NOTES ON ELEMENTARY STATISTICAL MECHANICS

Federico Corberi

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Contents

Preface

These notes are for my students and for me. For my students, because studying Physics may be an hard task and a reference text where all the arguments are collected and discussed along the same lines as they were presented in the class may help, and for me basically for the same reasons, since preparing Physics lessons may be an hard task as well.

The ambition of these notes is not to replace books, to which I invite anyone to make reference as often as possible, nor to be rigorous neither exhaustive, but to provide a basic, friendly (as far as possible :-)*), self-contained and familiar text to help against any difficulty. They are thought as a work in progress, to be improved and extended day by day on the basis of everyday's teaching experience. In preparing them I started from the excellent notes "Elementary course in Statistical Mechanics" by my former Ph.D. supervisor and dear friend Antonio Coniglio to which I am profoundly indebted. The idea is to gradually adapt this original text to my personal way of teaching and to the ever changing needs of University courses. In doing that, everyone's help will be greatly appreciated, particularly from the students.*

Federico Corberi

Chapter 1

Overview of Thermodynamics

1.1 Preliminaries

Thermodynamics is the study of macroscopic systems independent of their microscopic constituents. Statistical Mechanics is the study of macroscopic systems starting from the knowledge of their microscopic constituents - e.g., atoms and molecules - and the way in which they obey laws of physics such as those of classical mechanics and quantum mechanics. The scope of Statistical Mechanics is therefore to build bridge between the microscopic and the macroscopic world.

As quantum mechanics reproduces classical mechanics in the limit in which the Planck constant approaches zero and special relativity contains classical mechanics in the limit in which the velocity compared to the speed of light is negligible, similarly Statistical Mechanics encompasses Thermodynamics in the case of the thermodynamic limit, where the number of particles N and the volume V of the system both tend to infinity while the ratio $\rho \equiv N/V$ remains finite.

In Thermodynamics, the state of a system is defined by fixing some (hopefully few) macroscopic variables (which will be denoted as control variables or parameters) in such a way that two states characterized by the same variables are macroscopically indistinguishable. A relation among the state variables is called an equation of state. Since the number of microscopic variables needed to describe a system is at least of the order of its constituents, which, roughly speaking, is of the order of the Avogadro number, a natural question is: why fixing a relatively small number of macroscopic control variables should be sufficient to make all the microscopic state macroscopically equivalent? Nowadays an answer to this question can only be given for *equilibrium* states. A thermodynamic system is in equilibrium if the thermodynamic variables do not change over time (i.e. there is time-translation invariance, the system is stationary) and, in addition, there are no fluxes (of matter, energy or other) across the sample. Examples of stationary systems which are not in equilibrium states are: systems in contact with two thermal baths at different temperatures, a metallic ring where an electrical current is induced, a river which is regularly flowing etc... In all this systems a flux is present. Equilibrium states should not be confused with long-lived stationary metastable states, like supercooled liquid or gases or superheated liquids. This states have a finite lifetime and hence, strictly speaking, cannot be thought of as stationary (however, in some cases, this can be considered as temporary realizations of equilibrium states). According to the principles of Statistical Mechanics, to systems in equilibrium a very restricted number of macroscopic control variables can be associated (e.g., for a mole of a perfect gas, the pressure and the temperature, or alternatively the volume and the temperature etc...). This property, however, does not hold for a non-equilibrium state whose description, in general, cannot be given in terms of a small number of macroscopic variables (at least, this

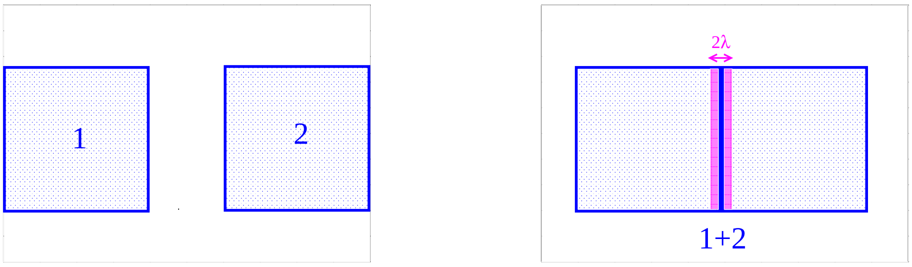

Figure 1.1: Left: The two separated systems 1 and 2. Right: The combined system 1+2. The magenta area is the interaction region.

Thermodynamic variables can be either intensive or extensive. The former do not depend on the dimension of the system. Typical examples are temperature and pressure. The temperature of the boiling water does not depend on the amount of water we put in the pot. Analogously the vapor pressure is not influenced by the amount of vapor. Extensive variables, instead, are linear functions (are proportional) of the dimension of the system, as expressed by the volume V or the number of particles N. As an paradigm let us focus on the internal energy U. Let us consider two identical isolated systems of volume V, denoted as 1 and 2, with energy U_1 and U_2, as in Fig. 1.1. Imagine now to bring the two parts in close contact so as to form a new system that will be denoted as $1+2$. Which is its internal energy U_{1+2}? Clearly one has

$$U_{1+2} = U_1 + U_2 + U_{int}, \tag{1.1}$$

where U_{int} is the interaction energy between the components (particles, molecules, atoms etc...) of system 1 and those of 2. If interactions are short ranged, so that they become negligible for interparticle distances larger than some threshold λ, then U_{int} will be roughly proportional to the number N_{AB} of couples AB of interacting particles such that A belongs to 1 and B to 2. There are $n_1 \simeq S \cdot \lambda$ particles in a slab of system 1 of width λ around the contact surface S between 1 and 2. Each of them interact with all the particles in a volume $V_i = B_d \lambda^d$ around it, where d is the Euclidean dimension and B_d is geometric constant (in an isotropic case it is the volume of a unitary radius sphere in d dimension, e.g. $(4/3)\pi$ in $d = 3$). Clearly, not all the particles contained in V_i contribute to N_{AB} since they do not necessarily belong to system 2, however it is clear (can you prove it?) that the number of those belonging to 2 is also proportional to λ^d. Hence $U_{int} \propto N_{AB} \propto n_1 \cdot \lambda^d = S \cdot \lambda^{d+1}$, Reasoning in the same way one also has that $U_1 = U_2 \propto V \cdot \lambda^d$. In the thermodynamic limit $V \to \infty$ faster than S and hence U_{int} can be neglected in Eq. (1.1) (is it true also in an infinite-dimensional space with $d = \infty$?). This shows that U is an extensive quantity. Notice that the same argument does not apply in system with long-range interactions. In the limiting case when every particle interact with all the others (usually denoted as mean-field limit) one has $U_1 = U_2 \propto V^2$ while $U_{1+2} \propto (2V)^2$. Hence $U_{1+2} \neq U_1 + U_2$ and the additivity property is spoiled. For this reason, if nothing will be explicitly stated, in the following we will always refer to short-range systems.

An isolated system that is not in equilibrium and is not maintained out of equilibrium by some external agent (like, for instance, by injecting energy into the system as in all the previous examples of non-equilibrium stationary states) transforms or evolves over time until equilibrium is reached. Hence equilibrium is generally a limit state, an attractor. In nature, the typical relaxation process towards equilibrium is irreversible, since the system does not spontaneously evolve in the reverse direction. A transformation can be made (quasi) reversible if some external control parameter (e.g. T or V) is varied in a very *smooth* way. For instance, we can gently cool a gas by putting it in contact with a large thermostat whose temperature is decreased sufficiently slow. In this case the transformation is called reversible if (a) the non-equilibrium trajectory of the system can be approximated as a succession of equilibrium states and (b) it is such that the system passes through the same states when the variation of external parameters change sign (is reversed in time). Notice that (a) and (b) are deeply related, since only for equilibrium states the value of few external parameters fully determine the state of the system. In an irreversible transformation (i.e. any transformation that is not reversible) non-equilibrium states are assumed whose control cannot be obtained by means of few thermodynamic variables.

1.2 Laws of Thermodynamics

1.2.1 Zeroth Law of Thermodynamics

Two systems are in thermal contact if they do not exchange matter but exchange energy without doing work on each other. If they are in thermal contact and in equilibrium they are said to be in thermal equilibrium. The zeroth law of Thermodynamics states that if two systems are in thermal equilibrium with a third system, then they are also in thermal equilibrium with each other. When two systems are in thermal equilibrium, we say they have the same temperature. To define precisely the temperature of a system A we use a particular system, called a thermometer, that has a property such that one of its macroscopic parameters (e.g., volume) is sensitive when it is brought into thermal contact with another system with which it is not in thermal equilibrium. Once we put the thermometer in contact with system A, the macroscopic parameter will assume a particular value. This value is defined operatively as the temperature of system A. We will see in Sec. 1.4 a different (assiomatic) definition of the temperature.

1.2.2 First Law of Thermodynamics

The first law of Thermodynamics deals with the conservation of energy. In classical mechanics, the work ΔW done on a system of n objects of coordinates $\vec{r_i} \ldots \vec{r_n}$ is given by

$$\Delta W = \sum_i \vec{F_i} \cdot \Delta\vec{r_i} \tag{1.2}$$

where $\vec{F_i}$ is the force acting on object i and $\Delta\vec{r_i}$ the displacement caused by the force. This expression is written in terms of (many) microscopic variables. If $\vec{F_i} = PS\hat{n}$, where P is the external pressure exherted on a gas, S the surface of the system exposed to that pressure and $\hat{n}$ the unit vector perpendicular to S, one has $\Delta W = -P\cdot\Delta V$. This provides an expression for the work in terms of (few) thermodynamic (i.e. macroscopic) variables. In general, other thermodynamic forces can do work on the system. For example, a chemical potential μ can cause a certain amount ΔN of particles to leave (or enter) the system. In this case one has $\Delta W = \mu \cdot \Delta N$. In general, the work can be written as the product of an intensive variable f (e.g. P or μ) times the variation of an extensive one X. f and X are said to be conjugate. If there are several *forces* f_i the thermodynamic work can be expressed as

$$\Delta W = \sum_i f_i \Delta X_i. \tag{1.3}$$

In a thermodynamic transformation in which there is no work done on the system, the amount of energy ΔQ exchanged by the system with a reservoir due to a difference in temperature ΔT, is called heat. The thermal capacity is defined by

$$C \equiv \frac{\delta Q}{\delta T} \equiv \lim_{\Delta T \to 0} \frac{\Delta Q}{\Delta T}. \tag{1.4}$$

The specific heat is the thermal capacity of a sample of unitary mass.

In a generic thermodynamic transformation, the first law of Thermodynamics states that

$$\Delta U = \Delta Q - \Delta W \tag{1.5}$$

where ΔU is the energy increment of the system, which depends only on the initial state and the final state.

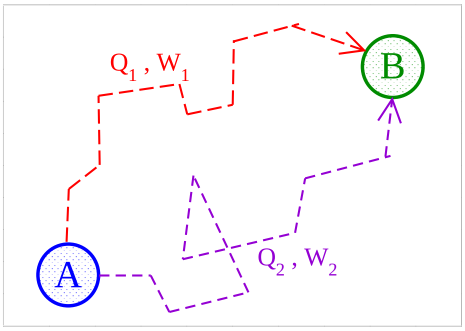

Figure 1.2: A thermodynamic transformation from a state A to another B.

For an infinitesimal transformation Eq. (1.5) becomes

$$dU = \delta Q - \delta W, \tag{1.6}$$

where δQ and δW are infinitesimal amounts of heat and work or, using Eq. (1.3)

$$dU = \delta Q - \sum_i f_i \Delta X_i. \tag{1.7}$$

The content of the first law is that dU is an exact differential, while δQ and δW are not. By integrating (1.6) from an initial state A to a final state B, we have

$$U_B - U_A = Q - W \tag{1.8}$$

where Q is the total heat absorbed by the system, W the work done on the system, and U a function of the state of the system, so $U_B - U_A$ is independent of the path between states A and B. Thus while Q and W depend on the particular transformation, $Q - W$ depends only on the initial and final state. Thus for two distinct transformations 1 and 2, which transform the system from state A to state B (Fig. 1.2),

$$Q_1 - W_1 = Q_2 - W_2, \tag{1.9}$$

where Q_1 and Q_2 are the heat absorbed by the system during transformations 1 and 2, and W_1 and W_2 are the work done by the system on the external world during the the transformations 1 and 2.

1.2.3 Second law of Thermodynamics

The second law of Thermodynamics imposes some limitations on the possible transformations in which the energy is conserved. There are many equivalent formulations of the second law of Thermodynamics. The equivalent formulations of Clausius and Kelvin are based on common experience.

Clausius Formulation

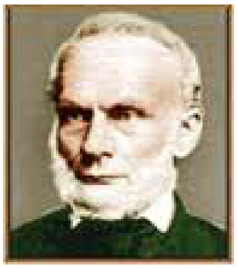

Figure 1.3: Rudolf Julius Emanuel Clausius (Köslin, 02/01/1822 - Bonn, 24/08/1888)

It is impossible to realize a thermodynamic transformation in which heat is transferred *spontaneously* from a low-temperature system to a high-temperature one (Fig. 2) without work being done on the system.

Kelvin Formulation

Figure 1.4: Lord William Thomson, I barone Kelvin (Belfast, 26/06/1824 - Largs, 17/12/1907)

It is impossible to realize a thermodynamic transformation whose unique result is to absorb heat from only one reservoir and transform it entirely into work. Namely, it is impossible to realize an engine that is able to transform heat into work using only one reservoir at temperature T (Fig. 3). If this were possible, we could extract heat from the ocean and transform it entirely in useful work.

Consequences

From these statements it is possible to derive important consequences concerning the efficiency of an engine. Kelvin's statement implies that to produce work an engine needs to operate at least between two reservoir (Fig. 4). If Q_1 is the heat absorbed from the reservoir at temperature T_1 and Q_2 the heat absorbed from the reservoir at temperature T_2, in one cycle from the first law $\Delta U = 0$. Therefore

$$Q_1 - Q_2 = W. \tag{1.10}$$

The efficiency of any engine can be defined as

$$\eta \equiv \frac{Q_1 - Q_2}{Q_1}. \tag{1.11}$$

It is possible to show that the efficiency of a reversible engine η_{rev} is always greater than the efficiency η of any other engine working between the same temperatures

$$\eta_{rev} \geq \eta. \tag{1.12}$$

As a corollary of (1.12), it follows that two reversible engines which work between two reservoirs respectively at the same temperatures T_1 and T_2 have the same efficiency. It follows that η_{rev} is a universal function of T_1 and T_2 (Fig. 4b). To find this universal function, we calculate the efficiency of one particular engine, called the Carnot Engine, which is an ideal reversible engine made of a cylinder filled with an ideal gas. The engine performs a cyclic transformation made of two isothermal and two adiabatic transformations (Fig. 1.5). Each point in the $P-V$ plane represents an equilibrium state. ab is the isotherm at temperature T_1 during which the system absorbs an amount of heat Q_1. cd is the isotherm at temperature T_2 ($T_2 < T_1$) in which the system rejects an amount of heat Q_2. bc and ad are adiabatic. Due to the simplicity of the cycle, the efficiency η_{rev} can be calculated and is found to be given by

$$\eta_{rev} = \frac{T_1 - T_2}{T_1}. \tag{1.13}$$

Therefore all reversible engines working between temperatures T_1 and T_2 have an efficiency given by (1.13). Using inequality (1.12) and definition (1.11), it follows that any engine working between two temperatures T_1 and T_2 satisfies the inequality

$$\frac{Q_1 - Q_2}{Q_1} \leq \frac{T_1 - T_2}{T_1}, \tag{1.14}$$

namely

$$\frac{Q_1}{T_1} - \frac{Q_2}{T_2} \leq 0, \tag{1.15}$$

the equality being valid for a reversible engine.

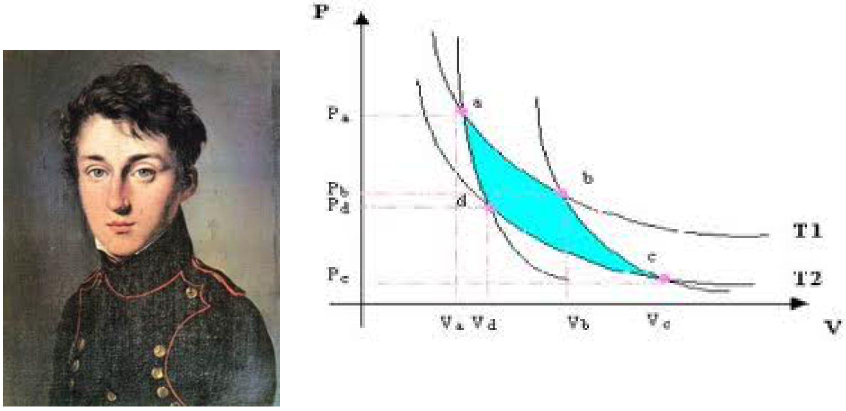

Figure 1.5: Left: Nicolas Léonard Sadi Carnot (Parigi, 01/06/1796 - Parigi, 24/08/1832). Right: The Carnot cycle.

The relation (1.15) can be extended to an engine that works with many reservoirs. Let ΔQ_i be the quantity of heat that the system exchanges with reservoir i at temperature T_i. Provided $\Delta Q_i > 0$, if the heat is absorbed and $\Delta Q_i < 0$ if the heat is rejected, relation (1.15) becomes

$$\sum_i \frac{\Delta Q_i}{T_i} \leq 0. \tag{1.16}$$

In the ideal limit in which the number of reservoirs becomes infinite and the heat exchanged with a reservoir is infinitesimal, relation (1.16) becomes

$$\oint \frac{\delta Q}{T} \leq 0. \tag{1.17}$$

Namely, in any cyclic transformation in which the engine exchanges an infinitesimal amount of heat δQ with a reservoir at temperature T, relation (1.17) holds. The equality holds for reversible cyclic transformations.

1.3 Entropy

In a reversible transformation the integral through any cycle is zero, so the integral must be an exact differential. Therefore we can define

$$dS \equiv \frac{\delta Q}{T}, \tag{1.18}$$

where δQ is the heat exchanged in a reversible transformation with a reservoir at temperature T . The function S whose differential is given by (1.18) is called the entropy, and it depends only on the thermodynamic state. From (1.18) we have

$$S_A - S_B = \underset{(rev)}{\int_A^B} \frac{\delta Q}{T}, \tag{1.19}$$

where the integral is defined along any reversible transformation. The function S is defined up to a constant. By chosing an arbitrary fixed state O to which we attribute zero entropy $S_O = 0$, the entropy of a state A can be defined as

$$S = \underset{(rev)}{\int_O^A} \frac{\delta Q}{T}, \tag{1.20}$$

In this definition we assume that any state A can be reached by a reversible transformation which starts in O. However this is not in general the case. The problem can be circumvented by using the third law of Thermodynamics, which states that any state at $T = 0$ has the same entropy. Therefore for any state A, we can chose a suitable state O at $T = 0$ to which can be attributed zero entropy such that A can be reached by a reversible transformation which starts at O. Let us now illustrate some properties of the entropy. Let us consider an irreversible transformation which transforms the system from a state A to a state B. We can always imagine another reversible transformation that brings the system from B to A. Let us apply relation (1.17) to the entire cycle

$$\oint \frac{\delta Q}{T} = \underset{(irr)}{\int_A^B} \frac{\delta Q}{T} + \underset{(rev)}{\int_B^A} \frac{\delta Q}{T} \leq 0, \tag{1.21}$$

It follows from (1.19) that

$$\underset{(irr)}{\int_A^B} \frac{\delta Q}{T} \leq S_B - S_A \tag{1.22}$$

If the irreversible transformation from A to B is adiabatic, namely, without exchange of heat with external reservoirs, then $\delta Q = 0$. Hence

$$S_B - S_A \geq 0. \tag{1.23}$$

If a system evolves naturally for one state to another without exchanging heat with the external world, the entropy of the system increases until it reaches a maximum value, which corresponds to a state of equilibrium (Fig. 7). Equation (1.22) and its corollary (1.23) are a direct consequence of the second law of Thermodynamics as stated by Clausius and Kelvin. An adiabatic system evolves naturally towards states with higher entropy, and this is another equivalent way to express the second principle:

Entropy (Assiomatic) Formulation

There exists an extensive function S of the thermodynamic control variables, called Entropy, such that, given two generic thermodynamic states A and B, B is *adiabatically* accessible from A ony if

$$S_B \geq S_A, \tag{1.24}$$

where the equality holds for a reversible transformation.

Consequences

Equation (1.23) has a dramatic consequence: it implies there exists a *time arrow*, since time must flow in the direction in which entropy increases. In an isolated system the entropy must always increase, so natural phenomena are irreversible. According to the second law of Thermodynamics, if a system evolves naturally from state A to state B, it cannot spontaneously evolve from B to A. Our everyday experience fully confirms this result. Two systems that come into contact initially at different temperatures will evolve towards a state at an intermediate temperature after which heat no longer flows from one to the other. The inverse process in which the two systems begin at a uniform temperature and then move to a state in which they have different temperatures is never realized. Any event such as the explosion of a bomb or an out-of-control fire dramatically confirms the validity of the second law of Thermodynamics. At first sight, the second law of Thermodynamics seems to contradict the microscopic laws of dynamics. These laws, both classical and quantum- mechanical, are invariant under time reversal, implying that if a phenomenon occurs in nature, the phenomenon obtained by reversing the time in principle can also occur. How can the microscopic laws of dynamics be reconciled with the macroscopic laws of Thermodynamics? Later we will consider this question within the framework of Statistical Mechanics, when a probabilistic interpretation of the concept of entropy will clarify many of the questions associated with the second law of Thermodynamics.

1.4 Temperature

Let us stipulate to describe the state of a system by its energy U and by a set $\{X_i\}$ of other extensive thermodynamic variables. then we have $S \equiv S(U, \{X_i\})$ and

$$dS = \left.\frac{\partial S}{\partial U}\right|_{\{X_i\}} \cdot dU + \sum_i \left.\frac{\partial S}{\partial X_i}\right|_{U,\{X_{j\neq i}\}} \cdot dX_i \qquad (1.25)$$

Using the first law (1.7) we arrive at

$$dS = \left.\frac{\partial S}{\partial U}\right|_{\{X_i\}} \cdot \delta Q + \sum_i \left[\left.\frac{\partial S}{\partial X_i}\right|_{U,\{X_{j\neq i}\}} + \left.\frac{\partial S}{\partial U}\right|_{\{X_i\}} \cdot f_i \right] \cdot dX_i \quad (1.26)$$

Let us now consider an adiabatic and reversible transformation, i.e. $\delta Q = dS = 0$. Eq. (1.26) becomes

$$\left.\frac{\partial S}{\partial X_i}\right|_{U,\{X_{j\neq i}\}} = - \left.\frac{\partial S}{\partial U}\right|_{\{X_i\}} \cdot f_i \qquad ; \qquad \forall i \qquad (1.27)$$

Since this is a relation among state variables it must not depend on the particular transformation we have used to derive it. Making the position

$$\left.\frac{\partial S}{\partial U}\right|_{\{X_i\}} = \frac{1}{T}, \qquad (1.28)$$

where T is presently a generic symbol (in a while it will be recognized to be the temperature), so that

$$\left.\frac{\partial S}{\partial X_i}\right|_{U,\{X_{j\neq i}\}} = -\frac{f_i}{T}. \tag{1.29}$$

Plugging these definitions into Eq. (1.25) we arrive at

$$dE = TdS + \sum_i f_i \cdot dX_i \tag{1.30}$$

which one recognizes as the first principle, provided that T is the temperature. Hence Eq. (1.28) is the (assiomatic) definition of the temperature.

1.5 Thermal Equilibrium

Let us consider two systems denoted 1 and 2 which are put in contact (like on the right panel of Fig. 1.1). Assume that the contact surface between 1 and 2 allows heat flows between the two system. The system 1+2 is initially in equilibrium, hence no net heat flows are present and the entropy $S_{1+2} = S_1 + S_2$ (we assume additivity) is at its maximum. At some time, by some apparatus, we slightly perturb the system by forcing an infinitesimal amount of heat to flow from 1 to 2, while all the other thermodynamic variables X_i are kept constant. The whole sample 1+2 is adiabatically isolated from the universe, hence the energy $U_{1+2} = U_1 + U_2$ is conserved $\delta U_{1+2} = 0$. This implies

$$\delta U_1 = -\delta U_2. \tag{1.31}$$

Since the system was at equilibrium S_{1+2} was at its maximum and this implies $\delta S_{1+2} = 0$ (i.e. entropy variations occur *at second order* but these are negligible since the perturbation is infinitesimal). Hence we can write

$$\begin{aligned} 0 = \delta S_{1+2} = \delta S_1 + \delta S_2 &= \qquad (1.32) \\ \left.\frac{\partial S_1}{\partial U_1}\right| \{X_i\} \cdot \delta U_1 + \left.\frac{\partial S_2}{\partial U_2}\right| \{X_i\} \cdot \delta U_2 &= \left(\frac{1}{T_1} - \frac{1}{T_2}\right)\delta U_1 \end{aligned}$$

This implies

$$T_1 = T_2 \tag{1.33}$$

We have derived in this way the condition of thermal equilibrium in an assiomatic way. Notice the procedure by which we have derived this result: We have perturbed the system around the equilibrium condition thus deducing in this way informations on the equilibrium state itself by the response of the system to the perturbation. This is a first example (we wil find many others in the following) of *response theory.*

1.6 Heat flows

Let us consider the same situation of the previous Sec. 1.5 but now the two sub-systems 1 and 2 are not initially in equilibrium because $T_1 \neq T_2$. The system is then left to relax towards equilibrium. In this case the total entropy S_{1+2} must increase during the process. Then we have

$$\begin{aligned} 0 \leq \delta S_{1+2} = \delta S_1 + \delta S_2 &= \qquad (1.34) \\ \left.\frac{\partial S_1}{\partial U_1}\right| \{X_i\} \cdot \delta U_1 + \left.\frac{\partial S_2}{\partial U_2}\right| \{X_i\} \cdot \delta U_2 &= \left(\frac{1}{T_1} - \frac{1}{T_2}\right) \delta U_1 \end{aligned}$$

Then, if $T_2 > T_1$ it must be $\delta U_1 > 0$. This shows that some heat has flown from 2 to 1. If $T_2 < T_1$ the heat flows in the opposite direction. Hence we arrived to establish that heat flow from the hotter systems to the colder.

1.7 Thermal Capacity

The definition (thermcap) does not relate the thermal capacity to state functions. In order to do that let us write

$$C = \frac{\delta Q}{dT} = \frac{\frac{\delta Q}{T}}{dT} = T \frac{\partial S}{\partial T}. \qquad (1.35)$$

This expression is somewhat vague because, since S is a function of more than one variable (for instance it may depend on $U, \{X_i\}$), it does not specify how the derivative on the r.h.s. is taken. In particular we can introduce

$$C_f = T \left(\frac{\partial S}{\partial T}\right)_{\{f_i\}}, \qquad (1.36)$$

the thermal capacity at constant *generalized force*, or

$$C_X = T\left(\frac{\partial S}{\partial T}\right)_{\{X_i\}}, \tag{1.37}$$

the thermal capacity at constant *generalized displacement.* Typical examples are C_P and C_V, the thermal capacities at constant pressure or volume, respectively.

1.8 Thermodynamic Potentials

Let us now consider, for simplicity, the case in which there is only one *generalized displacement* which is the volume of the system $X_1 = V$. The conjugate intensive variable is the pressure P. From Eqs. (1.17,1.18), recalling that $\delta W = PdV$, the first law of Thermodynamics for an infinitesimal reversible transformation of a fixed number of particles can be written

$$dU = TdS - PdV. \tag{1.38}$$

Since from (1.38) $U = U(S,V)$ is a function of S and V and dU is a perfect differential, it follows that

$$\left(\frac{\partial U}{\partial S}\right)_V = T \qquad \left(\frac{\partial U}{\partial V}\right)_S = -P \tag{1.39}$$

Because the derivative of the energy with respect to S gives T , S and T are called conjugate variables. Similarly, V and $-P$ are conjugate variables. Sometimes it is convenient to consider a thermodynamic potential function of T instead of its conjugate S. Indeed from a practical point of view it is impossible to use S as a control parameter, while T can be easily controlled by putting the system in contact with a large thermostat (a thermal bath, or reservoir). Accordingly, we introduce the Helmholtz potential A, obtained from U by subtracting the product of the conjugate variables TS

$$F = U - TS \tag{1.40}$$

By differentiating $dF = dU - TdS - SdT$ and from (1.38), we find

$$dF = -PdV - SdT \tag{1.41}$$

We note that the free energy is a function of V and T, $F = F(V,T)$, and that

$$\left(\frac{\partial F}{\partial T}\right)_V = -S \qquad \left(\frac{\partial F}{\partial V}\right)_T = -P \tag{1.42}$$

Similarly, we can define the enthalpy

$$H(S,P) = U + PV \tag{1.43}$$

By differentiating (1.43) and taking (1.38) into account we find

$$dH = TdS + VdP, \tag{1.44}$$

from which

$$\left(\frac{\partial H}{\partial S}\right)_P = T \qquad \left(\frac{\partial H}{\partial P}\right)_S = V \tag{1.45}$$

Finally, in the practical case of a system contained in a floppy container and in contact with a reservoir it may be useful to consider a quantity whose natural variables are P and T. This is the Gibbs free energy

$$G(T,P) = F + PV. \tag{1.46}$$

By differentiating (1.46) and taking (1.41) into account we find

$$dG = VdP - SdT, \tag{1.47}$$

with

$$\left(\frac{\partial G}{\partial P}\right)_T = V \qquad \left(\frac{\partial G}{\partial T}\right)_P = -S \tag{1.48}$$

Relations (1.39), (1.42), (1.45) and (1.48) can be reproduced using the Born diagram:

$$\begin{array}{ccc} V & F & T \\ U & & G \\ S & H & P \end{array} \tag{1.49}$$

The functions U , F , G and H are located on the square edges between their natural variables. The derivative with respect to one variable with the other fixed can be found following the diagonal. If the direction is opposite to the arrow, one uses a minus sign, e.g.,

$$\left(\frac{\partial F}{\partial T}\right)_V = -S. \tag{1.50}$$

Be careful, however, that it is possible to exchange only conjugate variables, but not any other. For instance we cannot have a description in terms of P, V or S, T.

1.9 Legendre Transformations

Figure 1.6: Adrien-Marie Legendre (Parigi, 18/09/1752 - Parigi, 10/01/1833)

The operation that we have done to substitute one variable with its conjugate is called the Legendre transform. In general, if $f(x)$ is a function of x with the differential

$$df = udx \qquad \text{with} \qquad u \equiv \frac{df}{dx}\,, \tag{1.51}$$

the Legendre transform of f is

$$g \equiv f - xu, \tag{1.52}$$

where x and u are conjugate variables. By differentiating (1.52)

$$dg = df - xdu - udx = -xdu, \tag{1.53}$$

which shows that g is a function solely of u. To obtain explicitly $g(u)$, one must infer $x = x(u)$ from the second part of (1.51), and substitute in (1.52). the Legendre transformation can be generalized to functions of more than one variable. If $f(x_1, x_2, \ldots, x_n)$ is such a function one has

$$df = \sum_{i=1}^{n} u_i dx_i \qquad \text{with} \qquad u_i \equiv \left.\frac{\partial f}{\partial x_i}\right|_{\{x_{j\neq i}\}}\,, \tag{1.54}$$

The Legendre transform with respect to $x_{r+1}, \ldots, x_n$ is

$$g = f - \sum_{i=r+1}^{n} u_i x_i \tag{1.55}$$

By differentiating one has

$$dg = df - \sum_{i=r+1}^{n} [u_i dx_i + x_i du_i] = \sum_{i=1}^{r} [u_i dx_i - \sum_{i=r+1}^{n} x_i du_i. \tag{1.56}$$

Thus $g = g(x_1, x_2, \ldots, x_r, u_{r+1}, \ldots, u_n)$. Clearly, one can go back from g to f, since the two functions contain the same informations. Geometrically, the Legendre transformation descrive f through the envelope of its tangents (up to an arbitrary constant).

1.10 Grand Potential

Thus far, we have considered the number of particles N to be fixed. If in a transformation the number of particles also changes, then the mechanical work in the first law of Thermodynamics contains an extra term, $-\mu dN$, where μ is the chemical potential that represents the work done to add one more particle to the system. The first law of Thermodynamics (1.38) is then written

$$dU = TdS - PdV + \mu dN. \tag{1.57}$$

If there are more species of particle, a term $\mu_i dN_i$ needs to be added for each species. If, in addition, there are forms of work other than mechanical work PdV , then additional terms will appear in (1.57). From (1.57) it follows that $U = U(S, V, N)$ is a function of the variables S, V, N and that

$$\left(\frac{\partial U}{\partial S}\right)_{V,N} = T, \qquad \left(\frac{\partial U}{\partial V}\right)_{S,N} = -P, \qquad \left(\frac{\partial U}{\partial N}\right)_{S,V} = \mu. \tag{1.58}$$

Since U is an extensive function of the extensive variables S, V, N , it follows that

$$U(\lambda S, \lambda V, \lambda N) = \lambda U(S, V, N), \tag{1.59}$$

where λ is a scale factor. Since λ is arbitrary, we can differentiate with respect to λ. Setting $\lambda = 1$, we obtain

$$U = \left(\frac{\partial U}{\partial S}\right)_{V,N} S + \left(\frac{\partial U}{\partial V}\right)_{S,N} V + \left(\frac{\partial U}{\partial N}\right)_{S,V} N. \tag{1.60}$$

Taking (1.58) into account,

$$U = TS - PV + \mu N, \tag{1.61}$$

from which we obtain an expression for the Gibbs potential (1.46)

$$G \equiv U - TS + PV = \mu N. \tag{1.62}$$

It is also useful to consider the grand potential

$$\Phi \equiv F - \mu N, \tag{1.63}$$

which is a Legendre transform of the Helmholtz potential. From (1.63) and (1.39), we have

$$\Phi = -PV. \tag{1.64}$$

1.11 Variational principles and Thermodynamic Potentials

The second law expresses the fact that the entropy of an isolated system is a maximum at equilibrium. For an isolated systems, therefore, the quantity $-S$ (the minus sign in the definition of S has historical reasons) plays the role of a potential energy in a mechanical system, thus justifying the name of *thermodynamic potential.* We show now that also the other thermodynamic potential may interpreted analogously. Consider the two subsystems of Sec. 1.5, but now let us assume that subsystem 2 is much larger than subsystem 1. System 2 can therefore be considered as a reservoir Fig. 7) at a fixed temperature T (we drop the index $_2$). From (**??**) and using the fact that

$$\left(\frac{\partial S_2}{\partial U_2}\right)_V = \frac{1}{T} \tag{1.65}$$

we have

$$\left(\frac{\partial S_{tot}}{\partial U_1}\right)_V = \frac{\partial S_1}{\partial U_1} - \frac{1}{T} = 0. \tag{1.66}$$

This equation corresponds to minimize the free energy of subsystem 1

$$F = U_1 - TS_1(U_1). \tag{1.67}$$

The maximum of the total entropy corresponds then to the minimum of the free energy of subsystem 1 and, restricting the attention to this system, F plays the role of a thermodynamic potential. Similar arguments can be developed for systems kept in a floppy envelope, i.e. at constant T, P, N, showing that, in this case, the potential G

is minimized, and for all the other potentials introduced before. We arrive therefore at the following variational principles

$$\begin{cases} d(-S)|_{E,V,N} \geq 0 \\ dF|_{T,V,N} \geq 0 \\ dG|_{T,P,N} \geq 0 \\ dH|_{S,P,N} \geq 0 \\ d\Omega|_{T,V,\mu} \geq 0, \end{cases} \tag{1.68}$$

where the equalities hold for a reversible transformation.

1.12 Maxwell Relations

Figure 1.7: James Clerk Maxwell (Edimburgo, 13/06/1831 - Cambridge, 05/11/1879)

Suppose we want to express the quantity

$$\left.\frac{\partial S}{\partial V}\right|_{T,N}. \tag{1.69}$$

Notice that we are considering here S as a function of T, V, N, which however are not its *natural* variables but, instead, those of F. In order to obtain a Maxwell relation one has to start from the *natural* potential F and to derive it twice, with respect to V, as in the original quantity (1.73), and in addition with respect to the variable (T) which is conjugate to the one (S) we are deriving in (1.73). Indeed, in doing that, one recover expression (1.73) (possibly with a minus sign)

$$\left.\frac{\partial}{\partial V}\frac{\partial F}{\partial T}\right|_{V,N} = -\left.\frac{\partial S}{\partial V}\right|_{T,N}. \tag{1.70}$$

Proceeding in the reverse order one has

$$\frac{\partial}{\partial T}\frac{\partial F}{\partial V}\bigg|_{T,N} = -\left.\frac{\partial P}{\partial T}\right|_{V,N} . \tag{1.71}$$

Enforcing the equality of the mixed derivatives, one arrives to the Maxwell relation

$$\left.\frac{\partial S}{\partial V}\right|_{T,N} = \left.\frac{\partial P}{\partial T}\right|_{V,N} . \tag{1.72}$$

As a second example let us consider

$$\left.\frac{\partial S}{\partial P}\right|_{T,N} . \tag{1.73}$$

(P, T, N) are the natural variables of G, that we must then derive twice with respect to P and T. Proceeding as before we have

$$\frac{\partial}{\partial P}\frac{\partial G}{\partial T}\bigg|_{P,N} = -\left.\frac{\partial S}{\partial P}\right|_{T,N} , \tag{1.74}$$

and

$$\frac{\partial}{\partial T}\frac{\partial G}{\partial P}\bigg|_{T,N} = \left.\frac{\partial V}{\partial T}\right|_{P,N} . \tag{1.75}$$

We then arrive to a second Maxwell relation

$$\left.\frac{\partial S}{\partial P}\right|_{T,N} = -\left.\frac{\partial V}{\partial T}\right|_{P,N} . \tag{1.76}$$

Other Maxwell relations are, for instance,

$$\left.\frac{\partial T}{\partial V}\right|_{S,N} = -\left.\frac{\partial P}{\partial S}\right|_{V,N} . \tag{1.77}$$

and

$$\left.\frac{\partial V}{\partial S}\right|_{P,N} = -\left.\frac{\partial T}{\partial P}\right|_{S,N} . \tag{1.78}$$

Chapter 2

Random walk: An introduction to Statistical Mechanics

2.1 Preliminaries

Most of the systems we observe in nature - e.g. gases, liquids, solids, electromagnetic radiations (photons) - are made of a very large number of particles. The study of such systems is difficult. Even when the interactions among particles are rather simple, the huge number of particles involved generates a complexity that can produce quite unexpected behaviors. Examples include the sudden transition of a liquid into a solid, the formation of patterns such as those found in snow flakes, or the fascinating and extremely complex organization which occurs in biological systems.

Macroscopic systems began to be studied from a phenomenological point of view in the last century. The laws that were discovered belong to the realm of Thermodynamics, as we mentioned in the previous chapter. However, in the second half of the last century, due to the development of atomic theory, macroscopic systems began to be studied from a microscopic point of view. It was such an approach that gave rise to the field of Statistical Mechanics. Therefore, although both Thermodynamics and Statistical Mechanics study the same macroscopic systems, their approaches differ.

Thermodynamics studies macroscopic systems from a macroscopic point of view, considering macroscopic parameters that characterize the system such as pressure, volume, and temperature without questioning whether or not the system is made of particles (e.g., atoms or molecules). On the other hand, Statistical Mechanics studies macroscopic systems from a microscopic point of view, i.e., it examines how systems made up of particles - atoms or molecules - exhibit behaviors governed by the laws of classical or quantum mechanics; its goal is to predict the macroscopic behavior of the system in terms of the system's microscopic molecular dynamics. Unlike Thermodynamics, Statistical Mechanics also studies fluctuations from equilibrium values. These fluctuations vanish in the thermodynamic limit where the number of particles N and the volume V both tend to infinity while the ratio $\rho \equiv N/V$ remains finite. In such limit Statistical Mechanics reproduces the laws of Thermodynamics. So Statistical Mechanics not only contains Thermodynamics as a particular limit, but also provides a microscopic basis and therefore a deeper understanding of the laws of Thermodynamics.

How then do we study a macroscopic system made of about an Avogadro (10^{24}) number of particles? In principle, by assuming some reasonable interactions among the particles, we could study the equation of motion of a single particle and follow its evolution. But such a task for a huge number of particles is impossible. Suppose one attempted, in a single toss of a coin, to use the laws of classical mechanics to predict the evolution of the coin movement and thereby the final outcome. Even if one could take into account all the interactions with the hand and with the air, one would need to know exactly the initial conditions. These events are extremely sensitive to initial conditions. Any infinitesimal change in the initial conditions will be amplified dramatically, giving rise to a completely different trajectory (a property called *chaos*).

One must resort to new concepts based on a probabilistic approach. A detailed knowledge of the system gained by attempting to predict the exact evolution of all single particles is renounced. Instead of predicting the exact evolution of all individual particles, the probabilistic approach is concerned only with the probability that a given event occurs. Therefore the aim is to predict a distribution probability for all microscopic events. Such a prediction is made assiomatically. From the probabilistic distributions one can evaluate average quantities and the fluctuations around such averages.

In the case of a coin, which has no apparent asymmetry, it is natural to assume that the probability that one of the two events (e.g., heads) will occur is 1/2. This prediction obviously cannot be verified experimentally in a single event (i.e., one toss). How does the theory compare with experiments? The experiments must be the result of an average of many realizations. One needs to toss many coins or a single coin many times. The frequency of heads is given by

$$\omega_+ \equiv \frac{N_+}{N}, \tag{2.1}$$

where N_+ is the number of coins with an outcome of heads and N the total number of coins. This frequence is an experimental quantity that can be measured. In the limit $N \to \infty$, the result will approach 1/2 if the theory is correct.

2.2 A non-equilibrium example: Unbounded Random Walk

In this section we will develop the basic ideas of Statistical Mechanics. (In a later chapter we will present a more detailed and precise formulation.) To do this, we consider in detail the example of diffusing particles in a viscous medium. To fix the idea, consider a single molecule diffusing in air. The exact approach would be to solve the dynamical equations for the molecules of the entire system of {molecules + air}. The statistical mechanical approach is probabilistic, namely it aims to calculate the probability for each possible trajectory of the particle.

The essential ideas emerge if we first simplify the problem: we discretize space and time and consider the motion in one dimension (Fig. ?). Assume the particle begins at the origin and, at each interval of time τ, takes a step of length a_0 (lattice constant) to the right with probability p or to the left with probability $q \equiv 1 - p$. In practice, each step corresponds to a collision with air particles, and after each collision the molecule has lost completely any memory it might have of its past history (in this case the process is called a Markov process, and is said to be Markovian). The effect of the air is taken into account in a probabilistic way. If there is symmetry between left and right, we choose $p = q = 1/2$. Otherwise, if there is a drift which makes the right or the left more favorable, $p \neq 1/2$. We consider the general case with p being a parameter. The problem is called a random walk, or the drunkard's walk. We will also use the imagine of randomly moving ants.

Eventually we want to be able to determine the probability that a given ant that begins at time $t = 0$ at the origin will be at a distance $x = ma_0$ at time $t = N\tau$ (i.e. after N steps), where m is an integer. Consider first the following example

$$\begin{aligned} p(rrr\ell) &= pppq \\ p(rr\ell r) &= ppqp \\ p(r\ell rr) &= pqpp \\ p(\ell rrr) &= qppp, \end{aligned} \tag{2.2}$$

where, e.g., $p(rrr\ell)$ is the probability that the ant will take three steps to the right (r) and one to the left (ℓ). Each of the four sequences has the same probability of occurring, p^3q, so the probability $P_4(3)$ that the ant will make a walk of four steps in which three steps are to the right and one is to the left is the sum of the four probabilities (since the events are mutually exclusive) $P_4(3) = 4p^3q$. Sequences like those in Eqs. (2.2), i.e. $rrr\ell$ etc..., are the most complete description of the system in that the microscopic displacements of the walker at each step is provided. Quantities like $rrr\ell$ can be then denoted as *micro*-variables. Next to this description one can introduce a less detailed one by considering the variables n_1 and n_2, namely the steps the particle moves to the right or to the left, respectively. These are *coarse*, or *macro*-variables since their value alone is not sufficient to describe all the microscopic evolution of the system. For example all the microscopic sequences (2.2) have the same values $n_1 = 3, n_2 = 1$ of the *coarse* variables n_1, n_2.

In general, the probability that a walker moves n_1 steps to the right and $n_2 = N - n_1$ steps to the left is given by the binomial distribution

$$P_N(n_1) = C_N(n_1)p^{n_1}q^{n_2}, \tag{2.3}$$

where

$$N \equiv n_1 + n_2, \tag{2.4}$$

and the binomial coefficient

$$C_N(n_1) \equiv \left(\begin{array}{c} N \\ n_1 \end{array} \right) = \frac{N!}{n_1!(N - n_1)!} \tag{2.5}$$

is the degeneracy, i.e., the number of independent walks in which n_1 steps are right (see Appendix A). The displacement m is related to n_1 and n_2 by

$$m = n_1 - n_2. \tag{2.6}$$

First we calculate the mean displacement

$$\langle m \rangle = \langle n_1 \rangle - \langle n_2 \rangle. \tag{2.7}$$

To calculate $\langle n_1 \rangle$, we must add up all the mutually independent ways of taking n_1 steps to the right, each with the appropriate weight, i.e.,

$$\langle n_1 \rangle = \sum_{n_1=0}^{N} n_1 P_N(n_1) = \sum_{n_1=0}^{N} n_1 C_N(n_1) p^{n_1} q^{n_2}. \tag{2.8}$$

To evaluate (2.8), we introduce the *generating function* (or, borrowing a terminology from equilibrium Statistical Maechanics, *partition function*)

$$Z(x,y) \equiv \sum_{n_1=0}^{N} C_N(n_1) x^{n_1} y^{n_2}. \tag{2.9}$$

From (2.9) we get

$$x \left. \frac{\partial Z}{\partial x} \right|_{\substack{x=p \\ y=q}} = \left. \sum_{n_1=0}^{N} n_1 C_N(n_1) x^{n_1} y^{n_2} \right|_{\substack{x=p \\ y=q}} , \tag{2.10}$$

which coincides with $\langle n_1 \rangle$. Using the binomial expansion (see Appendix A), the sum in (2.9) is simply

$$Z(x,y) = (x+y)^N, \tag{2.11}$$

so

$$x \left. \frac{\partial Z}{\partial x} \right|_{\substack{x=p \\ y=q}} = N x (x+y)^{N-1} \Big|_{\substack{x=p \\ y=q}} = Np \tag{2.12}$$

Therefore

$$\langle n_1 \rangle = Np. \tag{2.13}$$

We calculate $\langle n_2 \rangle$ in exactly the same way,

$$\langle n_2 \rangle = y \left. \frac{\partial Z}{\partial y} \right|_{\substack{x=p \\ y=q}} = Nq \tag{2.14}$$

Substituting (2.13) and (2.14) into (2.7), we find the mean value for m after N steps,

$$\langle m \rangle = N(p-q). \tag{2.15}$$

In addition to the mean $\langle m\rangle$, it is important to calculate the fluctuation about the mean,

$$\langle(\Delta m)^2\rangle = \langle(m-\langle m\rangle)^2 = \langle m^2\rangle - \langle m\rangle^2. \qquad (2.16)$$

From (2.6), $n_1 = (m+N)/2$ and

$$\langle(\Delta m)^2\rangle = 4(\langle n_1^2\rangle - \langle n_1\rangle^2). \qquad (2.17)$$

To calculate $\langle n_1^2\rangle$, we again use the generating function approach

$$\langle n_1^2\rangle = \left[x\frac{\partial}{\partial x}\left(x\frac{\partial Z}{\partial x}\right)\right]_{\substack{x=p\\y=q}} . \qquad (2.18)$$

Straightforward calculation gives

$$\langle n_1^2\rangle = Np + N(N-1)p^2 = (Np)^2 + Npq = \langle n_1\rangle^2 + Npq \qquad (2.19)$$

Finally, from (2.16)

$$\langle(\Delta m)^2\rangle = 4Npq. \qquad (2.20)$$

The *width* of the range over which m is distributed, i.e., the root mean square displacement, is given by the square root of the fluctuation

$$w \equiv [\langle\Delta m^2\rangle]^{1/2} = \sqrt{4pqN}. \qquad (2.21)$$

What is the meaning of the mean value $\langle m\rangle$ and its root mean square w? If we consider many walkers, each performing random walks, then the average displacement of all the walkers coincides with the mean. But if we ask what should be a typical displacement m^* of one walker chosen at random, then m^* satisfies the following relation

$$\langle m\rangle - w \le m^* \le \langle m\rangle + w. \qquad (2.22)$$

Equation (2.22) places different bound on m^* depending if $p=q$ or $p\neq q$. If $p=q$, then $\langle m\rangle = 0$ from (2.15), and $-w \le m^* \le w$. However if $p\neq q$, $\langle m\rangle \sim N$ while $w\sim\sqrt{N}$, so for large N it is $\langle m\rangle \lesssim m^* \lesssim \langle m\rangle$. Hence

$$m^* \sim \left\{\begin{array}{cc} \sqrt{N} & p=q \\ N & p\neq q \end{array}\right. , \qquad (2.23)$$

If we interpret the random walker as a particle diffusing on a lattice with lattice constant a_0 , then the displacement after N collisions separated by a time interval τ is $\langle m\rangle a_0$, where $t = N\tau$ is the time. Hence the typical displacement after a time t is, from (2.23),

$$m^* a_0 \sim \left\{ \begin{array}{ll} \sqrt{Dt} & p=q \\ Vt & p \neq q \end{array} \right. , \tag{2.24}$$

where $D = a_0^2/\tau$ is the diffusion constant and $V = (p-q)a_0/\tau$ is the drift velocity. Eq. (2.24) was one of the main results of one of the famous 1905 papers by A. Einstein. This equation shows that the typical displacement of particles increases indefinitely with time. The system therefore does never become stationary and equilibrium is never reached. The (unbounded) random walk is indeed a prototypical example of non-equilibrium statistical-mechanical problem. Since the evolution of the particle is fully described by its position at each time instant, while n_1 only informs on the position after N steps, Eq. (2.3) provides the probability of occurrence of what we have called (in a somewhat broad sense) a *coarse*, or *macro*-variable, namely a quantity to which many more fundamental and detailed *micro*-variables contribute (see for instance the four possible ways of obtaining $n_1 = 3$ with $N = 4$ expressed by Eqs. (2.2), and is therefore not the most complete possible information on the system. Notice that this probability depends on time (i.e. on N), since the system is not stationary. The determination of $P_N(n_1)$ has been possible because, due to the simplicity of the considered model, the probability of the *detailed*, or *micro*-variables - i.e. those in Eqs. (2.2) - are explicitly known. Its computation is only doable for very few (simple) statistical model while it remains, in general, unknown. The situation is different for equilibrium system, where, as we will see, a general receipt exists.

2.2.1 Gaussian Approximation

We next show that the distribution (2.3) in the limit of very large N can be well approximated by a Gaussian distribution. To this end, we consider $P_N(n_1)$ for large N as a continuous function of the continuous variable n_1, and then we expand $\ln P_N(n_1)$ around its maximum value $n_1 = \overline{n}_1$

$$\ln P_N(n_1) = \ln P_N(\overline{n}_1) + \frac{1}{2} \left. \frac{\partial^2 \ln P_N(n_1)}{\partial n_1^2} \right|_{n_1=\overline{n}_1} (n_1 - \overline{n}_1)^2 + \ldots \tag{2.25}$$

where we omit the first derivative term since

$$\left.\frac{\partial \ln P_N(n_1)}{\partial n_1}\right|_{n_1=\overline{n}_1} = 0. \tag{2.26}$$

Ignoring higher order terms, we immediately find the Gaussian distribution

$$P_N(n_1) = P_N(\overline{n}_1)e^{-(1/2)\lambda(n_1-\overline{n}_1)^2}, \tag{2.27}$$

with

$$\lambda = -\left.\frac{\partial^2 \ln P_N(n_1)}{\partial n_1^2}\right|_{n_1=\overline{n}_1}. \tag{2.28}$$

We must now compute $\overline{n}_1$, λ and show that higher order terms in (2.25) can be neglected.

From expressions (2.3) and (2.5) it follows that

$$\ln P_N(n_1) = \ln N! - \ln(N-n_1)! - \ln(n_1)! + n_1 \ln p + (N-n_1)\ln q. \tag{2.29}$$

Stirling's approximation for large n (Appendix C) states that

$$\ln n! \simeq n \ln n - n. \tag{2.30}$$

Rewriting (2.29) in this approximation, and requiring that its first derivative be zero, we find that the value $\overline{n}_1$ is given by

$$n_1 = Np, \tag{2.31}$$

which shows that $\overline{n}_1$ is the exact average value $\langle n_1 \rangle$ of (2.8). The second derivative is given by

$$\lambda = -\left.\frac{\partial^2 \ln P_N(n_1)}{\partial n_1^2}\right|_{n_1=\overline{n}_1} = (Npq)^{-1}, \tag{2.32}$$

and, in general, the k^{th} derivative by

$$\left.\frac{\partial^k \ln P_N(n_1)}{\partial n_1^k}\right|_{n_1=\overline{n}_1} \sim \frac{1}{(Npq)^{k-1}}. \tag{2.33}$$

Hence, for large N, higher order terms in (2.25) can be neglected for large N (because of the higher negative power of N in the terms (2.33) with respect to the one in (2.32)). More precisely, by comparing the quadratic term in Eq. (2.25) with the following one, one concludes that the Gaussian approximation (2.27) is valid, provided that

$$|n_1 - \overline{n}_1| \ll Npq. \tag{2.34}$$

On the other hand, if

$$\frac{(n_1-\overline{n}_1)^2}{Npq} \gg 1, \tag{2.35}$$

$P_N(n_1)$ and its Gaussian approximation are much smaller than $P_N(\overline{n}_1)$. Therefore when (2.34) starts to be unsatisfied, namely $|n_1-\overline{n}_1| \sim Npq$, Eq. (2.35) is satisfied, provided that

$$Npq \gg 1. \tag{2.36}$$

Therefore condition (2.36) assures that the Gaussian approximation is valid in the entire region where $P_N(n_1)$ is not negligible. Close to $p=1$ or $p=0$ when (2.36) is no more satisfied, and a different approximation is more appropriate, leading to the Poisson distribution. Clearly, if the interest is focused in the region in which $P_N(n_1)$ is very small, meaning that a prediction on very rare fluctuations is required, the Gaussian approximation (or the Poisson one if $p=1$ or $p=0$) breaks down and a more sophisticated theory, the so-called *large deviation theory* must be introduced.

Finally, the value of $P_N(\overline{n}_1)$ can be obtained by using the constraint that the sum over all probabilities is unity

$$\sum_{n_1=0}^{N} P_N(n_1) = 1. \tag{2.37}$$

Using (2.27) and (2.32) and using the variable $x=\frac{n_1-\overline{n}_1}{\sqrt{N}}$ one arrives at

$$\sum_{n_1=0}^{N} P_N(n_1) = P_N(\overline{n}_1)\sqrt{N} \sum_{x=-\overline{n}_1/\sqrt{N}}^{(N-\overline{n}_1)/\sqrt{N}} e^{-\frac{1}{2}\frac{x^2}{pq}} \cdot \Delta x = 1, \tag{2.38}$$

where $\Delta x = 1/\sqrt{N}$ and in the sum the (non integer) variable x runs from $-\overline{n}_1/\sqrt{N}$ to $(N-\overline{n}_1)/\sqrt{N}$ in steps of amplitude Δx. In the limit of large N, for $p \neq q$ (i.e. $\overline{n}_1 \neq 0$), x runs over the whole interval from $x=-\infty$ to $x=\infty$, $\Delta x \to 0$ and the sum can be replaced by an integral, hence

$$\sum_{n_1=0}^{N} P_N(n_1) \simeq P(\overline{n}_1)\sqrt{N} \int_{-\infty}^{\infty} e^{-x^2/2pq} dx = 1. \tag{2.39}$$

(For $p = q$ ($\overline{n}_1 = 0$) one can proceed analogously but the integral runs only on positive values of x.) Evaluating the Gaussian integral, from (2.39) we have

$$P_N(\overline{n}_1) = \frac{1}{\sqrt{2\pi Npq}}. \tag{2.40}$$

Finally from (2.27), (2.32), and (2.40) the distribution $P_N(n_1)$ is given by

$$P_N(n_1) = \frac{1}{\sqrt{2\pi Npq}} exp\left[-\frac{(n_1 - \overline{n}_1)^2}{2Npq}\right], \tag{2.41}$$

which is a Gaussian distribution centered around $\overline{n}_1 \equiv pN$ of width $w = \langle (n_1 - \overline{n}_1)^2 \rangle^{1/2} = \sqrt{Npq}$. Expressing (2.41) in terms of the displacement $m = 2n_1 - N$, we obtain the probability $\overline{P}_N(m) = (1/2)P_N((m + N)/2)$ that after N steps the net displacement is m

$$\overline{P}_N(m) = \frac{1}{2}\frac{1}{\sqrt{2\pi Npq}} exp\left[-\frac{1}{8Npq}(m - \overline{m})^2\right], \tag{2.42}$$

which is also a Gaussian, with a different mean

$$\overline{m} = N(p - q), \tag{2.43}$$

and twice the width,

$$\langle (\Delta m)^2 \rangle = 4Npq. \tag{2.44}$$

Note that these results agree with (2.15) and (2.20).

The generalization of the random walk to higher dimensions can be carried out using the same approach. The Gaussian distribution will appear often in Statistical Mechanics. A given distribution $f(x)$ can have a Gaussian form based on the following general requirements: (i) $f(x)$ has a maximum for $x = x_0$; (ii) $\ln f(x)$ can be Taylor expanded around x_0

$$\ln f(x) = \ln f(x_0) + \frac{1}{2} \left.\frac{\partial^2 \ln f(x)}{\partial x^2}\right|_{x=x_0} (x - x_0)^2 + \ldots \tag{2.45}$$

and higher order terms can be neglected. Under such requirements one finds

$$f(x) = f(x_0) exp\left[-\frac{1}{2}\lambda(x - x_0)^2\right], \tag{2.46}$$

with λ given by

$$\lambda \equiv \left| \left(\frac{\partial^2}{\partial x^2} \ln f(x) \right)_{x=x_0} \right| . \tag{2.47}$$

An example is

$$f(x) = [g(x)]^N , \tag{2.48}$$

with

$$g(x) = xe^{-x/x_0} . \tag{2.49}$$

Hence $g(x)$ has a maximum around x_0 and can be expanded around x_0. This example also shows that by expanding not $\ln f(x)$ but rather $f(x)$ itself around x_0 , one would not allow the truncation of the expansion in the limit of N large.

2.3 An equilibrium example: Random Walkers in a Box

Consider an adiabatic box with N non-interacting particles which we ideally divide into two equal parts. Each particle performs a three-dimensional random walk analogous to the one considered in Sec. 2.2, except that now the walkers are restricted inside the box (we can imagine that they are reflected back on the boundaries). If we prepare the system with all the particles on one part of the box by compressing them by means of a moving wall, and then we remove the wall a non-equilibrium process will take place where the gas of particles freely expand in order to occupy all the available space, until equilibrium is reached. Imagine to take W consecutive pictures in a time interval τ . Each picture represents a microscopic configuration at a certain time. The microscopic (detailed) variables necessary to describe the system are the positions q_i $(i = 1, \dots , N)$ of all the particles and their momenta p_i at each instant of time. A macroscopic (coarse) variable associated with the system is the average number of particles $\langle n_1 \rangle$ in the left half of the box. This quantity depends on time except when equilibrium is reached. If we want to make a prediction of such a value, the approach of classical mechanics would be to solve the equation of motion, given the interaction potential among the particles and their initial conditions, positions and velocities. Once the coordinates of the particles are calculated as functions of time, one would have to value the number of particles in the left part of the box. As we have seen in the previous sections

Statistical Mechanics takes a probabilistic approach to this problem. The techniques of Sec. 2.2 needs to be upgraded however, because the reflections on the walls must be taken into account. This results in a more complicated problem. However, if we are only interested in the equilibrium state, the problem can be further simplified, as we discuss below.

Assuming the crude random walk model of the previous Section, we do not need to specify the velocity of the particles since any of them moves a quantity a_0 in a time interval τ, so that there is a unique velocity. A microstate is the state of the system at some time as detailedly described by all the necessary microvariables. In the present case, therefore, microstates can be labelled by the microvariables $\{q_i\}$. Since particles are independent, the probability of the microstate $P_N(\{q_i\})$ factorizes into the product of the single particle probability $P_N(\{q_i\}) = \Pi_{i=1}^N P_i(q_i)$. Since particles are identical all the P_i must have the same functional form, and they do not depend on time due to the stationarity of equilibrium. Moreover, because space is homogeneous in this model, the P_i's cannot depend on space either, so that $P_i(q_i) \propto V^{-1}$, where V is the volume of the system. One arrives then to the conclusion that all the microstates have the same probability. This is general property of isolated systems, denoted as *equi-probability a priori*, as we will see in the next sections.

Next, we want to compute the probability $P(n_1)$, namely the probability that the macrovariable n_1 assumes a certain value (notice that we improperly use the same symbol P also for this, different, probability). One can also use the terminology of *macrostate*, or macroscopic configuration, to denote the set of microstates which share the same value of n_1. As in the random walk problem of Sec. 2.2, the first step is to assume a form for the probability p that a given particle will be on the left side of the box (hence $q = 1 - p$ is the probability of being on the right side). In equilibrium p must not depend on time and the left-right symmetry leads to $p = 1/2$. Assuming the particles are distinguishable, a given configuration is characterized by indicating which particle is on the left and which is on the right. For example, 1 particle has 2 possible configurations, while 2 particles have 4 possible configurations (see Fig. XX). Since the particles are weakly interacting, we can assume that the probability for a configuration of two particles is the product of the probability of the configurations of a single particle. Each microscopic configuration has therefore the same probability of being realized: 1/4. The probability that one particle will be on the left and the other on the right is

$$p(1,1) = 2 \cdot \frac{1}{4} = \frac{1}{2}. \tag{2.50}$$

Since 2 is the number of configurations that realizes that event, it represents its degeneracy.

In general the probability of finding n_1 particles on the left and $n_2 = N - n_1$ on the right is given (see Appendix A) by

$$\mathcal{P}_N(n_1) = \left(\begin{array}{c} N \\ n_1 \end{array} \right) p^{n_1} q^{n_2} \tag{2.51}$$

where

$$\left(\begin{array}{c} N \\ n_1 \end{array} \right) = \frac{N!}{n_1!(N-n_1)!} \tag{2.52}$$

is the degeneracy, i.e., the number of microscopic configurations that realize the event that n_1 particles are on the left and $n_2 = N - n_1$ on the right. Eq. (2.51) is formally identical to the probability (2.3) of the non-equilibrium case. However N is now the number of particles, instead of time, and the distribution is time-independent, as it must be for a stationary state.

The probabilities p and q have been chosen insofar to be $p = q = 1/2$, but if the box is divided into two unequal volumes V_1 and V_2 , then

$$p = \frac{V_1}{V_1 + V_2} \qquad q = \frac{V_2}{V_1 + V_2}. \tag{2.53}$$

The important concept to be stressed here is degeneracy. For example, in the case of $p = q = 1/2$, although each microscopic configuration has the same weight, what makes a macroscopic configuration more or less probable is the number of configurations required to realize the macrostate. As we will see, this something related to the entropy, and the evolution of the system toward the macroscopic equilibrium state with maximum degeneracy corresponds in this case to the entropy increase in a non-reversible transformation (Sec. 1.3). As we have shown in the previous section, for large values of N , the probability distribution becomes

$$P_N(n_1) = \frac{1}{\sqrt{2\pi N pq}} exp\left[-\frac{1}{2Npq}(n_1 - \overline{n}_1)^2 \right] \tag{2.54}$$

with $\overline{n}_1 = Np = N/2$.

The fluctuation of particles is $\sqrt{N}$, which means that the typical number of particles n_1 , on the left of the box, is given by

$$\frac{N}{2} - \sqrt{N} \leq n_1 \leq \frac{N}{2} + \sqrt{N}. \tag{2.55}$$

Let us introduce the intensive quantity

$$x \equiv \frac{n_1}{N}, \tag{2.56}$$

where x is the fraction of particles on the left of the box. From (2.55)

$$\frac{1}{2} - \frac{\sqrt{N}}{N} \leq x \leq \frac{1}{2} + \frac{\sqrt{N}}{N}. \tag{2.57}$$

For $N \to \infty$, the only possible value is $x = 1/2$.

To study the fluctuations of x about the average value $x = 1/2$ when N is finite, we define $\mathcal{P}_N(x)dx$ as the probability of finding a fraction between x and $x + dx$. To calculate $\mathcal{P}_N(x)$, we first relate $\mathcal{P}_N(x)$ to $P_N(n_1)$ of (2.54),

$$P_N(n_1)dn_1 = \mathcal{P}_N(x)dx, \tag{2.58}$$

where, from (2.56),

$$dn_1 = Ndx. \tag{2.59}$$

From (2.53), (2.54), and (2.58) we find for the equivolume case, $p = q = 1/2$,

$$\mathcal{P}_N(x) = \frac{\sqrt{N}}{\sqrt{\pi/2}} exp\left[-2N\left(x - \frac{1}{2}\right)^2\right]. \tag{2.60}$$

Distribution (2.60) in the intensive variable x has a width proportional to $N^{-1/2}$ and an amplitude proportional to $N^{1/2}$ and, in the limit $N \to \infty$, tends to a delta function peaked around its mean value $x = 1/2$. This means that although every *microscopic* configuration is allowed and has the same probability, the *macroscopic* configuration corresponding to $x = 1/2$ is almost surely realized by those microscopic configurations that are dominant in the limit $N \to \infty$. Thus it occurs with probability 1 and all other macroscopic states corresponding to $x \neq 1/2$ have zero probability of occurring.

The examples of this Chapter teach us that it is possible to predict macroscopic properties of a system without following the motions of all the single particles. The approach is based on a probabilistic description and on some reasonable assumptions about a priori probability. In equilibrium cases, the average quantities calculated must be compared with time average measurements on the system. In the large N limit, the distribution $\mathcal{P}_N(x)$ tends to a Gaussian around the mean value, which also corresponds to the most probable one. The state characterized by this most probable value is extremely degenerate, i.e., the limit $N \to \infty$ coincides with the totality of microscopic configurations. All the other macroscopic states have zero probability of occurring.

In the next chapter, we will formalize these examples in a coherent conceptual framework, as we will address the fundamental postulates of statistical mechanics.

Chapter 3

The Postulates of Statistical Mechanics

3.1 Motion in Γ-Space

As already stated above, Statistical Mechanics studies macroscopic systems by examining their microscopic elements, elements that, according to specific cases, obey the laws of classical or quantum mechanics. Using the laws of quantum mechanics, one must find the solution – given the wave function ψ at $t = 0$ – to the time-dependent Schrödinger equation

$$i\hbar \frac{\partial \psi}{\partial t} = \mathcal{H}\psi, \tag{3.1}$$

where $\mathcal{H}$ is the Hamiltonian of the system and ψ is the wave function, the spatial coordinates of the particles.

In classical mechanics, a microscopic state of a 3-dimensional system is characterized by the coordinates $\mathbf{q} \equiv \{q_1, \ldots, q_{3N}\}$ and its conjugate momenta $\mathbf{p} \equiv \{p_1, \ldots, p_{3N}\}$. The evolution of the system is found solving the Hamiltonian equations

$$\left\{ \begin{array}{l} \dot{q}_i(t) = \partial\mathcal{H}/\partial p_i \\ \dot{p}_i(t) = -\partial\mathcal{H}/\partial q_i \end{array} \right. \qquad i = 1, \ldots, 3N. \tag{3.2}$$

For fixed initial conditions

$$\left\{ \begin{array}{l} q_i(t_0) = q_{i,0} \\ p_i(t_0) = p_{i,0} \end{array} \right. \qquad i = 1, \ldots, 3N, \tag{3.3}$$

there is only one solution

$$\left\{ \begin{array}{l} \mathbf{q}(t) \equiv \{q_1(t) \ldots q_{3N}(t)\} \\ \mathbf{p}(t) \equiv \{p_1(t) \ldots p_{3N}(t)\} \end{array} \right. , \tag{3.4}$$

which gives deterministically the $6N$ coordinates in both the future and the past.

Whatever the description is (classical or quantum) there is a number $\mathcal{N}$ of order N (the number of microscopic constituents) of variables, or quantum numbers, which depend on time. The evolution of such variables can be described as the motion of a representative point (see Fig. ...) in the $\mathcal{F}$-dimensional space ($\mathcal{F} = 6N$ for a classical system described by Eqs. (3.2)) of the microstates, denoted as Γ space (also phase-space for classical systems). More precisely, the representative point moves on the subspace (or iper-surface) which is compatible with the values of the control parameters. For instance, for an isolated systems only the microstates with an assigned energy are accessible. Since Γ is $\mathcal{F}$ dimensional, by fixing a small number of control parameters the allowed Γ space remains of very high dimensionality.

Practically, the motion of the representative point in Γ cannot be determined for the following reasons

- Since N is of the order of the Avogadro number ($\sim 10^{24}$) the number of coupled equations in (3.2) is by far impossible to be managed even by the most powerful computer.

- Even if some thecnique to solve all these coupled equations would exist, we would need the initial conditions of all the $\mathcal{F}$ variables, which is impossible to measure. Not only this, every inaccuracy in the determination of such initial values would make any prediction invalid due to the chaotic nature (extreme sensitivity to initial conditions) of the equations.

Statistical Mechanics provides a way out of this discouraging scenario, by resorting to s probabilistic approach. The following considerations suggest its predictive power:

- Despite the incredible complication of the governing equations of classical or quantum mechanics, at least in equilibrium the very small number of thermodynamic control parameter needed to describe a macroscopic state suggests that some statistical regularity of a collective type underlys the problem.

- Despite the statistical description is only probabilistic, so that only averages can be obtained, the effect of fluctuations turn out to be very so small, due to the incredibly large value of N, to render Statistical Mechanics practically exact. For example, by considering only 10^{-2} moles of a perfect gas in contact to a reservoir at room temperature, it is possible to compute the relative fluctuations of its internal energy U. One has a number as small as $\delta U/U \simeq 10^{-11}$. In an instantaneous measurement the probability of finding a relative deviation from the average of order 10^{-6} is of order $10^{-3 \cdot 10^{15}}$!!

3.2 Measuring is averaging

Any macroscopic variable A is a function of the $6N$ coordinate $A = A[\mathbf{q}(t), [\mathbf{p}(t)]$. Since any instrument has a finite measurement time $\overline{t}$ any measure of the macroscopic variable A corresponds to doing an average A_{obs} over a suitable interval of time $\overline{t}$

$$A_{obs} \equiv \overline{A} = \frac{1}{\overline{t}} \int_0^{\overline{t}} A[\mathbf{q}(t), \mathbf{p}(t)] dt. \tag{3.5}$$

For example, the pressure is obtained by using an apparatus which does not measure the instantaneous value of the force exerted by the particles on the unit surface, but a time average over a time interval τ that depends on the apparatus. Analogously, to measure the temperature, a thermometer gives the average value of the kinetic energy. Thermodynamic systems in equilibrium are chaotic in the sense that the evolution at some time $t + \tau$, where t is a generic instant and τ a short time interval denoted as *correlation time*, does not keep memory (in not correlated with) the microstate assumed at the earlier time t. Then Eq. (3.5) amount to say that an average over $\overline{t}/\tau$ *independent* instantaneous measurements is done. This, however, is not the only source of averaging hidden in a usual measure. Indeed any instrument has a finite measuring *tip*, of a certain size (volume) $\overline{v}$. Then, if $A(\vec{r})$ is the (instantaneous) local value of the observable A at position $\vec{r}$, the value read on the instrument is

$$A_{obs} \equiv \overline{A} = \frac{1}{\overline{v}} \int_{\overline{v}} A[\mathbf{q}(t), \mathbf{p}(t)] d\vec{r}. \tag{3.6}$$

Thermodynamic systems in equilibrium have usually a short *coherence length* ξ. Similiarly to τ, but in the realm of space instead of time, ξ is the typical distance over which the behavior of the system becomes *independent*. Then Eq. (3.6) amount to say that an average over $\overline{v}/\xi^d$ *independent* local measurements is done.

3.3 Statistical Ensembles

In principle, to find the theoretical outcome of a given measurement, one should be able to solve the equation of motion and then calculate the integral (3.5), which we have already discussed to be impossible. How, then, does one calculate $\overline{A}$? We must renounce any notion involving the coordinates of the system at each instant of time and substitute the time average with another average called the *ensemble* average, which we will see gives (under certain hypotheses) the same value of the time average but in a much simpler way.

Consider an isolated system of N classical particles described by Eqs. (3.2) with certain control parameters (e.g. a fixed energy E and a volume V). Consider an ensemble made of N copies macroscopically identical to the given system, i.e., with the same values of the control parameters. At any given instant of time t_0 , each system will be in a given configuration $\{\mathbf{q}, \mathbf{p}\}^{(k)}$ in which k labels the systems of the ensemble $k = 1, 2, \dots, \mathcal{N}$. Any macroscopic dynamical variable will assume a value $A_k \equiv A(\mathbf{q}_k, \mathbf{p_k})$ in the system k. The ensemble average is given by

$$\langle A \rangle_{ens} = \frac{1}{\mathcal{N}} \sum_{k=1}^{\mathcal{N}} A_k, \tag{3.7}$$

with $\mathcal{N}$ extremely large ($\mathcal{N} \to \infty$).

To characterize the ensemble and calculate the ensemble average, we must give the distribution of the systems over all microscopic configurations described by the coordinates

$$\{\mathbf{q}, \mathbf{p}\} \equiv \{q_1 \dots q_{3N}, p_1 \dots p_{3N}\}. \tag{3.8}$$

Since this cohordinates represent a point in Γ, the microstates of the $\mathcal{N}$ systems of the ensemble can be represented by $\mathcal{N}$ points in phase space.

The distribution that characterizes the ensemble is described by a function $\rho(q, p)$ defined in phase space such that

$$d\mathcal{N} = \rho(\mathbf{q}, \mathbf{p}) d\mathbf{q} d\mathbf{p}, \tag{3.9}$$

where $d\mathcal{N}$ is the number of systems characterized by a microscopic state represented in phase space in the elementary volume $d\mathbf{q}d\mathbf{p}$. The ensemble average is given by

$$\langle A \rangle_{ens} = \frac{\int A(\mathbf{p}, \mathbf{q}) \rho(\mathbf{p}, \mathbf{q}) d\mathbf{q} d\mathbf{p}}{\int \rho(\mathbf{p}, \mathbf{q}) d\mathbf{q} d\mathbf{p}}, \tag{3.10}$$

where

$$\int \rho(\mathbf{q}, \mathbf{p}) d\mathbf{q} d\mathbf{p} = \mathcal{N}. \tag{3.11}$$

As we will see, the form of ρ is done assiomatically.

3.4 Liouville Theorem

Figure 3.1: Joseph Liouville (Saint-Omer, 24/03/1809 - Parigi, 08/09/1882)

The distribution of points in phase space at time t_0 is characterized by the distribution $\rho(\mathbf{q}, \mathbf{p}) \equiv \rho(\mathbf{q}, \mathbf{p}, t_0)$. As time evolves, each point in phase space moves according to the Hamiltonian equations. If this fundamental postulate describes a system in equilibrium, then the distribution (3.24) at time t_0 must equal the distribution at any time t. At time t, the points will in principle be described by a new function $\rho(\mathbf{q}, \mathbf{p}, t)$. However, we will show that such a distribution is time-independent as a consequence of Liouville's Theorem, namely

$$\rho(\mathbf{q}, \mathbf{p}, t_0) \equiv \rho(\mathbf{q}, \mathbf{p}, t). \tag{3.12}$$

This result will support the validity of the postulate of the equal a priori probability that applies to equilibrium systems.

The purpose of the Liouville Theorem is to give the evolution equation for $\rho(\mathbf{q}, \mathbf{p}; t)$. Since the number of points represents the number of systems $\mathcal{N}$, this number is conserved. Therefore we can write a continuity equation

$$\vec{\nabla} \cdot \vec{J} + \frac{\partial \rho}{\partial t} = 0, \tag{3.13}$$

where ρ is the density of points, $\vec{J} = \rho \vec{v}$ the flux, and $\vec{v} = \vec{v}(\mathbf{q}, \mathbf{p})$ the velocity of the point $(\mathbf{q}, \mathbf{p})$ in phase-space. The components of the phase-space velocity are

$$\vec{v} \equiv (\dot{q}_1 \ldots \dot{q}_{3N}, \dot{p}_1 \ldots \dot{p}_{3N}). \tag{3.14}$$

Therefore

$$\begin{aligned} \vec{\nabla} \cdot \vec{J} &= \sum_{i=1}^{3N} \left(\frac{\partial}{\partial q_i}(\rho \dot{q}_i) + \frac{\partial}{\partial p_i}(\rho \dot{p}_i) \right) \\ &= \sum_{i=1}^{3N} \left[\dot{q}_i \frac{\partial \rho}{\partial q_i} + \rho \frac{\partial \dot{q}_i}{\partial q_i} + \dot{p}_i \frac{\partial \rho}{\partial p_i} + \rho \frac{\partial \dot{p}_i}{\partial p_i} \right]. \end{aligned} \tag{3.15}$$

From the Hamiltonian equations (3.2),

$$\frac{\partial \dot{q}_i}{\partial q_i} = \frac{\partial \mathcal{H}}{\partial q_i \partial p_i} \qquad \text{and} \qquad \frac{\partial \dot{p}_i}{\partial p_i} = -\frac{\partial \mathcal{H}}{\partial p_i \partial q_i}, \tag{3.16}$$

and (3.15) becomes

$$\begin{aligned} \vec{\nabla} \cdot \vec{J} &= \sum_{i=1}^{3N} \left[\dot{q}_i \frac{\partial \rho}{\partial q_i} + \rho \frac{\partial \mathcal{H}}{\partial q_i \partial p_i} + \dot{p}_i \frac{\partial \rho}{\partial p_i} - \rho \frac{\partial \mathcal{H}}{\partial p_i \partial q_i} \right] \\ &= \sum_{i=1}^{3N} \left[\dot{q}_i \frac{\partial \rho}{\partial q_i} + \dot{p}_i \frac{\partial \rho}{\partial p_i} \right], \end{aligned} \tag{3.17}$$

Finally, from (3.13) and (3.17),

$$\frac{\partial \rho}{\partial t} + \sum_{i=1}^{3N} \left[\dot{q}_i \frac{\partial \rho}{\partial q_i} + \dot{p}_i \frac{\partial \rho}{\partial p_i} \right] = 0. \tag{3.18}$$

The l.h.s. is readily recognized to be $\frac{d\rho}{dt}$, hence

$$\frac{d\rho}{dt} = 0. \tag{3.19}$$

This is the Liouville theorem, which states that the representative points move in Γ-space as an incompressible fluid. Notice that no assumptions on the state of the system (e.g. if in equilibtium or not) has been done. From (3.2) we can write (3.18) in the equivalent form

$$\frac{\partial \rho}{\partial t} + \sum_{i=1}^{3N} \left(\frac{\partial \rho}{\partial q_i} \frac{\partial \mathcal{H}}{\partial p_i} - \frac{\partial \rho}{\partial p_i} \frac{\partial \mathcal{H}}{\partial q_i} \right) = 0, \tag{3.20}$$

where the sum is called the Poisson bracket $\{\rho, \mathcal{H}\}$.

3.5 Ergodic Hypothesis

In order to proceed we must stipulate to substitute time averages with ensemble averages (further averaging over space does not change the discussion that follows and we forget it now). In order to simplify the discussion let us for the moment assume that the instrument is very slow, i.e. $\bar{t} \to \infty$. In this case the difference between the averages (3.5) and (3.10) is that the average in the latter runs over all the possible states (compatible with the control parameters), while in the former only on those actually reached by the dynamical trajectory of the representative point in Γ. Assuming that the two averages coincides is equivalent to introduce the so called *ergodic hypothesis*, which states that the trajectory of the given system must, in the course of time, visit in a uniform way all the accessible phase space.

There have been many efforts to prove the ergodic hypothesis but results are limited to very few (and somewhat physically trivial) cases.

The role of a finite $\bar{t}$ is even harder to be controlled theoretically. It is an empirical fact that, due to the smallness of τ (and of ξ), any experimental measurement *de facto* realizes an average over a sufficiently large number of independent instances to be assimilated to a situation with $\bar{t} = \infty$.

3.6 Guessing the correct ensemble

We now must choose an ensemble which has the property that (for an ergodic system) the ensemble average of any dynamical quantity coincides with the time average of the given system. To do so, we must make an intuitive choice and compare its consequences with experimental data. This intuitive approach can only be done for systems in equilibrium. For non-equilibrium systems a theory does not yet exists.

3.6.1 A Suggestion from Monsieur Liouville

Liuville's theorem can suggest us how to guess the correct form of ρ for a system of N particles whose control parameters are U and V. If $\rho(\mathbf{q}, \mathbf{p}, t)$ must describe an equilibrium distribution, then

$$\frac{\partial \rho}{\partial t} = 0, \tag{3.21}$$

so $\rho(\mathbf{q},\mathbf{p},t) = \rho(\mathbf{q},\mathbf{p})$. From Liouville's theorem (3.15) it follows

$$\sum_{i=1}^{3N} \left[\dot{q}_i \frac{\partial \rho}{\partial q_i} + \dot{p}_i \frac{\partial \rho}{\partial p_i} \right] = 0, \tag{3.22}$$

and therefore $\rho(\mathbf{p},\mathbf{q})$ must be necessarily a constant of motion. Then a possiblity is that ρ is a function only of constant of motion, like energy or momentum. Making the further assumption that ρ is chosen to be a function solely of the energy, i.e., $\rho(\mathbf{p},\mathbf{q}) = \widetilde{\rho}[\mathcal{H}(\mathbf{p},\mathbf{q})]$, and that the distribution must be equal to zero in the region of phase space not allowed, it follows

$$\widetilde{\rho}[\mathcal{H}(\mathbf{p},\mathbf{q})] \equiv \begin{cases} \text{const.} & \text{if } E \leq \mathcal{H}(\mathbf{p},\mathbf{q}) \leq \mathbf{E} + \delta\mathbf{E} \\ 0 & \text{otherwise,} \end{cases} \tag{3.23}$$

Note that we have allowed the energy to lie in a small range δE rather to be strictly fixed. This has some mathematical advantages and, moreover, conforms to real situations since it is impossible to completely isolate a system from the universe. Let us stress that a necessary consequence of (3.21) and Liouville's theorem is only that $\rho(q,p)$ must be a constant of motion, while the particular choice that $\rho(q,p)$ is a function of only the energy and not of all the other constant of motion, is an assumption.

3.6.2 Equal a Priori Probability and the Microcanonical Ensemble

An alternative route to infer the properties of the equilibrium ensemble for a system with fixed energy in $[E, E + \delta E]$ and volume V, is to make the hypothesis that the probability measure ρ is distributed uniformly over the allowed configurations. This hypothesis is known as the postulate of *equal a priori probability* and is expressed by saying that $\rho(\mathbf{q},\mathbf{p})$ is constant in the accessible phase space, i.e., the phase space corresponding to those microstates with a number of particles N confined to a volume V and with energy $E \leq \mathcal{H}(\mathbf{p},\mathbf{q}) \leq E + \delta E$, namely

$$\rho(\mathbf{q},\mathbf{p}) \equiv \begin{cases} \text{const.} & \text{in the region of allowed phase-space} \\ 0 & \text{otherwise.} \end{cases} \tag{3.24}$$

Clearly this is the same probability measure of Eq. (3.23). Let us anticipate that it is not necessary to fix δE since we will show that the calculations based on distribution (3.24) do not depend on the value of δE in the limit $N \to \infty$.

The postulate of equal a priori probability is based on the intuitive idea that all microscopic configurations are equivalent. The rationale for this hypothesis is that, since the energy is fixed, there is no reason to privilege some configurations by giving them a different weight. In the same way there is no reason to give a different weight to the toss of a coin or to the configurations of the particles in the box considered in the previous chapter.

There is no general proof for this hypothesis. We therefore assume it as a postulate, a working hypotesis, and then confront all the consequences with the experiments. As long as the agreement with the experiments is correct we accept the postulate. On the contrary in absence of agreement we should be ready to question the postulate (see, e.g., the book Grandi, Foundation of Statistical Mechanics for further insights).

If the given system is not in equilibrium, we cannot make the assumption (3.24). For example, in the case of the particles in a box, if we prepare the system at $t = t_0$ in which all particles are on the left side of the box, not all configurations have the same weight. In fact, the system in this case will evolve and a macroscopic quantity such as the fraction of particles in the left side of the box will change in time until it reaches its equilibrium value.

3.6.3 Consistency with the Liouville Theorem

Since the partial differential equation (3.18) contains only the first derivative with respect to time, a solution that satisfies (3.18) and coincides at $t = t_0$ with the initial condition $\rho(\mathbf{q}, \mathbf{p}; t_0) = \rho(\mathbf{q}, \mathbf{p})$ is the only solution. The distribution $\rho(\mathbf{q}, \mathbf{p}; t) = \text{const.}$ with respect to both the variable $\{\mathbf{q}, \mathbf{p}\}$ and the time t is a solution of (3.18) and coincides at $t = t_0$ with the initial condition $\rho(\mathbf{q}, \mathbf{p}; t_0) = \text{const.}$ Therefore a uniform distribution in phase space at time t_0 will remain uniform for all t,

$$\rho(\mathbf{q}, \mathbf{p}; t) = \rho(\mathbf{q}, \mathbf{p}; t_0). \tag{3.25}$$

Hence the hypothesis that the equal a priori distribution describes a system in equilibrium is consistent with Liouville's theorem. Let us notice, however, that this does not guarantees the equal a priori distribution to be the correct one. Indeed, we will see that such a distribution is not suited for an ensemble where the control parameters are not U, V, N.

Chapter 4

The Connection with Thermodynamics

4.1 Degeneracy

In the previous chapter we have stressed that Statistical Mechanics is based on a probabilistic approach. The basic postulate of Statistical Mechanics states that, given a system with fixed external parameters N, U, V, there is an equal probability of finding the system in any of its microscopic states. If the number of microscopic states allowed is very limited (e.g., one), we know exactly in what microscopic state the system is, while if it is large, our ignorance of which microscopic state the system is in is also large. Some explicit realizations of this fact have been discussed in Sec. 2. We shall see that this degeneracy of states plays a fundamental role in Statistical Mechanics, and is a new concept not contained in classical or quantum mechanics.

Before we explore the meaning of this degeneracy, we offer first an idea of how this quantity behaves as a function of the number of degrees of freedom $\mathcal{F}$. We define $\Omega(E)$ as the number of states between E and $E+\delta E$. Notice that we have assumed that microstates are countable. This is not the case for a classical system as, for instance, a gas, whose microstates are labelled by a set of continuous variables (positions and momenta of each molecule). An extension to the case of systems described in terms of continuous variables will be given in Sec. 4.5. If $\phi(E)$ is the number of states between the ground state E_0 and E

$$\Omega(E) = \frac{\partial \phi}{\partial E} \delta E \tag{4.1}$$

Let us consider a box of size L and N particles so weakly interacting that we can consider them to be free. We calculate $\phi(E)$ using quantum mechanics. Each particle has a quantized energy

$$\epsilon = \frac{\hbar^2 \pi^2}{2mL^2} n^2, \tag{4.2}$$

where $n^2 = n_1^2 + n_2^2 + n_3^2$ and $n_1, n_2, n_3 = 0, 1, 2 \ldots$ are quantum numbers referring to the three degrees of freedom of a free particle. For a single degree of freedom, the number of states between n and $n + \delta n$ is proportional to $n\,\delta n$ (a rough way to understand this is the following: if the n_i were continuous variables this number would have been the area $2\pi n \delta n$ of the region between the two circles of radii n and $n + \delta n$.) Therefore, the number of states $\varphi(\epsilon)$ between 0 and ϵ grows as $n \propto \sqrt{\epsilon}$, and

$$\varphi(\epsilon) \sim \sqrt{\epsilon}. \tag{4.3}$$

For each degree of freedom there is a factor as in (4.3). Therefore, for an $\mathcal{F} = 3N$ degrees of freedom,

$$\phi(E) \sim [\varphi(\epsilon)]^{\mathcal{F}} \sim \left(\frac{E}{\mathcal{F}}\right)^{\mathcal{F}/2} \tag{4.4}$$

with $E = \mathcal{F}\epsilon$.

More generally, for a system of interacting particles we may expect

$$\phi(E) \sim (E - E_0)^{\alpha \mathcal{F}}, \tag{4.5}$$

where we have introduced the possibility that the ground state has a finite energy E_0 and α is of the order of unity. From (4.1) we have

$$\Omega(E) = \alpha f (E - E_0)^{\alpha \mathcal{F} - 1} \delta E, \tag{4.6}$$

and, since $\alpha \mathcal{F} \gg 1$ one has

$$\Omega(E) \sim (E - E_0)^{\alpha \mathcal{F}}, \tag{4.7}$$

so $\Omega(E)$ has the same behavior as $\phi(E)$. Since we are interested in the order of magnitude and αf is of the order of $\mathcal{F}$, we write

$$\Omega(E) \sim (E - E_0)^{\mathcal{F}}. \tag{4.8}$$

Thus we see that Ω is a rapidly increasing function of the energy difference from the ground state energy.

4.2 Statistical Definition of the Temperature

Let us explore the properties of this function. Consider the systems 1 and 2 of the right panel of Fig. 1.1 separated initially by a barrier that does not allow the exchange of energy. If $E^{(1)}$ and $E^{(2)}$ are the energies of system 1 and 2, the total number of configurations allowed for the combined system $1+2$ is

$$\Omega_b^{(1+2)} = \Omega^{(1)}(E^{(1)})\Omega^{(2)}(E^{(2)}), \tag{4.9}$$

(the index $_b$ reminds that in this initial configuration there is the barrier (later it will be removed)) where $\Omega^{(1)}(E^{(1)})$ is the number of configurations relative to system 1 compatible with energy $E^{(1)}$ and similarly for $\Omega^{(2)}(E^{(2)})$. Since $\Omega^{(1)}(E^{(1)})$ and $\Omega^{(2)}(E^{(2)})$ are the degeneracies of the two subsystems, Eq. (4.9) follows from the fact that for each macroscopic state corresponding to an energy $E^{(1)}$ there are $\Omega^{(2)}(E^{(2)})$ states corresponding to an energy $E^{(2)}$.

What happens if the barrier between 1 and 2 is removed so that the two systems can exchange energy (for simplicity let us assume that they cannot exchange particles, i.e. we consider solids. One can trivially extend the following arguments to the case when also particles can be exchanged), keeping fixed all the external parameters (so that no work is done on the two systems)? In this new situation, all configurations that were allowed before are still allowed, but now that systems 1 and 2 can exchange energy, the full system $1+2$ can also be in microscopic states that correspond to configurations in which the energy of 1 and 2 could be different from before, provided the total energy is kept constant. If we call $\Omega^{(1+2)}$ the number of states accessible to the total system after removing the barrier, then

$$\Omega^{(1+2)} \geq \Omega_b^{(1+2)}. \tag{4.10}$$

Immediately after removing the barrier the system is not equally distributed in all of the $\Omega^{(1+2)}$ states but will only occupy a fraction $\Omega_b^{(1+2)}/\Omega^{(1+2)}$. If the system is not distributed in all its possible states, it is not in equilibrium because its distribution is not the one (3.24) of the microcanonic ensemble. We will see when we studying non-equilibrium Statistical Mechanics that a system which is not uniformly distributed in its microscopic accessible states will evolve towards an equilibrium macroscopic state in which all microscopic states are equally probable.

Once the system has reached equilibrium, what is the value of the average energy of system 1 at equilibrium? What is the energy probability distribution $P(E^{(1)})$?

Assuming additivity

$$E^{(1+2)} = E^{(1)} + E^{(2)}, \tag{4.11}$$

the number of configurations accessible to the combined system $1+2$ is

$$\Omega^{(1+2)}(E^{(1+2)}) = \sum_{E^{(1)}} \Omega^{(1)}(E^{(1)})\Omega^{(2)}(E^{(2)}). \tag{4.12}$$

Here $\Omega^{(1)}(E^{(1)})$ and $\Omega^{(2)}(E^{(2)})$ are the number of configurations accessible to subsystems 1 and 2 when they have energies $E^{(1)}$ and $E^{(2)}$.

If system $1+2$ has reached equilibrium in isolation for the equal a priori probability postulate, it has the same probability of being in one of the accessible microscopic states. Therefore the probability $P^{(1+2)}(E^{(1)})$ that system $1+2$ is in a macroscopic state such that the subsystem 1 is in a state of energy $E^{(1)}$ and 2 in a state of energy $E^{(2)}$ is given by the number of configurations $\Omega^{(1+2)}(E)$ which realize this event, divided by the total number of accessible configurations,

$$P^{(1+2)}(E^{(1)}) = \frac{\Omega^{(1)}(E^{(1)})\Omega^{(2)}(E^{(2)})}{\Omega^{(1+2)}}. \tag{4.13}$$

Since $P^{(1+2)}(E^{(1)})$ is the product of a rapidly increasing function $[\Omega^{(1)}(E^{(1)}) \sim (E^{(1)} - E_0^{(1)})^{\mathcal{F}^{(1)}}]$ and a rapidly decreasing function $[\Omega^{(2)}(E^{(1+2)} - E^{(1)}) \sim (E^{(1+2)} - E^{(1)} - E_0^{(2)})^{\mathcal{F}^{(2)}}]$ of $E^{(1)}$, $P(E^{(1)})$ has an extremely pronounced maximum around a value $\overline{E}^{(1)}$.

We will later see that this distribution becomes a Gaussian extremely peaked around the maximum value $\overline{E}^{(1)}$ if the degrees of freedom of the two subsystems $\mathcal{F}^{(1)}$ and $\mathcal{F}^{(2)}$ are both large. Therefore the $\overline{E}^{(1)}$ coincides with the average energy, which for the postulate of Statistical Mechanics also coincides with the value of the measurement.

To find this value $\overline{E}^{(1)}$, we therefore must find the maximum of the probability $P^{(1+2)}(E^{(1)})$ or, more conveniently, of $\ln P^{(1+2)}(E^{(1)})$. To this end, we consider the equation

$$\left.\frac{\partial \ln P^{(1+2)}(E^{(1)})}{\partial E^{(1)}}\right|_{E^{(1)}=\overline{E}} = 0. \tag{4.14}$$

Using the fact that $\partial E^{(2)}/\partial E^{(1)} = -1$ (due to Eq. (4.11)), (4.14) leads to

$$\left.\frac{\partial \ln \Omega^{(1)}(E^{(1)})}{\partial E^{(1)}}\right|_{E^{(1)}=\overline{E}} = \left.\frac{\partial \ln \Omega^{(2)}(E^{(2)})}{\partial E^{(2)}}\right|_{E^{(2)}=\overline{E}^{(2)}} \tag{4.15}$$

Let us define

$$\beta(E) \equiv \frac{\partial \ln \Omega(E)}{\partial E} \tag{4.16}$$

The relation that determines the value $\overline{E}^{(1)}$ for which $P^{(1+2)}(E^{(1)})$ has a maximum and that expresses the equilibrium condition is

$$\beta^{(1)}(E^{(1)}) = \beta^{(2)}(E^{(2)}). \tag{4.17}$$

Since Ω is a number and β has the dimensions of an inverse of the energy. We can introduce a parameter T (which we will see coincide with the absolute temperature), through the relation

$$\beta^{-1} = kT, \tag{4.18}$$

where k is the Boltzmann constant. We next show that β has the properties of an inverse temperature.

- (i) It is an intensive variable.
- (ii) It regulates the thermal fluxes, namely:

  j)Two systems separately in equilibrium characterized by the same value of β will be in equilibrium if put in thermal contact (namely they can exchange energy without doing work, i.e., with all the parameters fixed).

  jj)Two systems separately in equilibrium and characterized by different values of β , will not be in equilibrium if put in thermal contact. In this case heat flows from the one with smaller β to the one with larger β. This can be understood as follows: Suppose that, starting from equilibrium $\beta^{(1)} = \beta^{(2)}$ we increase $\beta^{(1)}$ by a small amount $\delta\beta^{(1)} > 0$ and decrease $\beta^{(2)}$ by $\delta\beta^{(2)} < 0$ by transferring a small heat $\delta E^{(1)}$ (positive or negative we don't know at the moment) from 2 to 1. Next to Eq. (4.14) the condition of $\ln P^{(1+2)}$ being maximum requires also $\left.\frac{\partial^2 \ln P^{(1+2)}(E^{(1)})}{\partial (E^{(1)})^2}\right|_{E^{(1)}=\overline{E}} < 0$, that is $\left.\frac{\partial\beta^{(1)}}{\partial E^{(1)}}\right|_{E^{(1)}=\overline{E}} - \left.\frac{\partial\beta^{(2)}}{\partial E^{(1)}}\right|_{E^{(1)}=\overline{E}} < 0$. Since this relation must hold for any kind of system (different materials, different sizes of the two sub-systems etc...) this implies that $\delta E^{(1)}$ is positive, namely heat is transferred from 2 ($\beta^{(2)}$ smaller) to 1 ($\beta^{(1)}$ larger).

4.2.1 Form of $\mathbf{P}(\mathbf{E}^{(1)})$

We now show that $P^{(1+2)}(E^{(1)})$ becomes a Gaussian distribution when the degrees of freedom $\mathcal{F}^{(1)}$ and $\mathcal{F}^{(2)}$ are large. We expand $\ln P^{(1+2)}(E^{(1)})$ around the maximum (as we did in Chapter 3 for the distribution of particles in a box)

$$\ln P^{(1+2)}(E^{(1)}) = \ln P^{(1+2)}(\overline{E}^{(1)}) + \frac{1}{2}\left.\frac{\partial^2 \ln P^{(1+2)}(E^{(1)})}{\partial {E^{(1)}}^2}\right|_{E=\overline{E}^{(1)}} (E^{(1)} - \overline{E}^{(1)})^2 + \ldots . \tag{4.19}$$

Neglecting higher order terms we have

$$P^{(1+2)}(E^{(1)}) = P^{(1+2)}(\overline{E}^{(1)}) \exp\left[-\lambda(E^{(1)} - \overline{E}^{(1)})^2\right], \tag{4.20}$$

where

$$\lambda \equiv -\frac{1}{2}\left(\frac{\partial^2 \ln P^{(1+2)}(E^{(1)})}{\partial {E^{(1)}}^2}\right)_{E^{(1)}=\overline{E}^{(1)}} \tag{4.21}$$

is positive since $\overline{E}$ is a maximum for $P^{(1+2)}(E)$. For simplicity we set to zero the ground energies $E_0^{(1)} = E_0^{(2)} = 0$, so

$$\Omega^{(1)}(E^{(1)}) \sim \left(E^{(1)}\right)^{\mathcal{F}^{(1)}} \quad , \quad \Omega^{(2)}(E^{(2)}) \sim \left(E^{(2)}\right)^{\mathcal{F}^{(2)}} . \tag{4.22}$$

Hence from (4.13)

$$\lambda \simeq \frac{1}{2}\left(\frac{\mathcal{F}^{(1)}}{{\overline{E}^{(1)}}^2} + \frac{\mathcal{F}^{(2)}}{{\overline{E}^{(2)}}^2}\right). \tag{4.23}$$

If both systems are macroscopic, we can for simplicity consider the case $\mathcal{F}^{(1)} \approx \mathcal{F}^{(2)} \approx \mathcal{F}$. Then

$$\overline{E}^{(1)} \sim \overline{E}^{(2)} \approx \overline{E} \qquad \text{and} \qquad \lambda \sim \mathcal{F}^{-1} \tag{4.24}$$

and the width of the Gaussian $w = 1/\sqrt{\lambda} \sim \sqrt{\mathcal{F}}$, hence

$$\frac{w}{\overline{E}} \sim \frac{1}{\sqrt{\mathcal{F}}}. \tag{4.25}$$

Thus the relative fluctuation approaches zero for $\mathcal{F}$ very large, and the n^{th} order derivative of P goes as $\mathcal{F}/\overline{E}^n \sim \mathcal{F}^{1-n}$. Therefore, using the argument of Chapter 2, we can neglect all the terms in the expansion (4.19) with powers larger than 2.

4.3 Definition of Entropy in Statistical Mechanics

In the previous section we have already observed that, after removing the constraint represented by the separation wall between the subsystems 1 and 2 the total number of allowed configurations increases and therefore $\ln \Omega$ increases. The increase of $\ln \Omega$ is completely general for any isolated system which is let to evolve naturally by removing a (internal) constraint. This suggests that this quantity might be related to the entropy.

We now demonstrate that the function S, defined as

$$S \equiv k \ln \Omega, \tag{4.26}$$

coincides with the entropy defined in Thermodynamics.

Let us consider a system characterized by an energy E in equilibrium. Let us now imagine to add an infinitesimal amount of energy δE from the outer world without doing work on the system (for instance by putting it in contact for a short time with a hotter object, and then isulating it again). Then we wait enough for the system to equilibrate again. In this process the number of states will change by an amount

$$d(\ln \Omega) = \frac{\partial \ln \Omega}{\partial E} \delta E. \tag{4.27}$$

Taking into account that the transfer of energy $\delta E = \delta Q$ is by definition the amount of heat exchanged (since all the external parameters – i.e., particle numbers, volume, etc. – are kept constant), we have from (4.16)

$$d(\ln \Omega) = \frac{\delta Q}{kT}. \tag{4.28}$$

Since $d(\ln \Omega)$ is an exact differential (because it is the variation of the number of microscopic states), it follows that $\beta = 1/kT$ is the integral factor that makes δQ an exact differential (it is possible to show that the integral factor is unique, apart from a multiplicative constant). Moreover, from the second law of Thermodynamics we know that

$$dS = \frac{\delta Q}{T}, \tag{4.29}$$

where dS is an exact differential and defines the entropy. Therefore the quantity T that appears in (4.28) coincides with the absolute temperature T which appears in (4.29) (we will see that the multiplicative constant is equal to unity) and, from (4.28) and (4.29), we have

$$dS = kd(\ln \Omega), \tag{4.30}$$

This differential relation defines the entropy apart from a multiplicative constant. In order to fix it we postulate that at zero temperature there is no degeneracy ($\Omega = 1$). Then by integrating (4.30) from a state at zero temperature to any other macroscopic state, we obtain the desired result (4.26). In this way by assuming $\Omega = 1$ at zero temperature we have given a physical interpretation to the third law of Thermodynamics, which states that $S \to 0$ as $T \to 0$.

4.4 Definition of other quantities (pressure, chemical potential etc...) in Statistical Mechanics.

We have shown that $kd(\ln \Omega)$ coincides with the differential entropy dS defined in Thermodynamics when the system exchanges an infinitesimal amount of energy with a reservoir, while all the other parameters are kept fixed. We now show that this identification also holds when in an infinitesimal transformation the external parameters also change. Let us consider for simplicity that only one external parameter changes from X to $X + dX$ (X, for example, could be the volume of the system). We denote by $\Omega(E, X)$ the number of states between E and $E + \delta E$. When the parameter X changes from X to $X + dX$, the generic state r with energy E_r belonging to the interval between E and $E + \delta E$ will change from E_r to $E_r + (\partial E_r/\partial X)dX$. As a consequence there will be a number of states that will enter into the interval $(E, E + \delta E)$ and some that will go out. This shift of states will therefore result in a change of $\Omega(E, X)$. To evaluate quantitatively such a change it is convenient to write

$$\Omega(E, X) = \sum_r g(E_r(X) - E), \tag{4.31}$$

where

$$g(E_r(X) - E) = \begin{cases} 1 & \text{if } \ 0 \le E_r(X) - E \le \delta E \\ 0 & \text{otherwise,} \end{cases} \tag{4.32}$$

Taking the derivative of (4.31) with respect to X we obtain:

$$\frac{\partial\Omega(E,X)}{\partial X} = -\sum_r \frac{\partial g(z_r)}{\partial E}\frac{\partial E_r}{\partial X}. \tag{4.33}$$

Here we have used the relations

$$\frac{\partial g}{\partial z_r} = -\frac{\partial g}{\partial E}, \qquad \frac{\partial z_r}{\partial X} = \frac{\partial E_r}{\partial X}. \tag{4.34}$$

with $z_r = E_r(X) - E$. From (4.33), it follows that

$$\frac{\partial\Omega(E,X)}{\partial X} = \frac{\partial}{\partial E}[\Omega(E,X)\overline{f}] = \left(\overline{f}\,\frac{\partial\Omega(E,X)}{\partial E} + \Omega(E,X)\,\frac{\partial\overline{f}}{\partial E}\right), \tag{4.35}$$

where $\overline{f}$ is the average value of $-\partial E/\partial X$

$$\overline{f} \equiv -\langle\partial E/\partial X\rangle \equiv \frac{-1}{\Omega(E,X)}\sum_r g(E_r(X)-E)\frac{\partial E_r}{\partial X}. \tag{4.36}$$

[Indeed using Leibenitz rule ($\frac{\partial\overline{f}}{\partial E} = -\frac{1}{\Omega}\frac{\partial\Omega}{\partial E}\overline{f} +$ *second term*), the first term on the r.h.s. of the equation above, plugged into the second term on r.h.s. of Eq. (4.35) cancels the first term, and what referred above as *second term* gives the result.]

Hence, from Eq. (4.36), $-\overline{f}dX$ is the internal variation of the energy, due to the change from X to $X+dX$ of the control parameter X and therefore

$$\overline{f}dX = \delta W, \tag{4.37}$$

is the work δW done by the system on the external world. For this reason $\overline{f}$ is the generalized force introduced in Sec. 1.2.2.

From (4.35), dividing by $\Omega(E,X)$,

$$\frac{\partial\ln\Omega}{\partial X} = \overline{f}\,\frac{\partial\ln\Omega}{\partial E} + \frac{\partial\overline{f}}{\partial E}, \tag{4.38}$$

For large values of the degree of freedom $\mathcal{F}$, evaluating the order of magnitude of the two terms on the right side of (4.38) gives

$$\overline{f}\,\frac{\partial\ln\Omega}{\partial E} \sim \overline{f}\,\frac{\mathcal{F}}{E}, \tag{4.39}$$

where we have used (4.8); moreover,

$$\frac{\partial\overline{f}}{\partial E} \sim \frac{\overline{f}}{E}. \tag{4.40}$$

In conclusion, in the limit of extremely large $\mathcal{F}$,

$$\frac{\partial \ln \Omega}{\partial X} = \beta \overline{f}. \tag{4.41}$$

In the particular case in which X is the volume V, then

$$\overline{f} dV = \delta W, \tag{4.42}$$

therefore $\overline{f} \equiv P$ is the pressure.

If X is the number of particles N, then

$$\overline{f} dN = \delta W, \tag{4.43}$$

and

$$\overline{f} = -\mu \tag{4.44}$$

is the chemical potential. If there are $X_\alpha (\alpha = 1 \dots k)$ different parameters, (4.41) can be generalized

$$\frac{\partial \ln \Omega(E, X_\alpha)}{\partial X_\alpha} = \beta \overline{f}_\alpha. \tag{4.45}$$

In conclusion, from $\ln \Omega$ we can calculate both the temperature

$$\frac{\partial \ln \Omega(E, X)}{\partial E} = \beta, \tag{4.46}$$

and the generalized force

$$\frac{\partial \ln \Omega(E, X)}{\partial X} = \beta \overline{f}. \tag{4.47}$$

If X is the volume, we can find the equilibrium condition for two systems that can exchange heat and volume. Using the same arguments as before (4.40), the equilibrium conditions are obtained by maximizing the probability. Namely, by imposing that both derivatives of the probability with respect to E and X must be zero, we obtain

$$\beta^{(1)} = \beta^{(2)} \qquad \text{and} \qquad \overline{f}^{(1)} = \overline{f}^{(1)}, \tag{4.48}$$

where $\overline{f}^{(1)}$ and $\overline{f}^{(2)}$ are the pressures of the two systems.

If the system can also exchange particles, then $X^{(1)}$ and $xX^{(2)}$ denote the numbers of particles, while $\overline{f}^{(1)}$ and $\overline{f}^{(2)}$ denote the corresponding chemical potentials. In general, the equilibrium conditions for two systems which can exchange heat and any parameter X_α is given by $\beta^{(1)} = \beta^{(2)}$ and $\overline{f}_{\alpha}^{(1)} = \overline{f}_{\alpha}^{(2)}$. These conditions will be studied in more detail for the particular case in which $X = N$ is the number of particles (see Chapter 8).

Finally we consider a transformation from one equilibrium state characterized by (E, X) to another equilibrium state characterized by $(E + \delta E, X + \delta X)$. We have

$$d \ln \Omega(E, x) = \frac{\partial \ln \Omega}{\partial E} dE + \frac{\partial \ln \Omega}{\partial X} dX = \beta dE + \beta \overline{f} dX, \qquad (4.49)$$

from which

$$dE = \beta^{-1} d(\ln \Omega) - \overline{f} dX = k_B T d(\ln \Omega) - \overline{f} dx, \qquad (4.50)$$

where dE is the variation of total energy and $f dX$ the mechanical work done. Thus $\beta^{-1} d(\ln \Omega)$ is by definition the heat exchanged δQ, and

$$kd(\ln \Omega) = \frac{\delta Q}{T}. \qquad (4.51)$$

In conclusion, we find that $dS = kd(\ln \Omega)$ for a general transformation.

We are now in a position to better understand the physical meaning of the second law of Thermodynamics. The increase of the entropy in any process that evolves spontaneously corresponds to the fact that the system evolves toward macroscopic states which are most probable. How do we explain the dichotomy between microscopic reversibility and macroscopic irreversibility? The laws of classical mechanics are invariant under time reversal. This means that if we start from a microscopic state and let it evolve in time, the laws of mechanics tell us that, if we reverse the velocities of all particles, the system will go back into the initial configuration following the same phase space trajectory in the opposite direction. For example, two liquids initially at different temperatures when put in thermal contact will reach an homogeneous state at some intermediate temperature. If we reverse the velocities of all the particles, the system will evolve towards the initial state in which one subsystem is at a temperature different from the other. Why do we never observe that a liquid separates into a warmer region and a colder region? In principle, this process is allowed by the laws of mechanics but, in order for it to occur, the system must be in a very special configuration, one that has the property of evolving towards a state characterized by two regions at different temperatures. The number of such configurations is extremely small compared to the total number of allowed configurations. Therefore the probability that one of these particular configurations occurs is infinitesimally small for a macroscopic system.

4.5 Continuous variables

The definition of entropy given previously is based on the number of configurations accessible to the system for a fixed value of the energy E, the number of particles N , and the volume V. Although this definition makes perfect sense for a quantum mechanical system in which the states are discrete, for a classical system described in terms of continuous variables this definition needs to be modified since the states are not discrete and the number of states accessible is always infinite. This problem can be circumvented by dividing the phase space in cells of volume

$$\omega_0^N = (\delta q \delta p)^{3N} \tag{4.52}$$

The cell can be chosen small enough that, loosely speaking, all points in the cell are representative of microstates which do not differ much from each other. If $\Delta\Gamma$ is the volume of phase space accessible to the system, the number of accessible cells is given by $\Omega = \Delta\Gamma/\omega_0^N$ and the entropy for classical systems can be defined as

$$S = k \ln \frac{\Delta\Gamma}{\omega_0^N}. \tag{4.53}$$

With this definition, all the properties obtained in the case of discrete states are valid also here. The only question now is the choice of ω_0. This choice will affect the entropy only by a constant. Later, in chapter 6 we will discuss in detail how to choose ω_0 (we anticipate $\omega_0 = h^3$ where h is the Planck constant) using a technique that compares the entropy of a classical ideal gas with that of a quantum ideal gas.

Chapter 5

Systems with finite energetic levels

5.1 Two level systems

Let us consider a system of N identical non-interacting constituents (we can think to particles here, but they can be different entities like for instance magnetic moments – see Sec. 5.2), for each of which two energetic states, denoted as 0 and 1, are only possible. Without loss of generality we can fix the energy of the two levels to be $e_0 = 0$ and $e_1 = \epsilon$. Then the Hamiltonian is

$$\mathcal{H} = \epsilon \sum_{i=1}^{N} n_i = \epsilon M \tag{5.1}$$

where i is an index which labels particles, $n_i = 0, 1$ is the single particle *occupation number* of the excited state ($n_i = 0$ if the i-th particle occupy the lowest energy level and $n_i = 1$ if it is in the high energy state). In the microcanonical ensemble the system is supposed to be isolated, the energy does not fluctuate and is given by Eq. (5.1).

The number Ω of microstates equals

$$\Omega(E, N) = \frac{N!}{(N-M)!M!} \tag{5.2}$$

namely the number of ways to accomodate N particles into two boxes (permutations of N objects allowing repetitions). Notice that Eq. (5.2) implies that we have assumed the identical particles indistinguishable, namely we do not count as different two states which only differ by the exchange of the particles inside the two levels. We will return on this important point in Sec. 6.3.

Using Stirling's approximation, for the entropy one finds

$$S(E,N) = k \ln \Omega \simeq k[N \ln N - M \ln M - (N-M) \ln(N-M)] \quad (5.3)$$

Notice that the entropy is extensive, as it should (indeed S/N is a function of the intensive variable N/M only). It is easy to check that this would not have been the case if the identical particles were considered distinguishable.

We are now in the position to compute, using the relations of Chapter 4, the temperature of the system

$$\beta = \frac{\partial S}{\partial E} = \frac{\partial S}{\partial M}\frac{\partial M}{\partial E} = \frac{k}{\epsilon} \ln\left(m^{-1} - 1\right), \quad (5.4)$$

where $m = \langle n_i \rangle = M/N$ is the average occupation number of the excited level (which does not depend on i since the particles are identical). Inverting this relation one finds

$$m = \frac{1}{1 + e^{\beta\epsilon}} \quad (5.5)$$

This shows that in the limit of low temperatures $T \to 0$ all the particles tend to occupy the lower energy level, while in the opposite situation $T \to \infty$ the two energy levels are randomly occupied. This shows that the high temperature limit corresponds to the most *disordered* state (the two states have equal occupancy probability), not to the most energetic one, as one could naively believe.

5.1.1 Negative temperatures

The behavior of S and β as a function of m are shown in Fig. 5.1.

The first observation is that the entropy has a maximum at $m = 1/2$. This implies that the temperature becomes negative when the occupation number is larger than 1/2. This particular behavior is typical of systems exhibiting a bounded set of energy levels. Usually for a system like a gas or liquid, the energy levels are unbounded, and S is a monotonic function of the energy. In this case, when T becomes sufficiently large, the system tends to be in states with high energy in order to make the entropy large. A peculiarity of the system with limited level energy, is that the entropy cannot increase indefinitely upon increasing the energy, since there is only

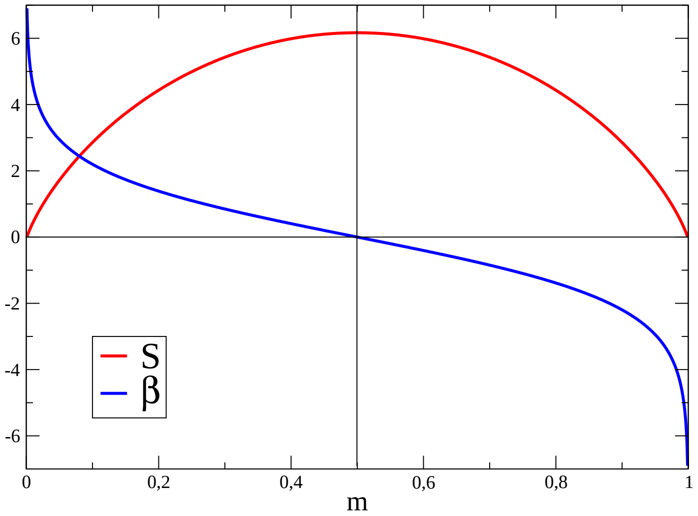

Figure 5.1: Entropy and inverse temperature of a two-level system.

one microstate corresponding to the maximum energy. Hence S must have a maximum for a certain value of the energy (in this case for $E = \epsilon N/2$), and above that value it decreases with E, producing a negative temperature.

A system with negative temperature in contact with a *normal* system with positive temperature will transfer energy until it reaches an equilibrium temperature. Since the *normal* system has always a positive temperature whatever the energy is, the final equilibrium temperature will always be positive. Negative temperature corresponds therefore to *superhot* systems, that only special systems can achieve.

Negative temperatures can be produced in the laboratory for instance when dealing with magnetic systems, how we will see in the next section.

5.2 Paramagnetism

The experiment of Stern and Gerlach showed that electrons have an intrinsic angular momentum called spin, which can be interpreted as due to the *rotation* of the electron around itself, and a magnetic dipole associated with the spin. In general, an atom has spin.

A material that has the property of possessing a magnetic moment proportional to an applied external field H is called a paramagnet. A simple model for a paramagnet is made of N magnetic atoms in fixed positions. Let us assume that each atom has a magnetic moment $\vec{\mu}_i$.

If the system is in an external field H and the magnetic moments of one atom do not interact with those of other atoms, then the Hamiltonian can be written as

$$\mathcal{H} = -\sum_{i=1}^{N} \vec{\mu}_i \cdot \vec{H} = -H \sum_{i=1}^{N} \mu_i^{(z)}, \tag{5.6}$$

where we have chosen the axis z along the direction of the field H, and $\mu_i^{(z)}$ is the projection of $\vec{\mu}_i$ along the z direction.

According to quantum mechanics, for spin 1/2 particles the component of the magnetic moment along the field can assume only the two values $\mu_i^{(z)} = \pm\mu_0$ where we have put $\mu_0 = \frac{1}{2}\mu_B$[1].

For convenience, let us introduce a *spin* variable that can assume two values $S_i = \pm 1$. The Hamiltonian (5.6) can then be written as

$$\mathcal{H} = -\mu_0 H \sum_{i=1}^{N} S_i. \tag{5.7}$$

where $S = \pm 1$ corresponds respectively to the spin up or down. Transforming the spin variables $S_i = \pm 1$ to $n_i = 0, 1$ by means of

$$n_i = 1 - 2S_i \tag{5.8}$$

the Hamiltonian reads

$$\mathcal{H} = 2\mu_0 H \sum_{i=1}^{N} n_i - 2N\mu_0 H. \tag{5.9}$$

With the position $\epsilon = 2\mu_0 H = \epsilon$ the Hamiltonian is identical (apart from an irrelevant additive constant $-2N\mu_0 H$) to that of Eq. (5.1). All the statistical mechanical tratment of Sec. 5 can therefore be repeated.

An experimental way to prepare a system with negative temperature is to apply a field to a crystal whose atoms possess a magnetic moment. By reversing the field, the system will be in an energy state

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[1] In general, spin is a vector $\vec{S}$ whose magnitude is given by $\sqrt{S(S+1)}\hbar$. The component of the spin along the z direction is given by $S_z = \hbar m_s$. The magnetic moment associated with the spin is proportional to $\vec{S}$ with a proportionality constant g, $\vec{\mu} = -g\vec{S}$; $\mu_z = \mu_B m_s$, where μ_B denotes the Bohr magneton and m_s is a discrete quantum number which assumes the value $-S, -S+1, \ldots, S$. The value of S can be integer (bosons) or half integer (fermions). For $S = 1/2$, $m_s = \pm 1/2$.

very large, corresponding to negative temperature. However, even if the system is isolated from the environment, the spins variable can release energy to the cristal lattice and hence they cannot be truely considered as isolated. Therefore, usually after a relaxation time, the spins will release energy to the lattice until a uniform temperature is reached. For this reason, a state with negative temperature does not live long and hence are rarely seen outside the laboratory.

Chapter 6

Ideal gases

6.1 Classical Ideal Gas

We calculate now the entropy for a classical ideal gas made of N monatomic particles of mass m in a volume V . The Hamiltonian can be written as

$$\mathcal{H}(p,q) = \sum_{i=1}^{3N} \frac{p_i^2}{2m}. \tag{6.1}$$

If we consider molecules belonging to an energy shell of size δE, than the accessible volume $\Delta\Gamma$ of phase space is

$$\Delta\Gamma = \int dq_1 dq_2 \dots dq_{3N} \int_{E \le \mathcal{H}(p,q) \le E+\delta E} dp_1 dp_2 \dots dp_{3N}. \tag{6.2}$$

The integral over the variable q is over the volume occupied by the particles and gives a factor V^N . The integral over the variable p can be computed by calculating first the accessible volume in phase space for all the states $0 \le \mathcal{H}(p,q) \le E$

$$\Gamma = V_N \int_{0 \le \mathcal{H}(p,q) \le E} dp_1 \dots dp_{3N}, \tag{6.3}$$

and then differentiate to get

$$\Delta\Gamma = \frac{d\Gamma}{dE} \delta E. \tag{6.4}$$

Given the form of the Hamiltonian (6.1), the integral over the momentum in (6.2) is given by the hypervolume in momentum space such that

$$\sum_{i=1}^{3N} \frac{p_i^2}{2m} \leq E. \tag{6.5}$$

For a fixed value of E, Eq. (6.5) describes a hypersphere of radius $R(E)$ in a $3N$ coordinate space, with

$$R(E) = (2mE)^{1/2}. \tag{6.6}$$

The volume of such a hypersphere is proportional to R^{3N}. Therefore

$$\int dq_1 dq_2 \dots dq_{3N} \int_{E \leq \mathcal{H}(p,q) \leq E+\delta E} dp_1 dp_2 \dots dp_{3N} = B_N R^{3N}, \tag{6.7}$$

where B_N is the unit sphere volume, which depends only on N and not on R

$$B_N = \frac{\pi^{3N/2}}{\Gamma(3N/2+1)}. \tag{6.8}$$

In the following, for simplicity, we will assume that $3N/2$ is an integer. Then the Γ function reduces to the usual factorial and

$$B_N = \frac{\pi^{3N/2}}{(3N/2)!}. \tag{6.9}$$

Thus

$$\frac{\Gamma}{\omega_0^N} = \left(\frac{V}{\omega_0}\right)^N B_N (2mE)^{3N/2}. \tag{6.10}$$

Differentiating with respect to E, we find

$$\frac{\Delta\Gamma}{\omega_0^N} = \frac{3}{2}\left(\frac{V}{\omega_0}\right)^N B_N (2mE)^{3N/2} \frac{N\delta E}{E} = \frac{3}{2}\frac{\Gamma}{\omega_0^N}\frac{N\delta E}{E}. \tag{6.11}$$

Taking the logarithm of (6.11), and using Stirling's approximation for B_N (6.9), we find for $\Omega = \Delta\Gamma/\omega_0^N$

$$\ln\Omega = N \ln\left[\frac{V}{\omega_0}\left(\frac{4\pi m E}{3N}\right)^{3/2}\right] + \frac{3}{2}N, \tag{6.12}$$

where we neglect terms of order of $\ln N$ such as $\ln(N\delta E/E)$. In fact, E is of the order of N while δE is, at most, of the order of the energy E, and therefore, at most, of the order of N.

Note that if N is very large – of the order of 10^{24} for macroscopic systems – then $\ln N/N \sim 10^{-22}$ and terms of $\ln N$ are completely negligible compared to N. For this reason, from Eqs. (6.10) and (6.11), $\ln \Delta\Gamma$ and $\ln \Gamma$ are practically identical. Namely, the volume of a hypersphere coincides with the volume of the infinitesimal shell when the number of space dimensions approaches infinity.

The entropy can be readily obtained from Eq. (6.12) by the relation $S = k \ln \Omega$. Notice that this quantity is not extensive (there is an extra V in the ln). This implies that our theory is yet incomplete (we anticipate that the question is how to distinguish among identical particles). We will discuss how this problem can be solved in the next section 6.3 by considering an appropriate correction to the theory. For the moment let us find the relations between E, T, P and V which, how it will be clear in Sec. 6.3, are not spoiled by that correction.

Using the equations relating the absolute temperature and the pressure derived in Chapter 4,

$$\beta = \frac{\partial \ln \Omega}{\partial E} \tag{6.13}$$

and

$$\beta P = \frac{\partial \ln \Omega}{\partial V}, \tag{6.14}$$

we obtain from Eq. (6.12)

$$E = \frac{3}{2} NkT \tag{6.15}$$

and

$$PV = NkT. \tag{6.16}$$

Relation (6.16) shows that the temperature $T = 1/k\beta$ defined through (6.13) coincides with the absolute temperature of the ideal gas. Eq. (6.15) is a manifestation of the so called *equipartition theorem*, stating that each independent quadratic variable in the Hamiltonian provides an average energy $(1/2)kT$. We will prove this theorem in Sec. 7.7.

6.2 Quantum Ideal Gas

Now we consider the energy spectrum for a system of particles that obey quantum mechanics. We treat the system quasi-classically in the sense that we consider only the quantization of the energy. The full quantum treatment will be presented later.

The energy spectrum of a particle in a 3-dimensional box of volume $V \equiv L^3$ is

$$\epsilon = \frac{\hbar^2 \pi^2}{2m} \frac{1}{L^2} (n_1^2 + n_2^2 + n_3^2), \tag{6.17}$$

where $n_1, n_2, n_3 = 0, 1, 2, \ldots$. For a system of N particles,

$$\epsilon = \frac{\hbar^2 \pi^2}{2m} \frac{1}{V^{2/3}} \sum_{i=1}^{3N} n_i^2. \tag{6.18}$$

As in the classical case, we calculate the number of states corresponding to an energy between 0 and E. The states correspond to the set of integers $\{n_i\}$ for which

$$0 \leq \sum_{i=1}^{3N} n_i^2 \leq \frac{2m}{\hbar^2} \frac{V^{2/3}}{\pi^2} E = R^2, \tag{6.19}$$

namely, all the points with integer coordinates inside a hypersphere of radius R. The number of points coincides with the volume of such a region if we consider the n_i's as continuous coordinates. The discrepany is anyway negligible in the limit of very large N. To calculate the volume of such region one needs to calculate the the volume of the hypersphere of radius R in $3N$ dimensions, devided by 2^{3N} (this is because the single particle quantum numbers n_1, n_2, n_3 in Eq. (6.17) can only be positive. This is exactly the same problem as in the classical case with the replacement $R_{classic} \to R_{quant} = V^{1/3}/(2\pi\hbar)$ (but in the classical case there was an extra volume coming from the integration over the positions).

In conclusion repeating the calculation along the same lines as done in the classical case, we obtain for the number of configurations Ω with energy between E and $E + \delta E$ the same result of the classical case but with the value of the elementary cell given explicitly as $\omega_0 = h^3$. It follows that

$$\ln \Omega = N \ln \left[\frac{V}{h^3} \left(\frac{4\pi m E}{3N} \right)^{3/2} \right] + \frac{3}{2} N. \tag{6.20}$$

The receipt to fix ω_0, that we have derived in a specific example, is completely general. Let us observe that we have to resort to the quantum properties of the system to fix ω_0. Indeed, its physical origin is related to Heisenberg's uncertainty principle: we cannot resolve states within a precision of order $\Delta q \Delta p \simeq \hbar/2$.

6.3 Identical particles

From the expressions (6.12) and (6.20) of $S/k = \ln \Omega$, we note that the entropy does not have the property of being an extensive quantity, namely, if we double volume V , energy E, and number of particles N , the entropy should also double. To generalize, if we make the transformations

$$V \to \lambda V \qquad E \to \lambda E \qquad N \to \lambda N. \tag{6.21}$$

the entropy should transform: $S \to \lambda S$. The lack of this property is due to the presence of the volume alone in the log term (6.12), unlike the energy which appears divided by N.

6.3.1 Gibbs paradox

Another (related) unsatisfying feature of the theory comes about, as pointed out originally by Gibbs, when one considers a system of two gases in a, adiabatic container as the one in Fig. 1.1 (right panel). Here the two subsystem have volumes V_1 and V_2 and are filled with N_1 and N_2 molecules of the two perfect gases, respectively. The two subsystems are initially separated by an internal wall, i.e. the two gas are unmixed, and at some instant of time the wall is removed and the two gases mix. According to Eq. (6.12) before removing the wall the entropy is given by

$$S_{unmix} = k \left(N_1 \ln a_1 V_1 + N_2 \ln a_2 V_2 + \frac{3}{2} N \right), \tag{6.22}$$

where $N = N_1 + N_2$ and $a_1 = \frac{1}{\omega_0} \left(\frac{4\pi m E_1}{3N_1} \right)^{3/2}$ and similarly for a_2. After removing the wall, the system attains a new equilibrium state with entropy

$$S_{mix} = k \left(N_1 \ln a_1 V + N_2 \ln a_2 V + \frac{3}{2} N \right), \tag{6.23}$$

where $V = V_1 + V_2$. The mixing entropy is therefore

$$\Delta S = k \left(N_1 \ln \frac{V}{V_1} + N_2 \ln \frac{V}{V_2} \right) > 0 \tag{6.24}$$

If the two gases are different this result is perfectly natural and states that the entropy of mixing is the thermodynamic force which drives the mixing process (the two gases mix because in doing so the entropy increases). However, if 1 and 2 contained initially the same gas this result is a disaster. Indeed this would imply that the entropy of a system (without the wall) containing a certain gas depends on whether it was initially prepared into two separate boxes or not. In other words a thermodynamic quantity (S) would depend on the history of the system, and hence it would not be a state variable.

6.3.2 Solution of the paradox

This paradox was resolved by Gibbs who introduced an *ad hoc* hypothesis – which, although intuitive, does not find justification with classical mechanics. The idea is that two states which are obtained by exchanging the coordinates of two particles should not be considered as two distinct states, since the particles should be indistinguishable. Assuming that each state of single particle is occupied by no more than one particle, the number of configurations calculated before has overestimated the number of states by a factor of $N!$ – the number of permutations of N particles.

The correct number of states Ω_{corr} is then given by

$$\Omega_{corr} = \frac{\Omega}{N!}. \tag{6.25}$$

This is usually denoted as the *correct Boltzmann counting.* By using the expression for Ω (6.12) and applying Stirling's approximation, one finds

$$S = k \ln \Omega_{corr} = N \ln \left[\frac{V}{h^3 N} \left(\frac{4\pi m E}{3N} \right)^{3/2} \right] + \frac{5}{2} k N, \tag{6.26}$$

which now has the correct additive property, since the volume V now is divided by N. This is the so called *Sackur-Tetrode* expression of the ideal gas entropy. Note that this extra factor N does not affect the calculation for the equation of state and the temperature since these calculations arise from derivatives of the entropy with respect to E and V by Eqs. (6.13) and (6.14). The correct Boltzmann counting tame also the mixing paradox. Indeed, keeping it into account one has, instead of Eq. (6.23)

$$S_{unmix} = k \left[N_1 \ln(a_1 v_1) + N_2 \ln(a_2 v_2) + \frac{5}{2} N \right], \tag{6.27}$$

where $v_1 = V_1/N_1$ is the specific volume (and similarly for v_2). Notice that, if the two gases are identical, in the sense that they have the same energy and volume per particle, then

$$a_1 = a_2 = a = \frac{1}{\omega_0}\left(\frac{4\pi mE}{3N}\right)^{3/2} \tag{6.28}$$

(see definition (6.27) of a_1, a_2) and

$$v_1 = v_2 = v = V/N, \tag{6.29}$$

and Eq. (6.27) can be written as

$$S^{(eq)}_{unmix} = k\left[N\ln(av) + \frac{5}{2}N\right], \tag{6.30}$$

After the mixing, instead of Eq. (6.27) one finds

$$S^{(diff)}_{mix} = k\left[N_1\ln\left(a_1\frac{V}{N_1}\right) + N_2\ln\left(a_2\frac{V}{N_2}\right) + \frac{5}{2}N\right], \tag{6.31}$$

if the two gases are different, and

$$S^{(eq)}_{mix} = k\left[N_1\ln\left(a_1\frac{V}{N}\right) + N_2\ln\left(a_2\frac{V}{N}\right) + \frac{5}{2}N\right] = k\left[N\ln(av) + \frac{5}{2}N\right], \tag{6.32}$$

with $a = a_1 = a_2$ (because, being equal, the two gases after mixing must have the same energy per particle, see definition (6.27) of a_1) and $v = V/N$,

if they are equal. Hence one finds

$$\Delta S^{(diff)} = k\left[N_1\ln\frac{V}{V_1} + N_2\ln\frac{V}{V_2}\right] > 0 \tag{6.33}$$

when the two gases are different and

$$\Delta S^{(eq)} = 0 \tag{6.34}$$

if they are equal. The paradox is then resolved.

In conclusion, to treat a classical system one must introduce two *ad hoc* requirements: (i) the elementary cell ω_0 in phase space must be chosen $\omega_0 = h^3$; (ii) the particles must be considered indistinguishable. These two requirements have no proper justification within classical mechanics. We will show later that a proper quantum mechanical treatment of a system of N particles in the *classical* limit of high temperature and low density reproduce the classical result, corrected by these two ad hoc requirements.

Chapter 7

Canonical Ensemble

7.1 The Ensemble Distribution

In Chapter 3, we considered an isolated system and we postulated that, at equilibrium, such a system is described by an ensemble that is uniformly distributed over all microstates (microcanonical ensemble), i.e., we postulated that the system at equilibrium can be found in each of its many allowed configurations with equal probability. Most often we deal with systems that are in contact with a heat reservoir at constant temperature. What is the probability that we will find such a system in one of its allowed configurations?

To be more specific, consider a system A in thermal contact with a system A', where A' is much larger than A, and assume the systems A and A' have reached equilibrium. We consider the case in which the interaction between systems A and A' is so small that we can consider the states of system A independent of system A'. We also consider here the case of discrete states. The extension to the classical case appears in the next section of this chapter. We address the question: If r is a particular microstate of A corresponding to an energy E_r , what is the probability P_r of finding A in such a microstate?

Although A can exchange energy with A' , system $A + A'$ is isolated. Since the system is in equilibrium, we can apply to such an isolated system the postulate of equal a priori probability. Therefore P_r is proportional to the number of configurations relative to system $A + A'$, in which subsystem A is in the configuration r and subsystem A' is in any of its configurations r' compatible with configuration r. Since system $A + A'$ is isolated, the total energy is fixed, so the sum of the energy of A and A' must always equal the total energy E_{tot} . Hence the configurations r' of A' compatible with r are those corresponding to an energy E' such that $E' + E_r = E_{tot}$.

Since A and A' are weakly interacting and by definition there is only one microstate r, the number of states $\Omega_{A+A'}(r, \{r'\})$ such that A is in state r and A' in any of the possible states r' is

$$\Omega_{A+A'}(r, \{r'\}) = 1 \cdot \Omega_{A'}(E'), \tag{7.1}$$

where $\Omega_{A'}(\{r'\})$ is the number of r' states. P_r is the ratio between the number of states $\Omega_{A+A'}(r, \{r'\})$ compatible with r and the total number of possible states $\Omega^{tot}_{A+A'}$ of the composite system $A+A'$. Using Eq. (7.1) one has

$$P_r = \frac{\Omega_{A'}(E')}{\Omega^{tot}_{A+A'}}. \tag{7.2}$$

Since we are considering the case where A and A' can only exchange energy (the number of particles and the volume of A and A' are kept fixed), states r can only differ by their energy. Hence we can write

$$P_r = \frac{\Omega_{A'}(E')}{\Omega^{tot}_{A+A'}} = \frac{\Omega_{A'}(E_{tot} - E_r)}{\Omega^{tot}_{A+A'}}. \tag{7.3}$$

If we take the logarithm of P_r in (7.3) and expand around $E_r = 0$, we find

$$\ln P_r = C - \left(\frac{\partial \ln \Omega_{A'}(E')}{\partial E'}\right)_{E'=E_{tot}} E_r + \ldots, \tag{7.4}$$

where C is a constant that does not depend on r. Since E_r is very small compared to E_{tot}, higher order terms can be neglected $\left(\text{In fact: } \Omega_{A'}(E') \sim E'^f \Rightarrow \left.\frac{\partial^k \ln \Omega_{A'}(E')}{\partial E'^k}\right|_{E'=E_{tot}} \sim \frac{f}{E^k_{tot}}\right)$. From (7.4)

$$P_r = \frac{1}{Z} e^{-\beta E_r}, \tag{7.5}$$

where

$$\beta = \left(\frac{\partial \ln \Omega_{A'}(E')}{\partial E'}\right)_{E'=E_{tot}}, \tag{7.6}$$

is the inverse temperature of system A' when its energy is $E' = E_{tot}$. Since system A' is much larger than system A, the energy of A' – when in equilibrium with A – practically coincides with energy E_{tot}.

The normalization factor Z is obtained by imposing $\sum_r P_r = 1$, so from (7.5)

$$Z = \sum_r e^{-\beta E_r} \tag{7.7}$$

The exponential factor $e^{-\beta E_r}$ is called the Boltzmann factor and Z is called the partition function. An ensemble of equivalent systems all in contact with a reservoir at a given temperature T that is distributed over all microstates according to distribution (7.5) is called a *canonical ensemble.*

7.2 The partition function

We now analyze the properties of the partition function. The average value of the energy $\langle E\rangle$ is given by

$$\langle E\rangle \equiv \sum_r E_r P_r = \sum_r \frac{E_r e^{-\beta E_r}}{Z}. \tag{7.8}$$

Therefore, from (7.7),

$$-\frac{\partial \ln Z}{\partial \beta} = -\frac{1}{Z}\frac{\partial Z}{\partial \beta} = \langle E\rangle. \tag{7.9}$$

Similarly, the mean square fluctuation is defined as

$$\langle \Delta E^2\rangle \equiv \langle E^2\rangle - \langle E\rangle^2 = \sum_r \frac{E_r^2 e^{-\beta E_r}}{Z} - \left(\sum_r \frac{E_r e^{-\beta E_r}}{Z}\right)^2. \tag{7.10}$$

Therefore,

$$\frac{\partial^2 \ln Z}{\delta \beta} = -\frac{\partial \langle E\rangle}{\partial \beta} = \langle E^2\rangle - \langle E\rangle^2. \tag{7.11}$$

Moreover, from $\beta = (kT)^{-1}$

$$\frac{\partial \langle E\rangle}{\delta \beta} = -kT^2\frac{\partial \langle E\rangle}{\delta T} \tag{7.12}$$

Since the variation of the energy is done at fixed external parameters, it is due only to the exchange of heat and not to any mechanical work. Therefore, from Eq. (1.5) of Chapter 1, C_V , the specific heat at constant volume, is

$$C_V \equiv \frac{\partial \langle E\rangle}{\partial T}. \tag{7.13}$$

From (7.9)(7.13) we have

$$kT^2C_V = \langle E^2\rangle - \langle E\rangle^2. \tag{7.14}$$

Equation (7.14) is one of many relations classified as fluctuation-dissipation relations. It connects the spontaneous fluctuations of the energy in equilibrium to the variations of the energy induced by an infinitesimal change of the temperature. The C_V term denotes the response (change of energy) of the system to the change of the external temperature. Relation (7.14) implies that if a system exhibits large fluctuations in energy, i.e., the system can spontaneously change its energy value around the average value, then the average value of the energy is very sensitive to external changes in temperature.

From the partition function Z it is also possible to obtain the generalized forces (see Chapter 4) defined as

$$\overline{f} \equiv -\sum_r \frac{\partial E_r}{\partial X}P_r, \tag{7.15}$$

where X is an external parameter such that the work done by the system due to a change δX is given by

$$\delta W = \overline{f}\delta X. \tag{7.16}$$

On the other hand, one has

$$\frac{\partial \ln Z}{\partial X} = \frac{1}{Z}\frac{\partial}{\partial X}\sum_r e^{-\beta E_r} = -\beta\sum_r \frac{\partial E_r}{\partial X}P_r. \tag{7.17}$$

Comparing with Eq. (7.15) we see that

$$\overline{f} = \frac{1}{\beta}\frac{\partial \ln Z}{\partial X}. \tag{7.18}$$

In the particular case in which X is the volume V, $\overline{f}$ is the pressure p, (7.18) becomes

$$p = \frac{1}{\beta}\frac{\partial \ln Z}{\partial V}. \tag{7.19}$$

7.3 Energy Distribution

The distribution probability (7.5) gives the probability that a system in contact with a reservoir at temperature T is in a particular configuration r characterized by an energy E_r. What is the probability that such a system will be in a configuration characterized by an energy between E and $E + \delta E$? $P(E)$ is given by the sum over the probabilities of each event that has an energy between E and $E + \delta E$,

$$P(E) = \sum_{E \le E_r \le E+\delta E} P_r = \frac{\Omega(E) e^{-\beta E}}{Z}, \tag{7.20}$$

where $\Omega(E)$ is the number of configurations with energies between E and $E + \delta E$.

We can write (7.20) as

$$P(E) = \frac{e^{-F(E)/kT}}{Z}, \tag{7.21}$$

where

$$F(E) = E - TS(E), \tag{7.22}$$

and

$$S(E) = k \ln \Omega(E). \tag{7.23}$$

We can follow the same procedure we used in Chapter 4 and expand $\ln P(E)$ around its maximum value $\overline{E}$. This is equivalent to expanding $F(E)$ around its minimum,

$$F(E) = F(\overline{E}) + \frac{1}{2} \left. \frac{\partial^2 F}{\partial E^2} \right|_{E=\overline{E}} (E - \overline{E})^2 + \dots, \tag{7.24}$$

where $\overline{E}$ is the value that minimizes $F(E)$, i.e.,

$$\left. \frac{\partial F(E)}{\partial E} \right|_{E=\overline{E}} = 0. \tag{7.25}$$

Hence, from (7.22),

$$\left. \frac{\partial S(E)}{\partial E} \right|_{E=\overline{E}} = \frac{1}{T}, \tag{7.26}$$

where T is the temperature of the reservoir. As discussed in Chapter 4, the value E that maximizes the probability corresponds to the value of the energy at equilibrium. Equation (7.26) states that at equilibrium the entropy of system A satisfies the thermodynamical relation. Using (7.23), we can express the second derivative of $F(E)$

in (7.22). Since T is the temperature of the reservoir and does not depend on E, we have

$$\left(\frac{\partial^2 F(E)}{\partial E^2}\right)_{E=\overline{E}} = -T\left(\frac{\partial^2 S(E)}{\partial E^2}\right)_{E=\overline{E}}, \tag{7.27}$$

and

$$\left(\frac{\partial^2 S(E)}{\partial E^2}\right)_{E=\overline{E}} = \left(\frac{\partial}{\partial E}\frac{1}{T(E)}\right)_{E=\overline{E}} = -\frac{1}{T^2(\overline{E})}\left(\frac{\partial T(E)}{\partial E}\right)_{E=\overline{E}}, \tag{7.28}$$

where $T(\overline{E})$ is the temperature of system A when it is in equilibrium with the reservoir at temperature T. Therefore

$$T(\overline{E}) = T \qquad ; \qquad \left(\frac{\partial T(E)}{\partial E}\right)_{E=\overline{E}} = \frac{1}{C_V}, \tag{7.29}$$

where C_V is the specific heat at constant volume. Therefore from (7.28) and (7.29), (7.27) gives

$$\left(\frac{\partial^2 F}{\partial E^2}\right)_{E=\overline{E}} = \frac{1}{TC_V}. \tag{7.30}$$

Finally, using the argument of Chapter 4, for very large N (the thermodynamic limit of system A) we can neglect higher order terms in (7.24), and, from (7.21) and (7.30),

$$P(E) = A\,\exp[-(E-\overline{E})^2/(2kT^2C_V)], \tag{7.31}$$

where the factor $A = e^{-F(\overline{E})/kT}/Z$ does not depend on E. We find that the distribution $P(E)$ is a Gaussian centered around the average value $\overline{E} = \langle E\rangle$ with variance $\langle E^2\rangle - \langle E\rangle^2 = kT^2C_V$ in agreement with Eq. (7.14). We note that the equilibrium is reached for $E = \overline{E}$ where $P(E)$ is maximum. This value in turn corresponds to the value which minimizes $F(E)$,

$$F(E) = E - TS(E), \tag{7.32}$$

namely, for a system in thermal contact with a reservoir at constant temperature T , the equilibrium is reached for that value of the energy that minimizes the free energy function defined in Thermodynamics, Eq. (7.32).

The free energy contains two terms: energy and entropy. In the high-temperature limit, the energy term can be neglected, and the minimum of free energy corresponds to maximizing the entropy. In the opposite limit of small temperatures, the entropy term can be neglected and the minimum of the free energy coincides with the minimum of the energy. For intermediate temperatures, for the system to reach equilibrium, it must reach a compromise between entropy and energy.

The width of the Gaussian (7.31) (i.e., the root mean square energy fluctuation) divided by the average value gives, since $\overline{E} = \langle E \rangle$

$$\frac{\sqrt{\langle E^2 \rangle - \langle E \rangle^2}}{\langle E \rangle} \sim \frac{\sqrt{C_V}}{\langle E \rangle} \sim \frac{1}{\sqrt{N}}, \tag{7.33}$$

where we have taken into account that C_V and E are proportional to the number of particles N. From (7.33), it follows that the relative fluctuation goes to zero in the thermodynamic limit. As explained in Chapter 2, this implies that the distribution of the energy per particle $e \equiv E/N$ in the thermodynamic limit tends to a delta function peaked around its mean value $\langle e \rangle$. Hence, for a system at equilibrium with a reservoir at temperature T , in the thermodynamic limit there is only one macroscopic state that is realized corresponding to equilibrium. All other macroscopic states corresponding to other values of the energy have zero probability of being realized in the $N \to \infty$ limit.

Thus we have found that in the thermodynamic limit the canonical ensemble coincides with the microcanonical ensemble. In fact, in the thermodynamic limit only one energy density is allowed, so the system behaves as if the energy were fixed – as it is in the microcanonical ensemble. In fact, for a fixed value of the energy, the probability distribution is constant in the canonical ensemble. Hence all calculations performed in the canonical and microcanonical ensembles in the thermodynamic limit will give the same result. This equivalence will be exemplified later when we return to the case of the ideal gas. Although the microcanonical ensemble is equivalent to the canonical ensemble in the thermodynamic limit, fluctuations around the average energy may be important for a finite system. The choice of the ensemble will depend on whether the system is isolated or in contact with a reservoir.

7.4 Free Energy

From the partition function Z, we have calculated the average energy $\langle E\rangle$ with its fluctuation $\langle E^2\rangle - \langle E\rangle^2$, and the generalized force $\overline{f}$. We now show that in the thermodynamic limit the free energy defined thermodynamically coincides with the quantity

$$F = -kT \ln Z, \tag{7.34}$$

where Z is the partition function (7.7). First we note that

$$Z = \sum_r e^{-\beta E_r} = \sum_E \Omega(E) e^{-\beta E} = \sum_E g(E) e^{-\beta E} \delta E, \tag{7.35}$$

where $g(E)\delta E = \Omega(E)$ is the number of states between E and $E+dE$ and the sum is over all the energy intervals δE. In the thermodynamic limit

$$\ln g(E) = \ln \Omega(E), \tag{7.36}$$

since $\ln(\Delta E)$ is at most of the order of $\ln N$, and is negligible compared with $\ln \Omega \sim N$. Since in (7.35) the energy interval δE is small compared to E, we can substitute an integral for the sum

$$Z = \int e^{-\beta F(E)} dE. \tag{7.37}$$

where $F(E) = E - TS(E)$. Using the Gaussian approximation (7.31) for $P(E)$, we find

$$Z = e^{-\beta F(\overline{E})} \int_0^\infty e^{-(E-\overline{E})^2/(2kT^2 C_V)} dE. \tag{7.38}$$

The Gaussian integral is evaluated in Appendix, so

$$\int_{-\infty}^{\infty} e^{-\alpha x^2} dx = \sqrt{\frac{\pi}{\alpha}}, \tag{7.39}$$

it follows from (7.38) that

$$-kT \ln Z = F(\overline{E}) - kT \ln \sqrt{2\pi k T^2 C_V}. \tag{7.40}$$

In the limit of infinite N , the last term in (7.40) can be neglected since C_V is of the order of N, so

$$-kT \ln Z = \overline{E} - TS. \tag{7.41}$$

Another way to obtain the same result is by differentiating $\ln Z$

$$d(\ln Z) = \frac{\partial \ln Z}{\partial x} dx + \frac{\partial \ln Z}{\partial \beta} d\beta, \tag{7.42}$$

where x is an external parameter (such as V). From (7.38) and (7.40)

$$d(\ln Z) = \beta \overline{f} dx - \overline{E} d\beta = \beta \delta W - d(\beta \overline{E}) + \beta d\overline{E} = \beta(\delta W + d\overline{E}) - d(\beta \overline{E}), \tag{7.43}$$

where δW is the work done by the system from Eq. (7.16), and $d\overline{E}$ the variation of the internal energy. Therefore $\delta W + \delta \overline{E} = \delta Q$, where δQ is the heat absorbed by the system.

In conclusion, from (7.43)

$$d(\ln Z + \beta \overline{E}) = \beta \delta Q = dS, \tag{7.44}$$

and on integrating, we find

$$-kT \ln Z = \overline{E} - TS. \tag{7.45}$$

Comparing (7.45) with (7.32) shows that $F = -kT \ln Z$ is the free energy.

From (7.45) we can derive a useful expression for the entropy in the canonical ensemble. Substituting (7.8) into (7.45), we find

$$S = \sum_s P_s \left(\frac{E_s}{T} + k \ln Z \right), \tag{7.46}$$

where we have used $\sum_s P_s = 1$. From (7.5) follows

$$\frac{E_s}{T} = -k \ln P_s - k \ln Z. \tag{7.47}$$

Hence substituting (7.47) into (7.46), the expression for the entropy in the canonical ensemble can be written in the form

$$S = -k \sum_s P_s \ln P_s = -k \langle \ln P_s \rangle. \tag{7.48}$$

The form of Eq. (7.48) is familiar in information theory. If P_s denotes the probability of finding the system in a given state s, then (7.48) is a measure of the information content of that system.

For example, if we know the system to be in a given state s_0, then $p_{s_0} = 1$ for $s = s_0$ and $p_s = 0$ for $s \neq s_0$. In this case (7.48)

$S = -k\sum_s P_s \ln P_s$ assumes its minimum value $S = 0$ corresponding to maximum information. If we know nothing about the system, then $P_s = 1/\Omega$ where Ω is the number of states. In this case

$$S = k \ln \Omega \tag{7.49}$$

assumes its maximum value, corresponding to minimum information.

Note that definition (7.48) applies also to the microcanonical ensemble where $P_s = 1/\Omega$ and the entropy (7.48) gives (7.49), which is the expression used in the microcanonical ensemble.

7.5 First Law of Thermodynamics

Let us write the variation of energy for a reversible transformation

$$\overline{E} = \sum_r E_r P_r \tag{7.50}$$

so that

$$d\overline{E} = \sum_r E_r dP_r + \sum_r P_r dE_r. \tag{7.51}$$

This relation expresses the first law of Thermodynamics. The second term on the right hand side is the work done by the external world acting on the system and is due to changes of levels while the distribution is the same. Using Eq. (7.47) and the property $\sum_r dP_r \equiv 0$, since due to the normalization $\sum_r P_r \equiv 1$, the first term can be written as

$$\sum_r E_r dP_r = -kTd\left(\sum_r P_r \ln P_r\right) = -TdS, \tag{7.52}$$

and represents the heat absorbed (the transfer of energy not due to mechanical work). This term induces a change of energy caused by the change of distribution of the level population while the levels are kept fixed.

In conclusion, in an infinitesimal transformation the work done increases the internal energy by shifting the energy levels and leaving the distribution unchanged. On the contrary, the heat absorbed increases the internal energy by changing the distribution probability P_r. It is this second contribution that leads to the change of entropy, which is in fact linked only to the distribution probability P_r.

7.6 Canonical Distribution for Classical Systems

In the previous section, the canonical distribution was obtained for a system with discretized energy levels. We want to find the canonical distribution for a system of N classical particles. The question is what is the probability to find a system in contact with a reservoir at temperature T, whose generalized coordinates $\{q, p\}$ are in the *volume* range $(q, q+dq)$ and $(p, p+dp)$. Each configuration $\{q, p\}$ has a weight $\rho(q, p) \equiv exp(-\beta\mathcal{H}(q, p))$ where $\mathcal{H}(q, p)$ is the Hamiltonian of the system. The number of configurations in such a phase space volume is $dqdp/N!h^{3N}$. Hence the probability of finding a system in a configuration in the range $(q, q + dq)$ and $(p, p + dp)$ is given by

$$P(q,p)dqdp = \frac{e^{-\beta\mathcal{H}(q,p)}}{Z}\frac{dqdp}{N!h^{3N}}. \tag{7.53}$$

Here Z is the partition function, which can be obtained using the normalization condition $\int P(q, p)dqdp = 1$,

$$Z = \frac{1}{N!h^{3N}}\int e^{-\beta\mathcal{H}(q,p)} \tag{7.54}$$

and we include the Gibbs correction factor $1/N!$ due to the indistinguishability of the particles.

The ensemble average of any quantity $A(q, p)$ in the canonical ensemble is given by

$$\langle A\rangle = \frac{\int A(q,p)e^{-\beta\mathcal{H}(q,p)}dqdp}{\int e^{-\beta\mathcal{H}(q,p)}} \tag{7.55}$$

7.7 Energy Equipartition Theorem

Consider a classical system of N particles with Hamiltonian

$$\mathcal{H}(q,p) = \sum_{i=1}^{3N}\frac{p_i^2}{2m} + V(q_1 \dots q_{3N}) + \sum_i U(q_i). \tag{7.56}$$

Here $V(q_1, \dots, q_N)$ is the interaction potential among the particles and $U(q_i)$ is an external potential acting on a single particle, which could represent the box in which the particles are confined if $U(q_i) = 0$ when the coordinates q_i falls within the box and ∞ when q_i is at the borders of the box. We shall prove the following general theorem,

$$\left\langle x_i \frac{\partial \mathcal{H}}{\partial x_j} \right\rangle = kT\delta_{ij}, \tag{7.57}$$

where x_i indicates any of the the generalized coordinates q_i or p_i, and δ_{ij} is the Kronecker delta which is 1 if $i = j$ and zero otherwise. The proof will be given in the canonical ensemble; a similar proof can be given also in the microcanonical ensemble, but it is more cumbersome.

If the average is taken over the canonical ensemble, then

$$\left\langle x_i \frac{\partial \mathcal{H}}{\partial x_j} \right\rangle = \frac{\int x_i \left(\frac{\partial \mathcal{H}}{\partial x_j}\right) e^{-\beta \mathcal{H}} d\omega}{\int e^{-\beta \mathcal{H}} d\omega}, \tag{7.58}$$

where for simplicity we have put

$$d\omega \equiv dx_1 \dots dx_{6N}. \tag{7.59}$$

Note that

$$\frac{\partial e^{-\beta \mathcal{H}}}{\partial x_j} = -\beta \left(\frac{\partial \mathcal{H}}{\partial x_j}\right) e^{-\beta \mathcal{H}}, \tag{7.60}$$

so (7.58) can be written as

$$\left\langle x_i \frac{\partial \mathcal{H}}{\partial x_j} \right\rangle = -\frac{1}{\beta} \frac{\int x_i \left(\frac{\partial e^{-\beta \mathcal{H}}}{\partial x_j}\right) d\omega}{\int e^{-\beta \mathcal{H}} d\omega}. \tag{7.61}$$

Integrating the numerator by parts, we find

$$-\frac{1}{\beta} \int x_i \left(\frac{\partial e^{-\beta \mathcal{H}}}{\partial x_j}\right) d\omega = -\frac{1}{\beta} \left\{ \int \left[x_i e^{-\beta \mathcal{H}}\right]_{x_j^{min}}^{x_j^{max}} d\omega_j - \int \frac{\partial x_i}{\partial x_j} e^{-\beta \mathcal{H}} d\omega \right\}. \tag{7.62}$$

where x_{min} and x_{max} are the extremum values of the coordinate x_j and $d\omega_j \equiv d\omega/dx_j = dx_1 \dots dx_{j-1} dx_{j+1} \dots dx_{6N}$. The first term is zero

$$\left[x_i e^{-\beta \mathcal{H}}\right]_{x_j^{min}}^{x_j^{max}} = 0, \tag{7.63}$$

since the Hamiltonian evaluated at its extrema is ∞. In fact, if x_j is one component of the momentum, the extrema of the momenta are $-\infty$ and $+\infty$ and the first term in the Hamiltonian (7.56) diverges. On the other hand, if x_j is one of the spatial coordinates, then the external potential $U(q_j)$ becomes infinite at the extrema of the box. Therefore only the second term in (7.62) is nonzero, and (7.61) becomes

$$\left\langle x_i \frac{\partial \mathcal{H}}{\partial x_j} \right\rangle = \frac{kT \int \frac{\partial x_i}{\partial x_j} e^{-\beta \mathcal{H}} d\omega}{\int e^{-\beta \mathcal{H}} d\omega}. \tag{7.64}$$

Since $\partial x_i / \partial x_j = \delta_{ij}$ from (7.64) follows the relation (7.61), which proves the theorem.

Next we demonstrate an interesting consequence of this theorem. From the Hamiltonian (7.56),

$$p_i \frac{\partial \mathcal{H}}{\partial p_i} = \frac{p_i^2}{m}. \tag{7.65}$$

From (7.61) for $x_i = x_j = p_i$,

$$\left\langle p_i \frac{\partial \mathcal{H}}{\partial p_i} \right\rangle = kT. \tag{7.66}$$

Therefore from (7.65) and (7.66),

$$\left\langle \frac{p_i^2}{2m} \right\rangle = \frac{1}{2} kT. \tag{7.67}$$

Equation (7.67) expresses the fact that due to thermal motion any kinetic degree of freedom possesses on average a kinetic energy equal to $kT/2$. Since there are $3N$ momentum coordinates, the average total kinetic energy is

$$\sum_{i=1}^{3N} \left\langle \frac{p_i^2}{2m} \right\rangle = \frac{3}{2} NkT \tag{7.68}$$

Relations (7.67) and (7.68) are quite general and hold for almost any potential and hence for many systems in nature. Moreover, (7.68) offers an interesting interpretation of the thermodynamic temperature that is associated with the kinetic energy of the particles.

If the Hamiltonian contains also quasi-static terms in the q coordinates, like for N harmonic oscillators, then the Hamiltonian can be written as

$$\mathcal{H} = \sum_{i=1}^{3N} (a_i p_i^2 + b_i q_i^2). \tag{7.69}$$

it easy to show that

$$\mathcal{H} = 3NkT, \tag{7.70}$$

so the total energy is comprised of two terms, $3NkT/2$ from the $3N$ coordinatesp_i and $3NkT/2$ from the $3N$ coordinates q_i.

7.8 Maxwell-Boltzmann Distribution

To study the momentum distribution $f(\vec{p})$ of a single particle in a given system at fixed temperature T we use the canonical ensemble. Here $f(\vec{p})d\vec{p}$ is the probability of finding a given particle with momentum $\vec{p}$ in the range $(\vec{p}_i, \vec{p}_i + d\vec{p}_i)$. $i = 1, 2, 3$ labels the components of the momentum. This distribution can be evaluated by integrating over the q and p coordinates of all the particles and the q coordinates of the given particle

$$f(\vec{p}) = \frac{\int e^{-\beta\mathcal{H}} d^{3N-3}p d^{3N}q}{\int e^{-\beta\mathcal{H}} d^{3N}p d^{3N}q} \tag{7.71}$$

For a general Hamiltonian of the form

$$\mathcal{H} = \sum_{i=1}^{3N} \frac{p_i^2}{2m} + V(q_1, \ldots, q_{3N}), \tag{7.72}$$

the integral in (7.71) can be performed, and we find

$$f(\vec{p}) = \frac{e^{-\beta p^2/(2m)}}{(2\pi mkT)^{3/2}}. \tag{7.73}$$

The prefactor in the denominator ensures the normalization

$$\int f(\vec{p}) d^3p = 1. \tag{7.74}$$

Expression (7.73) for $f(\vec{p})$ is the Maxwell-Boltzmann distribution and is rather general.

Using $p^2 = \sum_{i=1,3} p_i^2$ Eq. (7.73) can be cast as $f(\vec{p}) = f_{sing}(p_1) \cdot f_{sing}(p_2) \cdot f_{sing}(p_3)$, where the single component distribution reads

$$f_{sing}(p_i) = \frac{e^{-\beta p_i^2/(2m)}}{(2\pi mkT)^{1/2}}. \tag{7.75}$$

Hence the average kinetic energy for each component is given by

$$\frac{\langle p_i^2 \rangle}{2m} = \frac{1}{2}kT, \tag{7.76}$$

which is another way of obtaining one of the consequences, (7.67), of the energy equipartition theorem.

7.9 Effusion

7.10 Ideal Gas in the Canonical Ensemble

Let us calculate the free energy for a system of N classical non-interacting particles of mass m. Since $V = 0$, from (7.72) the Hamiltonian is the sum of all the kinetic energies of each particle

$$\mathcal{H} = \sum_{i=1}^{3N} \frac{p_i^2}{2m}. \tag{7.77}$$

The partition function is, from (7.54),

$$Z = \frac{1}{h^{3N}N!} \int exp \left(-\beta \sum_i \frac{p_i^2}{2m} \right) d^{3N}q d^{3N}p. \tag{7.78}$$

The integral over the $3N$ q variables is made over the volume V of the box gives a factor V^N , while the integral over the momenta can be factorized

$$Z = \frac{V^N}{h^{3N}N!} \left[\int e^{-\beta p_i^2/(2m)} dp_i \right]^{3N}. \tag{7.79}$$

Since the Hamiltonian contains no terms coupling the $6N$ position and momentum coordinates, the partition function can be written as

$$Z = \frac{1}{N!} Z_1^N, \tag{7.80}$$

where

$$Z_1 \equiv \frac{V}{h^3} \left[\int e^{-\beta p_i^2/(2m)} dp_i \right]^3. \tag{7.81}$$

is the partition function of a single particle which can easily be carried out

$$Z_1 = \frac{V}{h^3} (2\pi mkT)^{3/2}. \tag{7.82}$$

Hence from (7.80),

$$Z = \frac{V^N}{h^{3N}} \frac{1}{N!} (2\pi mkT)^{3N/2}. \tag{7.83}$$

Using Stirling's approximation (Appendix C), we find for large N

$$F = -kT \ln Z = NkT \left[\ln \left\{ \frac{N}{V} \left(\frac{h^2}{2\pi mkT} \right)^{3/2} \right\} - 1 \right]. \tag{7.84}$$

From (7.19)

$$p = -\frac{\partial F}{\partial V} = \frac{NkT}{V}, \tag{7.85}$$

which gives the equation of state of the ideal gas

$$pV = NkT. \tag{7.86}$$

From (7.9) the average energy is given by,

$$\langle E \rangle = -\frac{\partial \ln Z}{\partial \beta} = \frac{3}{2}NkT, \tag{7.87}$$

in agreement with the equipartition theorem (7.68).

The entropy S can be obtained using the relation 1.50, namely

$$S = -\frac{\partial F}{\partial T} = -\frac{\partial(-kT\ln Z)}{\partial T} = k\ln Z + \frac{kT}{Z}\frac{\partial Z}{\partial T} = k\ln Z + \frac{3}{2}Nk \tag{7.88}$$

where F is given by (7.84). In order to compare with the result obtained in the microcanonical ensemble one must express T in Eq. (7.87) in term of $\langle E \rangle$, which can be easily done using Eq. (7.87). Doing that, one readily obtains the Sackur-Tetrode expression, Eq. (6.26).

7.11 Harmonic Oscillators

A system of N decoupled harmonic oscillators can also be studied using the canonical ensemble.

7.11.1 Classic treatment

Let us consider a collection of d-dimensional harmonic oscillators. The Hamiltonian of the i-th oscillator is

$$\mathcal{H}_i = \frac{1}{2}m\omega^2 q_i^2 + \frac{p_i^2}{2m}. \tag{7.89}$$

The total for N Hamiltonian oscillators is

$$\mathcal{H} = \sum_{i=1}^{N} \mathcal{H}_i. \tag{7.90}$$

As in the case of the ideal gas, the Hamiltonian does not couple any of the $2N$ coordinates. Hence it is sufficient to calculate the partition function of a single harmonic oscillator,

$$Z_1 = \frac{1}{h} \int e^{-\beta(\frac{1}{2}m\omega^2 q_1^2)} d\vec{q}_1 \int e^{-\beta p_1^2/(2m)} d\vec{p}_1 = \frac{1}{(\beta\hbar\omega)^d} \tag{7.91}$$

The partition function of the total number of harmonic oscillators is thus

$$Z = Z_1^N = (\beta\hbar\omega)^{-dN}. \tag{7.92}$$

In this case, there is no need to introduce the factor $N!$. The particles are localized; hence they are distinguishable and there is no volume dependence V^N in the partition function. As a simple rule, every time there is such volume dependence it is necessary to introduce the $N!$ factor so that $\ln(V^N/N!) \approx N(\ln \frac{V}{N} - 1)$ will be an extensive quantity.

It is straightforward to find expressions for F, $\overline{E}$, and S. Thus from the relation $F = -kT \ln Z$,

$$F = NdkT \ln \frac{\hbar\omega}{kT}, \tag{7.93}$$

from $\overline{E} = -\partial \ln Z/\partial\beta$,

$$\overline{E} = NdkT, \tag{7.94}$$

and from $S = (\overline{E} - F)/T$,

$$S = Ndk\left(\ln \frac{kT}{\hbar\omega} + 1\right). \tag{7.95}$$

Note that the energy agrees with the equipartition theorem.

A system of N harmonic oscillators can be considered as a model for a solid. In this case, the energy is given by Eq. (7.93) and the specific heat at constant volume is $C_V = Ndk$. This is known as the law of Dulong and Petit, and is satisfied for a large range of temperature. At low temperature, experimentally it breaks down. This difficulty is avoided in the quantum mechanical treatment.

7.11.2 Quantum mechanical treatment

The eigenvalues of the i-th harmonic oscillator are given by

$$\epsilon_{n_i} = \left(n_i + \frac{d}{2}\right)\hbar\omega \tag{7.96}$$

where $n_i = n_i^{(1)} + \cdots + n_i^{(d)}$ and $n_i^{(k)} = 0, 1, 2, \ldots$.

$$Z = \sum e^{-\beta E} = \sum_{\{n_i^{(k)}\}} e^{-\beta(\epsilon_{n_1} + \cdots + \epsilon_{n_N})} = \left(\sum_{\{n_1^{(k)}\}} e^{-\beta \epsilon_{n_1}} \right) \cdots \left(\sum_{\{n_N^{(k)}\}} e^{-\beta \epsilon_{n_N}} \right) = Z_1^N \tag{7.97}$$

where Z_1 is the partition function of a single harmonic oscillator,

$$\begin{aligned} Z_1 &= \sum_{\{n_1^{(k)}\}} e^{-\beta \epsilon_{n_1}} = e^{-\beta d \hbar \omega /2} \sum_{\{n_1^{(k)}\}} e^{-\beta \hbar \omega n_1} = \\ &= e^{-\beta d \hbar \omega /2} \left(\sum_{\{n_1^{(1)}\}} e^{-\beta \hbar \omega n_1^{(1)}} \right)^d = \frac{e^{-\beta d \hbar \omega /2}}{(1 - e^{-\beta \hbar \omega})^d}. \end{aligned} \tag{7.98}$$

The average energy is then given by

$$\langle E \rangle = -\frac{\partial \ln Z}{\partial \beta} = N \left[\frac{d \hbar \omega}{2} + \frac{d \hbar \omega}{e^{-\beta \hbar \omega} - 1} \right]. \tag{7.99}$$

and the specific heat $d\langle E \rangle / dT$ is

$$C_V = \begin{cases} N d k (\beta \hbar \omega)^2 e^{-\beta \hbar \omega} & \text{for} \quad T \to 0 \\ N d k \quad \text{for} \quad T \to \infty \end{cases} \tag{7.100}$$

Note that as $T \to \infty$, (7.99) and (7.100) are consistent with the classical result (7.94).

7.12 Paramagnetism

Consider again the system of Sec. 5.2, described by the Hamiltonian (5.7)

$$\mathcal{H} = -\mu_0 H \sum_{i=1}^{N} S_i, \tag{7.101}$$

where the sum is over all N spins. The partition function is therefore given by

$$Z = \sum_{\{S_i\}} \exp[-\beta \mathcal{H}(S_1, \ldots, S_N)] = \sum_{\{S_i\}} \exp[\beta \mu_0 H \sum_i S_i], \tag{7.102}$$

where the sum is over the configurations of spins $S_1 = \pm 1, S_2 = \pm 1, \ldots, S_N = \pm 1$. From (7.102), we have

$$\begin{aligned} Z &= \sum_{\{S_i\}} e^{\beta\mu_0 H \sum_i S_i} = \qquad (7.103) \\ &= \left(\sum_{\{S_1=\pm 1\}} e^{\beta\mu_0 H S_1} \right) \left(\sum_{\{S_2=\pm 1\}} e^{\beta\mu_0 H S_2} \right) \cdots \left(\sum_{\{S_N=\pm 1\}} e^{\beta\mu_0 H S_N} \right). \end{aligned}$$

Hence

$$Z = Z_1^N = \left(e^{\beta\mu_0 H} + e^{-\beta\mu_0 H} \right)^N, \qquad (7.104)$$

where Z_1 is the partition function of one single particle.

The magnetization is defined by

$$M = \mu_0 \left\langle \sum_{i=1}^N S_i \right\rangle = \mu_0 \sum_{i=1}^N \langle S_i \rangle = Nm \qquad (7.105)$$

where m is the magnetization of a single spin. This quantity can be computed as follows. In general, given a Hamiltonian which contains a term xX,

$$\mathcal{H} = \mathcal{H}_0 - xX, \qquad (7.106)$$

where x is a variable, X is an external field, and $\mathcal{H}_0$ is independent of x, the following relation holds:

$$\langle X \rangle = \frac{\partial \ln Z}{\partial(\beta x)}. \qquad (7.107)$$

In our case, $x = H$ and $X = \mu_0 S$, and m is obtained directly from the partition function (7.104) by taking the derivative with respect to βH. One has

$$m = \mu_0 \langle S \rangle = \mu_0 \frac{e^{\beta\mu_0 H} - e^{-\beta\mu_0 H}}{e^{\beta\mu_0 H} + e^{-\beta\mu_0 H}} = \mu_0 \tanh(\beta\mu_0 H). \qquad (7.108)$$

Figure 7.1 shows the magnetization as a function of the field variable $\mu_0 H$. For $h \gg kT$, the magnetization asymptotically reaches its saturation value $m = \mu_0$. Physically, this means that for a fixed temperature for values of the field such that $\mu_0 H \gg kT$, the thermal energy is much less than the magnetic energy and almost all the spins are aligned with the magnetic field. For $\mu_0 H \ll kT$, the hyperbolic tangent can be approximated with the first term of its

Taylor expansion, and the magnetization is linear in H – i.e., for H small enough that $\mu_0 H \ll kT$, the thermal energy is large enough that not all the spins are aligned to the field. The smaller the field, the fewer is the number of spins that are aligned, on average, with the field.

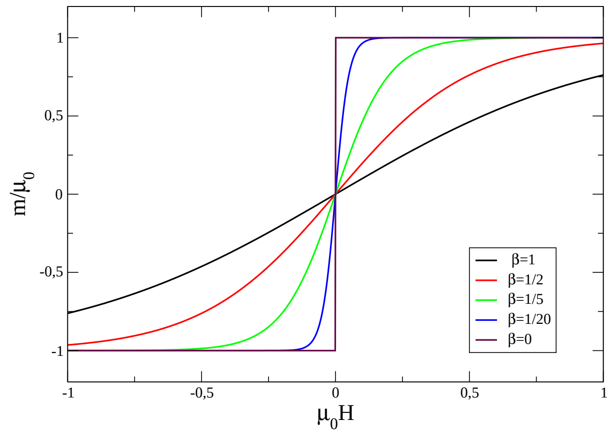

Figure 7.1: The magnetization m/μ_0 of a paramagnet (Eq. (7.108)) is plotted against $\mu_0 H$ for different values of β (see key).

Another quantity of interest is the magnetic isothermal susceptibility, which is defined as

$$\chi_T \equiv \left(\frac{\partial M}{\partial H}\right)_T . \tag{7.109}$$

To better understand the meaning, we rewrite (6.110) in the following way:

$$\chi_T \delta H = \delta M. \tag{7.110}$$

Therefore χ_T is a response function, measuring the response of the magnetization to an infinitesimal increase in field. The larger is χ_T, the more susceptible is the system to a variation of the external field.

The susceptibility at $H = 0$ can be easily computed from (7.108),

$$\chi_T = \left(\frac{\partial M}{\partial H}\right)_T \bigg|_{H=0} = N\frac{\mu_0^2}{kT}. \tag{7.111}$$

Note that as T decreases, χ increases and diverges as $T \to 0$. In fact, from Fig. 7.1 we see that the slope of M at $H = 0$ increases as

T decreases. Thus as $T \to 0$, the system passes from $M = 0$ to $N\mu$ when the field changes by a small amount.

Chapter 8

Grand Canonical Ensemble

8.1 Introduction

The grand canonical ensemble applies to those systems that can exchange both energy and particles. To find the probability distribution that characterizes the grand canonical ensemble, we proceed in the same manner as we did in the previous chapter for the canonical ensemble. We first study the equilibrium conditions for the systems A and A' in thermal contact, and find that they can exchange both energy and number of particles. For this purpose, we ask what is the probability $P(E, N)$ that the system A has energy E and number of particles N and system A' has energy E' and number of particles N' under the conditions that for both systems the total energy

$$E_{tot} = E + E' \tag{8.1}$$

and number of particles

$$N_{tot} = N + N' \tag{8.2}$$

must be constant and equal to the total energy E_{tot} and N_{tot} for the isolated system $A + A'$. Under the assumption that the two systems are in equilibrium, the probability $P(E, N)$ is given by the total number of configurations for the system $A + A'$ such that the subsystem A is in a macroscopic state of energy E and number of particles N and the subsystem A' is in a macroscopic state of energy E' and number of particles N' , divided by the total number of accessible configurations Ω_{tot} for the system $A + A'$. Under the assumption that the two subsystems A and A' are weakly interacting,

$P(E,N)$ is given by

$$P(E,N) = \frac{\Omega(E,N)\Omega'(E',N')}{\Omega_{tot}} \tag{8.3}$$

where $\Omega(E,N)$ is the number of configurations for the system A to be in a macroscopic state characterized by an energy lying between E and $E+\delta E$ and number of particles N . Similarly, $\Omega'(E',N')$ is the number of configurations for the system A' to be in a macroscopic state characterized by an energy lying between E' and $E'+dE'$ and number of particles N'.

The probability distribution (8.3) arises from the equal a priori probability postulate, which applies to the total system $A + A'$ which is assumed to be in equilibrium and isolated.

The value of $\overline{E}$ and $\overline{N}$ which corresponds to the maximum probability will coincide with the average energy and number of particles since $P(E,N)$ for N and N' very large is extremely sharply peaked around the values $\overline{E}$ and $\overline{N}$. Since $P(E,N)$ is the equilibrium distribution, $\overline{E}$ and $\overline{N}$ are the mean values for the system A when in equilibrium.

The conditions that $\overline{E}$ and $\overline{N}$ must satisfy are therefore the conditions for the system A to be in equilibrium with the system A'. These conditions are found by requiring that $P(E,N)$ is a maximum – or, equivalently, that $\ln P(E,N)$ is a maximum,

$$\left.\frac{\partial \ln P(E,N)}{\partial E}\right|_N = 0, \tag{8.4}$$

and

$$\left.\frac{\partial \ln P(E,N)}{\partial N}\right|_E = 0, \tag{8.5}$$

Condition (8.4) gives, from (8.3),

$$\left.\frac{\partial \ln \Omega(E,N)}{\partial E}\right|_N = \left.\frac{\partial \ln \Omega'(E',N')}{\partial E'}\right|_{N'}. \tag{8.6}$$

The relation (8.6), found already for the canonical ensemble, requires that the temperatures of systems A and A' coincide,

$$\beta(E,N) = \beta'(E',N'), \tag{8.7}$$

where we recall

$$\beta(E,N) = \left.\frac{\partial \ln \Omega(E,N)}{\partial E}\right|_N. \tag{8.8}$$

On the other hand, the condition (8.5) gives

$$\left.\frac{\partial \ln \Omega(E,N)}{\partial N}\right|_{E} = \left.\frac{\partial \ln \Omega'(E',N')}{\partial N'}\right|_{E'} . \tag{8.9}$$

which requires that

$$\beta\mu(E,N) = \beta'\mu'(E',N'), \tag{8.10}$$

where μ is the chemical potential, given by

$$\beta\mu(E,N) = \left.\frac{\partial \ln \Omega(E,N)}{\partial N}\right|_{E} . \tag{8.11}$$

Condition (8.7), $\beta = \beta'$, implies that

$$\mu(E,N) = \mu'(E',N') \tag{8.12}$$

Relations (8.7) and (8.12) are the conditions for systems A and A' to be in equilibrium.

Next, making the hypothesis that system A' is much larger than A, so that A' can be considered to be a reservoir of energy and particles, we can calculate the grand canonical probability distribution P_r that at equilibrium system A in contact with reservoir A' is in a particular configuration r characterized by energy E_r and number of particles N_r. Following the same arguments as for the canonical ensemble (Chapter 7), we find

$$P_r = \frac{\Omega_{A'}(\{r'\})}{\Omega^{tot}_{A+A'}}, \tag{8.13}$$

where

$$E_{tot} = E_r + E'_{r'} \tag{8.14}$$

and

$$N_{tot} = N_r + N'_{r'}. \tag{8.15}$$

For $E_r \ll E_{tot}$ and $N_r \ll N_{tot}$, we can expand $\ln P_r$ around $E_r = 0$ and $N_r = 0$,

$$\ln P_r = C - \beta' E_r + \mu'\beta' N_r + \ldots , \tag{8.16}$$

where

$$\beta' = \left.\frac{\partial \ln \Omega_{A'}(\{r'\})}{\partial E'}\right|_{\substack{N' = N_{tot} \\ E' = E_{tot}}} \tag{8.17}$$

and

$$-\mu'\beta' = \left.\frac{\partial \ln \Omega_{A'}(\{r'\})}{\partial N'}\right|_{\substack{N' = N_{tot} \\ E' = E_{tot}}} . \tag{8.18}$$

Since system A' is a reservoir, at equilibrium the number of particles N' and the energy E' will essentially coincide with N_{tot} and E_{tot}. This implies that β' and μ' are the inverse temperature and chemical potential of system A' when it is in equilibrium with system A. Therefore due to conditions (8.7) and (8.12), they coincide with the inverse temperature and chemical potential of system A – i.e.,

$$\beta' = \beta \qquad \text{and} \qquad \mu' = \mu. \tag{8.19}$$

Following the arguments of Chapter 7 for the canonical distribution, we can neglect higher order terms in (8.13) and write

$$P_r = \frac{e^{-\beta E_r + \beta\mu N_r}}{\mathcal{Z}}, \tag{8.20}$$

where $\mathcal{Z}$ is a normalization constant called the grand canonical partition function. Imposing $\sum_r P_r = 1$, we find

$$\mathcal{Z} = \sum_r e^{\beta\mu N_r} e^{-\beta E_r}, \tag{8.21}$$

where the sum is now taken over all the states r independently of the number of particles they are characterized by. Notice that the grand-partition function can equivalently be written as

$$\mathcal{Z} = \sum_N e^{\beta\mu N} \sum_r{}' e^{-\beta E_r}, \tag{8.22}$$

where the the first sum runs over all possible values of N and the second sum runs over all microscopic states r such that $N_r = N$ (indeed one immediately recognizes that $\sum_N \sum_r' \equiv \sum_r$).

Now $\mathcal{Z}$ can be written as

$$\sum_N e^{\beta\mu N} Z_N, \tag{8.23}$$

where

$$Z_N = \sum_r{}' e^{-\beta E_r}, \tag{8.24}$$

is the partition function of the canonical ensemble for N particles.

The grand canonical partition function has the properties that

$$\left(\frac{\partial \ln \mathcal{Z}}{\partial(\beta\mu)}\right)_\beta = \frac{\sum_r N_r e^{-\beta E_r+\beta\mu N_r}}{\mathcal{Z}} = \langle N\rangle, \tag{8.25}$$

and

$$\left(\frac{\partial^2 \ln \mathcal{Z}}{\partial(\beta\mu)^2}\right)_\beta = kT\left(\frac{\partial\langle N\rangle}{\partial\mu}\right)_T = \langle N^2\rangle - \langle N\rangle^2 \equiv \langle(\Delta N)^2\rangle, \tag{8.26}$$

where

$$\langle N^2\rangle = \sum_r \frac{N_r^2 e^{-\beta Er+\beta\mu N_r}}{\mathcal{Z}}. \tag{8.27}$$

Thus the grand canonical partition function (8.23) can be used to calculate fluctuations. Equation (8.26) relates the fluctuation of the number of particles to the derivative of $\partial\langle N\rangle/\partial\mu$. This last quantity is not easily accessible experimentally. Therefore it is better to express it in terms of pressure P and volume V. We will show that

$$\left(\frac{\partial\langle N\rangle}{\partial\mu}\right)_{V,T} = -\frac{\langle N^2\rangle}{V^2}\left(\frac{\partial V}{\partial P}\right)_{N,T}. \tag{8.28}$$

From (8.26) and (8.28),

$$\frac{\langle(\Delta N)^2\rangle}{\langle N\rangle^2} = -kT\frac{1}{V^2}\left(\frac{\partial V}{\partial P}\right)_{N,T}. \tag{8.29}$$

from which

$$\frac{\langle(\Delta\rho)^2\rangle}{\langle\rho\rangle^2} = \frac{kT}{\langle N\rangle}\left(\frac{\partial\langle\rho\rangle}{\partial P}\right)_{N,T} = \frac{kT}{\langle N\rangle}\chi_T. \tag{8.30}$$

Here $\rho \equiv \langle N\rangle/V$, $\langle(\delta\rho)^2\rangle$ is the density fluctuation and $\chi_T = \left(\frac{\partial\langle\rho\rangle}{\partial P}\right)_{N,T}$ is the so called *isothermal compressibility.*

Equation (8.30) relates the compressibility to the density fluctuation. This is one of the fluctuation-dissipation relations, which we have already introduced in the canonical ensemble. The compressibility represents the response function. Physically it gives the density variation due to an infinitessimal variation of the external pressure. Relation (8.30) says that the larger the equilibrium density fluctuation is the larger will be the variation of the density induced by the change of the external pressure. We will now offer a proof of relation (8.28).

Differentiating the thermodynamic relation $G = N\mu$, we obtain

$$dG = \mu dN + N d\mu. \tag{8.31}$$

From (1.62) and (1.57) we also have

$$dG = \mu dN - SdT + V dP. \tag{8.32}$$

Combining (8.31) and (8.32)

$$N d\mu = -SdT + V dP, \tag{8.33}$$

which gives

$$d\mu = vdP - sdT, \tag{8.34}$$

in which we have introduced the intensive variables $v \equiv V/N$ and $s \equiv S/N$. From (8.34)

$$\left(\frac{\partial \mu}{\partial P}\right)_T = v. \tag{8.35}$$

Using the mathematical relation (Appendix)

$$\left(\frac{\partial \mu}{\partial P}\right)_T = \left(\frac{\partial \mu}{\partial v}\right)_T \left(\frac{\partial v}{\partial P}\right)_T \tag{8.36}$$

it follows that

$$\left(\frac{\partial \mu}{\partial v}\right)_T = v \left(\frac{\partial P}{\partial v}\right)_T, \tag{8.37}$$

in which v can change either by changing V and keeping N fixed or by keeping V fixed and changing N . Therefore the left-hand side of (8.37) can be written as

$$\left(\frac{\partial \mu}{\partial v}\right)_T = -\frac{N^2}{V} \left(\frac{\partial \mu}{\partial N}\right)_{T,V}. \tag{8.38}$$

Therefore

$$v \left(\frac{\partial P}{\partial v}\right)_T = -\frac{N^2}{V} \left(\frac{\partial \mu}{\partial N}\right)_{T,V}. \tag{8.39}$$

Since the left-hand side of (8.39) can be written as

$$v \left(\frac{\partial P}{\partial v}\right)_T = V \left(\frac{\partial P}{\partial V}\right)_{T,N}, \tag{8.40}$$

then (8.39) becomes

$$-\frac{N^2}{V}\left(\frac{\partial\mu}{\partial N}\right)_{T,V} = V\left(\frac{\partial P}{\partial V}\right)_{T,N}, \tag{8.41}$$

and

$$\left(\frac{\partial N}{\partial\mu}\right)_{T,V} = -\frac{N^2}{V^2}\left(\frac{\partial V}{\partial P}\right)_{T,N}, \tag{8.42}$$

which coincides with (8.28) if one considers that the Thermodynamics variable $N = \langle N\rangle$.

8.2 Particle Number Distribution and the Grand Thermodynamic Potential

The grand partition function $\mathcal{Z}$ of system A in contact with a reservoir is, from (8.23),

$$\mathcal{Z} = \sum_N e^{\beta\mu N - \beta F(N,\beta)}, \tag{8.43}$$

where

$$F(N,\beta) = -kT\ln Z(N,\beta) \tag{8.44}$$

is the free energy of system A and $Z(N,\beta)$ is its partition function. We want to show that in the thermodynamic limit, $-kT\ln\mathcal{Z}$ is the grand potential $\Phi = -PV$ of (1.64).

We first will show that the particle number distribution P_N is extremely peaked around its most probable value $\overline{N}$, and becomes a delta function in the thermodynamic limit

$$P_N = \frac{e^{-\beta[-\mu N + F(N,\beta)]}}{\mathcal{Z}}. \tag{8.45}$$

We can expand $\ln P_N$ around its maximum value $\overline{N}$ or, equivalently, expand the exponent $-\mu N + F(N,\beta)$ around its minimum

$$-\mu N + F(N,\beta) = -\mu\overline{N} + F(\overline{N},\beta) + \frac{1}{2}\left(\frac{\partial^2 F}{\partial N^2}\right)_{N=\overline{N}}(N-\overline{N})^2 + \ldots. \tag{8.46}$$

The condition for the minimum gives

$$\left(\frac{\partial F}{\partial N}\right)_{N=\overline{N}} = \mu \tag{8.47}$$

which gives the thermodynamic relation between free energy and chemical potential. The second derivative of F gives

$$\left(\frac{\partial^2 F}{\partial N^2}\right)_{N=\overline{N}} = \left(\frac{\partial \mu}{\partial N}\right)_{N=\overline{N}}. \tag{8.48}$$

Therefore the particle number probability distribution is

$$P_N = \frac{e^{-\beta[-\mu\overline{N}+F(\overline{N},\beta)]}}{\mathcal{Z}} e^{-(N-\overline{N})^2/2\Delta^2} \tag{8.49}$$

where, from (8.42), the particle number fluctuation is

$$\Delta^2 = \frac{\overline{N}^2}{V^2}\left(\frac{\partial V}{\partial P}\right)_{T,\overline{N}}. \tag{8.50}$$

Now Δ^2 is proportional to volume V in the thermodynamic limit,

$$\frac{\Delta}{\langle\overline{N}\rangle} \propto \frac{1}{\sqrt{\overline{N}}}. \tag{8.51}$$

Therefore the probability distribution becomes a delta function in the density variable $\rho \equiv N/V$, when $N \to \infty$ and $V \to \infty$. Hence, in the thermodynamic limit, the only macroscopic state that is realized is the one with density $\rho = \overline{\rho}$, and the grand canonical ensemble becomes equivalent to the canonical ensemble.

Finally, the grand partition function is

$$\mathcal{Z} = \exp[\beta(\mu\overline{N} - F(\overline{N},\beta))] \sum_N \exp\left[-\frac{1}{2\Delta^2}(N-\overline{N})^2\right], \tag{8.52}$$

from which we find

$$\ln \mathcal{Z} = \beta[\mu\overline{N} - F(\overline{N},\beta)] \tag{8.53}$$

when we have neglected the term $\ln\sum_N \exp[-(N-\overline{N})^2/2\Delta^2]$ which is of order $\mathcal{O}(\ln N)$. Finally, recalling that

$$F(\overline{N},\beta) = \overline{E} - TS, \tag{8.54}$$

and that

$$G = \mu\overline{N} = \overline{E} - TS + PV, \tag{8.55}$$

we find from (8.53),

$$-kT\ln\mathcal{Z} = -PV, \tag{8.56}$$

which is the desired relation.

8.3 Adsorbiment

Chapter 9

Alternative approach: Entropy Maximization

9.1 Boltzmann entropy

In Chapter 7, we obtained the canonical ensemble for a system in contact with a reservoir. We now offer a rather different formulation, based more on the idea of a statistical ensemble. We will also be able to reformulate the equal a priori probability postulate of Statistical Mechanics in a more general form, which may help gain better understanding of the fundamentals of Statistical Mechanics.

Consider a macroscopic isolated system comprised of $\mathcal{N}$ subsystems. Each subsystem is macroscopically equivalent to all the others, they may or may not exchange energy and particles with all the others (we will distinguish these cases in the following), which act as a reservoir for that particular subsystem. The only constraint is that the total energy E_{tot} and number of particles N_{tot} is constant. This is the ensemble that we will see can be used to describe the statistical properties of any given subsystem A.

Under the hypothesis that the $\mathcal{N}$ subsystems interact weakly with one another, we can characterize the microscopic state by an index r, an associated energy E_r, and a number of particles N_r. We ask how the system distributes at a given time over the available microscopic configurations. If n_r is the number of subsystems in the microstate r, then we must have

$$\sum_r n_r = \mathcal{N}, \tag{9.1}$$

$$\sum_r E_r n_r = E_{tot} = \mathcal{N} UE, \tag{9.2}$$

and

$$\sum_r n_r N_r = N_{tot} = \mathcal{N} N, \tag{9.3}$$

The first condition implies that the total number of subsystems $\mathcal{N}$ is fixed, the second and third conditions imply that the total energy $\mathcal{N}E$ and the total number of particles $\mathcal{N}N$ are fixed. Every distribution n_r which satisfies (9.1), (9.2) and (9.3) represents a possible macroscopic state of the entire system. Each distribution or macrostate can be realized in many ways. The number of configurations that realize a given distribution n_r is given by the combinatoric factor

$$\mathcal{W}\{n_r\} = \frac{\mathcal{N}!}{n_1! n_2! \dots n_r! \dots}. \tag{9.4}$$

Indeed this is the number of ways to arrange $\mathcal{N}$ objects (represented as blue balls in Fig. 9.1) into urns (represented as green boxes) labeled by an index r each of which can only accomodate n_r balls. In order to do that we start to put one ball, that we can chose in $\mathcal{N}$ ways into the first urn, than we put the second, that can be chosen in $\mathcal{N} - 1$ ways in the urn and so on. When the first urn is full we move to the second and so on. This operation can be done in $\mathcal{N}$ ways, which appairs at the numerator in Eq. (9.4). However configurations where the n_1 balls in the first urn are arranged in a different order must not be counted as different, and the same for the other urns. This accounts for the denominator in Eq. (9.4).

Since the total system is isolated at equilibrium, each microscopic configuration is equally probable. Therefore the probability to find a given distribution $\{n_r\}$ is proportional to $\mathcal{W}\{n_r\}$. Using Stirling's approximation in (9.4) and the condition (9.1), we find

$$\ln \mathcal{W}\{n_r\} = \mathcal{N} \ln \mathcal{N} - \sum_r n_r \ln n_r, \tag{9.5}$$

or, in terms of the normalized distribution $p_r = n_r/\mathcal{N}$,

$$\ln \mathcal{W}\{n_r\} = \mathcal{N} \ln \mathcal{N} - \sum_r n_r \ln n_r = -\mathcal{N} \sum_r p_r \ln p_r. \tag{9.6}$$

Notice that, since $\mathcal{W}$ is the number of configurations associated with

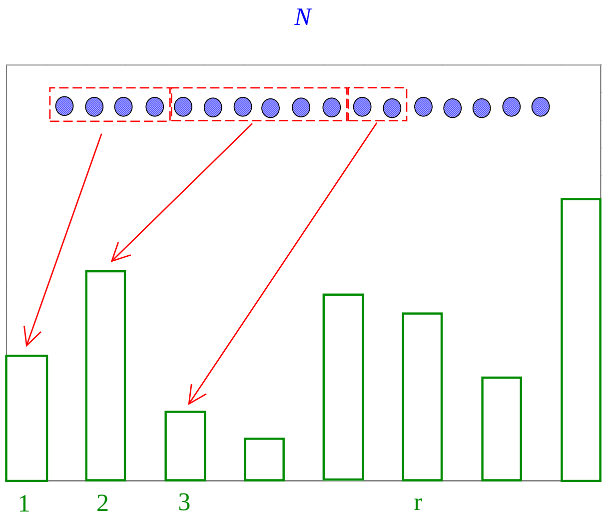

Figure 9.1: Explanation of the combinatorial factor of Eq. (9.4).

the distribution p_r, the quantity $S = \mathcal{N}^{-1} k \ln \mathcal{W}$ given by

$$S = -\sum_r p_r \ln p_r \tag{9.7}$$

is by definition the entropy (per system) corresponding to that distribution. Eq. (9.7) is the celebrated Boltzmann (or, sometimes, Gibbs, or Shannon) entropy formula.

Figure 9.2: Ludwig Boltzmann (Vienna, 20/02/1844 - Duino, 05/09/1906).

9.2 Entropy maximization

The most probable distribution $\{n_r^*\}$ is the distribution that maximizes $\mathcal{W}\{n_r\}$ – or, equivalently, the distribution that maximizes $\ln \mathcal{W}\{n_r\}$, the entropy, subject to the conditions (9.1), (9.2) and (9.3).

9.2.1 Microcanonical Ensemble

In this case each system has the same (non-fluctuating) energy $E_r \equiv E$ and particle number $N_r \equiv N$. Hence the three conditions (9.1), (9.2) and (9.3) are equivalent. Using the method of Lagrange multipliers (Appendix D), we calculate the maximum of

$$\ln \mathcal{W}_{const}\{n_r\} = \ln \mathcal{W}\{n_r\} - \alpha \left(\sum_r n_r - \mathcal{N} \right) \tag{9.8}$$

where α is the single Lagrange parameters that will be fixed to satisfy the three equivalent conditions (9.1), (9.2) and (9.3).

Substituting (9.5) into (9.8) and maximizing with respect to the quantity n_s, using Eq. (9.5) we have

$$\frac{\partial \ln \mathcal{W}_{const}}{\partial n_s} = - \ln n_s - 1 - \alpha = 0, \tag{9.9}$$

from which for the solution n_s^* we find

$$n_s^* = C, \tag{9.10}$$

where the constant $C = e^{-(1+\alpha)}$ can be fixed by requiring condition (9.1),

$$C = \frac{\mathcal{N}}{\Omega}, \tag{9.11}$$

where $\Omega = \sum_s 1$ is the number of microstates. Hence, for the normalized variable p_r one has

$$p_r^* = \frac{1}{\Omega}, \tag{9.12}$$

namely the same distribution obtained for an insulated system by means of the postulate of equal probability.

9.2.2 Canonical Ensemble

In this case each system has the same (non-fluctuating) particle number $N_r \equiv N$. Hence the two conditions (9.1) and (9.3) are equivalent. Using again the method of Lagrange multipliers, we calculate the maximum of

$$\ln \mathcal{W}_{const}\{n_r\} = \ln \mathcal{W}\{n_r\} - \alpha \left(\sum_r n_r - \mathcal{N} \right) - \beta \left(\sum_r E_r n_r - \mathcal{N} E \right), \tag{9.13}$$

where α and β are the two Lagrange parameters that will be fixed to satisfy conditions (9.1) and (9.2).

Substituting (9.5) into (9.13) and maximizing with respect to the quantity n_s, we have

$$\frac{\partial \ln \mathcal{W}_{const}}{\partial n_s} = -\ln n_s - 1 - \alpha - \beta E_s = 0, \tag{9.14}$$

from which we find

$$n_s^* = C e^{-\beta E_s}. \tag{9.15}$$

The constant $C = e^{-(1+\alpha)}$ can be fixed by requiring condition (9.1),

$$C = \frac{\mathcal{N}}{\sum_s e^{-\beta E_s}}. \tag{9.16}$$

Hence, introducing the normalized variable

$$p_r = \frac{n_r}{\mathcal{N}} \tag{9.17}$$

we finally find

$$p_r^* = \frac{e^{-\beta E_r}}{\sum_s e^{-\beta E_s}}, \tag{9.18}$$

where β is fixed by requiring the condition (9.2). This is the same distribution obtained previously in a canonical setting starting from the equal a priori postulate for the insulated system.

9.2.3 Grand Canonical Ensemble

Using again the method of the Lagrange multipliers, we must calculate the maximum of

$$\begin{aligned}\ln \mathcal{W}_{const}\{n_r\} &= \ln \mathcal{W}\{n_r\} - \alpha\left(\sum_r n_r - \mathcal{N}\right) \qquad (9.19)\\ &- \beta\left(\sum_r E_r n_r - \mathcal{N}U\right) - \gamma\left(\sum_r N_r n_r - \mathcal{N}N\right).\end{aligned}$$

Proceeding as before one readily arrives at

$$p_r^* = \frac{e^{-\beta E_s + \beta\mu N_r}}{\sum_s e^{-\beta E_s + \beta\mu N_s}}, \qquad (9.20)$$

where β and μ are fixed by requiring the condition (9.2) and (9.3). Again, this is the canonical distribution that we obtained starting from the postulate of equal a priori probability for the microcanonical system.

9.2.4 Entropy maximization postulate

The formalism above has been developed starting from the equal a priori postulate. However it indicates an alternative way of deriving the ensemble distributions without assuming the equal a priory postulate. Indeed from the results of Secs. 9.2.1, 9.2.2, 9.2.3 it is clear that the basic postulate of Statistical Mechanics can be replaced by the following one: *the ensemble distribution relative to a system in equilibrium, is given by that distribution that maximizes the entropy (9.6).* However, this is correct only after showing that the distributions obtained are unique, which will be shown in the next section.

9.3 Unicity of the distribution

We next show that the most probable distribution $\{n_r^*\}$ found in Secs. 9.2.1, 9.2.2, 9.2.3, in the $\mathcal{N} \to \infty$ limit of the number of systems in the ensemble, is the only distribution that is realized. To this end, we expand (9.13) around the value n_r^*,

$$\ln \mathcal{W}_{const}\{n_r\} = \ln \mathcal{W}_{const}\{n_r^*\} + \frac{1}{2}\sum_r \left(\frac{\partial^2 \ln \mathcal{W}_{const}\{n_r\}}{\partial n_r^2}\right)_{n_r = n_r^*} (n_r - n_r^*)^2 + \ldots. \qquad (9.21)$$

The first derivative is zero, while the second derivative is given by

$$\frac{\partial^2 \ln \mathcal{W}_{const}}{\partial n_r^2} = \frac{\partial^2 \ln \mathcal{W}}{\partial n_r^2} = -\frac{1}{n_r}. \tag{9.22}$$

Moreover, due to the conditions (9.1) and (9.2), $\ln \mathcal{W}_{const}\{n_r\} = \ln \mathcal{W}\{n_r\}$. Therefore from (9.21) and (9.22), we find a Gaussian distribution

$$\mathcal{W}\{n_r\} = \mathcal{W}\{n_r^*\}\, exp\left[-\frac{1}{2}\sum \frac{(n_r - n_r^*)^2}{n_r^*}\right], \tag{9.23}$$

with average value $\langle n_r \rangle = n_r^*$, and width (a measure of the rms fluctuations)

$$\Delta n_r^* = \left[\langle (n_r - n_r^*)^2 \rangle\right]^{1/2} = \sqrt{n_r^*}. \tag{9.24}$$

Therefore, considering that $n_r^* \sim \mathcal{N}$, we have in the $\mathcal{N} \to \infty$ limit

$$\frac{\Delta n_r^*}{n_r^*} \sim \frac{1}{\sqrt{\mathcal{N}}} \to 0. \tag{9.25}$$

Or, proceeding similarly to what done in 2.3, considering the *intensive* quantity associated to n_r, namely the probability p_r with probability $W\{p_r\}$ one has

$$W\{p_r\} = \mathcal{W}\{p_r^*\}\, exp\left[-\frac{1}{2}\sum \frac{\mathcal{N}(p_r - p_r^*)^2}{p_r^*}\right], \tag{9.26}$$

Hence we find that the probability $W(\{p_r\})$ to find a distribution $\{p_r\}$ is extremely peaked around the distribution p_r^* and becomes a delta function in the limit $\mathcal{N} \to \infty$.

Chapter 10

Strongly Interacting Systems and Critical Phenomena

10.1 Generalities

Thus far we have considered systems of non-interacting (or weakly interacting) particles, or constituents, degrees etc..., or systems which are interacting but where the interaction can be eliminated by a suitable transformation introducing the so called *normal modes*. We have seen many prototypical examples, as e.g. paramagnets, perfect gases (classical or quantum), phonon gases, or the black body radiation. In these cases all the thermodynamic functions can be deduced from the knowledge of the *energy levels* of the single constituents and are generally continuous quantities, with the notable exception of the boson gas case.

In *truely* interacting systems the interaction terms cannot be eliminated by means of any known transformation and cannot be considered in any case negligible or small. Typical examples of systems where this happens are materials close to a phase transition, as for instance condensing gases or melting solids, phase-separating mixtures and solutions, magnetic materials, alloys undergoing an order-disorder transition etc... In all these cases the single *particle* energy levels are not sufficient to determine the Thermodynamics, since a cooperative behavior sets in which often produces singularities in the thermodynamic functions as phase-transitions are approached. As a consequence, the mathematical description of these systems is very complicated and one usually resorts to extremely simplified models where the form and the range of the interactions, the nature of lattice, the properties of the constituents etc... are oversimplified. This simplification procedure is nevertheless meaningful because universal properties, namely properties which only rely on the collective behavior of the system and not on specific details, naturally emerge when interactions and correlations are strong. Nevertheless, even these oversimplified models are hardly tractable and new techniques are needed to tame the mathematical difficulties.

10.2 Gas-Liquid-Solid transition

A paradigmatic example of phenomena that exhibit sharp changes as a function of thermodynamic variables is the sudden density change that occurs when a vapor, like water vapor, turns into liquid, or when liquid water turns into ice (when pressure is kept constant as the temperature steadily drops). In order to visualize these transition lines, we construct a *phase diagram* (Fig. 10.1), starting with the equation of state, which indicates that, at equilibrium, the pressure P , the volume V, and the temperature T of a one-component homogeneous system satisfies the functional relation $f(P, V, T) = 0$. This equation of state defines a surface in a three-dimensional space with coordinates P, V, and T . Projecting the equation onto a plane P, T (left side of Fig. 10.1) gives rise to three regions, which correspond to the solid, liquid, and gas phases. The solid and gas phases are in equilibrium along the sublimation curve, the solid and liquid along the melting curve, and the gas and liquid along the vapor-pressure curve. The point of intersection of these three lines – where the three phases coexist – is called the triple point. By crossing one of the lines, the system exhibits a sudden density change going from one phase to another.

Note that while the solid-liquid equilibrium line never ends, the liquid-gas equilibrium line ends at a given point – called the critical point – whose coordinates P_c, V_c, and T_c are called critical pressure, critical volume, and critical temperature. This means that it is possible to change the liquid into a gas continuously by going around the critical point.

In the following, we will study the behavior of the system close to the critical point. To achieve this aim, we consider the projection onto the plane P, V (right part of Fig. 10.1). At a sufficiently high

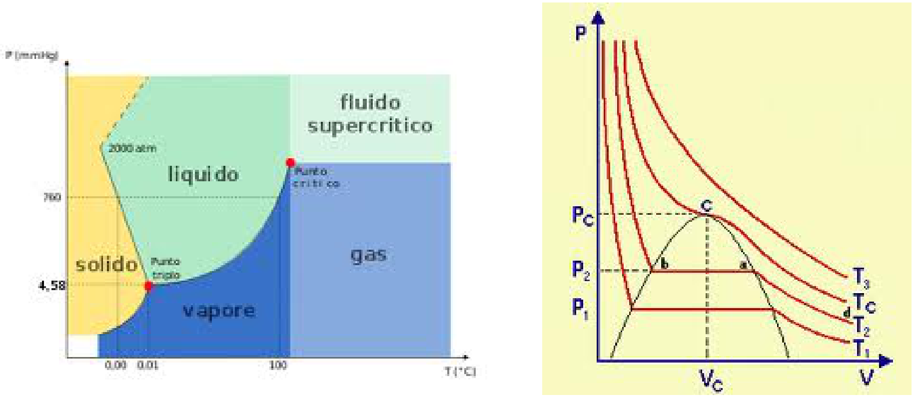

Figure 10.1: $p-T$ phase-diagram (left) and $p-V$ phase diagram (right).

temperature, we expect the fluid to follow the equation of state for ideal gases, $PV = Nk_BT$, which, for any fixed T , is characterized by an hyperbola. As the temperature decreases, the effect of the attractive interaction is felt and the curve shows a departure from the hyperbola until, for $T = T_c$, the curve exhibits an inflection point at $V = V_c$. For T below T_c there is a phase separation between the gas and the liquid. For any value of the pressure all the volume values between the values V_a and V_b are possible, corresponding to the coexistence of the gas and the liquid of densities $\rho_G = N/V_a$ and $\rho_L = N/V_b$ in various proportions. As function of T, ρ_G and ρ_L (or V_a and V_b) define a curve that joins at ρ_c (or V_c). The entire curve is called the coexistence curve.

The difference $M \equiv \rho_L - \rho_G$ is a measure of the difference between the two phases and is call the order parameter. As $T \to T_c$ from below, the order parameter tends toward zero,

$$\rho_L - \rho_G \to 0 \qquad \text{as} \qquad T \to T_c, \tag{10.1}$$

so the two phases become indistinguishable. Phenomenologically, we discover that for $T = T_c$ the curve at ρ_c has a flex. This implies that the compressibility

$$\chi_T \equiv \left(\frac{\partial \rho}{\partial P}\right)_T \to \infty \qquad \text{as} \qquad T \to T_c^+, \tag{10.2}$$

as T approaches T_c from above. Below T_c we must define the compressibility along the coexistence curve in the liquid and gas phases. Phenomenologically, we discover that both these compressibilities diverge as $T \to T_c$. The divergence of χ_T at T_c implies that in the vicinity of the critical point the response of the system to a small change in pressure is extremely large. It is this extremely nonlinear behavior that characterizes a critical point.

From the fluctuation-dissipation relation (8.30) we can relate the density fluctuation to the compressibility,

$$\frac{\langle \rho^2 \rangle - \langle \rho \rangle^2}{\langle \rho \rangle^2} = \frac{k_B T}{N} \chi_T. \tag{10.3}$$

The divergence of the compressibility at the critical point implies an extremely large density fluctuation in the vicinity of the critical point. The presence of large density fluctuation gives rise to a spectacular macroscopic phenomenon called critical opalescence. Consider a gas contained in a baker at fixed density ρ_c . For $T \gg T_c$, the system is homogeneous and looks transparent to visible light. As $T \approx T_c$, the system becomes opalescent. Below T_c, the two phases separate, the liquid at the bottom and the gas at the top. Critical opalescence occurs because, close to T_c, the system is dominated by large density fluctuations. These fluctuations can be viewed as droplets of the high density phase. When the linear size of those droplets is comparable with the wavelength of the light, the light is scattered in all directions, giving rise to a phenomenon visible to the naked eye. As we will discuss at the end of this section the intensity of the light scattered can be related to the density-density correlation function $g(\vec{x} - \vec{x}')$, defined as

$$g(\vec{x} - \vec{x}') \equiv \langle [\rho(\vec{x}) - \langle \rho(\vec{x}) \rangle][\rho(\vec{x}') - \langle \rho(\vec{x}') \rangle] \rangle \tag{10.4}$$

where $\rho(\vec{x})$ is the particle density at position $\vec{x}$, so that $\int \rho(\vec{x}) d\vec{x} = \rho$. The brackets stand for the average over all the configurations in the grand canonical ensemble. Usually the particles interact via a two-body potential that depends only on the distance between them. Consequently, in the thermodynamic limit (when surface effects are negligible), the system is translationally invariant: $\langle \rho(\vec{x}) \rangle$ does not depend on the position $\vec{x}$ and $\langle \rho(\vec{x}) \rangle = \langle \rho \rangle$ (the average density). For the same reason $g(\vec{x} - \vec{x}')$ depends only on the distance between $\vec{r}$ between $\vec{x}$ and $\vec{x}'$. Most systems are isotropic, implying that g depends only on the modulus r of $\vec{r}$.

The density-density pair correlation function measures the correlation between the density fluctuation at $\vec{x}$ and $\vec{x}'$. In the $T \to \infty$

limit where the effect of interactions is negligible, the system behaves as a collection of independent particles. Therefore the density at point $\vec{x}$ is independent of the density at point x', namely

$$g(r) \equiv \langle(\rho(\vec{x}) - \langle\rho\rangle)(\rho(\vec{x}') - \langle\rho\rangle)\rangle \simeq \langle\rho(\vec{x}) - \langle\rho\rangle\rangle\langle\rho(\vec{x}') - \langle\rho\rangle\rangle = 0. \tag{10.5}$$

For lower temperatures one cannot neglect interparticle interactions and the factorization in (10.5) is not allowed. The more $g(r)$ differs from zero, the larger the correlation between the density fluctuations at $\vec{x}$ and $\vec{x}'$. The distance ξ within which $g(r)$ differs from zero represents the linear dimension of the droplet (fluctuation). More precisely, ξ can be defined as

$$\xi^2 \equiv \frac{\int g(r)r^2 d\vec{r}}{\int g(r)d\vec{r}}, \tag{10.6}$$

where the integral extends over the entire volume of the system.

We show now that $\int g(r)d\vec{r}$ is related to the density fluctuation and therefore diverges as $T \to T_c$. In fact, recalling that $\vec{r} = \vec{x} - \vec{x}'$ one has

$$\begin{aligned} V\int g(r)d\vec{r} &= \left[\int d\vec{x}'\right]\left[\int d\vec{r}\, g(r)\right] = \left[\int d\vec{x}'\right]\left[\int d\vec{x}\, g(r)\right] \\ &= \langle\left[\int d\vec{x}\rho(\vec{x})\right]\left[\int d\vec{x}'\rho(\vec{x}')\right]\rangle - V^2\langle\rho\rangle^2 \\ &= V^2[\langle\rho^2\rangle - \langle\rho\rangle^2]. \end{aligned} \tag{10.7}$$

Therefore, in view of (10.3),

$$\int g(r)d\vec{r} = k_B T\langle\rho\rangle\chi_T. \tag{10.8}$$

Since χ_T diverges, $\int g(\vec{r})d\vec{r}$ also diverges. This is due to the divergence of ξ. Indeed it is usually found that for large r

$$g(r) \sim \frac{e^{-r/\xi}}{r^\mu}, \tag{10.9}$$

where μ is a critical exponent usually denoted $d - 2 + \eta$, implying that (i) away from the critical point ξ is finite and the correlation decays exponentially and (ii) at the critical point $\xi = \infty$ and the correlation decays as a power law. Physically this means that although a perturbation decays exponentially in a *normal* system, at criticality it propagates over all the system and then decays very smoothly, i.e., *algebraically* – much less than an exponential. It is this long-range correlation that gives to a cooperative behavior that paves the way toward a new phase.

Not only χ_T diverges at the critical point. Indeed it is found experimentally that the specific heat at constant volume C_V also exhibits a divergence, although much weaker than the compressibility. Since the specific heat is proportional to the energy fluctuation, the divergence of C_V implies that closer to the critical point also the energy fluctuations are very large, although smaller than the density fluctuations.

Let us now explain what anticipated above, namely the relation between the scattering of light and the correlation function $g(r)$. The standard theory of scattering relates the scattered intensity of a monoatomic beam to the Fourier transform of $g(\vec{r})$,

$$\widetilde{g}(\vec{q}) = \int g(\vec{r}) e^{i\vec{q}\cdot\vec{r}} d\vec{r}. \tag{10.10}$$

More precisely if $\vec{k}$ is the wave vector of a monocromatic beam incident on a homogeneous fluid and $\vec{k}'$ is the wave vector of the diffracted beam (see Fig. xxx), the intensity of the scattered beam $I(\vec{q})$ is proportional to $\widetilde{g}(\vec{q})$ where $\vec{q} \equiv \vec{k} - \vec{k}'$. Therefore, on taking the Fourier transform of $I(\vec{q})$ one gets $g(\vec{r})$.

The forward scattering intensity $I(0)$ gives a quantity proportional to χ and the width of $I(\vec{q})$ gives a term proportional to ξ^{-2},

$$\xi^{-2} \propto \frac{\int I(\vec{q}) q^2 d\vec{q}}{\int I(\vec{q}) d\vec{q}}. \tag{10.11}$$

10.3 The Van Der Waals Theory

The Van der Waals equation is an equation of state for a fluid composed of particles that have a non-zero volume and a pairwise attractive inter-particle force (such as the Van der Waals force). It was derived in 1873 by Johannes Diderik Van der Waals, who received the Nobel prize in 1910 for "his work on the equation of state for gases and liquids". The equation is based on a modification of the ideal gas law and approximates the behavior of real fluids, taking into account the nonzero size of molecules and the attraction between them.

Consider first a gas which is composed of N non-interacting point particles that satisfy the ideal gas law

$$p = \frac{nRT}{V}, \tag{10.12}$$

where n the number of moles of the gas. Next assume that all particles are hard spheres of the same finite radius r (the Van der Waals radius). The effect of the finite volume of the particles is to decrease the available void space in which the particles are free to move. We must replace V by $V - nb$, where b is called the *excluded volume* (per mole). The corrected equation becomes

$$p = \frac{nRT}{V - nb}, \tag{10.13}$$

which is called Clausius equation. For hard spheres b is four times the proper volume $4\pi r^3/3$ of a molecule, but empirical values for b are usually lower than that due to the fact that molecules interact via a soft potential.

Next, we introduce a pairwise attractive force between the particles. Van der Waals assumed that, not withstanding the existence of this force, the density of the fluid is homogeneous. Further he assumed that the range of the attractive force is so small that the great majority of the particles do not feel that the container is of finite size. Given the homogeneity of the fluid, the bulk of the particles do not experience a net force pulling them to the right or to the left. This is different for the particles in surface layers directly adjacent to the walls. They feel a net force from the bulk particles pulling them into the container, because this force is not compensated by particles on the side where the wall is (another assumption here is that there is no interaction between walls and particles, which is not true as can be seen from the phenomenon of droplet formation; most types of liquid show adhesion). This net force decreases the force exerted onto the wall by the particles in the surface layer. The net force on a surface particle, pulling it into the container, is proportional to the number density $\rho = N/V$. The number of particles in the surface layers is (again assuming homogeneity) also proportional to the density. In total, the force on the walls is decreased by a factor proportional to the square of the density, and the same applies to the pressure on the walls $p \to p - a(n/V)^2$, where a is a constant.

Hence one arrives to the Van der Waals equation

$$p + a\frac{n^2}{V^2} = \frac{nRT}{V - nb}. \tag{10.14}$$

Notice that for $\rho \to 0$ it reduces to the perfect gas state equation.

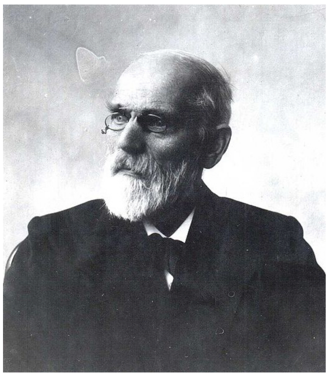

Figure 10.2: Johannes Diderik Van der Waals (Leida, 23/11/1837 - Amsterdam, 08/03/1923)

The Van der Waals equation (10.14) is plotted in Fig. 10.3. For high temperatures p is a monotonously decreasing function of the volume. At a particular temperature T_c - the critical temperature - an inflection point appairs at a certain volume V_c. The isothermal compressibility $\chi_T = (\partial\rho/\partial p)_{N,T} = -(N/V^2)(\partial V/\partial p)_{N,T}$ diverges in this point. In order to determine the critical point one has to solve the system

$$\begin{cases} p_c + a\frac{n^2}{V_c^2} = \frac{nRT_c}{V_c - nb} \\ \frac{\partial p}{\partial V}\Big|_{p_c,V_c,T_c} = 0 \\ \frac{\partial^2 p}{\partial V^2}\Big|_{p_c,V_c,T_c} = 0, \end{cases} \tag{10.15}$$

which yields

$$\begin{cases} p_c = \frac{a}{27b^2} \\ V_c = 3nb \\ T_c = \frac{8a}{27bR}. \end{cases} \tag{10.16}$$

Introducing the reduced variables

$$\begin{cases} \tilde{p} = \frac{p}{p_c} \\ \tilde{V} = \frac{V}{V_c} \\ \tilde{T} = \frac{T}{T_c} \end{cases} \tag{10.17}$$

the Van der Waals equation (10.14) can be written in the *universal* form

$$\left(\tilde{p}+\frac{3}{\tilde{V}^2}\right)\left(3\tilde{V}-1\right)=8\tilde{T}, \tag{10.18}$$

which is a parameter-free form obeyed by all the substances which are well described by the Van der Waals theory. This is called the law of corresponding states. It is interesting to note that also most of the substances which are not described by the Van der Waals theory obey a law of corresponding states, namely the relation between thermodynamic quantities is the same when the former are expressed in terms of reduced variables.

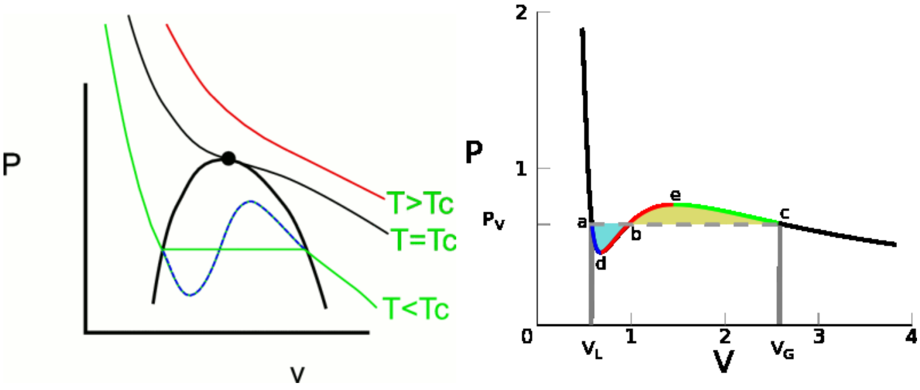

Figure 10.3: The Van der Waals equation in a pV diagram. The downward parabola is the coexistence region. In this area the Van der Waals curve is the dashed-blue one (the horizontal green line is the Maxwell construction, which is detailed in the right panel).

Below the critical temperature the Van der Waals isotherms oscillate. The red part of the isotherm between the points d and e in the right panel of Fig. 10.3 is unphysical, since $\chi_T < 0$ while Eq. (10.3) states that it must be $\chi_T \geq 0$ (notice that, instead the regions *ad* and *ec* of the curve do not violate any fundamental principle and, in fact, this states correspond to metastable states - the superheated liquid and the undercooled vapor). This happens because in the region below the downward parabola in Fig. 10.3 the fluid is no longer homogeneous since, as it is well known, a liquid and the vapor coexist. In this region the pressure does not depend on the volume and equals the vapor pressure P_V. Hence the oscillating part of the Van der Waals curve must be replaced by an horizontal line, the one from a to c in the right panel of Fig. 10.3. The height where this line must be placed, i.e. the vapor pressure p_V, can be inferred by an argument due to Maxwell, the so called *Maxwell construction.* In an isothermal process the variation of the Helmoltz free energy is $dF = pdV$. Since the free energy is a state function its variation in going from a state a to a state c must not depend on the path. Hence, going along the Van der Waals isotherm $adbec$ in Fig. 10.3 or along the straight line ac the quantity $\int pdV$ must be the same. In other words the areas $adba$ and $bceb$ must be equal. The Maxwell argument (at least as it is expressed here) is not correct, since the Van der Waals isotherm in the coexistence region does not describe the equilibrium states of the fluid. However its conclusion is correct, as it can be proven by refining the argument.

10.4 Ferromagnetic Transition

Other systems exhibit a phenomenology very similar to the liquid-gas transition. As we have seen in Sec. 7.12 a paramagnetic system has a macroscopic magnetization under the influence of an external magnetic field. According to the results of Sec. 7.12, when this external field approaches zero, the magnetization per particle m also goes to zero. However, there are other materials, called *ferromagnets* which even when there is no external magnetic field present, below a critical temperature T_c (called the Curie temperature), exhibit a *spontaneous* magnetization.

The equation of state $f(H, m, T) = 0$ defines a surface in a space of coordinates H, m, T. Projecting onto the plane H, T we obtain the phase diagram (Fig. 10.4, left panel) that shows the existence of a coexistence line for $H = 0$, $T \leq T_c$ separating the phase of positive magnetization and negative magnetization. As in the liquid-gas system, the line ends at the critical point, with coordinates $H = 0, T = T_c$. Projecting onto the (H, m) plane (Fig. 10.4, right panel), we have m as a function of H for a fixed temperature T. For high temperatures the system behaves as a non-interacting spin system. From Eq. (7.108) of Chapter 7 we expect $m = \tanh(\beta\mu_0 H)$, which for small H is a straight line passing through the origin. As the temperature decreases, the interaction among the spins becomes relevant and there is a deviation from the straight line until $T = T_c$ and the curve shows flexibility. Below T_c one observes a discontinuity in the magnetization at $H = 0$, corresponding to a first-order phase transition. As in the liquid-gas transition, we define an order parameter m that for $H = 0$ goes to zero as the critical temperature is approached from below, while the susceptibility $\chi_T = (\partial m/\partial H)$ and the specific heat at constant H, C_H diverge at the critical point.

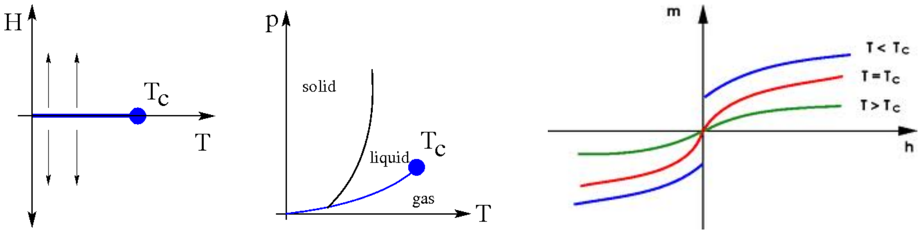

Figure 10.4: Left: $H-T$ phase-diagram which is analogous to the $p-T$ diagram in a liquid-vapor transition (also shown). Right: $m-H$ phase diagram (analogous to the $p-V$ diagram in Fig. 10.1).

The fluctuation dissipation relation $\chi_T \propto \langle m^2 \rangle - \langle m \rangle^2$ can be derived along the same lines as for Eq. (8.30). According to this relation the divergence of the susceptibility implies large fluctuations in the magnetization. The presence of large fluctuations in the magnetization gives rise to a phenomenon very similar to critical opalescence near the liquid-gas transition. This phenomenon is not manifested sending a beam of light on the sample, but instead sending a beam of neutrons. Since the neutrons possess a magnetic moment, they interact with the spins. When the wavelength associated with the neutrons become of the same order as the size of the fluctuations the neutrons are scattered. The analog of the droplets here are the magnetic domains of up and down spins. The intensity of the neutron scattering is proportional to the Fourier transform of the spin-spin pair correlation function, which is defined as

$$g_{ij} \equiv \langle (\vec{S}_i - \langle \vec{S}_i \rangle)(\vec{S}_j - \langle \vec{S}_j \rangle) \rangle, \tag{10.19}$$

where $\vec{S}_i$ is the value of the spin at site i. The phenomenology here is closely related to that of the liquid-gas transition: The correlation length, roughly the size of the droplets, diverges as the critical point is approached. In analogy with (10.7), it follows from (10.19) that

$$\sum_{i,j} g_{ij} = \langle \vec{M}^2 \rangle - \langle \vec{M} \rangle^2, \tag{10.20}$$

where $\vec{M} = \sum_i \vec{S}_i$ is the total magnetization.

Although the liquid-gas transition and the ferromagnet-paramagnet transition differ from each other in nature, they can nevertheless be described in the same way, and the same is true for other systems near their respective critical points, as we will be discuss in Sec. 10.7. The behavior of a system close to its critical point can be characterized by an order parameter $m \to 0$, a *susceptibility* $\chi \to \infty$, a specific heat $C \to \infty$, and a correlation length $\xi \to \infty$ as the critical point is approached. The order parameter is a measure of the ordered phase or, equivalently, the difference between the ordered and the disordered phase. The susceptibility is a measure of the response (variation) of the order parameter to an infinitesimal perturbation of the field that is coupled to the order parameter. The divergence of the susceptibility is a manifestation of a high nonlinear response to a small perturbation. At the same time, due to the fluctuation dissipation relations, it is also a manifestation of large fluctuations whose size ξ diverges at the critical point – which, in turn, leads to a power law behavior in the pair correlation function.

10.5 Critical Exponents

In the previous section we have seen that as a critical point is approached the order parameter goes to zero, and the susceptibility of specific heat and the correlation length diverge. These behaviors can be characterized quantitatively using critical exponents. For example, we generally assume that the magnetization goes to zero as

$$m = At^{\beta}(1 + Bt^{\Delta_1} + Ct^{\Delta_2} + \dots), \tag{10.21}$$

where

$$t \equiv \left| \frac{T - T_c}{T_c} \right|, \tag{10.22}$$

which represents the distance from the critical point. The critical exponents $\beta, \Delta_1, \Delta_2, \dots$ are positive numbers and the critical amplitudes $A, B, C, \dots$ are constants. The dots represent higher order terms in t. Very close to the critical point ($t \ll 1$) the term in parenthesis can be well approximated by 1 and the magnetization behaves asymptotically as

$$m \simeq At^{\beta}. \tag{10.23}$$

More generally, if a function $f(t)$ vanishes or diverges in $t = 0$, we define the critical exponent λ as

$$\lambda \equiv \lim_{t \to 0} \frac{\ln f(t)}{\ln t}. \tag{10.24}$$

Equation (10.25) implies that, close to $t = 0$, $f(t)$ can be well-approximated by $f(t) \sim At^{\lambda}$. If $\lambda > 0$, $f(t)$ vanishes, while if $\lambda < 0$, $f(t)$ diverges. For a function of the form in Eq. (10.21), the critical exponent, defined using definition (10.25), coincides with β.

Other quantities, such as χ_T , C_V, and ξ, diverge for $T \to T_c^-$ and as $T \to T_c^+$. In principle, one can introduce for each quantity two exponents, one for $T \to T_c^-$ and the other for $T \to T_c^+$. Experimental data and model calculations are consistent with the same divergences from above and below T_c. Therefore close to the critical point we write simply

$$M \sim At^{\beta}, \quad \chi \sim B_{\pm}t^{-\gamma}, \quad C_V \sim D_{\pm}t^{-\alpha}, \quad \xi \sim E_{\pm}t^{-\nu}, \quad (10.25)$$

where β, γ, α, and ν are critical exponents (because they characterize the critical behavior close to the critical point), B, D, and E are amplitudes, and $\pm$ stands for $T > T_c$ and $T < T_c$. Finally, right at T_c, since the spontaneous magnetization vanishes one must have $\lim_{H \to 0} M = 0$, which allows us to introduce the exponent δ as

$$M \sim H^{\frac{1}{\delta}}. \quad (10.26)$$

Again at T_c, after Eq. (10.9) for large values of r one has,

$$g(r) \sim \frac{1}{r^{d-2+\eta}}, \quad (10.27)$$

where d is the dimensionality of the system and η is another critical exponent.

Critical exponents are useful because they characterize critical behavior and can easily be compared among different systems (unlike entire functions, which are difficult to compare). Critical exponents also show themselves to be *universal* in that they allow all systems to be classified into a small number of universality classes, each class characterized by its distinct set of critical exponents. The attention focused on these critical exponents has been very important in the study of critical phenomena. They are, in fact, the key quantities by means of which any theory in critical phenomena is tested.

10.5.1 Critical exponents in the Van der Waals theory

Re-writing Eq. (10.18) in terms of the variables $\pi = \tilde{p} - 1$, $v = \tilde{V} - 1$ and $t = \tilde{T} - 1$, which describe the distance from the critical point

$\pi = v = t = 0$ one has

$$\pi = \frac{8(t+1)}{3v+2} - \frac{3}{(v+1)^2} - 1. \tag{10.28}$$

Along the critical isotherm $t = 0$ it is

$$\pi = \frac{-3v^3}{(3v+2)(v+1)^2} \tag{10.29}$$

from which, in the vicinity of the critical point ($v \to 0$) one has $\pi = -3v^3/2$ or

$$v \sim \pi^{1/\delta} \tag{10.30}$$

which is the analog of Eq. (10.26) in the liquid-gas transition, and $\delta = 3$.

Moreover, along the critical isocore ($v = 0$)

$$\left[\left. \frac{\partial p}{\partial V} \right|_T \right]_{v=0} = \frac{p_c}{V_c} \left[\left. \frac{\partial \pi}{\partial v} \right|_t \right]_{v=0} = -6 \frac{p_c}{V_c} t, \tag{10.31}$$

and hence $\chi_T = -\frac{\rho^2}{N} \left. \frac{\partial V}{\partial p} \right|_T = [N/(6p_c V_c)] t^{-1}$, or

$$\chi_T \sim t^{-\gamma} \tag{10.32}$$

which is the analog of the second equation in (10.25), and $\gamma = 1$.

Now we look at the region with t negative and small. From the shape of the Van der Waals isotherm in Fig. 10.3 we see that, fixing p appropriately there are three solutions for v. Indeed Eq. (10.28) is cubic in the variable v, as it can be seen writing it as

$$3v^3(1+\pi) + 8(\pi - t)v^2 + (7\pi - 16t)v + 2(\pi - 4t) = 0. \tag{10.33}$$

As $T \to T_c^-$ one solution tends to $v = 0$, and the remaining two become symmetric around $v = 0$. This means that in Eq. (10.33) the term of order v^0 must disappear upon approaching criticality, i.e. $\pi \simeq 4t$. With this result we write Eq. (10.33) as

$$v^3(1+4t) + 8tv^2 + 4tv = 0. \tag{10.34}$$

Neglecting the higher order terms in t term $4t$ for $t \to 0$ the two symmetric solutions are $v \simeq \pm 2(-t)^{1/2}$, and so

$$v \sim |t|^\beta \tag{10.35}$$

which is the analog of the first equation in (10.25), with $\beta = 1/2$. One can also show that the third equation in (10.25) is found with $\alpha = 0$.

10.6 Ising Model

From a theoretical point of view, the phenomenology of critical phenomena can be explained by starting with a realistic Hamiltonian, calculating all the quantities (using the appropriate ensemble), and comparing the results with experimental data. A realistic Hamiltonian is often very complicated to work with, however, and at a first level one simply wants to understand the mechanisms that drive the critical phenomenon. A simplified model, one that contains the essential ingredients for reproducing the phenomenon but leaves out the inessential, is needed. In this section we will study such a model, the Ising model, as it is applied to the paramagnet-ferromagnet transition.

The Ising model was introduced by Ising and Lenz as a simplified model for describing the transition between paramagnetic and ferromagnetic phases (characterized by the presence of magnetism below some critical temperature T_c, even for $H \to 0$). We recall that a paramagnetic system of N spins localized on the sites of a lattice and interacting with an external field H, is well described by the Hamiltonian

$$\mathcal{H} = -\mu_0 H \sum_{i=1}^{N} S_i, \tag{10.36}$$

where $S_i = \pm 1$ are the components of the spin i along the direction of the field. It was shown in Sec. 7.12 that the magnetization per spin $m = \mu_0 \tan(\beta \mu_0 H)$, and therefore approaches zero or any temperature T as $H \to 0$. Hamiltonian (10.36) neglects all the interactions among the spins. In the ferromagnetic Ising model, an interaction term $\mathcal{H}_{int}$ is added to Hamiltonian (10.36), i.e.,

$$\mathcal{H}_{int} = -J \sum_{\langle ij \rangle} S_i S_j, \tag{10.37}$$

where $J > 0$ is the strength of the interaction and the sum extends over all nearest neighbors on a lattice. To understand the effect of the interaction, consider two neighbor spins, e.g., 1 and 2: $-JS_1S_2 = -J$ if the two spins are parallel $S_1 = S_2 = \pm 1$, otherwise $-JS_1S_2 = +J$ if the two spins are antiparallel $S_1 = -S_2 = \pm 1$. We see that, in terms of energy, the spins tend to be parallel. For example, for $T = 0$ the system choses the configurations with minimum energy. For $H = 0$ these configurations are given by all spins up or all spins down. This consideration shows how the interaction term (10.37) may favor the alignment of the spins and therefore may induce the phenomenon of spontaneous magnetization. As usual, thermodynamic properties can be extracted, in the canonical ensemble, from the partition function,

$$Z = \sum_{\{S_i\}} \exp \left[\beta H \sum_i S_i + \beta J \sum_{\langle ij \rangle} S_i S_j \right], \tag{10.38}$$

where the sum is over all spin configurations, and for simplicity we have chosen $\mu_0 = 1$.

10.7 Other phase-transitions described by the Ising model

One of the features of the Ising model is that it is extremely versatile, e.g., it can be mapped onto other models which are suited to describe phase-transition in apparently very different systems.

10.7.1 Lattice-Gas

The lattice gas model is a simple model that describes the liquid-gas transition. One begins with a Hamiltonian for a simple fluid of the form

$$\mathcal{H} = \sum_{i=1}^{3N} \frac{p_i^2}{2m} + \sum_{i<j} U(|\vec{r}_i - \vec{r}_j|), \tag{10.39}$$

where the particles interact via a two-body potential. In the grand canonical ensemble, the grand partition function is

$$\mathcal{Z} = \sum_N e^{\beta \mu N} Z_N, \tag{10.40}$$

where Z_N is the partition function with N particles fixed. By integrating the momentum variables in Z_N and considering that

$$\lambda \equiv \int e^{-\beta[p^2/(2m)]} d\vec{p} = (2\pi mkT)^{3/2}, \tag{10.41}$$

we can write

$$\mathcal{Z} = \sum_N e^{\beta \mu_{eff} N} \frac{1}{N!} \int \exp\left[-\beta \sum_{i<j} U(|\vec{r}_i - \vec{r}_j|)\right] d\vec{r}_1 \ldots, d\vec{r}_N, \tag{10.42}$$

where $\mu_{eff} = \mu + kT \ln \lambda$.

Now we consider a simplification of (10.42) by assuming that the particle coordinates $\{\vec{r}_i\}$ can take only discrete values corresponding to the cells of a lattice. Morever, in analogy with the behavior of the Van der Waals potential for simple fluids (Fig. xx), the interparticle interaction is taken as a hard core plus an interactive potential,

$$U(\vec{r}_i - \vec{r}_j) = \begin{cases} \infty & \text{if } \vec{r}_i = \vec{r}_j \\ -\epsilon & \text{if } \vec{r}_i \text{ and } \vec{r}_j \text{ are nearest neighbors} \\ 0 & \text{otherwise} \end{cases} . \tag{10.43}$$

Each configuration in real space is given by $\{n_i\}$, where $n_i = 1$ or zero indicating whether a cell is occupied by a particle or not. Because of the hard core repulsion, two particles cannot occupy the same cell. This approximation is called the *lattice-gas*. The energy of a given configuration can be written $-\epsilon \sum_{\langle ij \rangle} n_i n_j$ and the integral in (10.41) is therefore replaced by

$$\frac{1}{N!} \int \exp\left[-\beta \sum_{i<j} U(|\vec{r}_i - \vec{r}_j|)\right] d\vec{r}_1 \ldots, d\vec{r}_N = \sum_{\{n_i\}}^{*} \exp\left[\beta\epsilon \sum_{\langle ij \rangle} n_i n_j\right] . \tag{10.44}$$

The sum is over all configurations and the asterisk indicates that the configuration must satisfy the condition$\sum_i n_i = N$, so $\sum_N \sum_{\{n_i\}}^* = \sum_{\{n_i\}}$. The correct Boltzmann counting $1/N!$ is disappeared in going to the representation in terms of the n_i's since cells cannot be overcounted (they are distinguishable because the sub-indexes i, j are now their positions).

Thus from (10.42) and (10.44) the lattice-gas grand-partition function follows

$$\mathcal{Z}_{LG} = \sum_{\{n_i\}} \exp\left[\beta \mu_{eff} \sum_i n_i + \beta\epsilon \sum_{\langle ij \rangle} n_i n_j\right], \tag{10.45}$$

where the sum is over all possible configurations of particles.

To make the connection with the Ising partition function, we note that the Ising variables can be expressed in terms of lattice gas variables

$$S_i = 2n_i - 1, \tag{10.46}$$

where $n_i = 0, 1$ for $S_i = +1, -1$. If we use (10.46) in (10.38), the Ising partition function Z_I becomes

$$Z_I\left(\frac{J}{kT},\frac{H}{kT}\right) = \sum_{\{n_i\}} \exp\left[\beta\mu_{eff}\sum_i n_i + \beta\epsilon\sum_{\langle ij\rangle} n_i n_j + W_0\right], \tag{10.47}$$

where

$$\begin{aligned} \mu_{eff} &= 2H - 2Jz \qquad (10.48)\\ \epsilon &= 4J \\ W_0 &= \beta(JNz/2 - HN), \end{aligned}$$

and z is the coordination number, namely the number of nearest-neighbor sites to a given site (be careful not to sum the interactions twice!)

From (10.47) we see that the Ising and lattice gas models are equivalent,

$$Z_I\left(\frac{J}{kT},\frac{H}{kT}\right) = \mathcal{Z}_{LG}\left(\frac{\epsilon}{kT},\frac{\mu_{eff}}{kT}\right)e^{W_0}, \tag{10.49}$$

where , ϵ, μ_{eff}, and W_0 are related to J and H through (10.49).

10.7.2 Antiferromagnets

An antiferromagnet is a material where the interactions among spins favor anti-alignement. Experimentally one observes a phase-transition at a critical temperature T_c. For $T > T_c$ spins are disordered, while below T_c there is a prevalence of anti-aligned neighboring spins. An antiferromagnet can be described by an Ising-like model with an interaction term $\mathcal{H}_{int}$ as in Eq. (10.37) but with $J < 0$. Let us consider the one-dimensional case to start with. Introducing the new spin variable $\sigma_i = (-1)^i S_i$ one has

$$\mathcal{H}_{int} = -J\sum_i S_i S_{i+1} = -J\sum_i -\sigma_i\sigma_{i+1} = -|J|\sum_i \sigma_i\sigma_{i+1}. \tag{10.50}$$

Then in term of the new variables the Hamiltonian can be written exactly as for a ferromagnet, namely with positive coupling constant. This implies that, with $H = 0$, the thermodynamic properties of an antiferromagnet are the same as those of a ferromagnet (notice however that in the presence of an external field the mapping between the two models cannot be done). A similar argument can be done in $d > 1$ if the lattice can be devided into two separated sub-lattices A and B such that two nearest neighbor spins always belong to different sub-lattices. In this case the transformation is $\sigma_i = \pm S_i$, where the symbol + applies to the spins belonging to the sub-lattice A and - in the other case. In $d = 1$ the two sub-lattices reduce to even or odd i. Such sub-lattices can be found e.g. in $d = 2$ for a square lattice but not for a triangular one.

10.7.3 Binary Mixtures

A binary mixture is a composite substance made of two kind of constituents, denoted as A and B. Experimentally one finds that a critical temperature T_c exists such that for $T > T_c$ the mixed state is stable while the two substances demix below T_c. If one imagines particles to jump on the sites of a lattice, these substances can be modeled by an Ising-like model where $S_i = +1$ corresponds to an A particle and $S_i = -1$ to a B particle. Assuming that interactions may occur only between neighboring sites we denote with ϵ_{AA}, ϵ_{BB},and ϵ_{AB} their strengths. An Ising Hamiltonian

$$\mathcal{H} = -J \sum_{\langle ij \rangle} S_i S_j - \mu_0 H \sum_i S_i + \frac{z}{2} N k \qquad (10.51)$$

can be introduced, where z is the coordination number of the lattice, N is the total number of lattice sites, and the last term, where k is a constant, does not influence the properties of the system being an additive constant to the energy.

In order to find the correspondence between $J, \mu_0 H, k$ and ϵ_{AA}, ϵ_{BB}, ϵ_{AB} let us consider the following three situations: 1) all the spins are up, 2) all the spins are down, and 3) all the neighboring spins are anti-aligned (when the lattice allows it). The total energies of these states are, respectively,

$$\frac{Nz\epsilon_{AA}}{2} = -\frac{NzJ}{2} - N\mu_0 H + \frac{z}{2} N k \qquad (10.52)$$

for state 1,

$$\frac{Nz\epsilon_{BB}}{2} = -\frac{NzJ}{2} + N\mu_0 H + \frac{z}{2}Nk \tag{10.53}$$

for state 2, and

$$\frac{Nz\epsilon_{AB}}{2} = \frac{NzJ}{2} + \frac{z}{2}Nk \tag{10.54}$$

for state 3. Eqs. (10.52,10.53,10.54) allows one to map the energy of the system into the Ising form (10.51).

10.8 Broken Symmetry

The Hamiltonian of the Ising model in a zero field is given by (10.37), and is invariant if we change $S_i \to S_i' = -S_i$, $\mathcal{H}\{S_i\} = \mathcal{H}\{S_i'\}$. The average total magnetization m per spin is given by

$$m \equiv \frac{1}{N}\sum_i m_i, \tag{10.55}$$

with

$$m_i \equiv \frac{1}{Z}\sum_{\{S_i\}} S_i e^{-\beta\mathcal{H}\{S_i\}}. \tag{10.56}$$

Since the sum is over all values of the spin variables, we can change variables $S_i' = -S_i$ and sum over all spin variables S_i' . From (10.56) and using the symmetry of the Hamiltonian

$$m_i \equiv -\frac{1}{Z}\sum_{\{S_i'\}} S_i' e^{-\beta\mathcal{H}\{S_i'\}} = -\frac{1}{Z}\sum_{\{S_i\}} S_i e^{-\beta\mathcal{H}\{S_i\}} = -m_i. \tag{10.57}$$

In conclusion, $m_i = -m_i$ implies $m_i = 0$. This result is not due to the simplicity of the Ising model, but is quite general, being valid for any realistic Hamiltonian that does not have a preferred axis of symmetry. This seems to contradict the fact that in many materials we observe a spontaneous magnetization below a critical temperature.

More generally, any realistic Hamiltonian system is usually invariant under many symmetry operations such as translations or rotations. We would therefore expect on the basis of pure symmetry arguments that the thermodynamic state should also be invariant under the same symmetry operation. This is in contradiction with everyday experience where we observe for example solid materials that are not invariant under translation. Indeed, many thermodynamic states we observe do not possess some of the symmetries that characterize the microscopic Hamiltonian that describes the system. When this happens, it is usually said that the system exhibits a spontaneously broken symmetry.

Coming back to the Ising model, in order to find a value $m \neq 0$ we must necessarily break the symmetry by introducing a field H in the Hamiltonian. Even if this does not seem to correspond to a case of spontaneous symmetry breaking, let us consider the issue more carefully and calculate the magnetization $m(H, T, N)$. By taking $H \to 0$ first and then $N \to \infty$ the result will be always zero, i.e.

$$\lim_{N \to \infty} \lim_{H \to 0} m(H, T, N) = 0. \tag{10.58}$$

This follows from the fact that, for finite N, $m(H, N)$ is an analytic function, since in Eq. (10.56) it is given by a sum of a finite number of analytic functions. Therefore, by definition, the limit $H \to 0$ is equal to the function calculated at $H = 0$, i.e.,

$$\lim_{H \to 0} m(H, T, N) = m(0, T, N) = 0, \tag{10.59}$$

where the second equality follows from the previous symmetry argument. On the other hand, by taking first the limit $N \to \infty$, the magnetization may be non-analytic below some temperature. Therefore the second limit $H \to 0$ does not necessarily coincide with the value calculated at $H = 0$ and it may happen that

$$\lim_{H \to 0} \lim_{N \to \infty} m(H, T, N) \neq 0 \tag{10.60}$$

We then say that there is a spontaneously broken symmetry if this happens for some range of the temperature.

Now let us see in more detail the mechanism giving rise to the spontaneous symmetry braking (10.60). We still consider the Ising model, but all the considerations and their validity are rather general. Given the Ising Hamiltonian for N spins, let us calculate the probability distribution $P(m, H, T, N)$ that at temperature T and external field H, the system has a magnetization $M = Nm$, i.e.,

$$P(m, H, T, N) = \frac{1}{Z} \sum_{\{S_i\}}^{(m)} e^{-\beta \mathcal{H}} = \frac{1}{Z} e^{\beta H M - \beta F_0(m, T, N)}, \tag{10.61}$$

where the $\sum^{(m)}$ means that the sum is over all configurations such that $\sum_{i=1}^{N} S_i = M$ and

$$\exp[-\beta F_0(m,T,N)] = \sum_{\{S_i\}}^{(m)} \exp\left[\beta J \sum_{\langle ij\rangle} S_i S_j\right]. \tag{10.62}$$

The partition function can be written as

$$Z = \sum_m \exp[\beta H M - \beta F_0(m,T,N)]. \tag{10.63}$$

Following the standard procedure in the canonical ensemble, the sum in Eq. (10.63) is dominated by the maximum of $HM - F_0(m,T,N)$ which satisfies the equation $H = (\partial f_0/\partial m)_{T,N}$, where we have introduces the free energy density $f_0 = F_0/N$. This value is a maximum for the probability (10.61) and a minimum for the free energy $F(m,H,T,N) = F_0(m,T,N) - HM$.

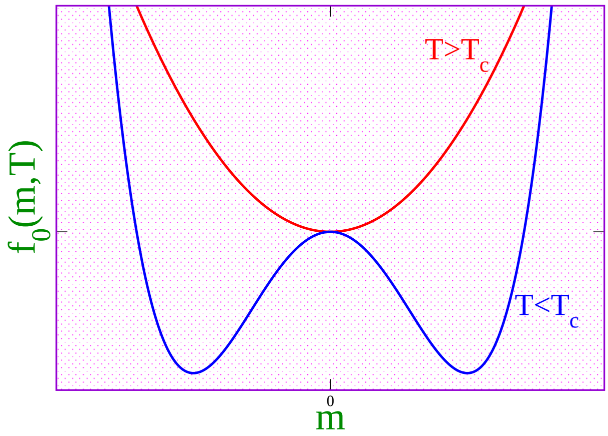

Figure 10.5: Free energy $f_0(m,T)$ of the Ising model as a function of the magnetization (per spin) m.

Consider first the case $H = 0$. Due to the symmetry $f_0(m,T) = f_0(-m,T)$, for high temperatures we expect a minimum in the free energy at $m = \overline{m} = 0$ and a maximum for the probability. For very low temperatures $T \to 0$, the free energy is dominated by the energy that has two minima, one at $+\overline{m}$ and one at $-\overline{m}$ with, in the $T = 0$ case, $\overline{m} = 1$. Therefore we also expect two minima in the free energy (Fig. 10.5) for temperature below some critical temperature T_c. Note that, in this case $H = 0$, the distribution is symmetric and the mean value of the magnetization is still zero. However the two distributions in the high and low temperature regimes are significantly different. In particular, since the exponent in Eq. (10.61) is an extensive quantity (proportional to N), in the limit $N \to \infty$, the probability distribution $P(m, T, N)$ in the magnetization per spin m, tends to the sum of two delta functions for $T < T_c$

$$\lim_{N\to\infty} P(m, T, N) = \frac{1}{2}[\delta(m - \overline{m}(T)) + \delta(m + \overline{m}(T))], \qquad (10.64)$$

and to a single delta function for $T > Tc$

$$\lim_{N\to\infty} P(m, T, N) = \delta(m). \qquad (10.65)$$

When we add a magnetic field, the free energy $f(m, H, T) \equiv f_0(m, T) - Hm$ for high temperatures has a minimum for positive values of m, while for low temperatures the free energy has two minima, the one at positive m being the lower. Correspondingly, the probability distribution has two maxima, one higher than the other. In the limit $N \to \infty$, the distribution gives a δ function that peaks around a value of $m(H, T)$ for high T, while for low T (no matter how small H is) the distribution approaches a δ function peaked around the largest maximum and the other relative maximum is suppressed (for sake of clarity we postpone the demonstration of this to the last part of this section). For high T the magnetization approaches zero as $H \to 0$, while for low T the magnetization approaches $m(0, T) > 0$, corresponding to one of the maxima of the distribution at $H = 0$.

Thus the symmetry of the paramagnetic phase is broken (i) because of the development of two maxima in the probability distribution $P(m, T, N)$, and (ii) because even a very small field gives rise to only one δ function in the limit $N \to \infty$.

On the other hand, if N is fixed in the limit $H \to 0^+$, the distribution does not become an exact δ function. It always contains a secondary maximum that, although very small for large values of H, becomes comparable to the primary maximum when H is of the order of $1/N$. Therefore in the limit $H \to 0$ the same two-peaked distribution as the one found for $H = 0$ is produced.

This discussion might imply that symmetries can be broken only in infinite systems. In reality, a macroscopic system with $N \sim 10^{23}$ particles, albeit large, is always finite. So how do we provide a realistic explanation for the broken symmetry found in systems that display spontaneous magnetization?

Suppose we take the limit $H \to 0$ for $N \sim 10^{23}$ fixed. The distribution develops two peaks centered at $-m$ and $+m$; however the system is trapped for a long time in a state corresponding to a magnetization m. If we evaluate the time τ in which the system is trapped, we realize that the system, to pass from the state with magnetization m to the state with magnetization $-m$, must pass through configurations of the phase space that are highly improbable. The dynamical process to go from one configuration to the other occurs via nucleation of a droplet. The droplet is a compact region (say a sphere) of dimension R made of overturned spins. The cost in energy is proportional to the surface of the sphere R^{d-1} and the probability that such event can occur is $p \sim e^{-R^{d-1}}$. The transition occurs when the droplet radius becomes of the order of the system size, $R \sim N^{1/d}$, where d is the space dimension. This implies that the transition probability is $p \sim \exp[-N^{(d-1)/d}]$ and the time for the transition occurrence $\tau \sim p^{-1} \sim \exp[N^{(d-1)/d}]$ sec. For $N \sim 10^{23}$, this time is of the order of $\tau \sim \exp[10^{15}]$ sec., which is much larger than the age of the universe.

Thus for measuring time scales that are negligible compared to τ, the system exhibits a breakdown of ergodicity; not all phase space is uniformly visited, and the system exhibits a *spontaneous* magnetization $\overline{m}$. Only for unrealistic measurements on time scales larger than τ will the system exhibit equal probabilities between states $-\overline{m}$ and $+\overline{m}$ and the net magnetization be zero.

In conclusion, for realistic time scales, the system behaves as if $\tau = \infty$ and as if $N = \infty$, enabling the spontaneous broken symmetry to be understood in terms of the partial breaking of ergodicity. Therefore the ensemble average, which usually gives zero, does not coincide with the time average, which gives m.

For completeness, we now show what we postponed above, namely that in the limit $N \to \infty$ the distribution $P(m, H, T, N)$ gives rise to a δ function peaked in the highest maximum. Dropping the explicit dependence on the variables H and T, Eq. (10.61) reads

$$P(m, N) = \frac{e^{-N\beta f(m)}}{\int e^{-N\beta f(m)} dm}. \tag{10.66}$$

Here we have substituted an integral for the sum. If $f(m)$ has only one minimum at $\overline{m}$ (high T) we can expand $f(m)$ around such a minimum

$$\exp[-N\beta f(m)] = \exp\left[-N\beta f(\overline{m}) - \frac{1}{2}N\beta\lambda(m-\overline{m})^2\right], \quad (10.67)$$

where

$$\lambda = -\left(\frac{\partial^2 f}{\partial m^2}\right)_{m=\overline{m}}. \quad (10.68)$$

Therefore, from (10.66),

$$P(m,N) = \frac{e^{-(1/2)N\beta\lambda(m-\overline{m})^2}}{\int e^{-(1/2)N\beta\lambda(m-\overline{m})^2}dm}, \quad (10.69)$$

which in the limit $N \to \infty$ tends to a δ function peaked around $\overline{m}$. If $f(m)$ has two minima at m_1 and m_2 with $f(m_2) > f(m_1)$ we can expand around the two minima and write

$$\begin{aligned}\exp[-N\beta f(m)] &= \exp\left[-N\beta f(m_1) - \frac{N}{2}\beta\lambda_1(m-m_1)^2\right] + \\ &+ \exp\left[-N\beta f(m_2) - \frac{N}{2}\beta\lambda_2(m-m_2)^2\right], \quad (10.70)\end{aligned}$$

with

$$\lambda_i = \left|\left(\frac{\partial^2 f}{\partial m^2}\right)_{m=m_i}\right| \quad ; \quad i = 1, 2. \quad (10.71)$$

Using (10.70), we can evaluate the integral

$$\int e^{-N\beta f(m)}dm = \sqrt{\frac{\pi}{N\beta\lambda_1}}e^{-N\beta f(m_1)} + \sqrt{\frac{\pi}{N\beta\lambda_2}}e^{-N\beta f(m_2)}. \quad (10.72)$$

Since $f(m_1) < f(m_2)$, in the limit $N \to \infty$ the second term can be neglected. From (10.66), (10.70) and (10.72)

$$\begin{aligned}P(m,N) &= \frac{\sqrt{N\beta\lambda_1}}{\sqrt{\pi}}\left(e^{-(1/2)N\beta\lambda_1(m-m_1)^2} + \right. \\ &+ \left. e^{-N\beta[f(m_2)-f(m_1)]}e^{-(1/2)N\beta\lambda_2(m-m_2)^2}\right). \quad (10.73)\end{aligned}$$

In the limit $N \to \infty$, the second term can be neglected and the distribution tends to a δ function centered at m_1.

10.9 Fluctuation-Dissipation theorem

We are now interested in the behavior of the correlation function

$$g(r) = \langle S_i S_j \rangle - \langle S_i \rangle \langle S_j \rangle. \tag{10.74}$$

Due to space homogeneity and isotropy this quantity depends only on the distance r between i and j. We also introduce the (local) susceptibility

$$\chi(r) = \left. \frac{\delta \langle S_i \rangle}{\delta H_j} \right|_{H=0} \tag{10.75}$$

describing the effect of a magnetic field $H_j = H$ present only on site j on the magnetization of a spin in i.

The two quantities g and χ are not independent. In order to see this, let us compute the latter in a canonical setting, as

$$\chi(r) = \frac{\delta}{\delta H} Z^{-1} \sum_{\{S_k\}} S_i e^{-\beta[\mathcal{H}_0 - H S_j]} \Bigg|_{H=0}, \tag{10.76}$$

where $\mathcal{H}_0$ is the Hamiltonian in the absence of H_j (for instance, but not necessarily, the one in Eq. (10.37)). One has

$$\chi(r) = Z^{-2}\beta \left[Z \sum_{\{S_k\}} S_i S_j e^{-\beta \mathcal{H}_0} - \sum_{\{S_k\}} S_i e^{-\beta \mathcal{H}_0} \cdot \sum_{\{S_k\}} S_j e^{-\beta \mathcal{H}_0} \right] \tag{10.77}$$

Hence one arrives at

$$\chi(r) = \beta g(r) \tag{10.78}$$

This fundamental relation is the Fluctuation-Dissipation theorem. It relates the response of the system to an external parameter, or perturbation, to the correlations which are present in the system when the perturbation is not present (notice, in fact, that the averages in Eq. (10.77) are taken with respect to the Hamiltonian H_0).

One might ask which is the relation between the (local) susceptibility introduced in Eq. (10.75) and the one ($\chi = \partial m / \partial H$, with H a constant magnetic field) considered before. In order to see this we can repeat the calculation done before, which now reads

$$\chi = \frac{\delta}{\delta H} Z^{-1} \sum_{\{S_k\}} S_i e^{-\beta[\mathcal{H}_0 - H \sum_j S_j]} \Bigg|_{H=0}. \tag{10.79}$$

Proceeding analogously one obtains

$$\chi = \sum_{\vec{r}} g(r) = \widetilde{g}(k=0), \tag{10.80}$$

where $\widetilde{g}(k)$, the so called *structure factor* is the Fourier transform of $g(r)$. This is the Fluctuation-Dissipation theorem for the global quantities. Notice that Eq. (10.80) implies also that

$$\chi = \sum_{\vec{r}} \chi(r). \tag{10.81}$$

In other words, if an uniform field H is applied on all the sites of the system, the global response of the system is the sum of all the local responses.

10.10 Mean-Field Theories

Mean-field theories offer a very simple and powerful theory of phase transitions requiring minimal assumptions.

10.10.1 Landau's Theory

We have shown how the partition function can be written for an Ising model,

$$Z = \int e^{-\beta N f(m,H,T)} dm, \tag{10.82}$$

where $f(m,H,T) = f_0(m,T) - Hm$ is the free energy density, which has the symmetry property $f_0(m,T) = f_0(-m,T)$. The partition function of any system that has the same symmetry properties can be written in the form (10.82), so what follows is rather general.

The idea is that close to the critical point the magnetization is small. This allows us, if we assume that the free energy is analytic, to develop the free energy f for small values of m and to stop at the 4-th order,

$$\widetilde{f}(m,H,T) = f(0,H,T) + a(T)m^2 + b(T)m^4 - Hm, \tag{10.83}$$

where we have used the fact that, since $f(m,T)$ is even in m, only even powers enter into the expansion. $a(T)$ and $b(T)$ are the coefficients of the expansion and are functions of the temperature. If we assume that $a(T)$ becomes zero for some temperature $T = T_c$ (which we will see corresponds to the critical temperature) and that $a(T)$ and $b(T)$ are analytic close to T_c, we can write the lowest order in $T - T_c$

$$a(T) = a_0(T - T_c) \quad , \quad b(T) = b_0, \tag{10.84}$$

with a_0 and b_0 constants that we assume to be positive. Inserting these values in (10.83), and plotting the free energy f as a function of m, we find one minimum for $T > T_c$ and two minima for $T < T_c$, as in Fig. 10.5. The minimum of the free energy gives the average value of m. From (10.83), equating the first derivative to zero gives

$$m[2a_0(T - T_c) + 4b_0 m^2] = H, \tag{10.85}$$

which represents the equation of state relating H, m, and T. For $H = 0$, (10.85) gives

$$m = \begin{cases} 0 & \text{if } T > T_c \\ \pm\sqrt{\frac{1}{2}\frac{a_0}{b_0}(T_c - T)} & \text{if } T < T_c \end{cases} . \tag{10.86}$$

There is also a solution $m = 0$ for $T < T_c$, but it corresponds to a maximum. Therefore the magnetization approaches zero at T_c, the critical temperature, with a critical exponent $\beta = 1/2$.

The susceptibility $\chi_T = (\partial m/\partial H)_T$ can also be calculated from the equation of state (10.85)

$$\chi_T^{-1} = \left(\frac{\partial H}{\partial m}\right)_T = 2a_0(T - T_c) + 12 b_0 m^2, \tag{10.87}$$

where m is also obtained from the equation of state. In the particular case $H = 0$, substituting the solution (10.86) for m one has

$$\chi_T = \begin{cases} [2a_0(T - T_c)]^{-1} & \text{if } T > T_c \\ [8a_0(T_c - T)]^{-1} & \text{if } T > T_c \end{cases} , \tag{10.88}$$

which predicts a critical exponent $\gamma = 1$. Note that the critical exponents above and below T_c are equal. Further, we see that the critical amplitudes (see Eq. (10.25) $B_+ = 4B_-$.

The specific heat C_H can easily be calculated from the free energy as $C_H = \partial E/\partial T = -\beta^{-1}\partial^2 F/\partial T^2$. The result for $H = 0$ gives a jump $C_H(T_c^+) - C_H(T_c^-) = kT_c a_0^2/(2b_0)$ with exponents $\alpha = \alpha' = 0$. Finally, Eq. (10.85) provides $m(T_c, H) \propto H^{1/3}$, and hence $\delta = 3$.

In conclusion, Landau's theory is a rather general theory based on symmetry considerations and on the assumption of analyticity in the order parameter of the free energy. It does not start from a specific Hamiltonian, so the parameters a_0 , b_0 , and T_c are not obtained within the theory and will depend on the particular system under consideration. On the other hand, the exponents of this particular model are universal and independent provided that the free energy is expanded to fourth order in the order parameter. Although we assume the free energy to be analytic in the order parameter, it does lead to quantities e.g. magnetization, susceptibility, and specific heat that are not analytic in T. We will see that the critical exponents of the Landau theory are not quite in agreement with most experimental data. The reason is that the basic assumption of the analyticity of the free energy, although it gives qualitatively the known experimental results, is not quite correct. This warns us that it is important in every physical problem to assume analyticity in the right quantities. To find the right results we have to search for analyticity in other quantities. We will do this later, within the framework of the renormalization group, a theory that goes beyond mean-field calculation.

10.10.2 Weiss Theory

The Weiss approximation is a theory that predicts the same critical exponents as those found in Landau's theory of critical phenomena. However, it starts with a microscopic Hamiltonian and calculates the free energy and other quantities of interest by introducing an approximation in which each spin feels the effect of the others through a mean field, whose strength is calculated self-consistently. The Weiss approach is similar in spirit to the Hartree-Fock theory in solid state physics in which a system of N interacting electrons is approximated by N independent electrons, each in a self- consistent field due to the presence of the other $N-1$ electrons.

We apply the Weiss theory to the Ising model in a field

$$\mathcal{H} = -J\sum_{\langle ij\rangle} S_iS_j - H\sum_i S_i = -\sum_i H_iS_i. \tag{10.89}$$

The quantity

$$H_i = H + J\sum_{\langle j\rangle_i} S_j \tag{10.90}$$

where $\langle j\rangle_i$ denote the nearest neighbors of i, is the so called *molecular* field, or Weiss field, and represents the effective field felt by S_i. By adding and and subtracting to each spin the average magnetization $m \equiv \langle S_i \rangle$, which does not depend on i due to space homogeneity (because the Hamiltonian is invariant under (discrete) translations) the Hamiltonian (10.89) can be cast as

$$\mathcal{H} = -H_{eff} \sum_i S_i + \frac{Jm^2Nz}{2} - J \sum_{\langle ij \rangle} (S_i - m)(S_j - m), \quad (10.91)$$

where z is the coordination number, i.e. the number of nearest-neighbor spins of spin i, and

$$H_{eff} = H + Jzm. \quad (10.92)$$

The key idea of the Weiss theory is to neglect the fluctuations of the variable S_j. Then, dropping the last term in Eq. (10.91) one has the mean-field approximation

$$\mathcal{H} \simeq \mathcal{H}_{eff} = -H_{eff} \sum_i S_i + \frac{Jm^2Nz}{2} \quad (10.93)$$

Notice that $H_{eff} = \langle H_i \rangle$. Then the mean-field approximation has replaced the original Hamiltonian (10.89) of N interacting spins by a new Hamiltonian $\mathcal{H}_{eff}$ (10.93) of N independent spins interacting with an effective external field H_{eff} that depends on m, which must be self-consistently calculated. Since the last term is a constant it does not influence the computation of average quantities (it cancels out). Hence the problem is formally identical to the one considered in Sec. 7.12, and we can borrow the result obtained there

$$m = \tanh(\beta H_{eff}) = \tanh[\beta(Jzm + H)]. \quad (10.94)$$

For $H = 0$ this is a transcendental equation that can be solved graphically by plotting the left-hand side and right-hand side as a function of m for each value of β. The intersection of the two curves gives the solution. The first term $y = m$ is a straight line with a slope 1. The second curve $y = \tanh(\beta Jzm)$ has at the origin a slope

$$\left. \frac{dy}{dm} \right|_{m=0} = \beta Jz. \quad (10.95)$$

If the slope is $\beta Jz < 1$ (high temperature), $m = 0$ is the only solution. When the slope is $\beta Jz > 1$ (low temperature), solutions can be $m = 0$ and $m = \pm\overline{m}$. The solution $m = 0$ corresponds to a maximum in the free energy and is unstable. The other two correspond to minima at $m = \pm\overline{m}$, where $\overline{m}$ goes to zero at the value $\beta_c Jz = 1$, corresponding to the critical temperature

$$k_B T_c = Jz. \tag{10.96}$$

The partition function is

$$Z = \left[e^{-\frac{\beta Jzm^2}{2}} \sum_{S_i} e^{-\beta H_{eff} S_i} \right]^N = \left[2\, e^{-\frac{\beta Jzm^2}{2}} \cosh(\beta H_{eff}) \right]^N , \tag{10.97}$$

from which the free energy (per spin) $f = -k_B T N^{-1} \ln Z$ reads

$$f = \frac{Jzm^2}{2} - k_B T \ln\left[\cosh(\beta Jzm)\right] - k_B T \ln 2. \tag{10.98}$$

We want now to establish a relation with the Landau's theory. In order to do this, we consider the region with small m and expand the free energy up to fourth order in m (we neglect the last irrelevant constant term on the r.h.s. of Eq. (10.98))

$$\begin{aligned} f &\simeq \frac{Jzm^2}{2} - k_B T \ln\left[1 + \frac{1}{2}(\beta Jzm)^2 + \frac{1}{4!}(\beta Jzm)^4\right] \\ &\simeq \frac{Jzm^2}{2} - k_B T \left[\frac{1}{2}(\beta Jzm)^2 + \frac{1}{4!}(\beta Jzm)^4 - \frac{1}{2}\left(\frac{1}{2}(\beta Jzm)^2\right)^2\right] \\ &= \frac{Jz}{2}(1 - \beta Jz)m^2 + \frac{k_B T}{12}(\beta Jzm)^4, \end{aligned} \tag{10.99}$$

or

$$f = a_0 (T - T_c) m^2 + b_0 m^4 \tag{10.100}$$

with

$$a_0 = \frac{Jz}{2T_c} \qquad \text{and} \qquad b_0 = \frac{(Jz)^4}{12(k_B T_c)^3}. \tag{10.101}$$

Eq. (10.100) is the same expression found in Landau's theory for the free energy density, but now the coefficients are explicitly known. Consistent with Landau's theory, $a(T)$ is zero at $T_c = Jz/k_B$. The critical exponents are therefore the same as in the Landau theory. Needless to say, these exponent could be easily derived within the present theory (without mapping it on Landau's theory). For instance β is easily derived from Eq. (10.94) by expanding $\tanh x$ to order x^3

$$m \simeq \beta Jzm - \frac{1}{3}(\beta Jzm)^3 \tag{10.102}$$

yielding

$$m^2 \simeq 3\,\frac{T_c - T}{T_c} \tag{10.103}$$

and hence $\beta = 1/2$. In the presence of the external field, expanding again Eq. (10.94) one has

$$m \simeq \beta Jzm + \beta H - \frac{1}{3}(\beta Jzm + \beta H)^3. \tag{10.104}$$

At $T = T_c$ this equation reads

$$m \simeq m + \beta_c H - \frac{1}{3}(m + \beta_c H)^3 \tag{10.105}$$

where we have used Eq. (10.96). Let us make the ansatz (to be verified shortly by consistency) that $m \propto H^{1/\delta}$ with $\delta > 1$. Then we can neglect the term proportional to H in the cubic term on the r.h.s. of Eq. (10.104), thus obtaining

$$m = m + \beta_c H - \frac{1}{3}m^3 \tag{10.106}$$

leading immediately to $\delta = 3$. Upon deriving Eq. (10.104) with respect to H and letting $H = 0$, for the spin susceptibility one has

$$\chi = \beta Jz\chi + \beta - (\beta Jzm)^2(\beta Jz\chi + \beta). \tag{10.107}$$

For $T > T_c$, letting $m = 0$ one has

$$\chi \simeq \beta_c \left(\frac{T - T_c}{T_c}\right)^{-1} \tag{10.108}$$

yielding $\gamma = 1$. The same result applies also for $T < T_c$. Indeed one sees that in this case the last term in Eq. (10.107) contributes only with a constant as $T \to T_c$ and does not change the exponent γ. Finally, in order to determine the specific heat exponent let us evaluate the energy $\langle E\rangle = -\frac{\partial \ln Z}{\partial \beta}$. Using Eq. (10.97) for $\ln Z$ one has

$$\langle E\rangle = \frac{Jzm^2}{2} + \beta Jzm\frac{\partial m}{\partial \beta} - Jz\tanh(\beta Jzm)\left(m + \beta\frac{\partial m}{\partial \beta}\right) = -\frac{Jzm^2}{2}. \tag{10.109}$$

Considering the specific heat $C = N^{-1}\partial E/\partial T$, from Eq. (10.109), letting $m = A_-(T_c - T)$ below T_c one finds

$$C \simeq \begin{cases} 0\,, & T > T_c \\ \frac{JzA_-^2}{2}\,, & T < T_c. \end{cases} \tag{10.110}$$

Hence the specific heat has a jump but not a singularity, and $\alpha = 0$.

We show now that the mean-field theory becomes exact for a system where the interaction is not restricted to the neighbours but any spin interact equally with all the others with strength J/N (normalization with N amounts to a redefinition of J when interaction is limited to neighbouring spins but is necessary to keep the global interaction strength finite when the interaction range goes to infinity). In this case Eq. (10.89) applies with

$$H_i = H + \frac{J}{N}\sum_{j\neq i} S_j \tag{10.111}$$

where, at variance with Eq. (10.90), the sum is extended to all the spins except the one in i. The molecular field in this case can be written as

$$H_i = H + \frac{J}{N}\left(\sum_j S_j - S_i\right) = H + J\left(m - S_i/N\right) \simeq H + Jm, \tag{10.112}$$

where the last equality holds in the thermodynamic limit in which $N \to \infty$. This is the form (10.92) of H_{eff} used in the mean-field approach. This shows that mean-field is exact for systems with an interaction strength that does not decay with distance. It can be shown that mean-field is also appropriate for systems where interactions decay sufficiently slowly (i.e. algebraically with a sufficiently small negative exponent) with distance.

There are many way to improve the Weiss mean-field result for a system with a finite interaction range. One way is to consider a cell made of one spin interacting with its z neighbors and an external field acting on the z neighbors as a result of the interaction due to all other spins. Increasingly better approximations can be obtained by taking larger and larger cells, within which the problem can be solved exactly and treating the remaining spins as a self-consistent field. In the limit of an infinite cell, one can expect to have solved the problem exactly. For a finite cell, even though such quantities as magnetization and susceptibility approach the correct results over a large temperature range, in the vicinity of the critical point there is always a mean-field behavior characterized by Landau's exponents.

Correct critical exponents are not found because solving the problem exactly in a finite cell implies summing up a finite number of degrees of freedom, which in turn implies analyticity in the free energy and thus in Landau's critical exponents. In other words, at temperatures away from the critical point the correlation length is finite. The system is made of cells with a size of the order of ξ that do not interact with each other. Therefore if we sum over a finite number of degrees of freedom inside a cell, we will get correct results. As $T \to T_c$ however, the correlation length becomes infinite and any approximation involving the sum over a finite number of degrees of freedom cannot give the correct critical exponents.

10.10.3 Bragg-Williams Theory

10.10.4 The Van der Waals Theory as a mean field theory

The partition function of a real gas is

$$Z(T,V,N) = \int d\vec{p}_1 \dots d\vec{p}_N e^{-\beta \sum_i \frac{p_i^2}{2m}} \int d\vec{r}_1 \dots d\vec{r}_N e^{-\beta \sum_{ij} V(|r_{ij}|)}, \tag{10.113}$$

where $r_{ij} = |\vec{r}_i - \vec{r}_j|$ is the distance between particles i and j. As it is the partition function (10.113) cannot be evaluated (in general) because of the interaction term V. Then, in order to proceed, we introduce a *mean field* approximation by saying that each particle i feels an effective potential $U(\vec{r}_i)$ due to the presence of all the other particles. We also assume that $U(\vec{r}_i)$ has the simple form

$$U(\vec{r}_i) = U(r_i) = \left\{ \begin{array}{ll} \infty & r < r_0 \\ \overline{u} < 0 & r \geq r_0, \end{array} \right. \tag{10.114}$$

namely there is an hard-core repulsion for small distances $r < r_0$ and a costant attraction otherways. We also make the reasonable assumption that $\overline{u}$ is proportional to the density $\overline{u} = -c\rho$, where c is a positive constant, which we can write as

$$\overline{u} = -a\frac{n^2}{NV}, \tag{10.115}$$

where n is the number of moles and $a = cN_A^2$, N_A being the Avogadro number. Plugging the form (10.114) into Eq. (10.113) one has

$$Z(T,V,N) = \left[\lambda \int d\vec{r}_i e^{-\beta U(r_i)}\right]^N, \tag{10.116}$$

where λ is the value of the momentum integration which does not depend on V. Using Eq. (10.114) one has

$$Z(T,V,N) = \left[\lambda\,(V-V_e)e^{-\beta\overline{u}})\right]^N, \tag{10.117}$$

where $V_e = \int_{r_i<r_0} d\vec{r}_i$ is the *excluded volume*. This quantity is proportional to the number of particles, $V_e = CN$, where C is a constant, so we can write

$$V_e = bn, \tag{10.118}$$

where $b = CN_A$. Computing the pressure as $p = -\left.\frac{\partial F}{\partial V}\right|_T = k_BT\left.\frac{\partial \ln Z}{\partial V}\right|_T$ one has

$$p = \frac{Nk_BT}{V-nb} - \frac{an^2}{V^2}, \tag{10.119}$$

which is the Van der Waals Equation (10.14) (recall that $Nk_B = nR$). This shows that the Van der Waals approach is a mean-field theory.

10.10.5 Correlation functions

Landau's theory describe the system directly in term of the macro-variable m and therefore, in the form of Sec. 10.10.1, it does not allow one to study correlations which are produced by the fluctuations of the micro-variables S_i. We then try to *upgrade* the theory by writing a Landau free energy of the form

$$F(T,H) = \int d\vec{r}\left[a(T)\phi^2(\vec{r}) + b(T)\phi^4 - H(\vec{r})\phi(\vec{r}) + c(T)|\vec{\nabla}\phi(\vec{r})|^2\right], \tag{10.120}$$

where $\phi(\vec{r})$ is a field with the meaning of the magnetization at position $\vec{r}$, i.e. $\int d\vec{r}\phi(\vec{r}) = m$. By assuming $\phi(\vec{r}) = m =$ const., Eq. (10.120) reduces to the Landau's free energy introduced in Sec. 10.10.1. Eq. (10.120), therefore, represents a generalization to the case in which there is a spatially varying magnetization. Notice that, in this case, the last term represent the lowest order term compatible with the required symmetry for $\phi \to -\phi$ for $H = 0$ in a gradient expansion. As explained in Sec. 10.10.1, to lowest order one assumes $a(T) = a_0(T-T_c)$, $b(T) = b_0$ and, analogously, $c(T) = c_0$. It can be shown that the free energy (10.120) provides the correct description of the critical properties (e.g. it gives the correct critical exponents). However this theory is not analytically solvable.

We now minimize the free energy

$$\frac{\delta F(T,H)}{\partial \phi(\vec{x})} = 2a(T)\phi(\vec{x}) + 4b_0\phi^3(\vec{x}) - H(\vec{x}) - 2c_0\nabla^2\phi(\vec{x}) = 0. \tag{10.121}$$

To obtain the last term we have used

$$\frac{\partial}{\partial \phi(\vec{x})}\int d\vec{r}\,|\vec{\nabla}\phi(\vec{r})|^2 = 2\int d\vec{r}\;\vec{\nabla}\phi(\vec{r})\cdot\vec{\nabla}\delta(\vec{x}-\vec{r}) \tag{10.122}$$

$$= \quad -2\int d\vec{r}\,[\vec{\nabla}\cdot\vec{\nabla}\phi(\vec{r})]\cdot\delta(\vec{x}-\vec{r}) + [\vec{\nabla}\cdot\phi(\vec{r})]\delta(\vec{x}-\vec{r})\Big|_{Border},$$

and neglected the border term which is located at infinity (if this is not sufficiently clear one can try to do the computation first in one dimension, and, as a second step, to perform the computation in arbitrary dimension by introducing the components). In order to obtain the susceptibility of Eq. (10.75) we derive Eq. (10.121) with respect to $H(\vec{y})$ obtaining

$$2a(T)\chi(r) + 12b_0\phi^2(\vec{x})\chi(r) - \delta(\vec{r}) - 2c_0\nabla^2\chi(r) = 0 \tag{10.123}$$

Since this equation cannot be solved, in order to be able to proceed, we resort to a mean-field-like approximation in which we substitute $\phi^2(\vec{x})$ with $\langle\phi^2(\vec{x})\rangle = S$, which does not depend on space due to homogeneity. Going to Fourier space one arrives at

$$[2a(T) + 12b_0S + 2c_0k^2]\widetilde{\chi}(k) = 1. \tag{10.124}$$

Hence, using the Fluctuation-Dissipation theorem (10.78) one has

$$\widetilde{g}(k) = \frac{kT}{2c_0}\,\frac{\xi^2}{k^2\xi^2+1}, \tag{10.125}$$

where

$$\xi = \sqrt{2c_0}\,[2a(T) + 12b_0S]^{-\frac{1}{2}}. \tag{10.126}$$

Since this quantity has the dimension of a length and there are no other lengths present in expression (10.125), ξ is the coherence length. Indeed we will show below that $C(r)$ decays over a typical distance $r \sim \xi$. Using the form (10.84) of $a(T)$ one has

$$\xi = \xi_0\left(\frac{|T-T_c|}{T_c}\right)^{-\nu} \tag{10.127}$$

with the critical exponent $\nu = 1/2$ and

$$\xi_0 = \begin{cases} \left(\frac{c_0}{a_0 T_c}\right)^{1/2} & , \quad T > T_c \\ \left(\frac{c_0}{4a_0 T_c}\right)^{1/2} & , \quad T < T_c \end{cases} \tag{10.128}$$

Eq. (10.125) is known as the Ornstein-Zernike form of the correlation. It states that

$$\widetilde{g}(k) \sim k^{-(2-\eta)} \tag{10.129}$$

for $k\xi \gg 1$, with the critical exponent $\eta = 0$. Transforming Eq. (10.129) back to real space one obtains

$$g(r) = \frac{kT}{2c_0} r^{-(d-2+\eta)} Y\left(\frac{r}{\xi}\right), \tag{10.130}$$

where, in $d = 3$, it is

$$Y(z) \propto e^{-z}. \tag{10.131}$$

This shows that ξ is the typical length over which $C(r)$ decays.

10.10.6 Ornstein-Zernike Theory

The mean-field version that we have treated thus far has allowed the calculation of such quantities as order parameter, susceptibility, and specific heat. These quantities do not depend on coordinates. Now we want to apply a mean-field theory to the pair-correlation function originally proposed by Ornstein and Zernike. As in Landau's theory, we start with a generic system and assume that some quantity we define has analyticity.

To fix the ideas, we consider the density-density pair correlation function $g(\vec{r})$ for a fluid, but the procedure will also be valid for spin systems. Remember that $g(\vec{r})$ measures the correlation between two points at a distance $\vec{r}$, i.e., it quantifies the effect that one density fluctuation at a given point has on the density fluctuation at another point separated by a distance $\vec{r}$. The range within which the effect is felt, i.e., the range within which $g(\vec{r}) = 0$, is called the correlation length ξ and has been precisely defined in Eq. (10.6). Thus, near the critical point, $g(\vec{r})$ develops long-range correlation. In fact, $\int g(\vec{r}) d\vec{r}$, which is proportional to the compressibility, diverges at the critical point. Therefore if we consider the Fourier transform, $\widetilde{g}(\vec{k}) = \int g(r) e^{\vec{k}\cdot\vec{r}} d\vec{r}$, for $k = 0$, $\widetilde{g}(0) = \int g(\vec{r}) d\vec{r}$ diverges at T_c.

Therefore $\widetilde{g}(\vec{k})$ is not an analytic function at $T = T_c$ and $k = 0$. We can never develop a theory that assumes $\widetilde{g}(\vec{k})$ is an analytic function, and thus this cannot help us to find the desired divergence, even qualitatively.

We introduce another quantity, the direct pair correlation function, which is defined by

$$g(\vec{r}) \equiv C(\vec{r}) + \int C(\vec{r} - \vec{r}')g(\vec{r}')d\vec{r}'. \tag{10.132}$$

Taking the Fourier transform of (10.132), we have

$$\widetilde{g}(\vec{k}) = \widetilde{C}(\vec{k}) + \widetilde{C}(\vec{k})\widetilde{g}(\vec{k}), \tag{10.133}$$

from which

$$\widetilde{C}(\vec{k}) = \frac{\widetilde{g}(\vec{k})}{1 + \widetilde{g}(\vec{k})}. \tag{10.134}$$

So given the pair correlation function $\widetilde{g}(\vec{k})$, the direct pair correlation function $\widetilde{C}(\vec{k})$ is uniquely defined by (10.134). From (10.133) we can also express $\widetilde{g}(\vec{k})$ as a function of $\widetilde{C}(\vec{k})$,

$$\widetilde{g}(\vec{k}) = \frac{\widetilde{C}(\vec{k})}{1 - \widetilde{C}(\vec{k})}. \tag{10.135}$$

From (10.135) we note that if $\widetilde{C}(0)$ at T_c equals 1, $\widetilde{g}(0)$ diverges and $k = 0$. Therefore $\widetilde{C}(\vec{k})$ can be a well-behaved function at $T = T_c$, even if $\widetilde{g}(\vec{k})$ is not.

Before we proceed to the evaluation of $\widetilde{g}(\vec{k})$, we give a physical interpretation to the direct pair correlation function $C(\vec{r})$. From (10.132) we can perturbatively solve the integral equation as

$$g(\vec{r}) = C(\vec{r}) + \int C(\vec{r}_1)C(\vec{r}-\vec{r}_1)d\vec{r}_1 + \int C(\vec{r}_1)C(\vec{r}_2-\vec{r}_1)C(\vec{r}-\vec{r}_2)d\vec{r}_2 d\vec{r}_1 + \ldots. \tag{10.136}$$

Graphically, this series can be expressed as ...

The first term $C(\vec{r})$ can be interpreted as the contribution to $g(\vec{r})$ from the direct correlation, and the second term as the contribution to $g(\vec{r})$ from the product of two direct correlations, i.e., the two points $\vec{0}$, r are correlated by a direct correlation that propagates from $\vec{0}$ to an intermediate point $\vec{r}_1$ and from $\vec{r}_1$ to $\vec{r}_2$, and so on.

Thus although $C(\vec{r})$ is short-range, this propagation mechanism can give rise to long-range correlations.

We now proceed as in the Landau theory and expand $\widetilde{C}(\vec{k})$ as a power of k^2 (since $g(\vec{r})$ is a function of the modulus of $|\vec{r}|$, the first term is in k^2). Assume that we are at fixed density $\rho = \rho_c$ and $T > T_c$. Our concern is the behavior at large r, so we stop at the first order in k^2,

$$\widetilde{C}(\vec{k}, T) = \widetilde{C}(0, T) + B(T)k^2 + \dots, \tag{10.137}$$

From (10.135) it follows at T_c that $\widetilde{C}(0, T_c) = 1$. We assume analyticity near T_c, so

$$\widetilde{C}(0, T) = 1 + A_0(T - T_c) \qquad \text{and} \qquad B(T) = B_0. \tag{10.138}$$

For simplicity, we have assumed T to be above the critical temperature along the line where the order parameter is 0 ($\rho_L = \rho_G = \rho_c$ for a fluid); we could otherwise include a dependence on the order parameter M which would contribute a term proportional to M^2 in (10.138).

In conclusion, from (10.135), (10.137), and (10.138) we can write to the lowest order in k^2 and $T - T_c$,

$$\widetilde{g}(\vec{k}, T) = \frac{D}{\xi^{-2} + k^2}, \tag{10.139}$$

where

$$D = -B_0^{-1}, \qquad \xi^{-2} = \xi_0^{-2}\frac{T - T_c}{T_c}, \qquad \text{and } \xi_0^{-2} = T_c A_0 D. \tag{10.140}$$

For $k = 0$, we have

$$\widetilde{g}(0, T) = \frac{1}{A_0(T - T_c)}. \tag{10.141}$$

Since $\widetilde{g}(0, T)$ is the square of the density fluctuation, it must be positive. Therefore $A_0 > 0$. From (10.141) we also find the compressibility diverges with an exponent $\gamma = 1$, as found in the Landau theory.

Since the only divergence of $\widetilde{g}(\vec{k}, T)$ is at $k = 0$, B_0 also is negative. The form of (10.139), which is called a Lorentzian, is valid near $T = T_c$ and when $\vec{k}$ is small. By performing a Fourier transform

(10.139), we obtain $g(\vec{r})$ for large values of r

$$g(\vec{r}) \propto \frac{e^{-r/\xi}}{r^{d-2}}, \tag{10.142}$$

where d is the space dimension.

From (10.142), it follows that ξ coincides with the correlation length of (10.141), for which

$$\xi \simeq \xi_0 \left(\frac{T - T_c}{T_c} \right)^{-\nu}, \tag{10.143}$$

with an exponent $\nu = 1/2$. For $T > T_c$, therefore, the pair correlation function for large r decays exponentially while at T_c it decays algebraically,

$$g(\vec{r}) = \frac{1}{r^{d-2+\nu}}, \tag{10.144}$$

with $\nu = 0$.

As stated earlier, the Ornstein-Zernike theory does not begin with a particular model. It only assumes the analyticity of $\widetilde{C}(\vec{k}, T)$ near $T = T_c$ and $k = 0$. As in the Landau theory, T_c and the amplitudes of the divergences are not determined, and will depend on the particular model considered. The critical exponents are universal and will be valid for any model that satisfies the analyticity requirement for $\widetilde{C}(\vec{k}, T)$. To perform an explicit calculation including T_c and the amplitudes, we can calculate $\widetilde{C}(\vec{k}, T)$. This can be done starting from definition (10.134). By doing a series expansion in β, to the first order, it is possible to show (see Problem) that

$$\widetilde{C}(\vec{k}) = \frac{\widetilde{V}(\vec{k})}{kT}, \tag{10.145}$$

where

$$\widetilde{V}(\vec{k}) = \int V(\vec{r}) e^{i\vec{k}\cdot\vec{r}} d\vec{r}, \tag{10.146}$$

and $V(\vec{r})$ is the interacting potential. This result is also valid for the Ising model or lattice gas model, except that the discrete sum must be used instead of the integral over all lattice sites in (10.146). The critical temperature is therefore given by condition (10.139)

$$\frac{\widetilde{V}(0)}{kT_c} = 1. \tag{10.147}$$

In the case of the Ising model $\widetilde{V}(0) = zJ$, which gives the Weiss result $k_B T_c = zJ$. Other quantitites such as ξ can be obtained by calculating (10.146) to the order k^2.

10.10.7 Summary on mean-field critical exponents

In conclusion, the mean-field theory predicts for fluids and magnets the following behaviors and critical exponents:

$M \sim \epsilon^{\beta}$	$\beta = 1/2$	Order parameter
$\chi \sim \epsilon^{-\gamma}$	$\gamma = 1$	Compressibility or susceptibility
$C \sim \epsilon^{-\alpha}$	$\alpha = 0$	Spec. heat at const. volume or field
$g(r) \sim e^{-r/\xi}/r^{d-2+\nu}$	$\nu = 0$	Pair correlation function
$\xi \sim \epsilon^{-\nu}$	$\nu = 1/2$	Correlation length
$M \sim H^{1/\delta}$	$\delta = 1/3$	Order parameter at T_c

Note the unphysical prediction that for $d = 1$ and $d = 2$ the pair correlation function will not decay, and for $d = 1$ will increase with distance. This defect arises from the fact that the mean-field theory is based on an assumption of analyticity, which is not necessarily correct.

10.10.8 Mean-field breakdown: The Ginzburg criterion

As we have already pointed out, mean field theories provides in many cases a qualitatively correct description of phase-transitions but their quantitative predictions are wrong. It is known, for instance, that the mean-field critical exponents do not agree with the real critical ones observed in experiments or in the few exactly soluble cases (See Sec. 10.11 and table 10.1 specifically). This happens because the mean-field does not take into account appropriately the ever growing fluctuations that set in the system, as testified by the divergence of the susceptibility, as the critical point is approached. Consequently, the mean field picture is expected to get worst approaching T_c. Interestingly, the breakdown of mean field can be consistently predicted within the mean-field theory, as we show below.

Translating the discussion above into a formula, we can assume that, below T_c, the following inequality

$$\left\langle \left[\sum_{i \in V_\xi} (S_i - \langle S_i \rangle) \right]^2 \right\rangle \ll \left\langle \sum_{i \in V_\xi} S_i \right\rangle^2 , \qquad (10.148)$$

must hold in order for mean field to be valid. Eq. (10.148) indeed states that mean field is correct when the spin fluctuations are much smaller than the spin average. Notice that we have restricted the calculation inside a correlated volume V_ξ because, since correlations are felt only up to distances ξ, the system can be thought as made of many independent subsystems of volume V_ξ. We can re-write the r.h.s. of Eq. (10.148) as

$$\begin{aligned} \left\langle \left[\sum_{i \in V_\xi} (S_i - \langle S_i \rangle) \right]^2 \right\rangle &= \left\langle \sum_{i \in V_\xi} \sum_{j \in V_\xi} (S_i - \langle S_i \rangle)(S_j - \langle S_j \rangle \right\rangle \\ = \sum_{ij \in V_\xi} g(r) &= \sum_{i \in V_\xi} \sum_{\substack{\vec{r} \\ r < \xi}} g(r), \qquad (10.149) \end{aligned}$$

where in the last sum we sum only up to $r \simeq \xi$. Using Landau's theory (Eq. (10.130)) one has

$$\begin{aligned} \sum_{i \in V_\xi} \sum_{\substack{\vec{r} \\ r < \xi}} g(r) &\simeq \int_{V_\xi} d\vec{x} \int_{r<\xi} d\vec{r}\, g(r) \\ &= V_\xi \frac{kT}{2c_0} \int_{r<\xi} d\vec{r} |r|^{-(d-2)} Y\left(\frac{r}{\xi}\right) = A_d \frac{kT}{2c_0} \xi^{d+2}, \quad (10.150) \end{aligned}$$

where in the last passage we have transformed the integration variable into $\vec{r}/\xi$ and the result of the integration is contained in the d-dependent constant A_d. Plugging this result into Eq. (10.148) and writing the r.h.s. using again Landau's theory as

$$\left\langle \sum_i S_i \right\rangle^2 = B_d^2 \xi^{2d} \frac{a(T)}{2b_0}, \qquad (10.151)$$

where B_d is the volume of a system of unitary size in dimension d, upon expressing all the quantities in terms of ξ_0 (Eq.(10.128)), one arrives at

$$\left(\frac{\xi}{\xi_0}\right)^{d-4} \equiv \left(\frac{|T-T_c|}{T_c}\right)^{\frac{4-d}{2}} \gg C_d \xi_0^{-d}, \tag{10.152}$$

where $C_d = A_d kTb_0/(2B_d^2 a_0 T_c)$ is a constant. This equation is known as the Ginzburg criterion. Although we have shown it for $T < T_c$, one can arrive to a similar result also for $T > T_c$. This equation shows that for $d \geq 4$ the mean field theory is basically correct as T_c is approached, while it fails for $d < 4$. The special dimension $d_c = 4$, above which mean field breaks down, is called the upper critical dimension and is a general concept when dealing with phase-transition in general (not only those described by the Ising model). Eq. (10.152) informs us also on how far from T_c one must be in order to have the mean field being basically correct. Notice that mean field is more accurate in systems with a large bare correlation ξ_0, such as systems with long-range interactions, superconductors etc...)

10.11 Exactly Solvable Models

10.11.1 The One-Dimensional Ising Model

The one-dimensional Ising model is exactly soluble. In the zero field it has Hamiltonian

$$\mathcal{H} = -J \sum_{i=1}^{N} S_i S_{i+1}, \tag{10.153}$$

where now we consider periodic boundary conditions $S_{N+1} = S_1$. The partition function can be written as

$$Z = \sum_{\{S_i\}} \prod_{i=1}^{N} e^{KS_iS_{i+1}}, \tag{10.154}$$

where $K \equiv \beta J$. Using the identity $e^{KS_iS_{i+1}} = \cosh(KS_iS_{i+1}) + \sinh(KS_iS_{i+1})$ we have

$$\begin{aligned} Z &= \sum_{\{S_i\}} \prod_{i=1}^{N} \cosh(KS_iS_{i+1})[1 + \tanh(KS_iS_{i+1})] \\ &= [\cosh K]^N \sum_{\{S_i\}} \prod_{i=1}^{N} [1 + S_iS_{i+1} \tanh K] \qquad (10.155) \\ &= [\cosh K]^N \left[\sum_{\{S_i\}} [1 + \sum_i S_iS_{i+1} \tanh K + \sum_i \sum_j S_iS_{i+1}S_jS_{j+1} \tanh^2 K + \ldots] \right], \end{aligned}$$

where we have used the fact that $S_iS_{i+1} = \pm 1$ and the parity of the hyperbolic functions. Since the sum is over all values of spins, all the terms except the first (i.e. 1) are zero; therefore

$$Z = 2^N [\cosh K]^N. \qquad (10.156)$$

The free energy density is

$$f(K) = -kT \frac{\ln Z}{N} = -kT(\ln 2 + \ln \cosh K). \qquad (10.157)$$

The extension to the presence of a magnetic field H gives (see problem)

$$f(K, h) = -\beta^{-1} \left\{ K + \ln\{\cosh h + [\sinh^2 h + e^{-4K}]^{1/2}\} \right\}, \quad (10.158)$$

where $h \equiv \beta H$. The magnetization can be easily calculated by taking the derivative of the free energy with respect to H (see problem). The result shows that the magnetization is always zero for any finite temperture except at $T = 0$.

We now calculate the pair correlation function

$$g_{ij} \equiv \langle S_iS_j \rangle. \qquad (10.159)$$

Since the magnetization $\langle s_i \rangle = 0$, we do not need to subtract the term $\langle S_i\rangle\langle S_j\rangle$, and

$$\begin{aligned} g_{ij} &= \frac{1}{Z}\sum_{\{S_i\}} S_i S_j e^{K\sum_\ell S_\ell S_{\ell+1}} \qquad (10.160) \\ &= \frac{1}{Z}[\cosh K]^N \sum_{\{S_i\}} S_i S_j \prod_{\ell=1}^{N}(1+S_\ell S_{\ell+1}\tanh K) \\ &= \frac{1}{Z}[\cosh K]^N \sum_{\{S_i\}} S_i S_j [1+\sum_\ell S_\ell S_{\ell+1}\tanh K \\ &+ \sum_\ell\sum_m S_\ell S_{\ell+1} S_m S_{m+1}\tanh^2 K+\dots], \\ &= \frac{1}{Z}[\cosh K]^N(\tanh K)^{|i-j|}2^N \end{aligned}$$

The final result can be obtained by observing that for $i = j$ one has $S_i S_j \equiv 1$ and only the first (the 1) term survives after summing over the spin configurations, similarly to what done in Eq. (10.155). For $j = i + 1$ the only surviving term is the second with $\ell = i$, namely $S_i^2 S_{i+1}^2 \tanh K = \tanh K$. For $j = 1 + 2$ there the second term survives with $\ell = i$ and $m = i + 1$, namely $S_i^2 S_{i+1}^2 S_{i+2}^2 \tanh^2 K = \tanh^2 K$ and so on for any distance $|i - j|$.

From (10.158) we finally obtain

$$g_{ij} = [\tanh K]^{|i-j|}, \qquad (10.161)$$

which can be written in the form

$$g_{ij} = \exp\left[\frac{-r_{ij}}{\xi}\right], \qquad (10.162)$$

where $r_{ij} = a|i - j|$, with a being the lattice spacing and

$$\xi = \frac{a}{|\ln\tanh K|}, \qquad (10.163)$$

which shows that as $T \to \infty$ the correlation reduces to zero, while as $T \to 0$, the correlation length diverges as

$$\xi = \frac{a}{2}\exp\left[\frac{2J}{k_B T}\right]. \qquad (10.164)$$

Although the one-dimensional Ising model does not show any spontaneous magnetization at finite temperatures, $T = 0$ can be treated as a critical point where the correlation length diverges. In 2 and 3 dimensions, there is a transition at finite T_c.

10.11.2 Onsager solution in $d = 2$

An exact solution of the Ising model was provided by Onsager in 1944 for the 2-dimensional case in zero external field. He showed that in the thermodynamic limit, the free energy has a non-analyticity at the temperature $T = T_c = 2.269J/kB$. At this temperature, the specific heat diverges logarthmically, while the spontaneous magnetization behaves as $(T-T_c)^\beta$ with $\beta = 1/8$. The other exponents are $\gamma = 7/4$, $\nu = 1$, and $\eta = 1/4$.

10.11.3 Spherical model

10.12 Critical exponents in $d = 3$

Although there is no exact solution in three dimensions, the critical exponents can be estimated numerically by means of high-temperature or low- temperature series expansion, or by Monte Carlo calculations. We find that the critical exponents for $d = 3$ are close to, but still different from the mean-field results (see Table I).

	β	γ	α	ν	η
2d	1/8	7/4	0	1	1/4
3d	0.313	1.25	0.125	0.64	0.04
MF	1/2	1	0	1/2	0

Table 10.1: Critical exponents.

What about the critical exponents obtained from experimental data? As might have been anticipated from the lattice gas model, most critical exponents for both ferromagnets and fluids are numerically close to those of the 3-dimensional Ising model. From Table 10.1 we see that the critical exponents are highly dependent upon system dimension. In $d = 1$ there is not even a phase transition at finite temperatures.

10.13 Paths degeneracy

How can we understand the absence of phase transition in $d = 1$? The pair correlation function between two points at a distance of n lattice spacing is

$$[\tanh \beta J]^n = \exp[-n \ln |\tanh(\beta J)|]. \qquad (10.165)$$

Because the correlation decays by a factor $\tanh(\beta J)$ at each step, the pair correlation decays exponentially. Examples include the decay of a radioactive element and the decay of light or sound as it travels through a medium.

In higher dimensions there is more than one path connecting two points. We can make a rough estimate of the pair correlation function. Roughly the number of paths made of n steps between two points increases as a power of n, i.e., $\lambda^n = e^{n \ln \lambda}$, with $\lambda > 1$. On each path the correlation decays exponentially, but the number of paths increases exponentially. But summing over all the paths, we obtain roughly the pair correlation g_n after n steps, i.e, $g_n = [\lambda \tanh(\beta J)]^n$.

When these two effects compensate, the correlation length becomes infinite. Therefore the critical temperature is given by

$$\lambda \tanh\left(\frac{J}{k_B T_c}\right) = 1 \tag{10.166}$$

The pair correlation function between two points separated by a distance $\vec{r}$ is related to g_n by $4g(\vec{r})r^{d-1}dr = g(n)dn$. If we assume that the relation between r and n is

$$n^\nu = r, \tag{10.167}$$

we obtain

$$g(\vec{r}) = \exp\left[-\left(\frac{r}{\xi}\right)^{1/\nu}\right]\frac{1}{r^{d-2+\eta}}, \tag{10.168}$$

with

$$\eta = \frac{2\nu - 1}{\nu}, \tag{10.169}$$

and

$$\xi = \frac{1}{[\ln \lambda \tan(\beta J)]^\nu} \sim (T - T_c)^{-\nu}. \tag{10.170}$$

Therefore ν corresponds to the correlation length exponent. Finally we can speculate that the paths along which correlations propagate are nonintersecting random walks, the so-called self-avoiding walks (SAWs). The exponent ν, which relates the number of steps n and the end-to-end distance r, can be known to a good approximation using a formula derived by Flory, i.e.,

$$\nu = \begin{cases} 3/(d+2) & \text{if } d \leq 4 \\ 1/2 & \text{if } d \geq 4 \end{cases}, \tag{10.171}$$

which in fact is exact for any d except $d = 3$. We note that the above argument becomes exact in one dimension and in higher dimensions. In this case $\lambda = z$, and in the higher dimensions z is large, thus from (10.166) T_c is large and, if we expand the hyperbolic tangent to first order,

$$\frac{zJ}{k_B T_c} = 1. \tag{10.172}$$

From (10.169) and (10.171) we see that when $d \geq 4$, $\nu = 1/2$ and $\eta = 0$. This argument suggests that there exists an upper critical dimensionality $d_c = 4$ such that for $d \geq d_c$ the critical exponents do not change with the dimensionality and become identical to the mean-field exponents. This result in fact is true and can be derived within the renormalization group approach.

10.14 Scaling Laws and Universality

Until the beginning of the 1970s the mean-field theory was the only theory available for the study of critical phenomena, and there was no way to improve the theory to give better results for critical exponents. However, based on general thermodynamical properties, it was possible to prove some general relations among critical exponents. There are many examples, e.g.,

$$\alpha + 2\beta + \gamma \geq 2 \quad \text{and} \quad d\nu \geq 2 - \alpha. \tag{10.173}$$

It was remarkable to note that these relations were always satisfied as equalities as can be seen in Table I. Even the mean-field exponents satisfy the first relation as an equality. In fact, all the relations that do not involve the dimensionality d are also satisfied as an equality by the mean-field exponents. These relations are called scaling relations. The relations that involve the dimensionality d are called hyperscaling relations.

In addition to the scaling, a second property, *universality*, was observed. As clearly stated by Kadanoff, this is based on the empirical fact that all systems can be divided into groups, each group being characterized by the same critical exponents. The reason for such universal behavior was based on the following arguments: A system near the critical point is dominated by large scale fluctuations, the linear size being essentially the correlation length ξ. At these large scales, the details of the interactions are not important in determining the critical exponents, i.e., the critical exponents do not depend on the details of the interactions. For example, an Ising model with nearest-neighbor interactions and next-nearest-neighbor interactions will be characterized by the same exponents as the Ising model with only nearest-neighbor interactions.

The universality classes are therefore only characterized by global properties, i.e.,

(1) the dimensionality,
(2) the Hamiltonian symmetries, and
(3) the behavior of the interactions for large distances.

Apparently all systems in nature can be divided into a comparatively small number of universality classes characterized by the above global properties. Systems belonging to the same universality class have not only the same critical exponents but also the same *scaled* equation of state.

10.14.1 Homogeneity

Before proceeding on the scaling laws it is useful a short mathematical digression on homogeneous function. By definition, a function $f(x)$ is said homogeneous if

$$f(tx) = g(t)f(x), \tag{10.174}$$

where t is a parameter, that in the following will be denoted as *rescaling parameter*, and g a generic function. A function $f(x_1, x_2, \ldots, x_n)$ of n variables is homogeneous if

$$f(tx_1, tx_2, \ldots, tx_n) = g(t)f(x_1, x_2, \ldots, x_n). \tag{10.175}$$

A generalized homogeneous function is such that

$$f(t^{-\nu_1}x_1, t^{-\nu_2}x_2, \ldots, t^{-\nu_n}x_n) = g(t)f(x_1, x_2, \ldots, x_n). \tag{10.176}$$

As we will see soon, scaling relations among critical exponents are a direct consequence of the fact near the critical point thermodynamic function are (generalized) homogeneous functions of their arguments.

10.14.2 Scaling

Let us go back to Landau's theory (in the homogeneous case of Sec. 10.10.1). Introducing the quantity

$$m^* = \left(\frac{|a(T)|}{b_0}\right)^{\frac{1}{2}}, \tag{10.177}$$

the equation of state (10.85) can be cast as

$$\frac{H}{H^*} = 2\,\mathrm{sign}(t)\frac{m}{m^*} + 4\left(\frac{m}{m^*}\right)^3, \tag{10.178}$$

where $t = (T - T_c)/T_c$, and $H^* = b_0 m^{*3}$. Hence, in each sector $T > T_c$ and $T < T_c$, $\mathcal{H} = H/H^*$ is a function only of the variable $\mathcal{M} = m/m^*$

$$\mathcal{H} = \hat{\mathcal{H}}^{\pm}(\mathcal{M}), \tag{10.179}$$

with $\hat{\mathcal{H}}^{\pm} = \pm 2\mathcal{M} + 4\mathcal{M}^3$. This implies that the equation of state does not *really* involves three independent variables (namely m, H, T) but only two independent ones $\mathcal{H}, \mathcal{M}$. The procedure we have followed above to re-write the equation of state is in spirit analogous to the law of corresponding states previously introduced regarding the Van der Waals theory of the liquid-gas transition. The form (10.179) is expected to be *universal* while all the system-dependent features are hidden into the relations connecting $\mathcal{H}$ to H through H^*, $\mathcal{M}$ to m through m^*. Writing Eq. (10.179) as

$$H(t, m) = |t|^{\frac{3}{2}} \mathcal{H}^{\pm}\left(\frac{m}{|t|^{\frac{1}{2}}}\right) \tag{10.180}$$

we see that $H(T, m)$ seen as a function of m is a homogeneous function where t plays the role of the rescaling parameter.

Similar considerations can be done for other thermodynamic quantities. Let us start with the free energy, that we chose in the Landau form (10.83) (we set the irrelevant constant $f(0, H, T) = 0$ for simplicity). This can be re-written as

$$\frac{f(m, H, T)}{f^*} = \mathrm{sign}(t)\mathcal{M}^2 + \mathcal{M}^4 - \mathcal{H}\mathcal{M}, \tag{10.181}$$

with $f^* = b_0 m^{*4}$. Inverting the relation (10.179) to express $\mathcal{M}$ in terms of $\mathcal{H}$ we arrive at

$$f(t, H) = |t|^2 \mathcal{F}^{\pm}\left(\frac{H}{|t|^{\frac{3}{2}}}\right) \tag{10.182}$$

with $\mathcal{F}^{\pm} \propto \mathrm{sign}(t)\mathcal{M}^2(\mathcal{H}) + \mathcal{M}^4(\mathcal{H}) - \mathcal{H}\mathcal{M}(\mathcal{H})$.

The homogeneity property expressed by Eqs. (10.180, 10.182) is referred to as *scaling*, since the number of independent variables is reduced by considering *rescaled* quantities as $\mathcal{H}, \mathcal{M}$. Notice that all the rescaling quantities m^*, H^*, f^* can be expressed as powers of the reduced temperature t.

According to Eq. (10.130) the correlation function at $H = 0$ can be cast in a scaling form as follows

$$g(r,T) = |t|^{(d-2)\nu} \mathcal{G}\left(\frac{r}{t^{-\nu}}\right), \tag{10.183}$$

where $\mathcal{G} = (r/\xi)^{-(d-2)} Y(r/\xi)$. The physical meaning of Eq. (10.183) is that one can map two systems at different temperatures T_1 and T_2 by measuring (or rescaling) lengths in units of $\xi(T)$, and also by measuring the local magnetization, so to say, in units of $m^* = \xi(T)^{-(d-2)}$ (since C is the product of two local magnetizations). This means that as T_c is approached the local magnetization gets weaker and weaker. This shows that the scaling property is equivalent to the statement that the physics can be described in terms of a single dominant length $\xi(T)$ in the vicinity of T_c (this is not true if we are far from T_c).

So far we have considered the mean field theory. To proceed further we make the hypothesis that the scaling property (10.182) holds also beyond mean field, where in general

$$f(t,H) = |t|^{2-\alpha} \mathcal{F}^{\pm}\left(\frac{H}{|t|^{2-\alpha-\beta}}\right), \tag{10.184}$$

where α and β are two unknown exponents (but we will soon recognize that they are the specific heat and magnetization exponents, so we anticipate the use of their symbols). For the correlation function we generalize the form (10.183) by assuming

$$g(r,T,H) = |t|^{(d-2+\eta)\nu} \mathcal{G}\left(\frac{r}{|t|^{-\nu}}, \frac{H}{|t|^{2-\alpha-\beta}}\right), \tag{10.185}$$

where we have considered also the case with $H \neq 0$ and we the scaling of H with t is the same as in Eq. (10.184).

Notice that the free energy, from which all the thermodynamic properties can be obtained, is a function of only two exponents. This implies, as we will see shortly, that all the critical exponents introduced before are not independent and can be expressed in terms of α and β. In order identify α and β, let us start with the specific heat in zero field

$$\begin{aligned} C &= N^{-1}\frac{\partial E}{\partial T}\bigg|_{H=0} = -N^{-1}\frac{\partial}{\partial T}\frac{\partial \ln Z}{\partial \beta}\bigg|_{H=0} = \frac{\partial}{\partial T}\frac{\partial(\beta f)}{\partial \beta}\bigg|_{H=0} \\ &= -T\,\frac{\partial^2 f}{\partial T^2}\bigg|_{H=0} = -\frac{T}{T_c^2}\,\frac{\partial^2 f}{\partial |t|^2}\bigg|_{H=0} \\ &= -\frac{T}{T_c^2}(2-\alpha)(1-\alpha)|t|^{-\alpha}\mathcal{F}^{\pm}(0), \end{aligned} \tag{10.186}$$

which shows that, as anticipated, α is the specific heat exponent. For the magnetization one has

$$m(T,H) = -\left.\frac{\partial f}{\partial H}\right|_T = -|t|^{\beta}\mathcal{F}^{\pm\prime}\left(\frac{H}{t^{2-\alpha-\beta}}\right). \tag{10.187}$$

Evaluating at $H=0$ one finds

$$m(T,H) = -|t|^{\beta}\mathcal{F}^{\pm\prime}(0), \tag{10.188}$$

which allows to recognize β as the usual magnetization exponent.

Up to this point we have only identified the exponents contained in the scaling ansatz (10.184). Now we show that from this ansatz one can derive a number of scaling relations among critical exponents. To start with, let us compute the susceptibility from Eq. (10.187) as

$$\chi(T) = \left.\frac{\partial m}{\partial H}\right|_{H=0} = -|t|^{2\beta+\alpha-2}\mathcal{F}^{\pm\prime\prime}(0), \tag{10.189}$$

from which we obtain the relation

$$\gamma = 2-\alpha-2\beta. \tag{10.190}$$

Now we consider the magnetization at T_c, in order to determine the exponent δ. From Eq. (10.187), in order to have a finite result when $t\to 0$ it must necessarily be $\lim_{t\to 0}\mathcal{F}^{\pm\prime}(x) \sim x^{\frac{\beta}{2-\alpha-\beta}}$. Hence one finds $m(T_c,H)\propto H^{\frac{\beta}{2-\alpha-\beta}}$, and hence another scaling relation

$$\delta\beta = 2-\alpha-\beta. \tag{10.191}$$

The zero field susceptibility is

$$\chi = \beta\int d\vec{r}\,g(r,T,H=0) \propto |t|^{-(2-\eta)\nu}, \tag{10.192}$$

from which

$$\gamma = (2-\eta)\nu. \tag{10.193}$$

Finally, assuming that below T_c the correlator $g_{disc}(r,T,H) = \langle S_i S_j \rangle$ takes the same form as g in Eq. (10.185), since $\lim_{r\to\infty} g_{disc} = \langle S_i \rangle \langle S_j \rangle = m^2$, due to the statistical independence of the spins over lengths $r \gg \xi$, we obtain $m^2 = |t|^{(d-2+\eta)\nu}\mathcal{G}(\infty)$, from which the last scaling relation

$$\nu(d-2+\eta) = 2\beta \tag{10.194}$$

descends. This latter is an hyperscaling relation, since it contains spatial dimensionality, and is obeyed by mean field only letting $d = d_c = 4$. In conclusion, there are six critical exponents and four scaling relations among them (Eqs. (10.190,10.191,10.193,10.194)), and hence only two exponents are independent.

10.15 The Renormalization Group

10.15.1 General scheme

The basic idea is that at the critical point, where $\xi = \infty$, there is no finite characteristic length. Therefore if we examine the system at two different length scales we will see statistically the same picture. For example, if we could observe the critical opalescence of a fluid at its critical point with a microscope we would see a system made of droplets of all sizes, and each droplet would contain smaller droplets exhibiting an identical structure. If we could change the length scale at which we observe the system by zooming in and observing the detail of a single droplet, we would see the same picture: a self-similar stucture made up of smaller droplets inside of larger droplets and all droplets exhibiting the same configuration. The idea of self-similar system, a system in which a tiny piece of the system has the same structure as the entire system, is the basis for the concept of scaling invariance. The divergence of the coherence length as $T \to T_c$ and the scale-invariant configuration of the system is shown in Fig. 10.6 where the equilibrium configurations of the two-dimensional Ising model at different temperatures are numerically generated with a computer. At high temperature ($T = 2T_c$) the correlation length is small. Close to T_c large clusters begin to develop and, right at T_c there are clusters of any size (up to the largest one, i.e. the system size).

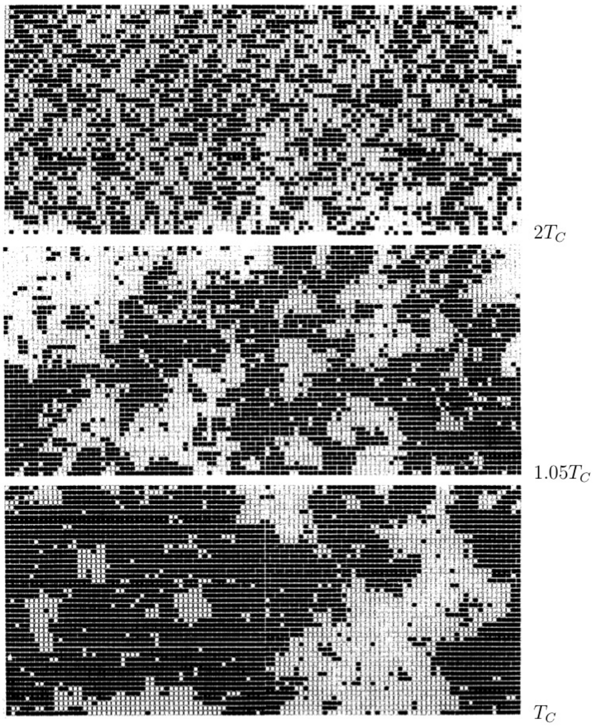

Figure 10.6: Equilibrium configurations of the $d = 2$ Ising model on a square lattice obtained by Montecarlo simulations. Black and white regions represent up and down spins. In the the three panels the temperature is (from top to bottom) $T = 2T_c$, $T = 1.05\,T_c$ and $T = T_c$.

Let us see how the idea of scale-invariance idea can be implemented to make predictions. To fix the ideas, we consider the Ising model in a zero external field. Close to T_c the correlation length ξ is very large. We divide the original system of spins into subsystems of linear dimension ℓ with $a < \ell < \xi$. Within each cell the spins are within a distance no greater than the correlation length and are therefore highly correlated. We can imagine that they will all behave coherently and that the cell can be roughly in two states: one in which up-spins are in the majority and one in which down-spins are in the majority. We can introduce a block variable s_α that assumes two values, up and down, corresponding to these two states. The majority rule introduced here must not be intended in a strict sense but only as a physically-motivated guideline to understand the basic passages. The correct procedure to introduce the block variables is that of summation over internal degrees of freedom, that will be discussed in Sec. 10.15.2. In order to proceed we further suppose that if the original spin Hamiltonian has the form

$$-\beta\mathcal{H} = K\sum_{\langle ij\rangle} S_i S_j + h\sum_i S_i, \tag{10.195}$$

with $K = J/k_BT$ and $h = H/k_BT$, the system of cells can be described by a Hamiltonian $\mathcal{H}'$ with the same form as the original spin systems, apart from a constant $W_0(K,h)$,

$$-\beta\mathcal{H}' = K'\sum_{\langle\alpha\beta\rangle} s_\alpha s_\beta + h'\sum_\alpha s_\alpha + W_0(K,h), \tag{10.196}$$

where the sum is over all nearest-neighbor cells, and K' and h' are the renormalized coupling constant and the magnetic field, respectively. Let us denote with $\xi(K,h)$ and with $\xi(K',h')$ the value of a certain length (we use this letter since we will be interested in the coherence length) before and after the block transformation. Since the distance between two *renormalized* spins s_α, s_β is ℓ times smaller than the distance between two original spins $S_i \in \alpha$, $S_j \in \beta$ one must have

$$\xi(K',h') = \frac{\xi(K,h)}{\ell} \tag{10.197}$$

We first consider the case in which $h = h' = 0$. The renormalized coupling constant depends on K and ℓ, i.e.,

$$K' = f(K,\ell). \tag{10.198}$$

Letting $K = K_c$ in Eq. (10.198), using Eq. (10.197) one has

$$\xi[f(K_c,\ell)] = \frac{\xi(K_c)}{\ell} = \infty. \tag{10.199}$$

Since $\xi[f(K_c,\ell)] = \xi[K_c]$, it follows that

$$f(K_c,\ell) = K_c. \tag{10.200}$$

Recalling the recurrence equation (10.198) this shows the important fact that that $K = K_c$ is a fixed point in the transformation of the coupling constant, and under rescaling it does not change. This is clearly seen in Fig. 10.7: at $T = T_c$ there an infinite coherence length, as shown in panel a) (in the present system of finite size ξ is as large as the system size). After repeated block transformations the block variable configurations is represented in the following panels. It is clearly seen that ξ remains as large as the whole system.

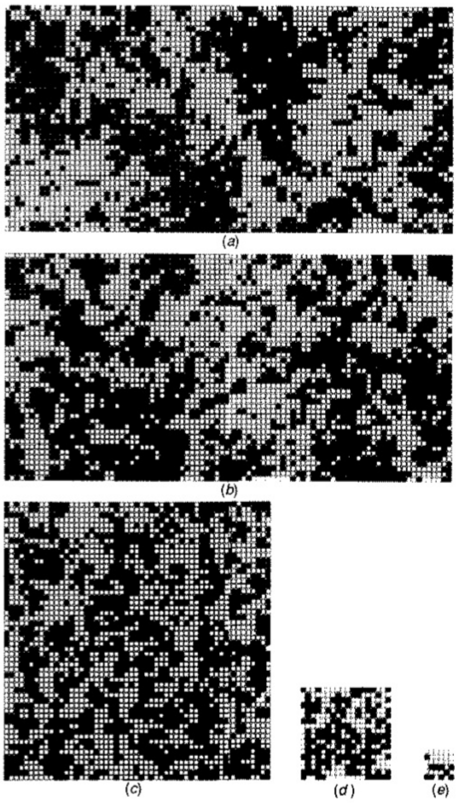

Figure 10.7: In the upper panel a configuration of the $d = 2$ Ising model at $T = T_c$ is shown. Panels b,c,d,e represent the effect of repeated block-spin transformations applied to such configuration.

Since K' was the result of a summation over a finite number of degrees of freedom, we can assume that $f(K, \ell)$ is analytic and thus can expand (10.198) to the first order near the critical point

$$K' = K_c + \left[\frac{\partial f(K, \ell)}{\partial K}\right]_{K=K_c} (K - K_c) + \ldots, \tag{10.201}$$

where we have used Eq. (10.200). Alternatively, introducing the distances from criticality $\epsilon = (K - K_c)/K_c$ and $\epsilon' = (K' - K_c)/K_c$, this equation can be cast as

$$\epsilon' = a(\ell)\epsilon, \tag{10.202}$$

where $a(\ell) = [\partial f(K,\ell)/\partial K]_{K=K_c}$. Eq. (10.201) implies that if the system is not exactly at criticality (i.e. $K \neq K_c$) it will move further away from K_c either towards $T = \infty$ (if the original coupling constant is $K < K_c$) or towards $T = 0$ (if $K > K_c$). This is clearly seen in Figs. (10.8, 10.9). Here one clearly see that after repeated block transformations one moves either towards a typical $T = \infty$ configuration (i.e. $\xi = 0$ and zero magnetization), or towards a typical configuration at $T = 0$ (i.e. $\xi = 0$ and $m = 1$).

Figure 10.8: As in Fig. 10.7 but at $T = 1.22T_c$.

Suppose now to rescale the spin system by a factor ℓ_1, so that from the above equation $\epsilon' = a(\ell_1)\epsilon$ and then to rescale again the cells by a factor ℓ_2, arriving finally at $\epsilon'' = a(\ell_2)\epsilon' = a(\ell_2)a(\ell_1)\epsilon$. We require that the transformation from ϵ to ϵ'' obeys group properties i.e. the same result for ϵ'' must be obtained if we directly tranform the system scaling by a factor $\ell_1\ell_2$. One can easily check that, using a naive majority rule (namely s_α will take the value of the majority of spins in the cell) to determine the value of s_α, the group property is obeyed in the cases which are expected to be most relevant (namely those in which there are not very large fluctuations between the distribution of spins inside the cells). From the group property it follows that $\epsilon'' = a(\ell_1\ell_2)\epsilon$, and hence

$$a(\ell_1\ell_2) = a(\ell_1)a(\ell_2). \tag{10.203}$$

This functional form has the only solution

$$a(\ell) = \ell^x. \tag{10.204}$$

Therefore (10.202) becomes

$$\epsilon' = \ell^x\epsilon, \tag{10.205}$$

where ϵ is the scaling field and x the scaling exponent given by (from Eq. (10.205))

$$x = \ln a(\ell)/\ln \ell. \tag{10.206}$$

We relate now x to the correlation exponent ν. Close to K_c, ξ shows the usual divergence $\xi(\epsilon) = \xi_0\epsilon^{-\nu}$. From (10.197) and (10.205) it follows

$$\xi(\epsilon) = \ell\,\xi(\ell^x\epsilon) = \xi_0\,\ell\,(\ell^x\epsilon)^{-\nu}, \tag{10.207}$$

and hence

$$x = \frac{1}{\nu} \tag{10.208}$$

Similarly, in the presence of a small field, the renormalized field is

$$h' = \ell^y h. \tag{10.209}$$

10.15.2 Summing over internal degrees of freedom

We now relate the free energy of the system of spins to the system of cells. In doing that we will provide a more precise procedure to define the block variables which amounts to a summation of it internal degrees of freedom.

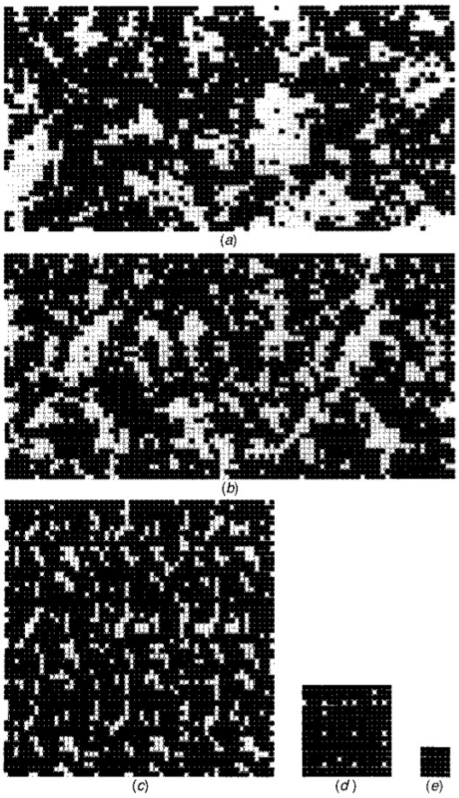

Figure 10.9: As in Fig. 10.7 but at $T = 0.99T_c$.

The partition function for the spin system $Z_N(K,h)$ can be written

$$Z_N(K,h) = \sum_{\{s_i\}} e^{-\beta\mathcal{H}} = \sum_{\{s_\alpha\}} \sum_{\substack{internal \\ s_\alpha}} e^{-\beta\mathcal{H}} = \sum_{\{s_\alpha\}} e^{-\beta\mathcal{H}'} = Z_{N'}(K',h')e^{W_0(K,h)}, \tag{10.210}$$

where we have partitioned the sum over the spin variables into the sum over the internal degree of freedom of the cells $\sum_{\substack{internal \\ s_\alpha}}$ (this means a restricted summation over all the configurations of spins S_i inside cell α which provide a value s_α of the block variable) and the sum over the degree of freedom of the cells $\sum_{\{s_\alpha\}}$. $N' = \ell^{-d}N$ is the number of cells. We have used also the relation

$$\sum_{\substack{internal\\ s_\alpha}} e^{-\beta\mathcal{H}} = e^{-\beta\mathcal{H}'} \tag{10.211}$$

which is the way to define $\mathcal{H}'$ and, in the last passage, the invariance of the form of the Hamiltonian (10.196). From Eq. (10.210) we have

$$-k_BT\frac{\ln Z_N(K,h)}{N} = -k_BT\frac{\ln Z_{N'}(K',h')}{N'}\frac{N'}{N} - k_BT\frac{W_0(K,h)}{N}. \tag{10.212}$$

Taking the limit $N \to \infty$, we obtain the relation between the free energy for spin $f(K,h)$ and the free energy per cell $f(K',h')$

$$f(K,h) = \ell^{-d}f(K',h') + B(K,h), \tag{10.213}$$

where $B(K,T) = k_BTW_0(K,T)/N$. We can assume that $B(K,h)$ is not singular at the critical point since $B(K,h)$ was the result of a summation over a finite number of degrees of freedom. Therefore if we define $f_{sing}(\epsilon,h)$ as the singular part of $f(K,h)$, from (10.213) we have

$$f_{sing}(\epsilon,h) = \ell^{-d}\mathcal{F}(\ell^x\epsilon,\ell^yh). \tag{10.214}$$

This relation (10.214) shows that the (singular part of) the free energy is a generalized homogeneous function (see Sec. 10.14.1).

We now examine the consequences of (10.214). Since (10.214) is valid for any ℓ, for any ϵ we can chose an ℓ such that $\ell^x\epsilon = 1$. From (10.214) immediately follows

$$f_{sing}(\epsilon,h) = \epsilon^{d/x}\varphi\left(\frac{h}{\epsilon^{y/x}}\right), \tag{10.215}$$

where $\varphi(z) = \mathcal{F}(1,z)$ is a function of only one variable. Taking into account that

$$\begin{aligned} C_H &\sim \left(\frac{\partial^2 f}{\partial t^2}\right)_{h=0} \sim t^{-\alpha}; \\ M &\sim \left(\frac{\partial f}{\partial h}\right)_{h=0} \sim t^{\beta}; \\ \chi &\sim \left(\frac{\partial^2 f}{\partial h^2}\right)_{h=0} \sim t^{-\gamma}, \end{aligned} \tag{10.216}$$

from (10.215), it follows

$$-\alpha = \frac{d}{x} - 2, \qquad \beta = \frac{d}{x} - \frac{y}{x}, \qquad -\gamma = \frac{d}{x} - \frac{2y}{x} \tag{10.217}$$

(in the first of these relations we have only kept the leading divergence as $t \to 0$). These relations show that all critical exponents can be expressed in terms of two independent quantities x and y. As a consequence, α, β, and γ are not independent, and it is easy to see that they satisfy the relation

$$\alpha + 2\beta + \gamma = 2, \tag{10.218}$$

which is the Rushbrooke relation with an equality sign. Note that from (10.208) and the first of Eqs. (10.217) it also follows that

$$d\nu = 2 - \alpha, \tag{10.219}$$

which reproduces the second scaling relation.

The scaling hypothesis not only predicts relations among critical exponents, but also predicts a kind of *data collapse*. From (10.215) we can calculate the magnetization $m = \partial g / \partial h$, we find

$$m = \epsilon^{\beta} \phi'(h \epsilon^{-y/x}) \tag{10.220}$$

If we plot m as a function of ϵ for each value of h we will find that the data are all scattered in the m-ϵ plane. If however we plot m/ϵ^{β} as a function of $h/\epsilon^{y/x}$, we will see that for all values of h the data will follow only one curve. This phenomenon is called data collapse and is a consequence of the form (10.215) of the free energy. This property is also useful in calculating critical exponents. In fact, we can find β and x/y until we obtain the best data collapse.

The scaling approach followed in the previous section was historically developed mainly by Leo Kadanoff to obtain the generalized form for free energy. Although the approach contained the basis for further development, no progress was made until 1972 when K. Wilson derived his renormalization group theory. In the phenomenological scaling approach, the cell variables are introduced but they are not precisely defined. To allow the explicit calculation of scaling transformation (10.220) and consequently of the critical exponent through relation (10.205) it was needed an implementation of (10.211), i.e., it was necessary to define the cell variables and the internal degree of freedom in terms of the spin variables . Then using (10.211) we can calculate the renormalization coupling constant. To illustrate how the renormalization group works, we consider in the next section a very simple case, the$1d$ Ising model, where the renormalization transformation can be carried over exactly.

10.15.3 Ising model in one dimension

Let us start by recalling that the exact solution of the model (Sec. 10.11.1) shows that for $H = 0$ the correlation length diverges as

$$\xi \sim e^{2J/(k_BT)}, \tag{10.221}$$

as T approaches absolute zero, which can therefore be considered a critical point. However it must be stressed that a zero-temperature critical point is quite different from the usual one at finite T_c because the system is (fully) magnetized at $T = 0$, at variance with what happens at $T_c > 0$. This implies for instance that the exponent β cannot be defined. From Eq. (10.221) it is clear that also the exponent ν cannot be defined in the usual way. However, introducing $u = e^{-2J/(k_BT)}$ - a quantity that goes to zero as $T \to T_c = 0$ playing the role of a distance from the critical point, analogously to $t = (T - T_c)/T_C$ is systems with $T_c > 0$, one can write

$$\xi \sim u^{-\nu}, \tag{10.222}$$

with $\nu = 1$.

The partition function for the 1d Ising model in a zero field can be written

$$Z = \sum_{\{s_i\}} e^{K(S_1S_2+S_2S_3+S_3S_4+\dots)}, \tag{10.223}$$

which can also be written as

$$Z = \sum_{S_1,S_3,\dots} \sum_{S_2,S_4,\dots} e^{K(S_1S_2+S_2S_3)} e^{K(S_3S_4+S_4S_5)} \dots . \tag{10.224}$$

We consider the system divided into cells of size $\ell = 2$ made of spins $(1, 2)(3, 4)(5, 6) \dots$. For convenience we consider the first spin in each cell (namely those on sites 1,3,5...) the cell variable and spin 2,4,6 the internal variable. In (10.224) the second sum is over the internal degree of freedom of the cell. After summation of the internal degrees of freedom the spins on odd sites become block variables which we denote with s_i instead of the original symbol S_i. Therefore, using (10.211), the renormalized Hamiltonian is given by

$$\sum_{S_2,S_4,\dots} e^{K(S_1S_2+S_2S_3)} e^{K(S_3S_4+S_4S_5)} \dots = e^{K'[s_1s_3+s_3s_5+s_5s_7+\dots+(N/2)W_0}, \tag{10.225}$$

where K' and W_0 can be easily calculated from

$$\sum_{S_2=\pm 1} e^{K(S_1S_2+S_2S_3)} = e^{K's_1s_3+W_0}. \tag{10.226}$$

From (10.226) we have

$$e^{K(S_1+S_3)} + e^{-K(S_1+S_3)} = e^{K's_1s_3+W_0}. \tag{10.227}$$

By fixing first $S_1 = s_1 = S_3 = s_3 = \pm 1$ and then $S_1 = s_1 = -S_3 = -s_3 = \pm 1$, we obtain two equations,

$$e^{2W_0} = 2(u+u^{-1}) \tag{10.228}$$

and

$$u' = \frac{2}{u+u^{-1}}, \tag{10.229}$$

where, for convenience, we have used the variable $u = e^{-2K}$; $u' = e^{-2K'}$. Here $u = 0$ corresponds to $T = 0$ and $u = 1$ to $T = \infty$. Our goal is to find the critical point and the critical exponent. From the previous section we know that the critical point is a fixed point. The fixed points are those that are invariant under the rescaling transformation (10.229). These are given by solving

$$u^* = \frac{2}{u^* + u^{*-1}}, \tag{10.230}$$

Equation (10.230) can be solved graphically by locating the intersection of $u'(u)$ given by (10.229) and $u' = u$. From Fig. 10.10 and Eq. (10.230) we see that there are two fixed points: $u^* = 0$ $(T = 0)$ and $u^* = 1$ $(T = \infty)$. From the previous section, we know that the critical point is a fixed point. But not all fixed points correspond to critical points. What is the meaning of the other fixed points?

In general, we must have at a fixed point for (10.227)

$$\xi(u^*) = \frac{\xi(u^*)}{\ell}. \tag{10.231}$$

This equation is satisfied when $\xi(u^*) = \infty$ or $\xi(u^*) = 0$. The first case corresponds to a critical point, the second case usually occurs at $T = 0$ or $T = \infty$ where the correlation length is zero. This second fixed point is called a trivial fixed point. How do we distinguish a trivial fixed point from a critical point?

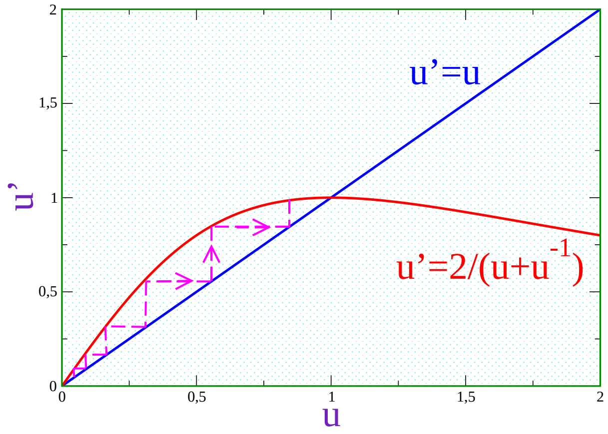

Figure 10.10: Graphical solution of Eq. (10.230) for $d = 1$. The dashed magenta line is the recurrence map.

Following the argument of the previous section, expanding the renormalized coupling constant near the fixed point

$$u' - u^* = a(\ell)(u - u^*), \tag{10.232}$$

we can associate the scaling exponent $x = \ln a/\ln \ell$ with the behavior of the correlation length at the fixed point, since $x = 1/\nu$ (see Eq. (10.208)). If $x > 0$, the correlation length diverges as $\xi \sim (u - u^*)^{-1/x}$. If, on the other hand, x is negative then the correlation length vanishes at the fixed point. Since $\ell^x = a \equiv (\partial u'/\partial u)_{u=u^*}$, x is positive or negative depending whether the slope at the fixed point $a \equiv (\partial u'/\partial u)_{u=u^*}$ is larger or smaller than 1. When the slope $a > 1$ the fixed point is also called unstable; when $a < 1$ it is called stable. This terminology become clear if we consider the evolution u_n of an initial point u_0 close to the fixed point under n successive iteration. From (10.232) we find

$$u_n - u^* = a^n(u_0 - u^*). \tag{10.233}$$

If $a > 1$ (unstable fixed point), after many iterations u_n moves away from the fixed point. If $a < 1$ (stable fixed point), $u_n \to u^*$, i.e., u_n is *attracted* by the fixed point. In conclusion we can say that an unstable fixed point corresponds to a critical point, while a stable fixed point corresponds to a trivial fixed point. In the 1d Ising model we can easily recognize that the fixed point $u^* = 0$ ($T = 0$) is unstable since $(\partial u'/\partial u)_{u=u^*} > 1$ and therefore corresponds to the critical point, while $u^* = 1$ ($T = \infty$) is unstable, corresponding to $T = \infty$. From the figure, it is easy also to pictorially recognize the stable from the unstable fixed point by representing the successive interaction and seeing how they are attracted or repelled by the two fixed points.

Finally, expanding near $u^* = 0$ (critical point), we find

$$u' = 2u, \tag{10.234}$$

therefore $a = 2$. Taking into account that the rescaling factor $\ell = 2$, recalling Eq. (10.206) we find the critical exponent ν given by

$$\nu = \frac{\ln \ell}{\ln a} = 1. \tag{10.235}$$

Therefore the correlation length close to $u = 0$ ($T = 0$) behaves as

$$\xi \sim \epsilon^{-\nu} \sim u^{-1} = e^{2J/k_BT}, \tag{10.236}$$

which coincides with the analytic result obtained from the exact solution. Notice that in the $1d$ case ϵ is not the usual quantity $(K - K_c)/K_c$ but instead $u - u_c = e^{-2K} - e^{-2K_c}$.

10.15.4 Ising model in two dimensions

In the one-dimensional model, the renormalization procedure has generated a new Hamiltonian for the cells identical in form to the original spin Hamiltonian apart from a constant. This usually is not the case. If we try the same procedure in two dimensions, we immediately realize that the renormalization procedure produces in general a new Hamiltonian which does not coincide with the previous one. In fact the new hamiltonian contains not only the original nearest neighbour spin interaction but many more interaction terms such as next nearest neighbour spin interactions, four spin interactions and so on. We therefore must resort to some approximation so that the original Hamiltonian generates itself under renormalization.

A simple procedure introduced by Migdal and developed by Kadanoff is based on some approximation that manages to reproduce the original nearest neighbor Ising Hamiltonian for any dimension. We will apply the Migdal-Kadanoff renormalization group to the two-dimensional case. This procedure is done in two steps. In the first step after dividing the sytem in cells of linear dimension $l = 2$ (dashed violet line in Fig. 10.11), one removes all the interactions coming out from the central spin A and adds these interactions to the other interactions in the cell. This is done uniformly in the entire lattice. It is easy to check that, in this way, the interactions along the perimeter of the cells are doubled. For instance, by stipulating to add the vertical bonds of spin A to the vertical ones of B by moving them to the right, and similarly we move the horizontal bonds of A upwards, half of the perimeter bonds are doubled. The remaining half (down and left edges of the box) are doubled due to the same procedure performed on the neighbouring cells. In conclusion, the bond-moving procedure ends up with an interaction $2K$ along the perimeter of the cell, while the central spins in the A positions now do not interact with any other spins and can be ignored.

After this first step the B spins interact with two neighbor spins only as in the one-dimensional chain. The second step then consists in applying the same decimation procedure of the one-dimensional case to the B spins. The final result is that spins of type A and B are removed and the surviving spins in position C interact with a new renormalized interaction K'. Thus the entire renormalization procedure consists in renormalizing K into K', having rescaled the system by a factor $\ell = 2$.

The calculation corresponding to the second step follows precisely the decimation procedure done in one dimension. The only difference now is that the intermediate interaction is $2K$. The recursion relation is therefore as in Eq. (10.229) with the replacement $u \to u^2$, i.e.

$$u' = \frac{2}{u^2 + u^{-2}} \tag{10.237}$$

Fig. 10.12 shows the presence of 3 fixed points

$$\begin{array}{llll} 1) & u^* & = 0 & (T = 0) \\ 2) & u^* & = 1 & (T = \infty) \\ 3) & u^* & = u_c & (T = T_c). \end{array} \tag{10.238}$$

The first two fixed points are stable. The third one $u_c = 0.54...$ is unstable. The critical exponent is

$$\nu = \frac{\ln 2}{\ln a_c} \simeq 1.33, \tag{10.239}$$

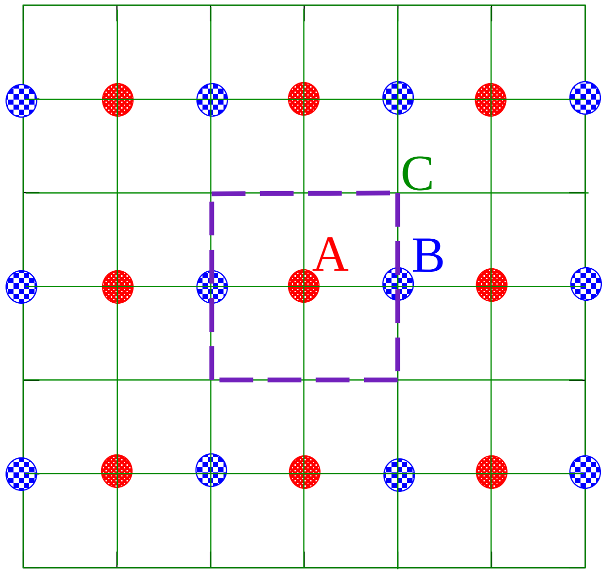

Figure 10.11: The Migdal-Kadanoff decimation procedure.

where

$$a_c = \left.\frac{du'}{du}\right|_{u=u_c} . \tag{10.240}$$

It is easy to see from the figures that if we renormalize the system starting from an initial value u_c, the coupling constant remains the same (scale invariant). If the initial value $u_0 > u_c$ ($T_0 > T_c$), under renormalization the system approaches the stable fixed point $u^* = 1$ ($T = \infty$). On the other hand, starting from $u_0 < u_c(T < T_c)$. The coupling constant under renormalization approaches $u = 0$ ($T = 0$). How do we understand physically this process? If $T > T_c$ in the original spin system two nearest-neighbor spins interact with a coupling interaction J. Under renormalization the cells interact via a new coupling interaction that is smaller than J, since $u = \exp(-2\beta J) \to 1$ and hence $J \to 0$. When under repeated renormalization the cell is of the order or larger than ξ, two nearest neighbor cells are practically independent and the renormalized interaction is almost zero. This explains why eventually the coupling constant tends towards zero. Similarly, if we start below T_c the majority of spins are up and at a coarse grained level if the majority of the spins in the cell are

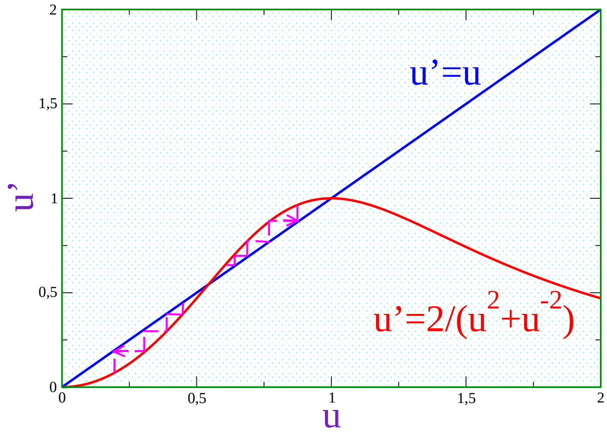

Figure 10.12: Graphical solution of Eq. (10.237) for $d = 2$. The dashed magenta line is the recurrence map.

up, the cell is in the up configuration so that in proportion a larger fraction of cells is up compared to the fraction of up spins. This induces coupling interactions among the cells larger than the interactions among the spins. As we continue renormalizing, the cells eventually reach the correlation length and almost all the cells look perfectly ordered, consequently the coupling interaction approaches infinity, consistently with $u = \exp(-2\beta J) \to 0$.

10.15.5 Universality

In the approximation involved in the Migdal-Kadanoff approach to the Ising model it is not possible to show how the renormalization group can explain the universal behavior of a group of systems. In a more elaborated renormalization group approach, other parameters of the Hamiltonian, other than K may be involved. For instance one could consider the model in the presence of an external magnetic field. Or one might deal with an Ising model with a nearest-neighbor coupling interaction K_1 plus a next-nearest-neighbor coupling interaction K_2. By mapping the original system onto a new one with a renormalized Hamiltonian with the same form as coupling constants K_1 and K_2 the recursion relation will have the form

$$\begin{aligned} K_1' &= f_1(K_1, K_2, \ell) \\ K_2' &= f_2(K_1, K_2, \ell). \end{aligned} \tag{10.241}$$

The fixed points are now points in a larger space. Let us suppose K_1^* and K_2^* are the unstable fixed points. Expanding (10.241) around the fixed point leads to

$$\begin{aligned} \epsilon_1' &= a_{11}\epsilon_1 + a_{12}\epsilon_2 & (10.242) \\ \epsilon_2' &= a_{21}\epsilon_1 + a_{22}\epsilon_2. & \\ & & (10.243) \end{aligned}$$

in which $\epsilon_i = (K_i - K_i^*)/K_i^*$ and

$$a_{ij} = \left(\frac{\partial f_i}{\partial K_j}\right)_{\substack{K_1 = K_1^* \\ K_2 = K_2^*}} \qquad i, j = 1, 2, \qquad (10.244)$$

which can be put in a matricial form

$$\begin{pmatrix} \epsilon_1' \\ \epsilon_2' \end{pmatrix} = \begin{pmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{pmatrix} \begin{pmatrix} \epsilon_1 \\ \epsilon_2 \end{pmatrix}. \qquad (10.245)$$

We can chose a linear combination of ϵ_1 and ϵ_2

$$\begin{aligned} u_1 &= c_{11}\epsilon_1 + c_{12}\epsilon_2 \\ u_2 &= c_{21}\epsilon_1 + c_{22}\epsilon_2, \qquad (10.246) \end{aligned}$$

which diagonalizes the matrix in Eq. (10.245), namely such that

$$\begin{aligned} u_1' = \lambda_1 u_1 = \ell^{x_1} u_1 \qquad (10.247) \\ u_2' = \lambda_2 u_2 = \ell^{x_2} u_2, \end{aligned}$$

or

$$\begin{pmatrix} u_1' \\ u_2' \end{pmatrix} = \begin{pmatrix} \lambda_1 & 0 \\ 0 & \lambda_2 \end{pmatrix} \begin{pmatrix} u_1 \\ u_2 \end{pmatrix}. \qquad (10.248)$$

Here u_1 and u_2 are the scaling fields and x_1 and x_2 the scaling exponents.

The fixed point is $u_1 = u_2 = 0$, which in the plane of the original coupling constants ϵ_1, ϵ_2 is a certain point (see Fig. 10.13). Sitting exactly on the fixed point one is not displaced by the renormalization group iterations. But what happens to a point slightly away from the fixed point? This depends on the sign of the exponents x_1, x_2. If $x_i > 0$ the corresponding scaling field u_i is said to be relevant. It is irrelevant if $x_i < 0$, and marginal if $x = 0$. A case in which both are relevant is, for instance, the case in which ϵ_1 is the coupling

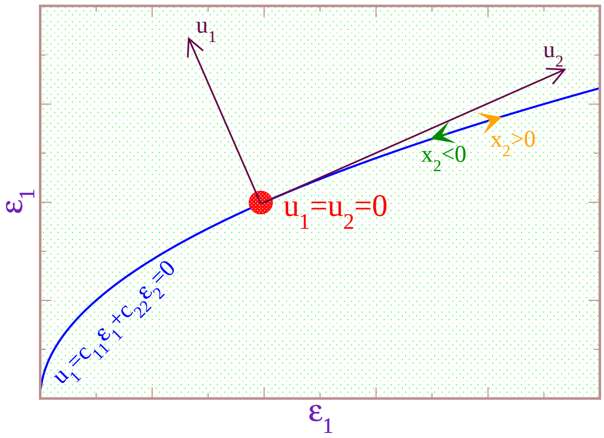

Figure 10.13: Trajectories of the renormalization group transformation.

constant K and ϵ_2 the magnetic field. In this case a point that is not initially exactly on the fixed point will move further away from it. As a particular case of a renormalization group trajectory in the presence of two relevant parameters, let us consider the situation where the representative point is on the curve defined as $u_1 = 0$, i.e., $c_{11}\epsilon_1 + c_{12}\epsilon_2 = 0$, but with $u_2 \neq 0$. Under renormalization one remains on the manyfold $u_1 = 0$ but u_2 will go away from $u_2 = 0$, so that the fixed point $u_1 = 0$, $u_2 = 0$ will be escaped. The situation is represented by the orange arrow in Fig. 10.13. In this case one can have the critical state only for $u_1 = u_2 \equiv 0$. Indeed we know that this is what happens when the scaling fields are the coupling constant and the magnetic field: criticality is obtained only for $H = 0$. Let us consider now the case in which $x_1 > 0$ but $x_2 < 0$. In this case if one is on the so called *critical surface* defined as $u_1 = 0$, i.e., $c_{11}\epsilon_1 + c_{12}\epsilon_2 = 0$, under renormalization u_2 will approach zero (green arrow in the figure). Therefore any point on the critical surface will approach the fixed point $u_1 = 0$, $u_2 = 0$. This shows that the presence of the parameter associated to u_2 does not produce any effect - it is irrelevant - since under renormalizations it goes to zero in any case. We can readily obtain this result by considering the correlation length near the fixed point

$$\xi(u_1', u_2') = \frac{\xi(u_1, u_2)}{\ell} \tag{10.249}$$

which, from (10.248) can be written

$$\ell\xi(\ell^{x_1}u_1,\ell^{x_2}u_2)=\xi(u_1,u_2). \tag{10.250}$$

Letting $\ell^{x_1}u_1=1$ we have

$$\xi(u_1,u_2)=u_1^{-1/x_1}\psi(u_2u_1^{|x_2|/x_1}), \tag{10.251}$$

where $\psi(s)=\xi(1,s)$, and we have taken into account that $x_2<0$. From (10.251) it follows that, as $u_1\to 0$, ξ diverges as

$$\xi\simeq\psi(0)u_1^{-1/x_1}\equiv\xi_0u_1^{-1/x_1}, \tag{10.252}$$

with $\xi_0=\psi(0)$, and an universal exponent $\nu=1/x$ which does not depend on the initial value of u_2. This shows how renormalization theory can predict the universal behavior of an entire family of model systems. All the irrelevant parameters flow to zero under renormalization and do not change the critical exponents. Models which differ only by irrelevant parameters belong to the same universality class. As an example, if we introduce next-nearest neighbourgh interactions in the Ising model with a coupling constant J_{nn}, this parameter turns out to be irrelevant.

10.15.6 Renormalization in momentum shell.

Performing the renormalization procedure in k-space on a model with an Hamiltonian in the form (10.120) (notice that in the mean field approach of Sec. 10.10.5 this form was considered already as the free energy), for $H=0$ and near $d=4$ one arrives at the following recurrences

$$\begin{aligned} r' &= \ell^2r+12c(\ell^2-1)u-\frac{3}{2\pi^2}\ell^2\ln\ell\, ru,\\ u' &= (1+\epsilon\ln\ell)u-\frac{9}{2\pi^2}\ln\ell\, u^2, \end{aligned} \tag{10.253}$$

where $\epsilon=4-d$, c is a constant, r is proportional to the distance $T-T_{MF}$ from the mean field critical temperature and u is proportional to the quantity b appearing in Eq. (10.120). Eq. (10.253) has two fixed points, one with

$$r^*=u^*=0, \tag{10.254}$$

denoted as the Gaussian fixed point, and the other with

$$r^*=\frac{24\pi^2c}{9}\epsilon \quad , \quad u^*=\frac{2\pi^2}{9}\epsilon, \tag{10.255}$$

the Heisenberg fixed point. Notice that at the Gaussian fixed point it is $dr'/dr|_{r=0,u=0} = \ell^2 > 1$, meaning that along the r direction (the *temperature*) the fixed point is repulsive. Analogously, regarding u, at the Gaussian fixed point one has $du'/du|_{r=0,u=0} = 1 + \epsilon \ln \ell$. Hence for $d > 4$ the Gaussian fixed point is attractive along u and it is repulsive below $d = 4$. Computing the critical exponents one discovers that those of the Gaussian fixed point are the mean field exponents. Hence for $d > 4$, if one starts with a theory with $u \neq 0$ and sets the temperature to the mean field critical value T_{MF} the renormalization group transformation leads to the Gaussian fixed point with $u = 0$, and the mean field behavior is found. Conversely, if $d < 4$ the recurrence relations (10.253) lead to a renormalized Hamiltonian at the Heisenberg fixed point. Computing the critical exponents, to lower order in ϵ one finds

$$\nu \simeq \frac{1}{2} + \frac{1}{12}\epsilon\,,\ \alpha \simeq \frac{1}{6}\epsilon\,,\ \beta \simeq \frac{1}{2} - \frac{1}{6}\epsilon\,,\ \gamma \simeq 1 + \frac{1}{6}\epsilon\,,\ \delta \simeq 3 + \epsilon\,,\ \eta \simeq 0. \tag{10.256}$$

Chapter 11

Dynamics

Thus far we have only considered systems that are at equilibrium. In this case Statistical Mechanics approaches the problem without describing the dynamics of the system. However, also in equilibrium, one could be interested to study how the kinetics occurs. Furthermore, if one wants to generalize the equilibrium distribution given by the microcanonical, canonical, and grand canonical ensembles to describe systems out of equilibrium one is forced to provide a dynamical description.

11.1 Hydrodynamic approach

We first consider the simple case of a drop of ink diffusing in water. As already stated, we do not consider the trajectory of each single ink particle resulting from the microscopic dynamic equation of the ink particles and the water, but instead consider a probabilistic description. To illustrate the idea, we use a simple approach based on the random walk model. This model, which has been developed in Chapter 2, predicts a Gaussian distribution for the probability that given the particle at the origin at time $t = 0$ it is at a distance r from the origin at time t [see Eq. (2.42)]. The same result can be obtained using the hydrodynamic approach which is based on Fick's law

$$\vec{J}(\vec{r}, t) = -D\nabla\rho(\vec{r}, t). \tag{11.1}$$

This law relates phenomenologically the flux of particles $\vec{J}(\vec{r}, t)$ at position $\vec{r}$ and time t to the gradient of the particle density $\rho(\vec{r}, t)$ via a constant D, which is called the diffusion coefficient. Physically

Eq. (11.1) means that if the density is not uniform, particles will move from a region of high density toward a region of low density.

To write an equation for the density, we consider the continuity equation that relates the density to the flux,

$$\nabla \cdot \vec{J} + \frac{\partial \rho}{\partial t} = 0. \tag{11.2}$$

From (11.1) and (11.2) the *diffusion equation* follows,

$$\frac{\partial \rho}{\partial t} = D\nabla^2 \rho(\vec{r}, t). \tag{11.3}$$

Equation (11.3) can be solved under the initial condition that all the ink particles at $t = 0$ are at the origin. In this case the solution has radial symmetry and is given by

$$\rho(\vec{r}, t) = \frac{N}{(4\pi Dt)^{3/2}} \exp\left(-\frac{r^2}{4Dt}\right), \tag{11.4}$$

where

$$N = \int \rho(\vec{r}, t) d\vec{r} \tag{11.5}$$

is the number of particles. Note that for $t = 0$, Eq. (11.4) gives a delta function, reproducing the initial conditions. Notice also that Eq. (11.4) is three dimensional analogous to Eq. (2.42) with the position $D = 2pq/\tau$.

11.2 The Langevin equation

Another approach to studying the diffusion of a particle in a medium is to write the equation of motion of the diffusing particle, assuming that the forces due to the particles of the medium can be replaced by a stochastic force $F(t)$. In this approach, which is due to Langevin, the equation of motion can be written as

$$m\frac{d\vec{v}}{dt} = \vec{F}(t), \tag{11.6}$$

where m and v are the mass and velocity of the diffusion particle, respectively.

Next it is assumed that the force can be composed of two parts: $\vec{F}_1(t)$ and $\vec{F}_2(t)$. The first is a deterministic force. It contains a term, due to the viscosity, proportional to the velocity of the particle plus any external force, if present. For the moment we will consider the case where external forces are absent and hence $F_1 = -(1/B)\vec{v}$, where B is the mobility coefficient. The second, $\vec{F}_2$, is a random force that has the property of having a zero time average over short intervals of time, namely

$$m\frac{d\vec{v}}{dt} = \frac{\vec{v}}{B} + \vec{F}_2(t), \tag{11.7}$$

with

$$\langle \vec{F}_2(t) \rangle = 0, \tag{11.8}$$

where the $\langle \dots \rangle$ stands for a time average or, equivalently, an ensemble average. For convenience we will only consider the ensemble average. Notice that Eq. (11.8) does not fully describe the statistical properties of F_2 which will be deduced in Sec. 11.2.1. Since Eq. (11.7) contains a random force it is a stochastic differential equation.

By taking the ensemble average over (11.7) and considering the property (11.8), the following equation is obtained for the average velocity $\langle \vec{v} \rangle$

$$m\frac{d\langle \vec{v} \rangle}{dt} = -\frac{\langle v \rangle}{B}, \tag{11.9}$$

from which

$$\langle \vec{v} \rangle = \vec{v}_0 e^{-t/\tau}, \tag{11.10}$$

with $\tau = mB$. Equation (11.10) tells us that the average velocity of a particle with initial velocity $\vec{v}_0$ goes to zero with a relaxation time τ, loosely speaking. After a time τ, due to the collisions with other particles, the particle loses the memory of its initial velocity. Note that (i) the larger the mass m of the particle, the longer it takes to lose its initial velocity and the larger is τ; (ii) the larger the mobility coefficient, the less resistance opposes the fluid and the larger is τ.

From Eq, (11.7) we can derive an equation for $\langle r^2 \rangle$. Taking the scalar product of both member of (11.7) with r, we obtain

$$\vec{r} \cdot \frac{d\vec{v}}{dt} = -\frac{\vec{r} \cdot \vec{v}}{\tau} + \frac{\vec{r} \cdot \vec{F}_2}{m}. \tag{11.11}$$

Using the identities

$$\frac{dr^2}{dt} = \frac{d}{dt}(\vec{r} \cdot \vec{r}) = 2\vec{r} \cdot \vec{v} \tag{11.12}$$

and

$$\frac{d^2r^2}{dt^2} = 2\frac{d}{dt}(\vec{r}\cdot\vec{v}) = 2v^2 + 2\vec{r}\cdot\frac{d\vec{v}}{dt}. \tag{11.13}$$

From (11.11) it follows

$$\frac{d^2r^2}{dt^2} + \frac{1}{\tau}\frac{d}{dt}r^2 = 2v^2 + \frac{2\vec{r}\cdot\vec{F}_2}{m}. \tag{11.14}$$

Taking the ensemble average from (11.14), we have

$$\frac{d^2\langle r^2\rangle}{dt^2} + \frac{1}{\tau}\frac{d}{dt}\langle r^2\rangle = 2\langle v^2\rangle, \tag{11.15}$$

where we have used the properties that $\langle\vec{r}\cdot\vec{F}_2\rangle = \vec{r}\cdot\langle\vec{F}_2\rangle = 0$. To solve (11.15), we need to know $\langle v^2\rangle$. We will calculate this quantity later for any value of t. However, for long times in which the particle has reached equilibrium with the system, we can use the theorem of equipartition of the kinetic energy, namely

$$\frac{1}{2}m\langle v^2\rangle = \frac{3}{2}kT. \tag{11.16}$$

Substituting (11.16) in (11.15),

$$\frac{d^2\langle r^2\rangle}{dt^2} + \frac{1}{\tau}\frac{d}{dt}\langle r^2\rangle = \frac{6kT}{m}. \tag{11.17}$$

The solution of (11.7) under the initial condition that $\langle r^2\rangle = 0$ and $d\langle r^2\rangle/dt = 0$ is given by (see Appendix F)

$$\langle r^2\rangle = \frac{6kT}{m}\tau^2\left\{\frac{t}{\tau} - \left(1 - e^{-t/\tau}\right)\right\}. \tag{11.18}$$

In the limit $t \ll \tau$, using the expansion $e^{-x} = 1 - x + (x^2/2) + \dots$ from (11.18) we have

$$\langle r^2\rangle = \frac{3kT}{m}t^2 = \langle v^2\rangle t^2, \tag{11.19}$$

while for $t \gg \tau$

$$\langle r^2\rangle = 6kTBt. \tag{11.20}$$

Equation (11.19) tells us that for time much less than the characteristic time τ, the particle moves as if it were free from collisions with a velocity equal to the thermal velocity (11.16). Equation

(11.20) gives a time-dependence identical to the one obtained in the random walk or hydrodynamic approach. In fact, from (11.4) and (B.4),

$$\langle r^2 \rangle = \frac{1}{N} \int \rho(\vec{r}, t) r^2 d\vec{r} = 6Dt, \tag{11.21}$$

which, compared with (11.20), gives a relation between the diffusion coefficient D and the mobility B,

$$kTB = D, \tag{11.22}$$

which is known as Einstein's relation.

Figure 11.1: Paul Langevin (Paris 23/01/1872 - 19/12/1946) and Albert Einstein (Ulma, 14/03/1879 - Princeton, 18/04/1955).

11.2.1 Statistical properties of the noise

In this section we deduce the statistical properties of the noise and, as a byproduct, we compute the time behavior of $\langle v^2 \rangle$ (in the previous section it was evaluated only in the long time regime).

Let us write the Langevin equation in the form

$$\frac{d\vec{v}}{dt} = -\frac{\vec{v}}{\tau} + \vec{a}(t) \tag{11.23}$$

where $\vec{a}(t) = \vec{F}_2(t)/m$. The general solution of this equation (see Appendix E) is

$$\vec{v} = \vec{v}(0)e^{-t/\tau} + e^{-t/\tau} \int_0^t \vec{a}(t_1)e^{t_1/\tau} dt_1. \tag{11.24}$$

Taking the square one has

$$\begin{aligned} v^2(t) &= v^2(0)e^{-2t/\tau} + e^{-2t/\tau}\int_0^t\int_0^t e^{(t_1+t_2)/\tau}\vec{a}(t_1)\cdot\vec{a}(t_2)dt_1dt_2 + \\ & \quad 2e^{-2t/\tau}\left[\vec{v}(0)\int_0^t e^{t_1/\tau}\vec{a}(t_1)dt_1\right], \end{aligned} \tag{11.25}$$

and, after averaging

$$\langle v^2(t)\rangle = \langle v^2(0)\rangle e^{-2t/\tau} + e^{-2t/\tau}\int_0^t\int_0^t e^{(t_1+t_2)/\tau}\langle\vec{a}(t_1)\cdot\vec{a}(t_2)\rangle dt_1dt_2, \tag{11.26}$$

since the last term in (11.25) gives zero contribution because $\vec{a}$ is not correlated with $\vec{v}(0)$ and $\langle\vec{a}(t)\rangle = 0$.

To proceed further, we must know the quantity $K(t_1,t_2) = \langle\vec{a}(t_1)\cdot\vec{a}(t_2)\rangle$, which appears in the integrand. This quantity is a measure of the correlation of $\vec{a}(t)$ at time t_1 with itself at time t_2. For this reason it is called the auto-correlation function of $\vec{a}(t)$. In a regime in which the fluid is stationary, any two-time function depends only on the time difference $s = t_1 - t_2$, hence

$$K(t_1,t_2) \equiv K(s) = \langle\vec{a}(t_1)\cdot\vec{a}(t_2)\rangle. \tag{11.27}$$

Next we assume that

$$K(s) = C\delta(s). \tag{11.28}$$

This assumption is physically justified by noting that the values of $\vec{a}(t_1)$ and $\vec{a}(t_1+s)$ for large enough s are highly uncorrelated. Because the force $\vec{F}_2$ is randomly fluctuating in time, for s larger than a characteristic s^*,

$$K(s) = \langle\vec{a}(t_1)\cdot\vec{a}(t_1+s)\rangle = \langle\vec{a}(t_1)\rangle\cdot\langle\vec{a}(t_1+s)\rangle. \tag{11.29}$$

Since $\langle\vec{a}(t_1)\rangle = 0$, it follows that $K(s) = 0$. Due to the molecular agitation, we can expect s^* to be extremely small. Therefore all calculations can be made by assuming that the autocorrelation is a delta function as in Eq. (11.28).

In conclusion, we assume that the force $\vec{F}_2$ appearing in the Langevin equation has zero mean and a delta correlation. Using (11.28), we can easily evaluate the integral in (11.26), giving

$$\langle v^2(t)\rangle = v^2(0)e^{-2t/\tau} + C\frac{\tau}{2}\left(1 - e^{-2t/\tau}\right). \tag{11.30}$$

This is the desired expression, which still contains the quantity C, which is unknown. However, by taking the limit $t \to \infty$ we find

$$\langle v^2(t) \rangle = C\frac{\tau}{2}, \tag{11.31}$$

and using the equipartition theorem we obtain

$$C = \frac{6kT}{\tau m} = \frac{6kT}{Bm^2}. \tag{11.32}$$

Consequently,

$$\langle \vec{F}_2(t_1) \cdot \vec{F}_2(t_2) \rangle = \frac{6kT}{B}\delta(t_1 - t_2). \tag{11.33}$$

This relation shows that the higher the strength of the fluctuating force, the higher the viscosity B^{-1}, showing that these two quantites have the same orgin in the collisions of the fluid particles.

11.2.2 Harmonic oscillator in a viscous medium

As an application let us consider a particle in a viscous medium subject to an elastic potential $\mathcal{H} = (1/2)\lambda r^2$. If the viscosity is high we can set $m \simeq 0$ (overdamped limit). I this limit, and in the presence of the harmonic force $-\lambda \vec{r}$ the Langevin equation becomes

$$\frac{d\vec{r}}{dt} = -B\lambda\vec{r} + B\vec{F}_2(t) \tag{11.34}$$

The solution is (see Appendix E)

$$\vec{r}(t) = \vec{r}(0)e^{-B\lambda t} + Be^{-B\lambda t}\int_0^t \vec{F}_2(t_1)e^{B\lambda t_1}dt_1, \tag{11.35}$$

which is similar to Eq. (11.24). Taking the average

$$\langle \vec{r}(t) \rangle = \langle \vec{r}(0) \rangle e^{-B\lambda t}, \tag{11.36}$$

which shows that the particle moves from the initial position to zero in an exponential way with rate $B\lambda$. Proceeding analogously to what done after Eq. (11.24), using the properties of the noise, one finds

$$\langle r^2(t) \rangle = \langle r^2(0) \rangle e^{-2B\lambda t} + \frac{3kT}{\lambda}\left(1 - e^{-2B\lambda t}\right). \tag{11.37}$$

Hence, starting from the initial value $\langle r^2(0)\rangle$ the mean square position of the particle converges to the asymptotic value $\langle r^2\rangle_{eq} = 3kT/\lambda$. This means that

$$\langle \mathcal{H}(\vec{r})\rangle = \frac{1}{2}\lambda\langle r^2\rangle = \frac{3}{2}kT, \tag{11.38}$$

which, recalling that the momenta degrees of freedom do not contribute due to $m \simeq 0$, gives the principle of equipartition of the energy.

11.3 Master Equation

In the Langevin approach we have considered the motion of a particle subject to random forces. Let us now write an equation for the distribution probability $f(x,t)$ of finding a particle between x and $x+dx$ at time t. For N particles diffusing in a medium in one dimension, $Nf(x,t)dx$ (the number of particles in the volume dx) satisfies

$$\begin{aligned} N\frac{\partial}{\partial t}f(x,t)dx &= -\int dx'[Nf(x,t)dxW(x,x')] + \\ &+ \int dx'[Nf(x',t)dx\,W(x',x)], \end{aligned} \tag{11.39}$$

where $W(x,x')dx'$ is the transition probability per unit time that a particle in x jumps in a volume between x' and $x'+dx'$. The first term in (11.39) represents the variation per unit of time of the number of particles in the volume dx. The second and third terms are the number of outgoing and incoming particles, respectively, in the volume dx. Notice the generality of Eq. (11.39), since the forces acting on the particles are encoded in the W's which are now left generic (we only assume that they do not depend on time, but this also could be released). Moreover the argument can be trivially extended to a generic space dimensionality. However, it must be noticed that the flux of incoming and outgoing particles in Eq. (11.39) does not depend on the velocity of the particles (which never appears in fact). This implies that we are implicitly working in the overdamped limit $m \to 0$. By dividing Eq. (11.39) by Ndx, we obtain the master equation,

$$\frac{\partial}{\partial t}f(x,t) = -\int f(x,t)W(x,x')dx' + \int f(x',t)W(x',x)dx'. \tag{11.40}$$

If space is discrete, instead of Eq. (11.40) one would have

$$\frac{\partial}{\partial t} f_i(t) = -\sum_{i'} f_i(t) W_{i,i'} + \sum_{i'} f_{i'}(t) W_{i',i}, \tag{11.41}$$

for the probability f_i of finding the particle on site i, where $W_{i,i'}$ is the transition rate for going from site i to i'. As an example let us consider the simple case of the unbiased ($p = q = 1/2$) one dimensional random walk of Sec. 2. In this case $W_{i,i'} = 1/2 \cdot \delta_{|i-i'|,1}$ and from Eq. (11.41) one obtains

$$\frac{\partial}{\partial t} f_i(t) = \frac{1}{2} \Delta f_i(t) \tag{11.42}$$

where the operator $\Delta(y_i)$, given by

$$\Delta(y_i) = -2y_i + [y_{i-1} + y_{i+1}], \tag{11.43}$$

is the discretized laplacian. It is trivial to show that Eq. (11.42) is arrived also in arbitrary dimension with the discretized laplacian

$$\Delta(y_i) = -zy_i + \sum_{\langle j \rangle_i = 1,z} y_{j_i} \tag{11.44}$$

where $\langle j \rangle_i$ are the z nearest neighbourgh of i. Eq. (11.42) is the diffusion equation (11.3) obtained with the hydrodynamic approach of Sec. 11.1. Notice however that here it is obtained for the probability f while in Sec. 11.1 the variable was the density of particles. This implies that ρ must be intended as an (ensemble) average quantity.

As a further example let us consider the particular case in which

$$\int W(x, x') dx' \equiv \frac{1}{\tau} \tag{11.45}$$

does not depend on x. Let us also assume that the (up to now generic) quantity $f_{st}(x)$, defined as

$$\int f(x', t) W(x', x) dx' \equiv \frac{1}{\tau} f_{st}(x), \tag{11.46}$$

does not depend on time. With these positions, Eq. (11.40) becomes

$$\frac{\partial}{\partial t} f(x, t) = -\frac{1}{\tau} f(x, t) + \frac{1}{\tau} f_{st}(x). \tag{11.47}$$

The solution of (11.47) under the initial condition $f(x,0) = f_0(x)$ gives (see Appendix E)

$$f(x,t) = f_{st}(x) + (f_0(x) - f_{st}(x)) \cdot e^{-t/\tau}. \tag{11.48}$$

This shows that $f_{st}(x)$ is the asymptotic distribution, i.e. the stationary state. In the absence of any external driving this is the equilibrium state, and hence the master equation describes the decay of a non-equilibrium state towards equilibrium. In this particular example the stationary state is reached exponentially fast with a characteristic time τ. Notice that, when it is reached, Eqs. (11.45,11.46) imply that

$$\int f(x',t)W(x',x)dx' = \int f(x,t)W(x,x')dx', \tag{11.49}$$

meaning that the flux of outgoing and ingoing probability probability in a point x are the same. This is an obvious property of stationarity.

11.4 Fokker-Planck Equation

In certain conditions the master equation can be reduced to a simpler equation, called the Fokker-Planck equation, which has the advantage of being a usual partial differential equation for f instead of an integro-differential one. In order to do that let us suppose that $W(x,x')$ is highly peaked around $x = x'$ and goes rapidly to zero for $x \neq x'$. This is reasonable if the particle can only jump nearby. Let us work in one dimension for simplicity and put $\xi = x' - x$. Equation (11.40) can then be written

$$\frac{\partial}{\partial t} f(x,t) = -\int f(x,t)W(x,x+\xi)d\xi + \int f(x+\xi,t)W(x+\xi,x)d\xi. \tag{11.50}$$

When we expand the integrand of (11.50) around $x_0 = x - \xi$, we get

$$f(x+\xi,t)W(x+\xi,x) = \sum_n \frac{1}{n!}\frac{\partial^n}{\partial x^n}[f(x+\xi,t)W(x+\xi,x)]\Bigg|_{x=x_0} \xi^n. \tag{11.51}$$

Notice that this is not a trivial expansion for small jumps $\xi \simeq 0$ (in this case, for instance, the zero-th order would be $f(x,t)W(x,x)$) but an expansion around $x - \xi$. In other words we re-write $f(x +$

$\xi, t)W(x+\xi, x)$ in terms of the *translated* quantity $f(x,t)W(x, x-\xi)$ by means of a Taylor expansion).

For small ξ, we can stop at the second order, so that

$$f(x+\xi,t)W(x+\xi,x) = f(x,t)W(x,x-\xi)+ \tag{11.52}$$

$$+\frac{\partial}{\partial x}[f(x+\xi,t)W(x+\xi,x)]\bigg|_{x=x_0}\xi+\frac{1}{2}\frac{\partial^2}{\partial x^2}[f(x+\xi,t)W(x+\xi,x)]\bigg|_{x=x_0}\xi^2$$

namely

$$f(x+\xi,t)W(x+\xi,x) = f(x,t)W(x,x-\xi)+ \tag{11.53}$$

$$+\frac{\partial}{\partial x}[f(x,t)W(x,x-\xi)]\xi+\frac{1}{2}\frac{\partial^2}{\partial x^2}[f(x,t)W(x,x-\xi)]\xi^2.$$

By putting $\xi' = -\xi$, we can easily shown that for integer n it is

$$\int_{-\infty}^{\infty} f(x,t)W(x,x-\xi)\xi^n d\xi = -(-1)^n \int_{\infty}^{-\infty} f(x,t)W(x,x+\xi')\xi'^n d\xi' =$$

$$= (-1)^n \int_{-\infty}^{\infty} f(x,t)W(x,x+\xi')\xi'^n d\xi'. \tag{11.54}$$

Therefore from (11.50), (11.53), and (11.54) we obtain the Fokker-Planck equation,

$$\frac{\partial}{\partial t}f(x,t) = -\frac{\partial}{\partial x}\{\mu_1(x)f(x,t)\}+\frac{1}{2}\frac{\partial^2}{\partial x^2}\{\mu_2(x)f(x,t)\}, \tag{11.55}$$

where

$$\mu_1(x) = \int_{-\infty}^{\infty} W(x,x+\xi)\xi d\xi, \tag{11.56}$$

and

$$\mu_2(x) = \int_{-\infty}^{\infty} W(x,x+\xi)\xi^2 d\xi. \tag{11.57}$$

Note that μ_1 and μ_2 can be written as

$$\mu_1 \equiv \frac{\langle \delta x\rangle}{\delta t} \equiv \langle v\rangle, \tag{11.58}$$

and

$$\mu_2 \equiv \frac{\langle (\delta x)^2\rangle}{\delta t}. \tag{11.59}$$

In order to better characterize these terms let us consider again the Langevin equation in the presence of an external force f_{ext},

$$m\frac{dv}{dt} = -\frac{v}{B} + F_2(t) + f_{ext}. \qquad (11.60)$$

In the overdamped limit $m \to 0$ we have considered in Sec. 11.3 this gives

$$\langle v \rangle = B f_{ext}. \qquad (11.61)$$

Since $f_{ext} = -\partial\mathcal{H}/\partial x$ where $\mathcal{H}$ is the Hamiltonian, we find

$$\mu_1 = -B\frac{\partial \mathcal{H}}{\partial x}. \qquad (11.62)$$

Moreover, from the Langevin equation in one dimension we find

$$\langle x^2 \rangle = 2kTBt \qquad t \gg \tau, \qquad (11.63)$$

which is the analogue of Eq. (11.20) in $d = 1$. Since we are considering the case $m \to 0$ ($\tau \to 0$), Eq. (11.63) is valid for any t. Therefore for a mean square displacement $\langle (\delta x)^2 \rangle$ in a time δt we have

$$\mu_2 = \frac{\langle (\delta x)^2 \rangle}{\delta t} = 2kTB. \qquad (11.64)$$

In conclusion, the Fokker-Planck equation becomes

$$\frac{\partial f}{\partial t} = B\frac{\partial}{\partial x}\left[\frac{\partial \mathcal{H}}{\partial x} \cdot f\right] + kBT\frac{\partial^2}{\partial x^2}f. \qquad (11.65)$$

The first term is a drift term due to external forces. The second is a diffusive term. In the absence of external forces, Eq. (11.65) coincides with the diffusive equation. Notice that the procedure we have followed implies that the Langevin and the Fokker-Plank equations are complementary approaches.

In the stationary regime $t \to \infty$, we have

$$0 = \frac{\partial}{\partial x}\left[\frac{\partial \mathcal{H}}{\partial x} \cdot f\right] + kT\frac{\partial^2}{\partial x^2}f, \qquad (11.66)$$

whose solution

$$f_{eq} \propto e^{-\beta\mathcal{H}}, \qquad (11.67)$$

gives the Boltzmann (canonical) distribution.

11.4.1 Harmonic oscillator in a viscous medium (revisited)

As an application, let us consider a particle in a viscous medium subject to an elastic potential $\mathcal{H} = (1/2)\lambda x^2$. The Fokker-Planck equation becomes

$$\frac{\partial f}{\partial t} = \lambda B \frac{\partial}{\partial x}[xf] + kBT \frac{\partial^2}{\partial x^2} f \tag{11.68}$$

under the initial condition that the particle is localized in x_0 at $t = 0$. The solution is given by (see Appendix to be done)

$$f(x,t) = \left\{ \frac{\lambda}{2\pi k_B T(1-e^{-2\lambda Bt})} \right\}^{1/2} \exp\left[-\frac{\lambda(x - x_0 e^{-\lambda Bt})^2}{2k_B T(1-e^{-2\lambda Bt})} \right]. \tag{11.69}$$

Equation (11.69) is a Gaussian distribution that becomes a delta function localized at x_0 for $t = 0$, while the average position $\langle x(t) \rangle$ moves towards the origin exponentially in time with rate $B\lambda$. For $t \to \infty$ is a Gaussian centered in $x = 0$ with width $\sqrt{k_B T/\lambda}$. In other words, a particle originally in x_0 will diffuse moving on average towards the origin $x = 0$ with an equilibrium distribution f_{eq} given by

$$f_{eq}(x) = \frac{1}{(2\pi kT/\lambda)^{1/2}} \exp\left[-\frac{\lambda x^2}{2kT} \right], \tag{11.70}$$

which coincides with the Boltzmann distribution of a particle subject to an elastic potential $U(x) = (1/2)\lambda x^2$. The mean square displacement in the equilibrium configuration is given by

$$\langle x^2 \rangle = \int f_{eq}(x) x^2 dx = \frac{kT}{\lambda}, \tag{11.71}$$

which can be written as

$$\langle \mathcal{H}(x) \rangle = \frac{1}{2}\lambda \langle x^2 \rangle = \frac{1}{2}kT. \tag{11.72}$$

which gives the principle of equipartition of the energy. Clearly, working in $d = 3$ we would have found Eq. (11.38). The results of this section are analogous to those found in Sec. 11.2.2 working with the Langevin equation. This shows that the Fokker-Plank and the Langevin approach are complementary.

11.5 General Master Equation

Here we want to generalize the master equation, discussed in Sec. 11.3. Given an ensemble of $\mathcal{N}$ equivalent systems, the probability $P_r(t)$ of finding a system of the ensemble in a state r is given by $P_r(t) = \mathcal{N}_r(t)/\mathcal{N}$, where $\mathcal{N}_r(t)$ is the number of systems in the state r at time t, and $\mathcal{N}$ tends to infinity. For instance, in Sec. 11.3 the states r could be described simply in terms of the particle's position x and we used the notation $f(x,t)$ for $P_r(t)$. In general a state r must be described by all the relevant variables, like, for instance, positions and momenta of all the particles etc... Using the same argument as in Sec. 11.3, we can write a differential equation for $P_r(t)$

$$\frac{\partial P_r}{\partial t} = -\sum_s P_r(t) W_{rs} + \sum_s P_s(t) W_{sr}, \tag{11.73}$$

where W_{rs} is the probability per unit time that a system goes from the microscopic state r to the microscopic state s and we are working with a discrite spectrum of states (the case with continuous variables is analogue). If we multiply each term of (11.73) by $\mathcal{N}$, the first term is the rate at which the number of systems in the microstate r in the ensemble changes. This is given by two terms. The first (with negative contribution) is the number of systems that in the unit time go from the state r to any state s. The second (with positive contribution) is the number of systems that in the unit time go from any state s into the state r.

To find an expression for W_{rs}, let us consider (11.73) at equilibrium where $\partial P_r/\partial t = 0$. From (11.73) we have

$$\sum_s P_r^{(eq)} W_{rs} = \sum_s P_s^{(eq)} W_{sr}, \tag{11.74}$$

where $P_r^{(eq)}$ is the (time-independent) equilibrium distribution. This equation is certainly satisfied if

$$P_r^{(eq)} W_{rs} = P_s^{(eq)} W_{sr}. \tag{11.75}$$

Equation (11.75) is called the *detailed balance equation.* Notice that, in general, Eq. (11.75) does not fix the transition rates W since it is a single equation for two unknowns.

For the microcanonical ensemble we have $P_r^{(eq)}$ = const for each accessible configuration r. Hence a possible solution is

$$W_{rs} = \text{const}. \tag{11.76}$$

For the canonical ensemble $P_r^{(eq)} = \text{const.} \cdot e^{-\beta E_r}$. Therefore, a possible solution of (11.75) is given by the so-called *heat bath* transition rates

$$W_{rs} = \text{const.} \cdot e^{-\beta E_s}. \tag{11.77}$$

Another possibility are the *Metropolis* transition rates

$$W_{rs} = \text{const.} \ \cdot \ \min\left[1, e^{-\beta(E_s - E_r)}\right]. \tag{11.78}$$

The constants in Eqs. (11.76,11.77,11.78) fix the unit time. If the system satisfies ergodicity, namely each state can be reached by any other state s, then Eq. (11.73) with W_{rs} given by (11.76) or (11.77) assure that, starting from any initial distribution, the ensemble evolves toward the equilibrium distribution.

For an isolated system for which the microcanonical ensemble applies we will show below that the H function

$$H = \sum_r P_r \ln P_r \tag{11.79}$$

satisfies

$$\frac{dH}{dt} = -\frac{1}{2} \sum_{r,s} W_{rs}(P_r - P_s)(\ln P_r - \ln P_s) \leq 0. \tag{11.80}$$

Since $S = -kH$, (11.80) implies that the entropy in an isolated system decreases with the time and reaches the maximum value when $P_r = \text{const.}$ for each r, namely when the equilibrium distribution is reached.

It remains to show the validity of Eq. (11.80). Taking the time derivative of H in Eq. (11.79), using the master equation (11.73) one gets

$$\frac{dH}{dt} = \sum_{r,s} \left(-W_{rs} P_r + W_{sr} P_s\right)\left(\ln P_r + 1\right) \tag{11.81}$$

In a microcanonical setting, chosing $W_{rs} = \text{const.}$ so that $W_{rs} = W_{sr}$, Eq. (11.82) can be written as

$$\frac{dH}{dt} = \sum_{r,s} W_{rs}\left(-P_r + P_s\right)\left(\ln P_r + 1\right) \tag{11.82}$$

Exchanging the indexes r, s one has

$$\sum_{r,s} W_{rs}\left(-P_r + P_s\right)\left(\ln P_r + 1\right) = \sum_{r,s} W_{rs}\left(P_r - P_s\right)\left(\ln P_s + 1\right), \tag{11.83}$$

where we have used again $W_{rs} = W_{sr}$. Enforcing this relation the r.h.s. of Eq. (11.82) can be written as

$$(1/2)\left[\sum_{r,s} W_{rs}\left(-P_r + P_s\right)\left(\ln P_r + 1\right) + \sum_{r,s} W_{rs}\left(P_r - P_s\right)\left(\ln P_s + 1\right)\right], \tag{11.84}$$

arriving then at Eq. (11.80).

11.6 Boltzmann Equation

Let us apply the master equation of the previous section to a gas of N particles obeying the laws of classical mechanics. The states r of the system are now labelled by the position and momentum of each particle, which are continuous variables. We will use the shorthand $\overrightarrow{R} \equiv \{\vec{r}_1, \dots, \vec{r}_N\}$ to denote the $3N$ positions, and $\overrightarrow{P} \equiv \{\vec{p}_1, \dots, \vec{p}_N\}$ for the momenta. We will also define $\overrightarrow{P}_{i,j,\dots}$ as the ensemble of all the variables $\overrightarrow{P}$ except those of the particles $i, j, \dots$, (and similarly for $\overrightarrow{R}_{i,j,\dots}$). Denoting the probability of a state as $\mathcal{P}$ Eq. (11.73) can be written as

$$\begin{aligned} \frac{\partial}{\partial t}\mathcal{P}(\overrightarrow{P}, \overrightarrow{R}, t) &= -\int d\overrightarrow{R}' d\overrightarrow{P}' \, W(\overrightarrow{P}, \overrightarrow{R}; \overrightarrow{P}', \overrightarrow{R}')\mathcal{P}(\overrightarrow{P}, \overrightarrow{R}, t) \\ &+ \int d\overrightarrow{R}' d\overrightarrow{P}' \, W(\overrightarrow{P}', \overrightarrow{R}'; \overrightarrow{P}, \overrightarrow{R})\mathcal{P}(\overrightarrow{P}', \overrightarrow{R}', t) \end{aligned} \tag{11.85}$$

From the joint probability distribution $\mathcal{P}(\overrightarrow{P}, \overrightarrow{R}, t)$ the single particle probability distribution $f_1 = f(\vec{p}_1, \vec{r}_1, t)$ of particle 1 can be obtained by marginalization, i.e. by integrating over the variables of all the remaining $N-1$ particles. In the case in which there are not external forces considered here this function does not depend on space.

$$f_1(\vec{p}_1, t) = \int d\overrightarrow{R}_1 d\overrightarrow{P}_1 \mathcal{P}(\overrightarrow{P}, \overrightarrow{R}, t). \tag{11.86}$$

Analogously, the two-particle joint probability is given by

$$h(\vec{p}_1, \vec{r}_1; \vec{p}_2, \vec{r}_2; t) = \int d\overrightarrow{R}_{1,2} d\overrightarrow{P}_{1,2} \mathcal{P}(\overrightarrow{P}, \overrightarrow{R}, t). \tag{11.87}$$

The transiton rate is given by two terms

$$W(\overrightarrow{P},\overrightarrow{R};\overrightarrow{P}',\overrightarrow{R}')=W_{trasl}(\overrightarrow{P},\overrightarrow{R};\overrightarrow{P}',\overrightarrow{R}')+W_{coll}(\overrightarrow{P},\overrightarrow{R};\overrightarrow{P}',\overrightarrow{R}'). \tag{11.88}$$

The first term is what one would have in the absence of collisions. It is

$$W_{trasl}(\overrightarrow{P},\overrightarrow{R};\overrightarrow{P}',\overrightarrow{R}')=\delta\left(\overrightarrow{R}'-\overrightarrow{R}-\frac{\overrightarrow{P}}{m}\delta t\right)\delta(\overrightarrow{P}'-\overrightarrow{P}). \tag{11.89}$$

The second δ-function ensures momentum conservation, and the first simply states that in the absence of collisions each particle is displaced by $(\vec{p}/m)\,\delta t$ in a time δt.

Regarding the collision term, in a sufficiently small time interval δt only a couple of particles can collide. Let us label them as particle 1 and 2 (this can always be done by re-labelling the particles). The collision term can be written as

$$W_{coll}(\overrightarrow{P}',\overrightarrow{R}';\overrightarrow{P},\overrightarrow{R})=\delta(\overrightarrow{P}'_{1,2}-\overrightarrow{P}_{1,2})\delta(\vec{r}_1-\vec{r}_2)V^{-N}w(\vec{p}_1,\vec{p}_2;\vec{p}_1',\vec{p}_2'). \tag{11.90}$$

The first δ function ensures that all the momenta except those of the colliding particles are unchanged, while the second implies that a collision can only take place if the two particles are on the same site. If these conditions are met the scattering probability is $V^{-N}w(\vec{p}_1,\vec{p}_2;\vec{p}_1',\vec{p}_2')$, where V is the volume of the system (this term appairs as a normalization, but does not matter much since it is a constant).

Due to Eq. (11.88), the r.h.s. of Eq. (11.85) can be splitted in to terms

$$\frac{\partial}{\partial t}\mathcal{P}(\overrightarrow{P},\overrightarrow{R},t)=\left(\frac{\partial}{\partial t}\mathcal{P}(\overrightarrow{P},\overrightarrow{R},t)\right)_{trasl}+\left(\frac{\partial}{\partial t}\mathcal{P}(\overrightarrow{P},\overrightarrow{R},t)\right)_{coll} \tag{11.91}$$

Let us concentrate on the collisional term

$$\begin{aligned}&\left(\frac{\partial}{\partial t}\mathcal{P}(\overrightarrow{P},\overrightarrow{R},t)\right)_{coll}=\\ -&\ V^{-N}\int d\overrightarrow{R}'d\overrightarrow{P}'\,\delta(\overrightarrow{P}'_{1,2}-\overrightarrow{P}_{1,2})w(\vec{p}_1,\vec{p}_2;\vec{p}_1',\vec{p}_2')\delta(\vec{r}_1-\vec{r}_2)\mathcal{P}(\overrightarrow{P},\overrightarrow{R},t)\\ +&\ V^{-N}\int d\overrightarrow{R}'d\overrightarrow{P}'\,\delta(\overrightarrow{P}'_{1,2}-\overrightarrow{P}_{1,2})w(\vec{p}_1',\vec{p}_2';\vec{p}_1,\vec{p}_2)\delta(\vec{r}_1'-\vec{r}_2')\mathcal{P}(\overrightarrow{P}',\overrightarrow{R}',t)\end{aligned} \tag{11.92}$$

Integrating over the variables of all the particles except the first one, one has

$$
\begin{aligned}
&\left(\frac{\partial}{\partial t} f_1(\vec p_1,t)\right)_{coll} = \\
- &\ V^{-N}\int d\overrightarrow{R}_1 d\overrightarrow{R}' d\overrightarrow{P}_1 d\overrightarrow{P}'\ \delta(\overrightarrow{P}'_{1,2}-\overrightarrow{P}_{1,2})\delta(\vec r_1-\vec r_2)w(\vec p_1,\vec p_2;\vec p_1',\vec p_2')\mathcal{P}(\overrightarrow{P},\overrightarrow{R},t) \\
+ &\ V^{-N}\int d\overrightarrow{R}_1 d\overrightarrow{R}' d\overrightarrow{P}_1 d\overrightarrow{P}'\ \delta(\overrightarrow{P}'_{1,2}-\overrightarrow{P}_{1,2})\delta(\vec r_1'-\vec r_2')w(\vec p_1',\vec p_2';\vec p_1,\vec p_2)\mathcal{P}(\overrightarrow{P}',\overrightarrow{R}',t) = \\
- &\int d\vec p_2 d\vec p_1' d\vec p_2' w(\vec p_1,\vec p_2;\vec p_1',\vec p_2')g(\vec p_1,\vec p_2,t) \\
+ &\int d\vec p_2 d\vec p_1' d\vec p_2' w(\vec p_1',\vec p_2';\vec p_1,\vec p_2)g(\vec p_1',\vec p_2',t), \qquad (11.93)
\end{aligned}
$$

where we have used all the δ functions to carry out the integrations and

$$g(\vec p_1',\vec p_2';t)=h(\vec p_1,\vec r_1;\vec p_2,\vec r_1;t) \qquad (11.94)$$

is the joint probability of the two particles to be in the same place $\vec r_1$ which does not depend on $\vec r_1$, similarly to f, due to space homogeneity. [Specifically (referring to the first integral): i) integrating over $d\overrightarrow{R}'$ cancels the V^{-N} in front; ii) integration over $d\overrightarrow{P}'_{1,2}$ can be carried over using the $\delta(\overrightarrow{P}'_{1,2}-\overrightarrow{P}_{1,2})$-function; iii) integration over $d\overrightarrow{R}'_{1,2}d\overrightarrow{P}'_{1,2}$ transforms $\mathcal{P}(\overrightarrow{P},\overrightarrow{R},t)$ into $h(\vec p_1,\vec r_1;\vec p_2,\vec r_2;t)$; iv) integration over $d\vec r_2$ can be carried out using the $\delta(\vec r_1-\vec r_2)$-function and transforms $h(\vec p_1,\vec r_1;\vec p_2,\vec r_2;t)$ into $g(\vec p_1',\vec p_2';t)$.]

Performing the same operations on the translation term one easily obtains

$$\left(\frac{\partial}{\partial t} f_1(\vec p_1,t)\right)_{trasl}=0. \qquad (11.95)$$

This equation simply express the fact that, since momentum is conserved in the absence of collisions, the only effect of an elapsed time δt is to transfer the particle from $\vec r_1$ to $\vec r_1+\frac{\vec p_1}{m}\delta t$ but since f_1 depends only on the momentum it is left unchanged.

Since it can be shown that the collision transition is symmetric, $w(\vec p_1',\vec p_2';\vec p_1,\vec p_2)=w(\vec p_1,\vec p_2;\vec p_1',\vec p_2')$ one arrives at

$$\left(\frac{\partial f_1(\vec p,t)}{\partial t}\right)=\int d\vec p_2 d\vec p_1' d\vec p_2' w(\vec p_1,\vec p_2;\vec p_1',\vec p_2')[g(\vec p_1',\vec p_2',t)-g(\vec p_1,\vec p_2,t)], \qquad (11.96)$$

This expression is exact for a diluted gas. However it contains the unknown correlation function g. We now introduce the crucial assumption

$$g(\vec{p}_1, \vec{p}_2, t) \simeq f(\vec{p}_1, t) f(\vec{p}_2, t) \tag{11.97}$$

This says that the momenta of two particles in the volume element are uncorrelated, so that the probability of finding them simultaneously is the product of the probability of finding each alone. This is known as assumption of *molecular chaos*. It is necessary to obtain a closed equation for the distribution function, but there is otherwise no justification. With this assumption we arrive at

$$\frac{\partial f_1}{\partial t} = \int d\vec{p}_2 d\vec{p}_1' d\vec{p}_2' \, w_{1,2} [f_2' f_1' - f_1 f_2], \tag{11.98}$$

where we have used the compact notation $w_{1,2} = w(\vec{p}_1, \vec{p}_2; \vec{p}_1', \vec{p}_2')$, $f_1 \equiv f(\vec{p}_1, t)$, $f_1' \equiv f(\vec{p}_1', t)$, and similarly for $\vec{p}_2$ and p_2'. Equation (11.98) is the famous Boltzmann equation that gives the single particle probability distribution as a function of time.

11.6.1 Alternative derivation

The master equation that we presented in Sec. 11.3 contains only the distribution in real space. It can be easily generalized to a distribution $f \equiv f(\vec{r}, \vec{p}, t)$ in the entire phase space, where $f d\vec{r} d\vec{p}$ is the probability of finding a particle at time t in a volume $d\vec{r}$ around the position $\vec{r}$ and with an impulse in a range $d\vec{p}$ around $\vec{p}$. Boltzmann derived an explicit equation for a one-particle distribution in a gas of particles using the laws of classical mechanics. The distribution changes in time because molecules enter and leave a given element $d\vec{r} d\vec{p}$ of Γ-space. Suppose there were no collisions among the molecules and no external forces. Then a molecule with coordinates $(\vec{r}, \vec{p})$ at time t will have coordinates $(\vec{r} + \vec{v}\delta t, \vec{p})$, with $\vec{v} = \vec{p}/m$, at the instant $t + \delta t$. We could then write

$$f(\vec{r} + \vec{v}\delta t, \vec{p}, t + \delta t) = f(\vec{r}, \vec{p}, t). \tag{11.99}$$

The presence of collisions can be taken into account by an extra term $(\partial f/\partial t)_{coll}$ defined through

$$f(\vec{r} + \vec{v}\delta t, \vec{p}, t + \delta t) = f(\vec{r}, \vec{p}, t) + \left(\frac{\partial f}{\partial t}\right)_{coll} \delta t. \tag{11.100}$$

Expanding the l.h.s. to first order in δt one arrives at

$$\left(\frac{\partial}{\partial t}+\vec{v}\cdot\nabla_{\vec{r}}\right)f(\vec{r},\vec{p},t)=\left(\frac{\partial f(\vec{r},\vec{p},t)}{\partial t}\right)_{coll}. \qquad (11.101)$$

In the absence of external forces it is consistent to assume that the gas is homogeneous, and hence f does not depend on $\vec{r}$. Then one has

$$\frac{\partial}{\partial t}f(\vec{p},t)=\left(\frac{\partial f(\vec{p},t)}{\partial t}\right)_{coll}. \qquad (11.102)$$

The collision term

$$\left(\frac{\partial f(\vec{p},t)}{\partial t}\right)_{coll}\delta t=\left[\overline{R}(\vec{p},t)-R(\vec{p},t)\right]\delta t \qquad (11.103)$$

can be written as the difference between the incoming and outgoing fluxes of particles, where specifically $R(\vec{p},t)\delta t d\vec{r}d\vec{p}$ is the number of collision events in which one particle leaves the volume element $d\vec{r}d\vec{p}$ in the interval $[t,t+\delta t]$ and $\overline{R}(\vec{p},t)\delta t d\vec{r}d\vec{p}$ that of those in which a particle enters the volume element. Notice that Eq. (11.103) is the analogous of Eq. (11.73) for $f(\vec{p},t)$. Let us consider a collision event where in the initial state S two particles 1 and 2 have impulses $\vec{p}_1$ and $\vec{p}_2$. while in the final state S' they are $\vec{p}_1'$ and $\vec{p}_2'$. Then we can write

$$R(\vec{p}_1,t)=\int d\vec{p}_1'\,d\vec{p}_2\,d\vec{p}_2'\,w_{1,2}g(\vec{p}_1,\vec{p}_2,t), \qquad (11.104)$$

where $g(\vec{p}_1,\vec{p}_2,t)$ is the joint probability that in a volume element around particle 1 there is particle 2 with momentum $\vec{p}_2$ (besides particle 1). Eq. (11.104) states that the number of particles which are leaving the volume element around molecule 1 can be obtained by integrating over all the possible final states of the two particles and over the initial state of particle 2 of the probability of finding particle 2 with impulse p_2 (i.e. g_2) times a scattering probability $w_{1,2}$ which describes as probable is the transition from the initial to the final state. The expression (11.104) is the analogous of the first term on the r.h.s. of Eq. (11.73), namely the statement that the decrease of probability of being in a state (here labelled by $\vec{p}_1,\vec{p}_2$) is given by the probability $g_2(\vec{p}_1,\vec{p}_2)$ of being in the state times the conditional probability $w_{1,2}$ of going to any other possible final state, and a sum over all these states (namely over $\vec{p}_1,\vec{p}_2$) is taken. With respect to Eq. (11.73) here also a sum over $\vec{p}_2$ is appairs, since we only interested in the loss of probability of particle 1, and hence the initial degree of freedom $\vec{p}_2$ of particle 2 is also traced out. Similarly, for the incoming flux one can write

$$\overline{R}(\vec{p}_1, t) = \int d\vec{p}_1' \, d\vec{p}_2 \, d\vec{p}_2' \, w_{1,2}' g(\vec{p}_1', \vec{p}_2', t), \tag{11.105}$$

where $w_{1,2}'$ is the transition rate from S' to S. Since it can be shown that the collision transition is symmetric, $w_{1,2} = w_{1,2}'$ one arrives at

$$\left(\frac{\partial f(\vec{p}, t)}{\partial t}\right)_{coll} = \int d\vec{p}_2 d\vec{p}_1' d\vec{p}_2' w_{1,2} [g(\vec{p}_1', \vec{p}_2', t) - g(\vec{p}_1, \vec{p}_2, t)], \tag{11.106}$$

This expression is exact for a diluted gas. However it contains the unknown correlation function g. We now introduce the crucial assumption

$$g(\vec{p}_1, \vec{p}_2, t) \simeq f(\vec{p}_1, t) f(\vec{p}_2, t) \tag{11.107}$$

This says that the momenta of two particles in the volume element are uncorrelated, so that the probability of finding them simultaneously is the product of the probability of finding each alone. This is known as assumption of *molecular chaos*. It is necessary to obtain a closed equation for the distribution function, but there is otherwise no justification. With this assumption we arrive at

$$\frac{\partial f_1}{\partial t} = \int d^3p_2 d^3p_1' d^3p_2' \, w_{1,2} [f_2' f_1' - f_1 f_2], \tag{11.108}$$

where we have used the compact notation $f_1 \equiv f(\vec{p}_1, t)$, $f_1' \equiv f(\vec{p}_1', t)$, and similarly for $\vec{p}_2$ and p_2'.

Equation (11.108) is the famous Boltzmann equation that gives the single particle probability distribution as a function of time.

11.6.2 Convergence to equilibrium

In the stationary case, $\partial f_1 / \partial t = 0$. It can be shown that the solution in this case has the form of the Boltzmann distribution $f_{eq}(\vec{p}) = e^{-\beta(p^2/2m)}$. A sufficient condition for $\frac{\partial f_1}{\partial t} = 0$ is,

$$f_2' f_1' - f_1 f_2 = 0 \tag{11.109}$$

in such a state (it can be shown that this condition is also necessary). Taking the logarithms

$$\ln f_1 + \ln f_2 = \ln f_1' + \ln f_2'. \tag{11.110}$$

Eq. (11.110) shows that $\ln f$ is a conserved quantity. Since the only conserved quantites are energy and momentum, $\ln f$ must be a linear combination of these quantities (plus a constant, which of course is another conserved quantity), and one can write

$$\ln f(p) = -A(\vec{p} - \vec{p}_0)^2 + \ln C \tag{11.111}$$

or

$$f(\vec{p}) = Ce^{-A(\vec{p}-\vec{p}_0)^2}, \tag{11.112}$$

where C, A and the three components of p_0 are five arbitrary constants. Since p_0 can be readily identified with the average momentum, if the gas has no translational motion it must be fixed to $\vec{p}_0 = 0$. C and A can be determined by fixing the density of particles ρ, and the energy of the system or, using equipartition, the temperature T. One arrives than to

$$f(p) = \frac{\rho}{(2\pi mkT)^{3/2}} e^{-\frac{p^2}{2mkT}}, \tag{11.113}$$

namely the Maxwell-Boltzmann distribution.

11.6.3 H-Theorem

A direct consequence of the Boltzmann equation is the famous Boltzmann H-theorem. Defining H as

$$H = \int d^3p\, f(\vec{p}, t) \ln f(\vec{p}, t), \tag{11.114}$$

we show that $dH/dt \leq 0$. Differentiating H with respect to time one has

$$\frac{dH(t)}{dt} = \int d^3p\, \frac{\partial f(\vec{p}, t)}{\partial t} [1 + \ln f(\vec{p}, t)], \tag{11.115}$$

and using the Boltzmann equation (11.108)

$$\frac{dH(t)}{dt} = \int d^3p_1 d^3p_2 d^3p_1' d^3p_2'\, w_{1,2}[f_2' f_1' - f_1 f_2][1 + \ln f_1]. \tag{11.116}$$

Interchanging $\vec{p}_1$ and $\vec{p}_2$ in the integrand leaves the integral unchanged because $w_{1,2}$ is symmetric. Making this change of integration variables and taking one-half of the sum of the new expression and of Eq. (11.116) one obtains

$$\frac{dH(t)}{dt} = \frac{1}{2} \int d^3p_1 d^3\vec{p}_2 d^3\vec{p}_1' d^3\vec{p}_2'\, w_{1,2}[f_2' f_1' - f_1 f_2][2 + \ln(f_1 f_2)]. \tag{11.117}$$

This integral is invariant under the interchange $p_1, p_2 \leftrightarrow p'_1, p'_2$ because for every collision there is an inverse one with the same transition matrix. Hence

$$\frac{dH(t)}{dt} = -\frac{1}{2}\int d^3p_1 d^3\vec{p}_2 d^3\vec{p}'_1 d^3\vec{p}'_2\, w_{1,2}[f'_2 f'_1 - f_1 f_2][2 + \ln(f'_1 f'_2)]. \tag{11.118}$$

Taking half the sum of Eqs. (11.118) and (11.117) one arrives at

$$\frac{dH(t)}{dt} = \frac{1}{4}\int d^3p_1 d^3p_2 d^3p'_1 d^3p'_2\, w_{1,2}[f'_2 f'_1 - f_1 f_2][\ln(f_1 f_2) - \ln(f'_1 f'_2)]. \tag{11.119}$$

Since the integrand in this equation is never positive, the theorem is proved.

If we associate the entropy with $-kH$, with k a constant, the theorem states that the entropy is an increasing function of the time that reaches a maximum in the equilibrium state. At the time, the results obtained by Boltzmann were considered a proof of the second law of Thermodynamics starting from the microscopic laws of classical dynamics. There was immediately a big debate about the validity of such results.

Two main objections were raised. The first concerned the Boltzmann equation. This equation is non-invariant for time reversal as it can be easily recognized by changing $t \to -t$ in the equation. How could such an equation be derived from the laws of dynamics which are invariant under time reversal? (Notice that also the Langevin equation, the Master equation and the Fokker-Plank equation are not invariant under time reversal, but in those cases, at variance with the present one, this is not surprising, due to the explicit presence of the viscous term whereby mechanical energy is transformed into heat).

The second objection is based on the recurrence cycles of Poincaré. Poincaré proved that in a closed system – given an initial configuration in phase space and a region around it, however small – there exists an interval of time long enough but finite after which the point representative of the system goes through this region. Therefore the quantity H cannot always decrease since it must assume values close to the initial one. In other words, Eq. (11.108) introduces a time arrow, which is absent in the laws of classical mechanics. According to classical mechanics, if a trajectory is realized, the same trajectory in the opposite direction is possible if the velocity of all the particles are reversed. According to the H Theorem, a trajectory that could increase the value of H would never be possible.

In reality, the Boltzmann equation has been proven only under the condition of "molecular chaos". This condition states that the probability distribution for two particles can be decomposed into the product of the probability functions of single particles, namely

$$f_2(\vec{p}_1, \vec{p}_2; t) = f_1(\vec{p}_1, t) f_1(\vec{p}_2, t), \tag{11.120}$$

which is equivalent to saying that the particles are not correlated. The Boltzmann equation is valid only if (11.120) is satisfied. If it is not satisfied, H can also increase. The Boltzmann result must then be interpreted by saying that in reality most of the time the condition of molecular chaos is satisfied, and therefore H decreases more than it increases, resulting on average in a monotonic decreasing function as is shown in Fig. XX.

How can we reconcile the reversibility implicit in classical mechanics with the H-Theorem? Imagine a gas that is initially confined in the left half of a box. This state corresponds to a high value of H. As the system evolves, the other half will start to be occupied until the particles are homogeneously distributed, resulting in a decrease of H. Classical mechanics states that if at a given time, say t_0 , one could reverse all the velocity then the system would evolve backwards and all the particles would eventually move to the left half of the box, resulting in an increase of H contrary to the H-theorem. The point is that the state that was prepared at t_0, by reversing all the velocities, is characterized by highly correlated particles. Each particle must take a particular velocity, depending on the velocities of all the other particles – otherwise the system will not go backwards. This high correlation implies an absence of molecular chaos and thus invalidates the H-Theorem. Note that such a highly-correlated state is extremely improbable and therefore it is extremely improbable that H could increase so much.

How can the second objection be answered? In reality, for a macroscopic system with N particles, the recurrence time is of the order of e^N. Therefore one has to expect a time interval, which cannot even be conceived, before H could start to increase (Fig. XX). To just have an idea for $N \sim 10^{24}$ this recurrence time τ should be of the order of $e^{10^{24}} sec.$. The age of the universe is estimated to be of the order of 10^{10} years $\sim 10^{16}$ sec. Therefore

$$\tau \simeq \frac{10^{10^{24}}}{10^{16}} \sim 10^{(10^{24}-16)} \sim 10^{10^{24}} \text{ ages of the universe.} \qquad (11.121)$$

Therefore one would never see such an event. This phenomenon is similar to the phenomenon of broken symmetry, which we have studied in the context of critical phenomena. Although the microscopic dynamic is invariant, under time reversal the macroscopic laws exhibit an asymmetry in time on a time scale comparable to our observation time. On a much larger time scale, the symmetry is restored as shown in Fig. XX. For an infinite system $\tau \to \infty$, the symmetry is never restored (see Chapter 10).

Chapter 12

Dynamical properties of stationary states

12.1 Time-dependent Fluctuation-Dissipation Relation

Let us consider a generic (one time) observable $\mathcal{A}(t) = \langle A(t) \rangle$ of a generic system whose microscopic variables are the positions $\vec{r}(t)$ and the momenta $\vec{p}(t)$ of all the N constituents, that we shortly indicate with $\vec{r}^N(t), \vec{p}^N(t)$. In a real system the value of $A(t)$ is a deterministic function of the initial state (at time $t = 0$), namely $A(t) = A[t; \vec{r}^N(0), \vec{p}^N(0)]$. As we have said several times this function is impossible to be practically computed, since one should solve an Avogadro number of coupled Newton equations. However here we are not interested in its direct computation but we will only use this formal expression to derive a general relation between correlations and response functions, as we will see shortly. The probability distribution $P_i = P[\vec{r}^N(0)\vec{p}^N(0)]$ of the microstates at the initial time $t = 0$ in the canonical ensemble is

$$P_i = \frac{e^{-\beta \mathcal{H}_i}}{Tr_i\left(e^{-\beta \mathcal{H}_i}\right)} \tag{12.1}$$

where we have introduced the short notation $\mathcal{H}_i = \mathcal{H}[\vec{r}^N(0), \vec{p}^N(0)]$ for the initial time value of the Hamiltonian and $Tr_i(\cdot) = \int d\vec{r}^N(0) d\vec{p}^N(0)\,(\cdot)$. One also has

$$\langle A(t) \rangle = \frac{Tr_i\left\{A[t; \vec{r}^N(0), \vec{p}^N(0)] e^{-\beta \mathcal{H}_i}\right\}}{Tr_i\left\{e^{-\beta \mathcal{H}_i}\right\}}. \tag{12.2}$$

The autocorrelation function associated to A is

$$C_A(t,t') = \langle A(t)A(t')\rangle - \langle A(t)\rangle\langle A(t')\rangle. \tag{12.3}$$

In an equilibrium state it is $C_A(t,t') = C_A(t-t',0) = C_A(s,0)$ ($s = t-t'$) due to stationarity, and the expression for $C_A(s,0) = \langle A(s)A(0)\rangle - \langle A\rangle^2$ is given by

$$C_A(s,0) = \frac{Tr_i\left\{A[s;\vec{r}^N(0),\vec{p}^N(0)]A[0;\vec{r}^N(0),\vec{p}^N(0)]e^{-\beta\mathcal{H}_i}\right\}}{Tr_i\left\{e^{-\beta\mathcal{H}_i}\right\}} - \langle A\rangle_{eq}^2, \tag{12.4}$$

where $\langle\dots\rangle_{eq}$ means an equilibrium ensemble average. The quantity $C_A(s)$ has the limiting behaviors

$$\begin{cases} \lim_{s\to 0} C_A(s,0) = \langle A^2\rangle_{eq} - \langle A\rangle_{eq}^2 \\ \lim_{s\to\infty} C_A(s,0) = 0 \end{cases} \tag{12.5}$$

The decay of the autocorrelation function is known as the *regression of fluctuations.*

Perturbation

Let us now apply to the system above (which up to now was unperturbed and in equilibrium) an external perturbation that changes the Hamiltonian as $\mathcal{H} \to \mathcal{H} + \Delta\mathcal{H}$. As an effect of this the system will be driven out of equilibrium. For simplicity let us assume that the perturbation couples linearly to the variable A, in the sense that

$$\Delta\mathcal{H} = -f(t)A(t), \tag{12.6}$$

where $f(t)$ is a generalized force. Denoting with $A_f(t)$ and with $A_0(t)$ the values of A in the perturbed and unperturbed systems respectively, the shift determined by the perturbation is

$$\delta A(t) = A_f(t) - A_0(t) \tag{12.7}$$

and its average

$$\delta\langle A(t)\rangle = \langle A_f(t)\rangle_f - \langle A_0(t)\rangle_{eq,0} \tag{12.8}$$

where $\langle\dots\rangle_f$ and $\langle\dots\rangle_{eq,0}$ are averages over the perturbed and unperturbed ensembles (the latter is an equilibrium one). Expanding $\langle\delta A(t)\rangle$ around $f(t) = 0$ one has

$$\langle\delta A(t)\rangle = \int_{-\infty}^{\infty} R(t,t')f(t')dt' + \mathcal{O}(f^2), \tag{12.9}$$

where we have used the fact that the zero order term is absent since $\langle \delta A(t) \rangle$ vanishes for $f(t) = 0$ and

$$R(t,t') = \left. \frac{\delta \langle A(t) \rangle}{\delta f(t')} \right|_{f=0} \tag{12.10}$$

is the so called response function which describes as $A(t)$ is modified by the perturbation with respect to the unperturbed system. Since we have arrested the expansion to linear order (which is meaningful only if the perturbation is small) R is the linear response function, but higher order responses, necessary to describe the case of larger perturbations, exists (but we will not considere them here). Eq. (12.9) can be read as the Taylor expansion of a function, $\langle \delta A(t) \rangle$ which depends on all the trajectory, i.e. on a continuous set of variables $f(t')$ labeled by t'. The theory whose aim is to predict the properties of the response functions is called response theory or, if it is restricted to first order, linear response theory. As any two-time average quantity at stationarity the response depends only on the time difference $R(t,t') = R(s)$. This quantity can be shown to be independent on the form of the perturbation, so we can make the simple choice

$$f(t) = \left\{ \begin{array}{ccc} f & , & t < 0 \\ 0 & , & t \geq 0 \end{array} \right. . \tag{12.11}$$

Then, using the equivalent of Eq. (12.2) for the perturbed system, for $t > 0$ one has

$$\langle A(t) \rangle_f = \frac{Tr_i \left\{ A_0[t; \vec{r}^N(0), \vec{p}^N(0)] e^{-\beta(\mathcal{H}_i + \Delta \mathcal{H}_i)} \right\}}{Tr_i \left\{ e^{-\beta(\mathcal{H}_i + \Delta \mathcal{H}_i)} \right\}}. \tag{12.12}$$

Notice that we have written A_0 in the numerator of this equation since $A_0 = A_f$ for $t > 0$. If the perturbation is small (i.e. $\Delta \mathcal{H}_i / \mathcal{H}_i \ll 1$) we can expand to first order the Boltzmann factors around the unperturbed Hamiltonian thus obtaining

$$\begin{aligned} \langle A(t) \rangle_f &\simeq \frac{Tr_i \left\{ A_0[t; \vec{r}^N(0), \vec{p}^N(0)] e^{-\beta \mathcal{H}_i} (1 - \beta \Delta \mathcal{H}_i) \right\}}{Tr_i \left\{ e^{-\beta \mathcal{H}_i} (1 - \beta \Delta \mathcal{H}_i) \right\}} \\ &\simeq Tr_i \left\{ A_0[t; \vec{r}^N(0), \vec{p}^N(0)] e^{-\beta \mathcal{H}_i} (1 - \beta \Delta \mathcal{H}_i) \right\} \cdot \\ &\quad \cdot \left\{ \frac{1}{Tr_i \left(e^{-\beta \mathcal{H}_i} \right)} + \frac{Tr_i \left(\beta \Delta \mathcal{H}_i e^{-\beta \mathcal{H}_i} \right)}{\left[Tr_i \left(e^{-\beta \mathcal{H}_i} \right) \right]^2} \right\} \\ &\simeq \langle A \rangle_{eq,0} - \beta \left[\langle \Delta \mathcal{H}_i A(t) \rangle_{eq,0} - \langle A \rangle_{eq,0} \langle \Delta \mathcal{H}_i \rangle_{eq,0} \right] \\ &= \langle A \rangle_{eq,0} + \beta f \left[\langle A(t) A(0) \rangle_{eq,0} - \langle A \rangle_{eq,0}^2 \right]. \end{aligned} \tag{12.13}$$

In this chain of equalities we have always kept only terms up to first order in $\Delta\mathcal{H}_i$, used the approximation $(x-\epsilon)^{-1} \simeq x^{-1} + \epsilon/x^2$ for small ϵ and the expression (12.6) of the perturbation. The result above can be written as

$$\delta\langle A(t)\rangle \simeq \beta f C_A(t,0). \tag{12.14}$$

Re-writing Eq. (12.9) taking into account the form (12.11) of f we obtain

$$\delta\langle A(t)\rangle = f\int_{-\infty}^{0} dt' R(t-t') = f\int_{t}^{\infty} ds R(s,0) \tag{12.15}$$

and hence

$$R(s,0) = -\frac{1}{f}\frac{d}{dt}\delta\langle A(t)\rangle \tag{12.16}$$

Hence, from Eq. (12.13) for $s>0$ we obtain

$$R(s) = -\beta\frac{dC_A(s)}{ds}, \tag{12.17}$$

where we have posed $C_A(s) \equiv C_A(s,0)$ and similarly for $R(s)$. For $s<0$ it is $R(s) \equiv 0$ due to causality (a system cannot respond before the perturbation is applied). Eq. (12.17) is the celebrated fluctuation-dissipation theorem (Callen and Welton 1951). As it is clear from its derivation it applies only to a system whose unperturbed state is an equilibrium one. There is no reason for its validity when this is not the case.

The fluctuation-dissipation theorem relates a property - the response function of a certain observable A - of a perturbed non-equilibrium system (but not to far from equilibrium, since the theorem is limited to linear terms in f) to a property (the fluctuations, or analogously the correlation function of A) of the corresponding unperturbed equilibrium system. The basic idea at the basis of the theorem, originally due to Onsager, is the so called *Onsager regression hypothesis.* Basically it amonts to the statement that the effect of a small perturbation is to displace the system from its equilibrium state not much differently than what commonly happens also in the unperturbed system as due to the spontaneous thermal fluctuations. This implies that a relation between the two *a priori* unrelated systems must exist. This relation is Eq. (12.17). Notice that it cannot be obtained with the usual methods of equilibrium statistical mechanics since it involves the dynamics (in fact we have invoked the deterministic evolution of the system, even if, fortunately, its solution has not been necessary). A derivation of the same result can be obtained for stochastic descriptions, such as those in terms of a Master equation, Langevin equation, Fokker-Planck or others.

12.2 Fluctuation Theorem

In the previous section we have discussed the origin of the time asymmetry in a non-equilibrium process. The probability of observing an event where entropy decreases is exponentially large in the number of constituents. However, in mesoscopic systems (with a large but not enormous number of components), the probability of such fluctuations is not completely negligible and may trigger important processes, notably biological ones. *Fluctuation theorems* allow one to determine the relative probability of occurrence of such *rare* events. In order to fix the ideas, let us consider a non-equilibrium setting where the two parts S_A and S_B of a system $S = S_A + S_B$ are put in contact with two reservoirs A and B at different temperatures T_A and $T_B < T_A$ (see Fig.). This system attains a stationary state where some average heat $\langle Q \rangle$ flows from A to B according to the laws of thermodynamic (i.e. heat is transferred from hotter systems to colder ones). Notice that, although stationary, this state is not an equilibrium one since there is a flux, or a current, which breaks the time-reversal symmetry of the equilibrium state (in other words, detailed balance is not obeyed).

Let us denote with Q the fluctuating heat flowing in some time interval τ through the system. Although the probability distribution $P(Q)$ is not in general known, fluctuation theorems provide a relation between $P(Q)$ and $P(-Q)$. Let us stipulate that $Q > 0$ when heat flows from A to B. Hence $\langle Q \rangle > 0$. The fluctuation theorem then informs us on the relative probability of observing a flux Q in the *normal* direction (i.e. in the same direction of the average) to that of observing the same amount of flux in the *strange* (opposite to the average) direction.

Let us denote with S_i the set of variables needed to specify the state of the i-th constituent (for instance position and momentum if it is a particle or the spin if it is a magnetic particle). We assume for simplicity that constituents are evolved sequentially according to a certain sequence that, by relabeling the variables, we can always assume to be $i = 1, 2, \ldots$. Since S_A and S_B are in contact with heat reservoirs a canonical setting is appropriate and we denote with $W^{q_i}_{S_i S'_i}$ the transition rate for the variable S_i to change to S'_i. This transition rate depends in principle on the whole configuration of the system (on all the $\{S_i\}$ and not only on S_i) even if in order to ease the notation this is not made explicit. The superscript ^{q_i} reminds us that during the transition the heat q_i has been exchanged with the reservoir which, since there is no work done, equals also the energy variation of the system in the move. Assuming that the i-th component is in contact with the heat bath A, due to detailed balance (11.75) its transition rates must obey

$$\frac{W^{q_i}_{S_i S'_i}}{W^{-q_i}_{S'_i S_i}} = e^{-\beta_A q_i}, \tag{12.18}$$

Since the constituents are updated sequentially and independently, the (conditional) probability of a trajectory $TR^{\{q_i\}}_{rs}$ going from a configuration r to another s after N elementary moves by exchanging the set of heats $\{q_i\}$ is

$$W_{TR^{\{q_i\}}_{rs}} \propto \prod_{i=1,N} W^{q_i}_{S_i S'_i}. \tag{12.19}$$

Using Eq. (12.18) one has

$$\frac{W_{TR^{\{q_i\}}_{rs}}}{W_{TR^{\{-q_i\}}_{sr}}} = e^{-(\beta_A Q_A + \beta_B Q_B)}, \tag{12.20}$$

where $Q_A = \sum_{i \in S_A} q_i$ is the total heat exchanged by the constituents in contact with the thermostat A (and similarly for Q_B) and $TR^{\{-q_i\}}_{sr}$ is the *time reversed* trajectory of $TR^{\{q_i\}}_{rs}$, i.e. the one going from s to r by exchanging the elementary amounts of heat $\{-q_i\}$.

Eq. (12.20) is the generalized detailed balance condition for a system in contact with two heat baths (clearly it can be straightforwardly generalized to the case of more than two reservoirs). The energy variation of the system in going from r to s is $\Delta E = E' - E = Q_A + Q_B$. For a finite system ΔE is also finite. On the other hand the typical values of the exchanged heats Q_A and Q_B in the time interval τ grow with τ. Then, in the large-τ limit one has $Q_B \simeq -Q_A$, and in this limit Eq. (12.20) reads

$$\frac{W_{TR^{\{q_i\}}_{rs}}}{W_{TR^{\{-q_i\}}_{sr}}} \simeq e^{-(\beta_A - \beta_B) Q_A}, \tag{12.21}$$

The probability of a certain heat $Q_A \simeq Q_B \simeq Q$ to flow in the system is

$$P(Q) = \sum_r \sum_s \sum_{TR_{rs}^{\{q_i\}}}' P_r W_{TR_{rs}^{\{q_i\}}}, \qquad (12.22)$$

where $\sum'$ indicates a sum over all the trajectories such that $\sum_i q_i = Q$. Analogously one can write

$$P(-Q) = \sum_s \sum_r \sum_{TR_{sr}^{\{-q_i\}}}' P_s W_{TR_{sr}^{\{-q_i\}}}. \qquad (12.23)$$

Eq. (12.23) can be readily obtained from Eq. (12.22) because, since $\sum'_{TR_{rs}^{\{q_i\}}}$ involves all the trajectories where the heat Q is exchanged, $\sum'_{TR_{sr}^{\{-q_i\}}}$ necessarily involves all those where $-Q$ is tranferred.

Using Eq. (12.21) one can write

$$\frac{P(Q)}{P(-Q)} = \frac{\sum_r \sum_s \sum_{TR_{rs}^{\{q_i\}}} P_r W_{TR_{rs}^{\{q_i\}}}}{\sum_s \sum_r \sum_{TR_{rs}^{\{q_i\}}} P_r W_{TR_{rs}^{\{q_i\}}} \frac{P_s}{P_r}\, e^{-(\beta_A-\beta_B)Q_A}}. \qquad (12.24)$$

Here we have used the fact that

$$\sum_s \sum_r \sum_{TR_{sr}^{\{-q_i\}}} P_s W_{TR_{rs}^{\{q_i\}}} = \sum_s \sum_r \sum_{TR_{rs}^{\{q_i\}}} P_s W_{TR_{rs}^{\{q_i\}}} \qquad (12.25)$$

since replacing the sum over the forward trajectories with that over their time reversed keeping the transition rates unchanged simply amounts to reshuffle the terms in the product in Eq. (12.19).

In a stationary state it can be proved that, quite generally, the ratio between the probability of two configuration is finite, i.e. $0 < K_1 < P_s/P_r < K_2 < \infty$. Hence, taking the logarithms of both sides in Eq. (12.24) one has

$$(\beta_A - \beta_B)Q - \ln K_2 < \ln \frac{P(Q)}{P(-Q)} < (\beta_A - \beta_B)Q - \ln K_1. \quad (12.26)$$

Since typical values of the exchanged heat Q grow with τ, neglecting $\ln K_1$ and $\ln K_2$ with respect to $(\beta_A - \beta_B)Q$ in the large-τ limit one has

$$\ln \frac{P(Q)}{P(-Q)} = (\beta_A - \beta_B)Q. \qquad (12.27)$$

This is one instance of the so called *fluctuation theorems* which generally relate the probability of observing a certain flux in the *right* direction to that of the reversed quantity. Although we have derived the theorem for a non-equilibrium stationary state obtained by keeping a system between two reservoirs, similar relations can be found for different systems in stationary non-equilibrium states generated, for instance, by mechanical stirring or other external drivings.

12.3 Spectral Analysis

In Chapter 11 we studied the motion of a diffusive particle using the Langevin equation. Figure XX shows a typical realization of such a noisy signal. In nature many signals exhibit this noisy, irregular behavior: the voltage at the end of a resistor, the daytime air temperature outside, any economic index, an earthquake signal. The question we want to consider here is how do we characterize such a $y(t)$ signal? We can assume the system has some periodicity $T \equiv 1/f_0$, take the limit $T \to \infty$ in the same way we take periodic boundary conditions in a finite system of volume V, and send the volume to infinity.

We can perform a Fourier analysis of the signal

$$y(t) = a_0 + \sum_n a_n \cos(2\pi n f_0 t) + \sum_n b_n \sin(2\pi n f_0 t). \qquad (12.28)$$

The coefficients are given by

$$\begin{aligned} a_0 &= \frac{1}{T}\int_0^T y(t)dt, & (12.29)\\ a_n &= \frac{2}{T}\int_0^T y(t)\cos(2\pi n f_0 t)dt, & (12.30)\\ b_n &= \frac{2}{T}\int_0^T y(t)\sin(2\pi n f_0 t)dt. & (12.31)\end{aligned}$$

Defining the time-average $\overline{h}(t) = T^{-1}\int_0^T h(t)$ of a generic quantity h, the time average of the signal is $\overline{y} = a_0$ which, for convenience, we can set equal to zero (otherwise we could consider another signal $x(t) = y(t) - a_0$, which has the property $\overline{x} = 0$). Instead of a time average, we could calculate equivalently an ensemble average over many equivalent signals. For example, for a fixed value t, we could take the ensemble average over many signals $y_k(t)$

$$\langle y(t)\rangle = \frac{1}{\mathcal{N}}\sum_k y_k(t). \tag{12.32}$$

If $\mathcal{N}$ is large enough, the time average and ensemble average will coincide, $\overline{y} = \langle y(t)\rangle = 0$. We can take then the ensemble average of a_n and b_n from (12.30) and (12.31) and since $\langle y(t)\rangle = 0$ we find

$$\langle a_0\rangle = 0 \tag{12.33}$$
$$\langle a_n\rangle = 0 \tag{12.34}$$
$$\langle b_n\rangle = 0 \tag{12.35}$$

Using the ortogonal properties of the trigonometric functions sine and cosine, the time average of $y^2(t)$,

$$\overline{y^2(t)} = \frac{1}{2}\sum_n (a_n^2 + b_n^2). \tag{12.36}$$

If we take the ensemble average of (12.36), we obtain

$$\langle y^2(t)\rangle = \frac{1}{2}\sum_n (\langle a_n^2\rangle + \langle b_n^2\rangle), \tag{12.37}$$

where we have used the fact that $\overline{y^2(t)} = \langle y^2(t)\rangle$. $\langle a_n^2\rangle$ and $\langle b_n^2\rangle$ are the contributions from the frequency nf_0 to the width of the signal. Since they correspond to the same frequency, and differ only by a phase, they are expected to be equal $\langle a_n^2\rangle = \langle b_n^2\rangle$ (can you grasp the hidden hypothesis under this assumption?). Therefore

$$\langle y^2(t)\rangle = \sum_n \langle a_n^2\rangle. \tag{12.38}$$

From (12.30) we have

$$\langle a_n^2\rangle = 4f_0^2\int_0^T\int_0^T \langle y(t_1)y(t_2)\rangle \cos(2\pi nf_0t_1)\cos(2\pi nf_0t_2)dt_1dt_2. \tag{12.39}$$

Considering stationary signals, the autocorrelation function that appears in the integrand will only depend on the time differences $s = t_2 - t_1$. Therefore we can write

$$K(s) = \langle y(t_1)y(t_2)\rangle, \tag{12.40}$$

where $K(s)$ is expected to be extremely peaked around $s = 0$. Using the properties of the trigonometric functions we can write (12.39) as

$$\langle a_n^2 \rangle = f_0^2 \int_0^T dS \int_{-T}^{T} ds K(s)[\cos(2\pi n f_0 s) + \cos(4\pi n f_0 S)], \quad (12.41)$$

where we have made the following change

$$s \equiv t_2 - t_1 \quad (12.42)$$

$$S \equiv \frac{1}{2}(t_2 + t_1) \quad (12.43)$$

The second term in the integral (12.41) gives zero contribution. Therefore from (12.41) we have

$$\langle a_n^2 \rangle = \frac{2}{T} \int_0^T K(s) \cos(2\pi n f_0 s) ds. \quad (12.44)$$

This is the Wiener-Khintchine relation. It relates the weight of the contributions of each frequency to the Fourier Transform of the autocorrelation functions. Hence, inverting the Fourier transform one has

$$K(s) = 2 \sum_n \langle a_n^2 \rangle \cos(2\pi n f_0 s) \quad (12.45)$$

Given the signal, one can calculate the autocorrelation function and therefore the width $\langle a_n^2 \rangle$ that characterizes the signal.

Figure 12.1: Norbert Wiener (Columbia, 26/11/1894 - Stoccolma, 18/03/1964) and Aleksandr Kinchin (Kondrovo (Kaluga Oblast) 19/07/1894 - Moscow 18/11/1959

Let us look at the physical meaning of Eqs. (12.44,12.45). For $s = 0$, from Eqs. (12.38,12.45) we have

$$K(0) = 2 \sum_n \langle a_n^2 \rangle = 2\langle y^2(t) \rangle, \quad (12.46)$$

namely the width of the signal is the integral of the weights over all frequencies. Note that signals with the same width (the same intensity) may differ completely from each other (Fig. XX). The fingerprint of a signal is $\langle a_n^2 \rangle$. A signal that contains all frequencies with the same Fourier amplitude is extremely noisy and is called white noise. In fact, from (12.44), if $\langle a_n^2 \rangle = \text{const}$, $K(s) \propto \delta_{s,0}$. This means that the signal at time t is completely uncorrelated with the signal at any time later $t + \delta t$, no matter how small δt is. The increments of the position of a random walker are an example of such an extremely noisy signal. In the $T \to \infty$ limit the Fourier frequencies $f = n f_0$ become a continuum and we denote with $W(f)$ the Fourier components. In this case pure white noise would give a width $K(0) = \infty$, which is not physically possible. Therefore white noise is an idealization. There is always a cutoff at some frequency f_0, namely

$$W(f) \equiv \left\{ \begin{array}{ll} W_0 & 0 \le f \le f_c \\ 0 & f > f_c \end{array} \right. . \qquad (12.47)$$

Consequently, using the properties of the Fourier transform, $K(s)$ will have a range $\Delta s \sim 1/f_c$, in which it is essentially different from zero. This means that the signal is correlated with itself within an interval of the order of $\Delta s \sim 1/f_c$. The more frequencies contribute to the signal (large f_c) the noisier it is.

Chapter 13

Quantum Statistical Mechanics

13.1 Fundamental Postulates and Density Matrix

We now extend the basic postulates of classical Statistical Mechanics to quantum Statistical Mechanics. In classical mechanics, a microstate is characterized by the variables $\{q, p\}$, which evolve according to the Hamiltonian equations. In quantum mechanics, a microstate is characterized by a wave function $\psi(x, t)$, which evolves according to the Shröedinger equation

$$i\hbar \frac{\partial}{\partial t}\psi(x,t) = \hat{\mathcal{H}}\psi(x,t), \tag{13.1}$$

where $\hat{\mathcal{H}}$ is the Hamiltonian operator.

The quantum mechanical (qm) mean value of any observable defined by an operator $\hat{A}$ at time t is

$$\langle A(t)\rangle_{qm} = \int \psi^*(x,t)\hat{A}\psi(x,t)dx, \tag{13.2}$$

where the wave function is normalized to unity. The result of a measurement A_{obs} is the time average over observable time,

$$A_{obs} \equiv \frac{1}{\tau}\int_0^\tau \langle A(t)\rangle_{qm} dt. \tag{13.3}$$

As in classical Statistical Mechanics, the goal in quantum Statistical Mechanics is to construct an appropriate ensemble such that temporal average and ensemble average coincide. We start with an isolated system characterized by N particles, volume V, and energy E. We consider therefore $\mathcal{N}$ copies of the system at time t macroscopically equivalent (with the same volume, same number of particles, and same energy) if ψ_K is the state of the K^{th} system of the ensemble. The mean value of the observable in such a state is

$$\begin{aligned} \langle A_K(t)\rangle_{qm} &= \int \psi_K^*(x,t)\hat{A}\psi_K(x,t)dx, && (13.4) \\ \langle A(t)\rangle_{ens} &\equiv \frac{1}{\mathcal{N}}\sum_K \langle A_K(t)\rangle_{qm}. && (13.5) \end{aligned}$$

How do we characterize the ensemble? In classical Statistical Mechanics, the ensemble is characterized by the distribution function $\rho(q,p)$. Here we will show that the ensemble is characterized by an operator $\hat{\rho}$. If $\phi_n(x)$ is a complete set of eigenfunctions at a given time t, then each wave function $\psi_K(x,t)$ can be expressed as the linear combination of the $\phi_n(x)$

$$\psi_K(x,t) = \sum_n C_n^{(K)}(t)\phi_n(x), \tag{13.6}$$

where the coefficients $C_n^{(K)}(t)$ satisfy the normalization condition

$$\sum_n |C_n^{(K)}(t)|^2 = 1. \tag{13.7}$$

Consequently (13.4) can be written

$$\langle A_K(t)\rangle_{qm} \equiv \sum_{mn} C_m^{*(K)}(t)C_n^{(K)}(t)A_{mn}, \tag{13.8}$$

where

$$A_{mn} \equiv \int \phi_m^*(x)\hat{A}\phi_n(x)dx \tag{13.9}$$

Consequently,

$$\langle A\rangle_{ens} \equiv \frac{1}{\mathcal{N}}\sum_K \langle A_K(t)\rangle_{qm} = \sum_{mn}\left[\frac{1}{\mathcal{N}}\sum_K C_m^{*(K)}(t)C_n^{(K)}(t)\right]A_{mn}. \tag{13.10}$$

If we define

$$\rho_{nm}(t) \equiv \frac{1}{\mathcal{N}}\sum_K C_m^{*(K)}(t)C_n^{(K)}(t), \tag{13.11}$$

then (13.10) can be written in a more complete form,

$$\langle A(t)\rangle_{ens} = \sum_{nm} \rho_{nm}(t) A_{mn}. \tag{13.12}$$

Here ρ_{nm} can be considered the element of a matrix associated with an operator $\hat{\rho}$ in the representation of $\phi_n(x)$. Namely, one can define an operator $\hat{\rho}$ such that

$$\rho_{nm} = \int \phi_n^*(x)\hat{\rho}(t)\,\phi_m(x)dx. \tag{13.13}$$

In fact, it is possible to check that when changing the base of the $\phi_n(x)$ into a new base by a unitary transformation the matrix elements transform as the element of a matrix associated with an operator.

Equation (13.12) can then be written as the trace of the product of $\hat{\rho}$ and $\hat{A}$. Indeed $(\hat{\rho}\hat{A})_{n,j} \equiv \sum_m \rho_{nm}A_{mj}$ and hence $\mathrm{Tr}(\hat{\rho}\hat{A}) \equiv \sum_n (\hat{\rho}\hat{A})_{nn} = \sum_{nm} \rho_{nm}A_{mn}$. Hence we can write

$$\langle A(t)\rangle_{ens} = \mathrm{Tr}\left(\hat{\rho}\hat{A}\right), \tag{13.14}$$

where we have assumed that the coefficients $C_m^{(K)}(t)$ are normalized to 1 [see Eq. (13.7)] (otherways it would be necessary to divide the r.h.s. by $\mathrm{Tr}\hat{\rho}$). Note that the trace of an operator is independent of the chosen base.

In conclusion, $\hat{\rho}$ characterizes the ensemble distribution; in fact once $\hat{\rho}$ is known the ensemble average can be carried out for any observable. Now we concentrate on the equilibrium case, where $\hat{\rho}$ does not depend on time. Just as in classical Statistical Mechanics we postulate the form of $\rho(p,q)$ for an isolated system, so also here we must postulate the operator $\hat{\rho}$. After specifying a particular base we then postulate

$$\rho_{nn} = \frac{1}{\mathcal{N}}\sum_K |C_n^{(K)}|^2 = \begin{cases} \Omega^{-1} & \forall n : E \le E_n \le E+\delta E \\ 0 & \text{otherwise} \end{cases}, \tag{13.15}$$

where Ω is the dimension of the basis (i.e. the number of states) and

$$\rho_{mn} = 0 \qquad \text{for} \qquad m \neq n. \tag{13.16}$$

The matrix is then written

$$(\rho_{mn}) \equiv \begin{pmatrix} \Omega^{-1} & & & & & & 0 \\ & \Omega^{-1} & & & & & \\ & & \ddots & & & & \\ & & & \Omega^{-1} & & & \\ & & & & 0 & & \\ & & & & & \ddots & \\ 0 & & & & & & 0 \end{pmatrix} \qquad (13.17)$$

and the diagonal elements that are zero correspond to those eigenfunctions of the energy that are not accessible, namely outside the energy interval $(E, E + \delta E)$.

The first part of postulate (13.15) corresponds to the equal *a priori* probability since ρ_{nn} is the probability of finding a given system of the ensemble in state n. Since $\rho_{nn} = \text{const.}$ for the accessible state, every accessible state is equally probable. The second part of the postulate does not have a correspondence in classical Statistical Mechanics and, for the reason that will be explained below, it is called the postulate of the random phases. Notice that, restricted on the states whose energy lies in the interval $(E, E + \delta E)$, the microcanonic density matrix is a multiple of the unity matrix. For this reason it takes the same form, namely it is diagonal, in any base. This property is specific to the microcanonical ensemble.

If we write the coefficients $C_n^{(K)}$ as the product of the modulus times the phase

$$C_n^{(K)} \equiv |C_n^{(K)}| e^{i\varphi_n^{(K)}}, \qquad (13.18)$$

then the non-diagonal elements are

$$\rho_{mn} = \frac{1}{\mathcal{N}} \sum_K |C_n^{(K)}||C_m^{(K)}| e^{i(\varphi_m^{(K)} - \varphi_n^{(K)})}. \qquad (13.19)$$

Therefore, according to random phase postulate (13.16), (13.19) must be zero for any $m \neq n$. This can occur only if the phases in the ensemble are uncorrelated with the moduli $|C_n^{(K)}||C_m^{(K)}|$ and their difference $\varphi_m - \varphi_n$ are completely random (as functions of K).

Indeed in such case, still for $m \neq n$ one has

$$\frac{1}{\mathcal{N}}\sum_K |C_n^{(K)}||C_m^{(K)}|e^{i(\varphi_m^{(K)}-\varphi_n^{(K)})} =$$
$$= \frac{1}{\mathcal{N}}\sum_K |C_n^{(K)}||C_m^{(K)}| \cdot \frac{1}{\mathcal{N}}\sum_K e^{i(\varphi_m^{(K)}-\varphi_n^{(K)})} = 0 \quad (13.20)$$

(in the first passage we have used the fact that, for independent variables, the average of a product equals the product of the averages. The final result is obtained because the second average is zero due to symmetry). In conclusion, the postulate of quantum Statistical Mechanics is that the time average of any observable is equal to the ensemble average in which the ensemble is specified by a density matrix given by (13.15) and (13.16).

In order to better understand the physical meaning of this postulate, we will reformulate the postulate in terms of only the evolution properties of the wave function of the system (as we did when we introduced the ergodicity postulate). From Eqs. (13.3,13.9) we have

$$A_{obs} \equiv \sum_{mn} \rho'_{mn} A_{mn}, \quad (13.21)$$

where

$$\rho'_{nm} \equiv \overline{C_m^*(t)C_n(t)}. \quad (13.22)$$

Here the bar indicates time average.

Now the postulate that the time average (13.21) and the ensemble average coincide implies

$$\rho_{mn} = \rho'_{mn} \quad (13.23)$$

The postulate on the density matrix implies

$$|\overline{C_n(t)}|^2 = \left\{ \begin{array}{ll} \text{const.} & E \leq E_n \leq E + \delta E \\ 0 & \text{otherwise} \end{array} \right. , \quad (13.24)$$

and

$$\overline{C_m^*(t)C_n(t)} = 0 \quad \text{for } m \neq n. \quad (13.25)$$

Equation (13.24) implies that the probability of finding the system in any of the accessible states is the same for all the states, while Eq. (13.25) states that interference (or non diagonal) terms vanish. Physically one says that the state of the system is a superposition of incoherent states or in a mixture of states. In conclusion, the postulates of quantum Statistical Mechanics are equivalent to the statement that the wave function of a macroscopic system is a superposition of incoherent states with coefficients satisfying (13.24) and (13.25). We remark that the properties (13.24,13.25) must hold for any representation of the density matrix, i.e. independently on the chosen basis.

13.2 Liouville Equations

We can show now that the density matrix in general satisfies an equation that is the analog of Liouville's equation in classical mechanics. Using this equation we will show that the density matrix (13.17) that has been postulated for a system in equilibrium is really a time-independent operator.

Let us consider the Shroedinger equation for the wave function $\psi^{(K)}$ relative to the K^{th} system of the statistical ensemble,

$$i\hbar\frac{\partial}{\partial t}\psi^{(K)}(x,t)=\hat{\mathcal{H}}\psi^{(K)}(x,t). \tag{13.26}$$

Fixing a base $\phi_m(x)$ (not necessarily eigenfunctions of the Hamiltonian $\hat{\mathcal{H}}$),

$$\psi^{(K)}(x,t)=\sum_m C_m^{(K)}(t)\phi_m. \tag{13.27}$$

Substituting (13.27) into (13.26) we have

$$i\hbar\sum_m\frac{d}{dt}C_m^{(K)}(t)\phi_m=\sum_m C_m^{(K)}(t)\mathcal{H}\phi_m. \tag{13.28}$$

Multiplying (13.28) by $\phi_n(x)$, integrating over x, and using the orthonormality conditions for $\phi_m(x)$, we have

$$i\hbar\frac{d}{dt}C_n^{(K)}(t)=\sum_m C_m^{(K)}(t)\mathcal{H}_{nm}. \tag{13.29}$$

where

$$\mathcal{H}_{nm}\equiv\int\phi_n^*\mathcal{H}\phi_m. \tag{13.30}$$

Recalling the definition of the density matrix

$$\rho_{nm}(t)\equiv\frac{1}{\mathcal{N}}\sum_K {C_m^*}^{(K)}(t)C_n^{(K)}(t), \tag{13.31}$$

from (13.29) we have

$$i\hbar\frac{\partial}{\partial t}\rho_{nm} = \frac{i\hbar}{\mathcal{N}}\sum_K \left(C_n^{(K)}\frac{d}{dt}C_m^{*\,(K)} + C_m^{*\,(K)}\frac{d}{dt}C_n^{(K)} \right) = \sum_\ell (\mathcal{H}_{n\ell}\rho_{\ell m} - \rho_{n\ell}\mathcal{H}_{\ell m}), \tag{13.32}$$

or, in terms of operators,

$$i\hbar\frac{\partial\hat{\rho}}{\partial t} = [\hat{\mathcal{H}}, \hat{\rho}]. \tag{13.33}$$

To make more transparent the connection with Liouville's equation derived in classical mechanics, we consider the definition of the operator $\hat{\rho}$ through the matrix ρ_{nm} (t) [see Eq. (XX)]

$$\rho_{nm} = \int \phi_n^*(x)\hat{\rho}(t)\phi_m(x)dx. \tag{13.34}$$

Equation (13.34) gives the intrinsic time dependence of the operator $\hat{\rho}(t)$. If we let the base $\phi_n(x)$ evolve in time, then we have

$$\rho_{nm}[t, \phi_n^*(t), \phi_m(t)] = \int \phi_n^*(x,t)\hat{\rho}(t)\phi_m(x,t)dx, \tag{13.35}$$

where we have indicated the time dependence through $\phi_n^*(x,t)$ and $\phi_m(x,t)$ explicitly.

The total derivation of (13.35) gives

$$i\hbar\frac{d}{dt}\ \rho_{nm}[t, \phi_n^*(t), \phi_m(t)] = -\int \phi_n^*(x,t)[\mathcal{H}, \hat{\rho}]\phi_m(x,t)dx + \\ i\hbar\int \phi_n^*(x,t)\frac{\partial\hat{\rho}(t)}{\partial t}\phi_m(x,t)dx, \tag{13.36}$$

which can be written formally as

$$i\hbar\frac{d\hat{\rho}}{dt} = [\hat{\rho}, \mathcal{H}] + i\hbar\frac{\partial\rho}{\partial t}, \tag{13.37}$$

which together with (13.33) gives

$$i\hbar\frac{d\hat{\rho}}{dt} = 0, \tag{13.38}$$

which is the analog of Liouville's equation in classical Statistical Mechanics. Both Eq. (13.33) and Eq. (13.35) are general equations and must be satisfied in any condition and by any ensemble distribution.

In particular, in equilibrium the basic postulates of quantum Statistical Mechanics have led to the choice of a density matrix that is diagonal in the energy base; therefore, the operator $\hat{\rho}$ commutes with the Hamiltonian H. It follows from (13.33) that the matrix $\hat{\rho}$ is time-independent. This result is thus consistent with the postulate that $\hat{\rho}$ describes a macroscopic system in equilibrium.

13.3 Ensembles

The statistical ensemble considered thus far is related to an isolated system and is called a microcanonical ensemble. In this case thermodynamic functions, can be obtained from the density matrix using the arguments developed in classical Statistical Mechanics, and the entropy is given by

$$S = k_B \ln \Omega. \tag{13.39}$$

If the system is not isolated and can exchange energy with a reservoir, the density matrix will still be diagonal in the base of the energy eigenfunctions and using the same considerations as those used in classical statistical mechanics, it is possible to show that in the energy representation only the diagonal elements do not vanish and are given by $\rho_{nn} = Z^{-1}e^{-\beta E_n}$, where the normalization constant Z is the partition function.

In terms of operators, we then have

$$\hat{\rho} = Z^{-1}e^{-\beta\hat{\mathcal{H}}}, \tag{13.40}$$

with the partition function given by

$$Z = \mathrm{Tr}\, e^{-\beta\hat{\mathcal{H}}} = \sum_n e^{-\beta E_n}, \tag{13.41}$$

and the free energy F given by

$$F = -k_B T \ln Z. \tag{13.42}$$

Similarly, for the grand canonical ensemble the matrix density is given by

$$\hat{\rho} = \mathcal{Z}^{-1}e^{-\beta\hat{\mathcal{H}}+\beta\mu\hat{N}}, \tag{13.43}$$

where μ is the classical potential and $\hat{N}$ the operator relative to the number of particles. The grand partition function $\mathcal{Z}$ is given by

$$\mathcal{Z} = \mathrm{Tr}\, e^{\beta\mu\hat{N}-\beta\hat{\mathcal{H}}} = \sum_r e^{\beta\mu N_r - \beta E_r}, \tag{13.44}$$

which is related to pressure P and volume V by

$$PV = k_B T \ln \mathcal{Z}. \tag{13.45}$$

13.4 Paramagnetism

Consider a particle with a two-component spin in a thermal bath in an external magnetic field $\vec{H}$. We want to determine the partition function and the average magnetization in the direction of the field. The Hamiltonian can be written

$$\hat{\mathcal{H}} = -\vec{\mu} \cdot \vec{H} = -\hat{\mu}_z H, \tag{13.46}$$

where μ_z is the component of the magnetic moment along the direction of the field (coincident with the z axis), and μ_z is given by a Pauli matrix

$$\hat{\mu}_z = \mu_0 \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \tag{13.47}$$

with μ_0 being the magnetic component along the z direction. The density matrix is partition function is given by

$$Z = \mathrm{Tr}\, e^{-\beta\hat{\mathcal{H}}} = e^{\beta\mu_0 H} + e^{-\beta\mu_0 H}. \tag{13.48}$$

Using Eq. (13.14), the average magnetization is given by

$$\langle \hat{\mu}_z \rangle = Z^{-1} \mathrm{Tr} \left(e^{-\beta\hat{\mathcal{H}}} \hat{\mu}_z \right) = \mu_0 \frac{e^{\beta\mu_0 H} - e^{-\beta\mu_0 H}}{e^{\beta\mu_0 H} + e^{-\beta\mu_0 H}}, \tag{13.49}$$

which coincides with the result obtained in classical Statistical Mechanics.

13.5 Density Matrix and Partition Function for Non-Interacting Particles

We will calculate now the density matrix for one particle in a box. We will extend the result to N particles with N very large and will show that – in a certain limit of low density and high temperature – we recover the partition function found classically with the two ad hoc assumptions: the correct Boltzmann counting and the size of a cell being equal to h^3.

We start with one particle in a box of volume L^3 with the Hamiltonian $\hat{\mathcal{H}} = \hat{p}^2/(2m)$ with the eigenvectors and eigenvalues given by

$$\hat{\mathcal{H}}|K\rangle = \epsilon_K|K\rangle, \tag{13.50}$$

where we use the Dirac notation where $|K\rangle$ is a vector corresponding to a microstate,

$$\epsilon_K = \frac{\hbar^2 K^2}{2m}, \tag{13.51}$$

and

$$\vec{K} = \frac{2\pi}{L}\vec{n}, \qquad \vec{n} \equiv \{n_x, n_y, n_z\}, \tag{13.52}$$

with n_x, n_y, and n_z are ± 1, ± 2, $\pm 3 \ldots$. In the representation of the coordinates, the wave function is

$$u_K(\vec{x}) = \langle x|K\rangle = \frac{1}{L^{3/2}} e^{i\vec{K}\cdot\vec{x}}. \tag{13.53}$$

Let us calculate the elements of the density matrix $\hat{\rho} = Z^{-1}e^{-\beta\hat{\mathcal{H}}}$ in the base of the eigenfunction of the position

$$\langle\vec{x}|e^{-\beta\hat{\mathcal{H}}}|\vec{x}'\rangle = \sum_{K,K_1}\langle x|K\rangle\langle K|\hat{\rho}|K_1\rangle\langle K_1|x'\rangle = \sum_K \langle x|K\rangle e^{-\beta\epsilon_K}\langle K|x'\rangle, \tag{13.54}$$

where we used the fact that there are no off-diagonal elements in $\hat{\rho}$. From (13.53) we have

$$\langle\vec{x}|e^{-\beta\hat{\mathcal{H}}}|\vec{x}'\rangle = \sum_K \frac{1}{L^3} e^{-\beta\epsilon_K} e^{i\vec{K}\cdot(\vec{x}-\vec{x}')}. \tag{13.55}$$

In the limit $L \to \infty$, the sum can be transformed into an integral, namely

$$\langle\vec{x}|e^{-\beta\hat{\mathcal{H}}}|\vec{x}'\rangle = \frac{1}{(2\pi)^3}\int e^{-\frac{\beta\hbar^2 K^2}{2m}} e^{i\vec{K}\cdot(\vec{x}-\vec{x}')} d\vec{K}, \tag{13.56}$$

where we have used the property (13.52)

$$\frac{\Delta n_x \Delta n_y \Delta n_z}{L^3} = \frac{\Delta K_x \Delta K_y \Delta K_z}{(2\pi)^3}. \tag{13.57}$$

Here $\Delta K_x, \Delta K_y, \Delta K_z$ correspond to the incremental $\Delta n_x = \Delta n_y = \Delta n_z = 1$.

The integral in (13.56) is the Fourier transform of a Gaussian distribution. This integral can be expressed as (see Appendix B (Eq. (B.5))

$$\langle\vec{x}|e^{-\beta\hat{\mathcal{H}}}|\vec{x}'\rangle = \lambda^{-3}e^{-2\pi\frac{(\vec{x}-\vec{x}')^2}{2\lambda^2}}, \tag{13.58}$$

and gives a Gaussian whose width is given by the De Broglie's thermal wavelength

$$\lambda = \frac{h}{\sqrt{2\pi m k_B T}}, \tag{13.59}$$

and is the inverse of the width of the original Gaussian in (13.56). Notice that the non-diagonal terms of the density matrix do not vanish here, since we are not in the energy representation.

The partition function is given by

$$Z = \mathrm{Tr}\, e^{-\beta\hat{\mathcal{H}}} = \int \langle\vec{x}|e^{-\beta\hat{\mathcal{H}}}|\vec{x}\rangle dx = \lambda^{-3}V, \tag{13.60}$$

where V is the volume of the box (notice that we have computed the trace over the position eingenvectors since the trace does not depend on the basis) . Note that we find the same result classically for one particle without making *ad hoc* hypotheses, whereas classical Statistical Mechanics uses an ad hoc hypothesis relative to the size of the cell in phase space. Clearly, since the partition function is the same as in the classical case, all the thermodynamic properties of the quantum system are inherited by the classical case (e.g. the equipartition theorem holds etc...).

Substituting the value of Z in Eq. (13.58) the density matrix elements in the cohordinates representation are obtained

$$\langle\vec{x}|\hat{\rho}|\vec{x}'\rangle = \frac{1}{V}\,e^{-2\pi\frac{(\vec{x}-\vec{x}')^2}{2\lambda^2}}, \tag{13.61}$$

Equation (13.61) is significant. For $x = x'$, (13.61) becomes

$$\langle\vec{x}|\hat{\rho}|\vec{x}\rangle = \frac{1}{V}, \tag{13.62}$$

which represents the density probability of finding the particle in x. Since the particle is equally distributed in the box, this probability is independent on x. The same result is also found classically.

However, the non-diagonal contribution $x \neq x'$ gives a result that has no analog in classical Statistical Mechanics. In fact $\langle x'\hat{\rho}x\rangle$ represents the average of the product of amplitude probability of finding the same particle in x and x'. In classical mechanics this quantity is a delta function since the particles are localized. Here we find instead a Gaussian whose width gives a measure of the wave packets associated with the particle. From (13.59) we note that as $T \to \infty$ the width $\lambda \to 0$. This means that the particle is localized and therefore behaves as a classical particle.

We want to extend the result to the case of two particles and then to N particles.

Let us start with two noninteracting particles. The eigenvalues and eigenfunctions of the Hamiltonian H are now

$$\mathcal{H}|\vec{K}_1\vec{K}_2\rangle = \epsilon(K_1,K_2)|\vec{K}_1\vec{K}_2\rangle, \tag{13.63}$$

where

$$\epsilon(K_1,K_2) = \frac{\hbar^2 K_1^2}{2m} + \frac{\hbar^2 K_2^2}{2m}. \tag{13.64}$$

The wave function for one particle is given by (13.53). For two particles, the wave function $\psi_E(\vec{x}_1,\vec{x}_2) = \langle \vec{x}_1\vec{x}_2|\vec{K}_1\vec{K}_2\rangle$ is given by

$$\psi_E(\vec{x}_1,\vec{x}_2) = \frac{1}{\sqrt{2}}[u_{K_1}(\vec{x}_1)u_{K_2}(\vec{x}_2) \pm u_{K_1}(\vec{x}_2)u_{K_2}(\vec{x}_1)], \tag{13.65}$$

where the symmetric wave function (with plus sign) refers to bosons while the antisymmetric (with minus sign) refers to fermions.

Consider now the density matrix elements

$$\langle \vec{x}_1\vec{x}_2|\hat{\rho}|\vec{x}_1'\vec{x}_2'\rangle. \tag{13.66}$$

Proceeding as in Eq. (13.54) one has

$$\begin{aligned} \langle \vec{x}_1\vec{x}_2|e^{-\beta\hat{\mathcal{H}}}|\vec{x}_1'\vec{x}_2'\rangle &= \sum_{\vec{K}_1,\vec{K}_2,\vec{K}_1',\vec{K}_2'}{}' \langle \vec{x}_1\vec{x}_2||\vec{K}_1\vec{K}_2\rangle\langle \vec{K}_1\vec{K}_2|e^{-\beta\hat{\mathcal{H}}}|\vec{K}_1'\vec{K}_2'\rangle\langle \vec{K}_1'\vec{K}_2'||\vec{x}_1'\vec{x}_2'\rangle = \\ &= \sum_{\vec{K}_1,\vec{K}_2}{}' e^{-\beta\epsilon(K_1,K_2)}\psi_E^*(\vec{x}_1',\vec{x}_2')\psi_E(\vec{x}_1,\vec{x}_2), \end{aligned} \tag{13.67}$$

where the prime indicates the constraint that in the sum are excluded all the states obtained by exchanging K_1 and K_2, since the effect of this operation has already been taken into account in Eq. (13.65) and we do not want here to sum over states which are not independent. Substituting (13.65) into (13.67), we note that each term in (13.67) is split in the sum of four separate terms which are obtained by exchanging K_1 with K_2. Therefore we can keep only two terms and remove the contraint from the sum. Therefore (13.67) becomes

$$\begin{aligned}
&\langle \vec{x}_1\vec{x}_2|e^{-\beta\hat{\mathcal{H}}}|\vec{x}_1'\vec{x}_2'\rangle = \frac{1}{2}\sum_{K_1,K_2} e^{-\beta(\hbar^2K_1^2/(2m))}e^{-\beta(\hbar^2K_2^2/(2m))}\,\cdot \\
&[u_{K_1}(\vec{x}_1)u_{K_2}(\vec{x}_2)u^*_{K_1}(\vec{x}_1')u^*_{K_2}(\vec{x}_2') \pm u_{K_1}(\vec{x}_2)u_{K_2}(\vec{x}_1)u^*_{K_1}(\vec{x}_1')u^*_{K_2}(\vec{x}_2')] = \\
= \; & \frac{1}{2V^2}\left[\sum_{K_1} e^{-\beta(\hbar^2K_1^2/(2m))}e^{i\vec{K}_1(\vec{x}_1-\vec{x}_1')}\cdot\sum_{K_2} e^{-\beta(\hbar^2K_2^2/(2m))}e^{i\vec{K}_2(\vec{x}_2-\vec{x}_2')}\pm\right. \\
\pm \; & \left.\sum_{K_1} e^{-\beta(\hbar^2K_1^2/(2m))}e^{i\vec{K}_1(\vec{x}_2-\vec{x}_1')}\cdot\sum_{K_2} e^{-\beta(\hbar^2K_2^2/(2m))}e^{i\vec{K}_2(\vec{x}_1-\vec{x}_2')}\right]. \qquad (13.68)
\end{aligned}$$

The diagonal elements are

$$\langle \vec{x}_1\vec{x}_2|e^{-\beta\hat{\mathcal{H}}}|\vec{x}_1\vec{x}_2\rangle = \frac{1}{2\lambda^6}\left[1 \pm e^{-2\pi(r_{12}^2/\lambda^2)}\right], \qquad (13.69)$$

where in the last passage we have transformed sums over K_1 and K_2 into integrals as done before in Eq. (13.56) and we have posed $r_{12} \equiv |\vec{x}_1 - \vec{x}_2|$. From this expression we can calculate the partition function

$$\begin{aligned}
Z \; &= \int \langle \vec{x}_1\vec{x}_2|\hat{e}^{-\beta\hat{\mathcal{H}}}|\vec{x}_1\vec{x}_2\rangle d\vec{x}_1 d\vec{x}_2 = \frac{1}{2\lambda^6}\int\left[1 \pm e^{-2\pi(r_{12}^2/\lambda^2)}\right]d\vec{x}_1 d\vec{x}_2 = \\
&= \frac{1}{2\lambda^6}\int\left[1 \pm e^{-2\pi(r_{12}^2/\lambda^2)}\right]d\vec{x}_1 d\vec{r}_{12} = \frac{1}{2}\left(\frac{V}{\lambda^3}\right)^2\left[1 \pm \frac{1}{2^{5/2}}\left(\frac{2\lambda^3}{V}\right)\right]. \qquad (13.70)
\end{aligned}$$

In (13.70) the term $n\lambda^3$ appears with $n = 2/V$ being the particle density.

Whenever

$$n\lambda^3 \ll 1, \qquad (13.71)$$

we can neglect the second term and the partition function becomes the same for both fermions or bosons,

$$Z = \frac{1}{2}\left(\frac{V}{\lambda^3}\right)^2, \qquad (13.72)$$

which means that quantum mechanical effects can be neglected. This result can be generalized to N non-interacting particles. Under conditions (13.71) where $n = N/V$ is the density, the partition function reduces to the classical limit

$$Z = \frac{1}{N!}\left(\frac{V}{\lambda^3}\right)^N, \tag{13.73}$$

which coincides with the classical derivation (7.83).

What is the physical meaning of condition (13.71)? Since the mean interparticle distance $r \sim n^{-1/3}$, (13.71) can be written as

$$\lambda \ll r, \tag{13.74}$$

this implies that the width of the wave packet associated with each particle is much less than the interparticle distance. When this condition is satisfied, the wave functions do not overlap and the quantum effect can be neglected. Nevertheless it is interesting to note that (13.73) still contains the fingerprints of quantum mechanics, namely the constant Planck h and the $1/N!$ that comes from the particle indistinguishibility, which were both introduced in classical Statistical Mechanics as ad hoc hypotheses.

Note also that while classical mechanics, which is obtained from quantum mechanics in the limit $\hbar \to 0$, loses completely any memory of the quantum effect, classical Statistical Mechanics cannot be obtained from quantum Statistical Mechanics putting $\hbar = 0$, which would result in a divergence of the partition function, but only neglecting powers of h.

13.6 Classical Descriptions of Quantum Particles

We consider here two noninteracting quantum particles in a box. According to Eq. (13.69), the density probability distribution is given by

$$\rho(\vec{x}_1, \vec{x}_2) \propto \left(1 \pm e^{-2\pi(r_{12}^2/\lambda^2)}\right). \tag{13.75}$$

In the classical limit, this distribution becomes spatially uniform, as expected for these noninteracting classical particles. Quantum effects creates instead a correlation, as can be seen from (13.75), implying that there is an effective interaction acting between the two particles. In particular note that for fermions the probability that two particles are located in the same place is zero, as if there were an effective repulsion due to the exclusion Fermi principle stating that two particles cannot be in the same state. On the contrary, bosons behave as if there were an effective attraction. What is the effective potential between two (identical) classical particles? If the effective potential is $V(r)$, then the density probability distribution for two classical particles is

$$\rho(\vec{x}_1, \vec{x}_2) \propto e^{-\beta V(r_{12})}. \tag{13.76}$$

Equating (13.76) with (13.75) gives

$$V(r_{12}) \propto -\beta^{-1} \ln \left(1 \pm e^{-2\pi(r_{12}^2/\lambda^2)}\right). \tag{13.77}$$

The plot of the potential in the case of bosons and fermions is shown in Fig. 13.1. In the Bose case it is attractive, a fact that can be interpreted as a *statistical attraction* among bosons. For fermions, instead, there is a *statistical repulsion.* Notice that in both cases the potential vanishes rapidly as r_{12} becomes larger than λ; accordingly its influence is weakened by raising the temperature.

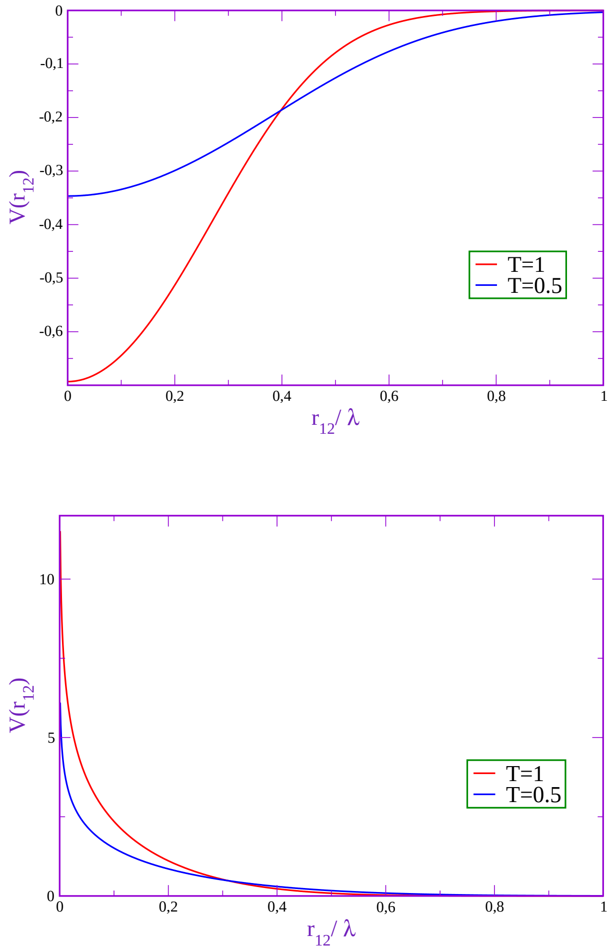

Figure 13.1: The statistical potential $V(r_{12})$ between a pair of particles obeying Bose-Einstein (upper panel) or Fermi-Dirac (lower panel) statistics. Two values of temperature are shown (see key).

Chapter 14

Statistics of Non-Interacting Particles

In this chapter we will calculate the energy distribution for non-interacting quantum particles, either bosons or fermions. There are many approaches to doing this. The simplest is to first calculate the partition function in the grand canonical ensemble. The previous chapter does this by tracing the density matrix. If we chose as a base the eigenfunctions of the energy and the number of particles, the partition function can be written

$$\mathcal{Z} = \sum_r e^{-\beta(E_r - \mu N_r)}, \tag{14.1}$$

where r denotes a microstate with N_r particles and energy E_r.

14.1 Occupation Numbers

Each state is characterized by a wave function given by the product of a single particle wave function made symmetrical or antisymmetrical, depending of whether the particles are bosons or fermions (see the previous chapter). As a consequence, the fermion particles cannot be in the same state, while bosons do not have such a constraint.

Each state is in one-to-one correspondence with the occupation number of each single particle state. Therefore each microstate r can be labelled by the set of occupation numbers $r \equiv \{n_1, n_2, \ldots, n_j, \ldots\}$, which represents the number of particles in single particle states $1, 2, \ldots, j, \ldots$. The energy E_r can then be written in terms of the energy of a single particle ϵ_K

$$E_r \equiv E_{n_1,n2,\ldots} = \sum_j n_j \epsilon_j. \tag{14.2}$$

The particle number N_r is given by

$$N_r \equiv N_{n_1,n_2,\ldots} = \sum_j n_j. \tag{14.3}$$

The partition function (14.1) can therefore be written as

$$\mathcal{Z} = \sum_{n_1,n_2,\ldots} e^{-\beta \sum_j (\epsilon_j - \mu) n_j}. \tag{14.4}$$

For bosons there is no limitation in the particle number, therefore the sum extends to all values $n_i = 0, 1, 2, \ldots$, while for fermions the sum is limited to the values $n_i = 0, 1$.

In (14.4) the exponential of the sum can be written as the product of exponentials, therefore

$$\mathcal{Z} = \prod_j \mathcal{Z}_j, \tag{14.5}$$

where

$$\mathcal{Z}_j = \sum_{n_j} e^{-\beta(\epsilon_j - \mu) n_j} \tag{14.6}$$

is the single particle grand-partition function and, according to Eq. (8.56)

$$\beta PV = \ln \mathcal{Z} = \sum_j \ln \mathcal{Z} j. \tag{14.7}$$

The average number of particles in the single particle state j is given by

$$\langle n_j \rangle = \frac{\sum_{n_1 n_2 \ldots} n_j e^{-\beta \sum_r (\epsilon_r - \mu) n_r}}{\mathcal{Z}} = \frac{\sum_{n_j} n_j e^{-\beta(\epsilon_j - \mu) n_j}}{\mathcal{Z}_j} \cdot \frac{\prod_{k \neq j} \mathcal{Z}_k}{\prod_{k \neq j} \mathcal{Z}_k}. \tag{14.8}$$

Hence, taking into account (14.6), one has

$$\langle n_j \rangle = \frac{\partial \ln \mathcal{Z}_j}{\partial(\beta\mu)} = z \frac{\partial \ln \mathcal{Z}_j}{\partial z}. \tag{14.9}$$

The last expression means that we consider β, z as independent variables (instead of the usual ones β, μ). The average total number of constituents is

$$\langle N \rangle = \frac{\partial \ln \mathcal{Z}}{\partial (\beta\mu)} = z \frac{\partial \ln \mathcal{Z}}{\partial z}. \tag{14.10}$$

Now we must calculate explicitely $\mathcal{Z}_j$ for bosons and fermions.

14.2 Bosons

14.2.1 Particles

The sum in (14.6) is over all values $n_j = 0, 1, 2, \dots$, and since this is a geometric series, one has

$$\mathcal{Z}_j = \sum_{n_j=0}^{\infty} e^{-\beta(\epsilon_j-\mu)n_j} = \frac{1}{1-e^{\beta(\mu-\epsilon_j)}}, \tag{14.11}$$

If the single-particle levels depend only on the wavevector $\vec{k}$ and the energy depends only on k one can also write

$$\mathcal{Z}_{\vec{k}} = \sum_{n_{\vec{k}}=0}^{\infty} e^{-\beta(\epsilon_k-\mu)n_{\vec{k}}} = \frac{1}{1-e^{\beta(\mu-\epsilon_k)}}, \tag{14.12}$$

If the single-particle levels depend, besides on $\vec{k}$, also on other discrete variables s which can take ℓ values, if the energy ϵ_j does not depend on s (s-degeneracy), Eq. (14.5) can also be written

$$\mathcal{Z} = \prod_{\vec{k}} \prod_{s=1,\ell} \mathcal{Z}_{\vec{k}s} = \prod_{\vec{k}} \mathcal{Z}_{\vec{k}}^{\ell} \tag{14.13}$$

where $\mathcal{Z}_{\vec{k}}$ on the r.h.s. of Eq. (14.13) is given in Eq. (14.11). This case is realized, for instance if particles have a spin. Indeed a particle of spin S may be found in $\ell = 2S+1$ spin states labelled by an index s.

From (14.9) we have

$$\langle n_j \rangle = \frac{1}{e^{\beta(\epsilon_j-\mu)}-1}, \tag{14.14}$$

which is called the Bose-Einstein distribution (see Fig. 14.1), and from (14.7)

$$\ln \mathcal{Z} = \beta p V = -\sum_j \ln\left[1-e^{-\beta(\epsilon_j-\mu)}\right]. \tag{14.15}$$

The chemical potential can be obtained by fixing the average number of particles in the system

$$\sum_j \langle n_j \rangle = \langle N \rangle. \tag{14.16}$$

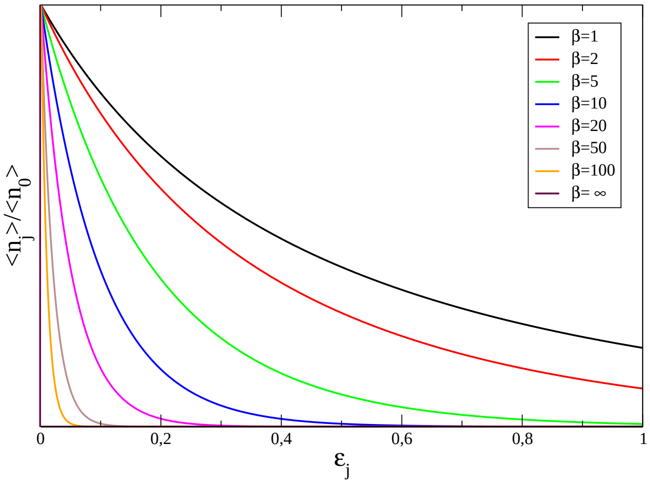

Figure 14.1: The Bose-Einstein distribution (14.14) is shown for different temperatures (see key). The chemical potential is $\mu = -0.5$ and the occupation number is normalized by $< n_0 >$ where $j = 0$ is the state of lower energy $\epsilon_0 = 0$.

Let us now consider the large-V limit in which $\vec{k}$ and hence ϵ become continuous variables. Letting $\ell = 1$ for simplicity and transforming the sums in Eq. (14.15) into integrals as $\sum_j \to [V/(2\pi)^3] \int d\vec{k}$ one arrives (in $d = 3$) at

$$\ln \mathcal{Z} = \frac{V}{\lambda^3} g_{\frac{5}{2}}(z), \tag{14.17}$$

where

$$z = e^{\beta\mu} \tag{14.18}$$

is the so called *fugacity*, the *thermal wavelength* λ is given in Eq. (13.59), and $g_{\frac{5}{2}}(z) = -\frac{4}{\sqrt{\pi}} \int_0^\infty x^2 \ln(1 - z e^{-x^2})$ is a special function which depends only on z. The average energy can be obtained from

Eq. (14.4) as $E = -\left.\frac{\partial}{\partial\beta}\ln\mathcal{Z}\right|_z$. From Eq. (14.17) one has

$$-\left.\frac{\partial}{\partial\beta}\ln\mathcal{Z}\right|_z = \frac{3}{2}\beta^{-1}\ln\mathcal{Z} \tag{14.19}$$

and hence

$$pV = \frac{2}{3}E. \tag{14.20}$$

Notice that this result is valid for bosonic, fermionic (as we will see), and classical (non-interacting) particles.

Bose-Einstein Condensation

Let us re-write Eq. (14.14) as

$$V^{-1}\langle n_j\rangle = V^{-1}\frac{z}{e^{\beta\epsilon_j}-z}, \tag{14.21}$$

where z is given in Eq. (14.18). Since $z \geq 0$ and $n_j \geq 0$ by definition, it must be $z \leq \min e^{\beta\epsilon_j}$. In the perfect gases $\min\epsilon_j = 0$ and hence $0 \leq z \leq 1$. However, $z = 1$ would be unphysical for any finite V, since Eq. (14.21) would imply an infinite number of particles on the fundamental level n_0 with $\epsilon_j = 0$. However, in certain conditions it may happen that $z \to 1$ as $V \to \infty$ in such a way that $\lim_{V\to\infty} 1-z \sim V^{-1}$. This would imply, through Eq. (14.21), that a finite fraction of particles would populate the fundamental state, a phenomenon that is called *condensation.* Let us state that this is a very peculiar condition, since in a *normal* state for $V \to \infty$ the particles are distributed among the infinite continuous levels, so that the $\langle n_j\rangle$ are all infinitesimal, as it happens for classical particles. Clearly, as we will see, condensation cannot happen for fermions because the Pauli principle does not allow to populate states with more than one particle. In the following we show how condensation occurs for a boson gas at sufficiently low (but finite) temperatures.

By using Eqs. (14.10,14.17) one has

$$n = \frac{1}{\lambda^3}g_{\frac{3}{2}}(z), \tag{14.22}$$

where $n = \langle N\rangle/V$ is the particle density and $g_{3/2}(z) = z(d/dz)g_{5/2}$ is another special function. $g_{3/2}(z)$ is plotted in Fig. 14.2. For small z it is $g_{3/2}(z) \simeq z$. Increasing z it gets steeper and steeper until its derivative $dg_{3/2}/dz$ becomes infinite at $z = 1$, where $g_{3/2}(1) \simeq$

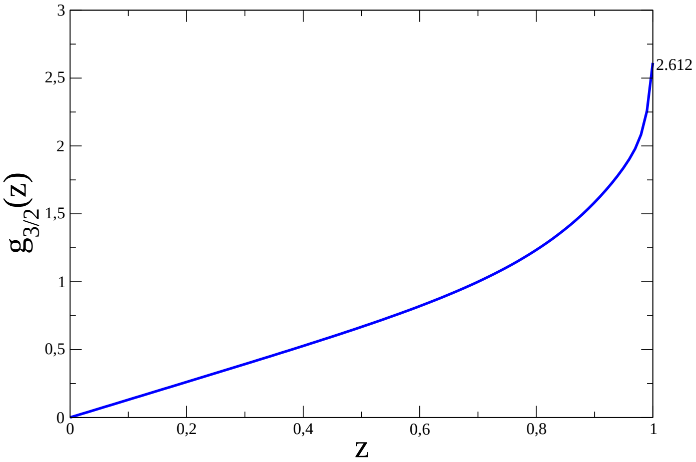

Figure 14.2: The function $g_{\frac{3}{2}}(z)$.

2.612.... Since $\lambda \propto T^{-1/2}$, by lowering T one arrives at a critical temperature T_c where

$$n = \frac{1}{\lambda^3} g_{\frac{3}{2}}(1), \tag{14.23}$$

below which Eq. (14.22) does not admit solution. One then has

$$T_c = \frac{2\pi\hbar^2 n^{\frac{2}{3}}}{mk[g_{\frac{3}{2}}(1)]^{\frac{2}{3}}}. \tag{14.24}$$

What does it happen for $T < T_c$? Recalling the discussion above, the only possible answer is that a single level, the fundamental one, becomes macroscopically populated. Since the behavior of $\langle n_0 \rangle$ is singular, we cannot keep it into the integral which defines the g functions when passing to the continuum. To keep this into account, in going from Eq. (14.15) to Eq. (14.17) we must single the term $\langle n_0 \rangle$ out of the integral for $g_{3/2}(z)$, thus arriving at

$$n = \frac{1}{\lambda^3} g_{\frac{3}{2}}(z) + \frac{1}{V}\frac{z}{1-z}. \tag{14.25}$$

With Eq. (14.25) one has a solution for any temperature with

$$\frac{\langle n_0 \rangle}{V} = \begin{cases} 0 & , \quad T > T_c \\ n - \frac{g_{\frac{3}{2}}(1)}{\lambda^3} = n\left[1 - \left(\frac{T}{T_c}\right)^{\frac{3}{2}}\right] & , \quad T < T_c \end{cases}, \tag{14.26}$$

(the latter can readily obtained recalling that $g_{\frac{3}{2}}(1)/[n\lambda^3(T_c)] = 1$) showing that, below T_c, $(T/T_c)^{3/2}$ is the fraction of particles continuously distributed among the excited levels. The quantity $\langle n_0 \rangle/V$ is plotted in Fig. 14.3. Clearly, we are in the presence of a phase transition which resembles the ferro-paramagnetic transition discussed in chapter 10, and $\langle n_0 \rangle/V$ has the meaning of the order parameter. Here, at variance with the magnetic case, there is no interaction among the particles, and the transition is due to the symmetry properties of the wavefunctions. The condensation phenomenon on the fundamental state is called *Bose-Einstein condensation*. Notice that, expanding in Eq. (14.26) for $T \simeq T_c$ one finds $\langle n_0 \rangle/V \simeq [3n/(2T_c)](T_c - T)$, and hence one has the critical exponent $\beta = 1$.

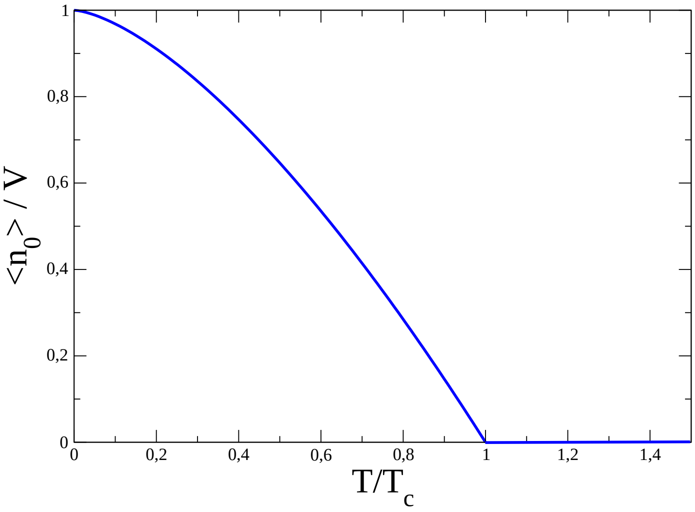

Figure 14.3: The occupation density $\frac{\langle n_0 \rangle}{V}$ of the fundamental state

One might ask how one passes from the situation with a finite V, where Eq. (14.22) admits a solution for every temperature and hence there is no phase-transition, to the case with infinite V where condensation occurs. Fig. 14.4 shows the graphical solution of Eq. (14.25), after multiplying both sides times λ^3, e.g.

$$n\lambda^3 = g_{\frac{3}{2}}(z) + \frac{\lambda^3}{V}\frac{z}{1-z}. \qquad (14.27)$$

The second term on the r.h.s. of Eq. (14.27), depicted in green in the first panel of the figure, diverges in $z = 1$. The strength of the divergence is regulated by V^{-1}. Hence, by drawing an horizontal line (depicted as dashed brown) it will intercept the green curve at a value of z whose distance from $z = 1$ is of order $1 - z \sim V^{-1}$. Since $g_{\frac{3}{2}}(z)$ (depicted in blue) does not diverge, the same property is shared also by the whole r.h.s. (depicted in red) of Eq. (14.27). Notice that the graphical solution of Eq. (14.27) can be obtained precisely with the same technique, namely by drawing an horizontal line at height $n\lambda^3$ and finding the proper value of z from the intercept with the red line. Increasing $n\lambda^3$ starting from zero also z increases, initially in a linear way, as shown in the second panel of Fig. 14.4. According to the previous discussion, when $n\lambda^3$ is of order $g_{\frac{3}{2}}(1) \simeq 2.612$ the solution z is at a distance V^{-1} from $z = 1$. If V is rigorously infinite, the curve for the solution z becomes discontinuous in $n\lambda^3 = g_{\frac{3}{2}}(1)$.

Now we study the equation of state (14.17). Also in this case below T_c one should single out the term with $k = 0$ from the integral. However it can be shown that it does not contribute to the equation of state. Hence one has

$$\beta p = \begin{cases} \lambda^{-3} g_{\frac{5}{2}}(z) & , \quad T > T_c \\ \lambda^{-3} g_{\frac{5}{2}}(1) & , \quad T < T_c \end{cases} . \tag{14.28}$$

Notice that p depends on n, and hence on V, through z (see Eq. (14.22) above T_c but becomes independent on V for $T < T_c$. The graphical solution of this equation is presented in Fig. 14.5. One clearly sees the phenomenon of phase coexistence, analogously to what observed in the gas-liquid transition. The independence of p on the volume is the analogue of the Maxwell construction for the gas-liquid transition. The two phases here are the normal phase, where the population of the quantum levels is distributed, and the condensed one with the macroscopic occupation of the fundamental state.

Let us consider now the internal energy. Combining Eqs. (14.20) and (14.28) one obtains

$$E = \frac{3N}{2n\beta\lambda^3} \cdot \begin{cases} g_{\frac{5}{2}}(z) & , \quad T > T_c \\ g_{\frac{5}{2}}(1) & , \quad T < T_c \end{cases} \tag{14.29}$$

For large T, when $z \to 0$, one can use (but we do not do it explicitly

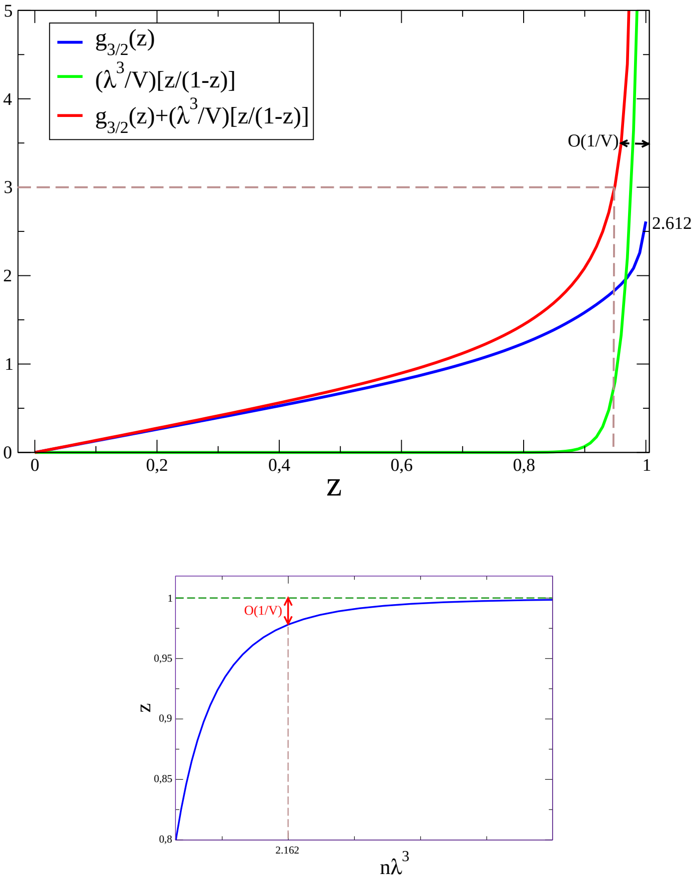

Figure 14.4: Graphical solution of Eq. (14.27). The distance of the red and green lines from $z = 1$ are of order V^{-1}.

here) the known small z behavior of $g_{5/2}$ obtaining

$$E = \frac{3}{2} NkT, \tag{14.30}$$

namely the equipartition theorem. Indeed, for large T the particles behave as classical ones. In the opposite limit, from Eq. (14.29) one directly reads $E \propto (kT)^{5/2}$, namely $C_V \propto T^{3/2}$ in the whole low-temperature phase $T < T_c$. In this phase the entropy $S = \int dT\,(C_V/T)$ goes to zero as $T^{3/2}$ as the absolute zero is approached, in agreement with the third principle of Thermodynamics. The behavior of the specific heat is shown in Fig. 14.6. It raises as

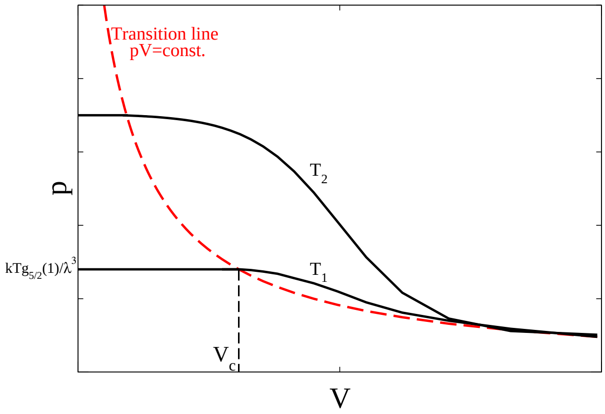

Figure 14.5: Two isotherms of the ideal Bose gas.

$T^{3/2}$ for low temperatures and then forms a cusp at the transition (which in fact is also called λ-point, due to the shape of C_V), and then converge to the Dulong-Petit law for large T.

It has been suggested that this transition is the basic mechanism for the superfluid transition in liquid helium. There are two isotopes of helium: ^4He and ^3He. An atom of ^4He has two protons and two neutrons, has an integer spin, and therefore is a boson. ^4He below a critical temperature $T_c \simeq 2.18^o K$ exhibits such unusual properties as an absence of viscosity when it flows through a capillary. That is why it is called a superfluid. At T_c there is a weak (logarithmic) divergence of C_V. Although the Bose condensation considered insofar applies to a noninteracting Bose gas, it has been suggested that also in the case of liquid helium made of interacting bosons, the Bose condensation is still present and the superfluid transition has been attributed to the Bose condensation phenomenon. The interaction is responsible for the discrepancies between the theoretical estimate of the critical temperature $T_c = 3.14^o C$ and the observed one, of the different behavior of C_V and other quantitative properties, but at a qualitative level the phenomenon is described by the perfect gas treatment discussed insofar. A confirmation of this suggestion comes from the observation that liquid ^3He, which has spin $1/2$ and is a fermion but chemically is the same as ^4He, does not possess the same superfluid properties as ^4He. In the same way, as we will see, also bosons with a non-conserved number, such as photons and

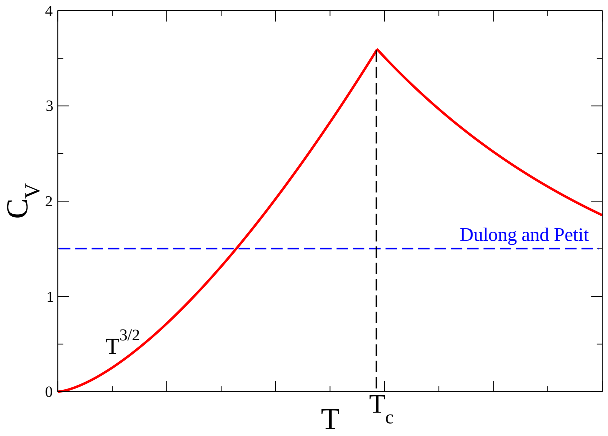

Figure 14.6: The specific heat of the Bose gas.

phonons do not condense, because they can instead annihilate.

14.2.2 Photons

The Hamiltonian of the electromagnetic field can be expanded in plane waves of different frequencies. After quantization one is left with a collection of bosons with no mass and spin 1. An important difference with the case of real particles is that the number of photons is not conserved. This means that $\mu = 0$. Each photon has 2 possible polarization states (there are 3 polarization states for a spin 1 particle but the transverse condition, e.g. for the electric field $\vec{\nabla} \cdot \vec{\mathcal{E}} = 0$, reduces the degrees of freedom to 2), and hence $\ell = 2$. The energy of a photon of momentum $\hbar \vec{k}$ is

$$\epsilon_k = \hbar c|k|. \tag{14.31}$$

When the radiation is contained in a box of volume V, boundary conditions imply Eq. (13.52). The electromagnetic radiation in equilibrium inside a box at temperature T is called the black body radiation. Experimentally one can observe it by studying the radiation emitted from a small hole in the box.

Since the energy of the photon does not depend on the polarization state, one has Eq. (14.11) with $\mu = 0$. Hence, proceeding similarly to Eq. (14.8) instead of Eq. (14.9) one finds

$$\langle n_{\vec{k}} \rangle = 2 \left. \frac{\partial \ln \mathcal{Z}_{\vec{k}}}{\partial(\beta\mu)} \right|_{\mu=0} = \frac{2}{e^{\beta\epsilon_k} - 1}. \tag{14.32}$$

Moreover

$$\ln \mathcal{Z} = \beta p V = -2 \sum_{\vec{k}} \ln \left[1 - e^{-\beta\epsilon_k} \right]. \tag{14.33}$$

Recalling that $\mu = 0$, the average energy can be evaluated from Eq. (14.4) as $E = -\frac{\partial}{\partial\beta} \ln \mathcal{Z}|_z$, which provides

$$E = \sum_{\vec{k}} \epsilon_k \langle n_{\vec{k}} \rangle \tag{14.34}$$

with a very transparent meaning. From Eq. (14.7) one also has

$$\beta p = \frac{\partial \ln \mathcal{Z}}{\partial V} = -2 \sum_j \frac{\beta e^{-\beta\epsilon_k} \frac{\partial \epsilon_k}{\partial V}}{1 - e^{-\beta\epsilon_k}} = \frac{\beta}{3V} \sum_{\vec{k}} \epsilon_k \langle n_{\vec{k}} \rangle, \tag{14.35}$$

where in the last passage we have used Eqs. (13.52) and (14.31). Hence one arrives at

$$pV = \frac{1}{3} E, \tag{14.36}$$

which should be compared with Eq. (14.20) which is valid for particles.

Let us now consider the large-V limit in which $\vec{k}$ and hence ϵ become continuous variables. Transforming the sums in Eq. (14.34) into integrals as done for the particles ($\sum_{\vec{k}} \to [V/(2\pi)^3] \int d\vec{k}$) one arrives at

$$\begin{aligned} E &= \frac{V}{(2\pi)^3} \int_0^\infty dk 4\pi k^2 \frac{2\hbar c k}{e^{\beta\hbar c k} - 1} = \\ &= \frac{V}{\pi^2 (\hbar c)^3 \beta^4} \int_0^\infty dx \frac{x^3}{e^x - 1} = \frac{\pi^2}{15} V \frac{(kT)^4}{(\hbar c)^3}. \end{aligned} \tag{14.37}$$

This is the well known Stephan-Boltzman law of the black body radiation, according to which the energy emitted is proportional to the fourth power of the temperature. Notice that the equipartition theorem is not recovered even in the large T limit, because the number of degrees of freedom is not fixed. Writing the argument of the last integral in Eq. (14.37) in terms of the frequency $\omega = \hbar^{-1}\epsilon$ one gets the celebrated Planck's law

$$u(\omega, T) = \frac{\hbar}{\pi^2 c^3} \frac{\omega^3}{e^{\beta\hbar\omega} - 1} d\omega \tag{14.38}$$

for the black body energy density in an interval $d\omega$ around the frequency ω. This law is in excellent agreement with the experimental results, providing also one of the first accurate proofs of the absence of mass of the photons.

14.2.3 Phonons

At low temperatures the interaction Hamiltonian among the N atoms of a cristal can be linearized and takes the form of a collection of coupled harmonic oscillators. Upon diagonalization one obtains $3N$ one-dimensional independent oscillators, the so called *normal modes*. After quantization one is left with a collection of independent spin 1 bosons, the phonons. The situation is similar to that of photons, except that there are now 3 polarization states (since there is no transverse condition for the sound waves), so $\ell = 3$. The other major difference is that there are a number $3N$ of energies for the phonons, whereas this constraint was not present for photons. Generally speaking, the relation between the wavevector and the energy can be much more complicated than Eq. (14.31). Assuming that Eq. (14.31), with c the speed of sound in an isotropic solid, is a reasonable approximation (this dispersion relation is the one obtained for the so-called acustic phonons far from the boundaries of the Brilluin's zone) one can proceed as for photons, thus obtaining Eq. (14.11) with $\mu = 0$. Then

$$\langle n_{\vec{k}} \rangle = \frac{3}{e^{\beta\epsilon_k} - 1}, \tag{14.39}$$

and

$$\ln \mathcal{Z} = \beta p V = -3 \sum_{\vec{k}} \ln\left[1 - e^{-\beta\epsilon_k}\right]. \tag{14.40}$$

Following exactly the same passages as done for the photons one arrives to Eq. (14.36) also for the phonons. The energy can be written analogously to Eq. (14.37), with the difference that the integral does not extend from 0 to ∞ but only from 0 to $\epsilon_M = \epsilon_{j_M}$, because there is a finite number ($3N$) of possible energies. ϵ_M is determined by the condition

$$\sum_{j=0}^{j_M} 1 = 3N, \tag{14.41}$$

or, in the continuum limit

$$3N = \frac{3V}{(2\pi)^3}\int_0^{k_M} dk 4\pi k^2 = \frac{3V}{2\pi^2(\hbar c)^3}\int_0^{\epsilon_M}\epsilon^2 d\epsilon = \frac{V}{2\pi^2(\hbar c)^3}\epsilon_M^3, \tag{14.42}$$

so that

$$\epsilon_M = \hbar c\left(\frac{6\pi^2 N}{V}\right)^{\frac{1}{3}} \tag{14.43}$$

Hence, proceeding as in Eq. (14.37) one has

$$\begin{aligned} E &= \frac{3V}{2\pi^2(\hbar c)^3\beta^4}\int_0^{\beta\epsilon_M} dx\frac{x^3}{e^x-1} \\ &= \frac{9(kT)^4N}{\epsilon_M^3}\int_0^{\beta\epsilon_M} dx\frac{x^3}{e^x-1}. \end{aligned} \tag{14.44}$$

This is the Debye formula which describes the energy and the specific heat of a solid. The quantity T_D defined by $kT_D = \epsilon_M$, the *Debye temperature*, is the characteristic temperature which separates the low and high temperature behaviors with

$$E = \begin{cases} 3NkT & , \quad T \gg T_D \\ \frac{3}{5}\pi^4 N\left(\frac{T}{T_D}\right)^3 kT & , \quad T \ll T_D \end{cases} \tag{14.45}$$

The first expression is obtained for $T \gg T_D$ by expanding the exponential $e^x \simeq 1 + x$ in Eq. (14.44). The second expression is obtained by letting the upper intergration limit equal to ∞ (since the integrand goes exponentially fast to zero for large x) so that the integral becomes a constant (it can be shown that this constant equals $\pi^4/15$). Notice that at high temperatures the systems behaves classically and obeys the equipartition principle (recall Eq. (14.41), namely that there are $3N$ normal modes, each with two quadratic degrees (position and momentum)). However, for extremely high temperatures the model of non-interacting bosons breaks down because phonons become interacting and the solid may eventually melt. The specific heat $C_V = \partial E/\partial T$ is plotted in Fig. 14.7. For most solids $T_D \simeq 200^o K$. This is why the Dulong and Petit law is usually observed at room temperatures. For low temperatures the specific heat of the solid goes to zero as T^3, a fact that is observed at low temperatures in solids. For extremely low temperatures, however, the specific heat is dominated by the fermionic term due to the electrons which, as we will see in Sec. 14.3.1 goes linearly in T. The entropy $S = \int dT\,(C_V/T)$ goes to zero as T^3 as the absolute zero is approached, in agreement with the third principle of Thermodynamics.

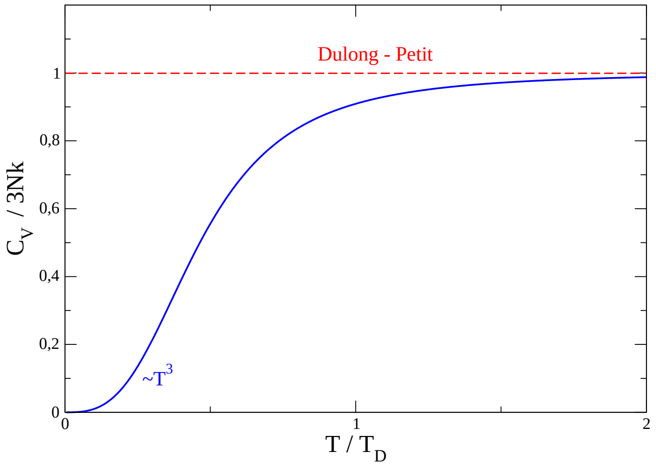

Figure 14.7: The specific heat in the Debye theory, as a function of temperature.

14.3 Fermions

Let us consider now fermions. The sum in (14.6) is limited only to values $n_j = 0, 1$; therefore,

$$\mathcal{Z}_j = 1 + e^{-\beta(\epsilon_j - \mu)}. \tag{14.46}$$

From (14.9) we have

$$\langle n_j \rangle = \frac{1}{e^{\beta(\epsilon_j - \mu)} + 1}, \tag{14.47}$$

which is called the Fermi-Dirac distribution (see Fig. 14.8), and from (14.7)

$$\ln \mathcal{Z} = \beta p V = \sum_j \ln\left[1 + e^{-\beta(\epsilon_j - \mu)}\right]. \tag{14.48}$$

The chemical potential is obtained as in Eq. (14.16).

14.3.1 Particles

The energy spectrum is $\epsilon(\vec{K}) = \hbar^2 K^2/(2m)$. Moreover, for particles of spin s each state has a degeneracy $\ell = 2s + 1$ due to two possible spin configurations. If N is the number of particles, the chemical potential is given by

$$N = \ell \sum_{\vec{k}} f[\epsilon(\vec{K})] = \frac{\ell V}{(2\pi)^3} \int f[\epsilon(\vec{K})] d\vec{K}, \tag{14.49}$$

where $< n_j >= f(\epsilon)$ is the Fermi distribution (14.47), namely

$$f(\epsilon) = \frac{1}{e^{\beta(\epsilon-\mu)} + 1}, \tag{14.50}$$

and using (14.6) we have transformed the sum into an integral. By integrating over the angle and then changing variable $K = (\sqrt{2m}/\hbar)\sqrt{\epsilon}$, we have

$$N = \frac{\ell V}{2\pi^2} \int_0^\infty K^2 f[\epsilon(\vec{K})] dK = \frac{(2m)^{3/2} \ell V}{4\pi^2 \hbar^3} \int_0^\infty \epsilon^{1/2} f(\epsilon) d\epsilon. \tag{14.51}$$

In the limit $T \to 0$, the Fermi distribution becomes a step function (see Fig. 14.8). If $\epsilon > \epsilon_f$, then $f(\epsilon) = 0$; if $\epsilon < \epsilon_f$, then $f(\epsilon) = 1$, where $\epsilon_f = \mu(T = 0)$ is the chemical potential at $T = 0$ and is called the Fermi energy. At $T = 0$ therefore the particles fill one by one all the available states until they reach the maximum energy ϵ_f. From (14.51) we have

$$N = \frac{(2m)^{3/2} V}{3\pi^2 \hbar^3} \epsilon_f^{3/2}, \tag{14.52}$$

which relates the density N/V to the Fermi level. For higher temperature, the Fermi distribution becomes a smooth function going from one to zero around the Fermi energy in a range of energy of the order $k_B T$ (see Fig. 14.8).

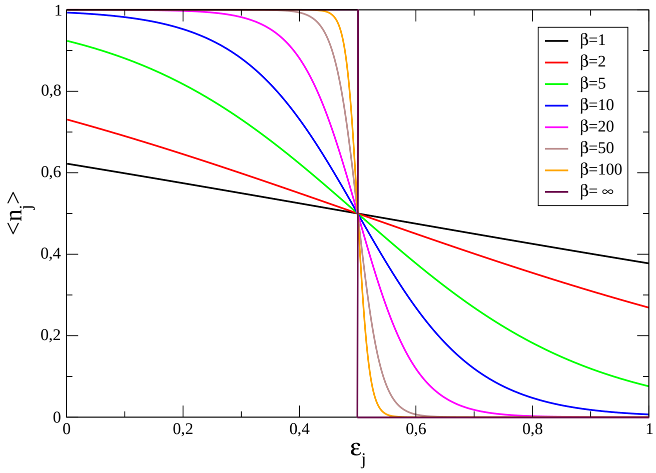

Figure 14.8: The Fermi-Dirac distribution (14.47) is shown for different temperatures (see key). The chemical potential is $\mu = 0.5$.

Transforming the sums in Eq. (14.48) into integrals similarly to what done for bosonic particles one arrives at

$$\ln \mathcal{Z} = \frac{V}{\lambda^3} f_{\frac{5}{2}}(z), \tag{14.53}$$

with the special function $f_{\frac{5}{2}}(z) = \frac{4}{\sqrt{\pi}} \int_0^\infty x^2 \ln(1+ze^{-x^2})$. Proceeding as for bosons one arrives at Eq. (14.20) also for fermions.

We want to calculate now the contribution of the electrons to the specific heat of a metal. To a good approximation, the electrons in the conduction band – those that conduct electricity – can be considered free. Let us calculate now the average energy. This can be obtained proceeding as for the average particle number N, thus arriving to an equation as Eq. (14.51) with an extra ϵ under the integral

$$E = A \int_0^\infty \epsilon^{3/2} f(\epsilon) d\epsilon, \tag{14.54}$$

where

$$A = \frac{(2m)^{3/2} V}{2\pi^2 \hbar^3}, \tag{14.55}$$

and we have used $\ell = 2$ for electrons. Integrating by parts in Eq.

(14.54) one has

$$E = -\frac{2}{5}A\int_0^\infty \epsilon^{\frac{5}{2}}\,\frac{df(\epsilon)}{d\epsilon}d\epsilon = -\frac{2}{5}A\beta^{-\frac{5}{2}}\int_{-\beta\mu}^\infty (x+\beta\mu)^{\frac{5}{2}}\,\frac{df(x)}{dx}dx, \tag{14.56}$$

where we have introduced the variable $x = \beta(\epsilon - \mu)$. For small temperatures $df(x)/dx$ is sharply peaked around $x = 0$, since f tends to a step-function. Hence we can expand $(x+\beta\mu)^{5/2}$ and extend the integration from $-\infty$ to ∞, thus obtaining

$$E = -\frac{2}{5}A\beta^{-\frac{5}{2}}\int_{-\infty}^\infty \left[(\beta\mu)^{\frac{5}{2}} + \frac{15}{4}(\beta\mu)^{\frac{1}{2}}x^2 + \dots\right]\frac{df(x)}{dx}dx, \tag{14.57}$$

where we have neglected the term proportional to x since $df(x)/dx = -(1/4)\cosh^{-2}(x/2)$ is a symmetric function. Using Eq. (14.20) we find

$$pV \simeq -\frac{4}{15}A\mu^{\frac{5}{2}}\int_{-\infty}^\infty \frac{df(x)}{dx}dx. \tag{14.58}$$

This shows that the pressure does not go to zero when $T \to 0$. This purely quantum phenomenon is due to the Pauli principle according to which only two particles (with opposite spin) can have zero momentum; the other contribute to the pressure.

The specific heat C_V is given by

$$C_V = \frac{\partial E}{\partial T} = BkT, \tag{14.59}$$

where $B = -(3/2)A\mu^{1/2}k\int_{-\infty}^\infty dx\,x^2 df(x)/dx$. This result has a simple interpretation. We have already noticed that the Fermi distribution goes from 1 to zero around the Fermi energy in a range of energy of the order k_BT (see Fig. 14.8). Only the fraction of electrons in this range can contribute to the specific heat, since the others at lower energy cannot be excited. In fact, consider an electron at very low energy ϵ. If this electron receives a small amount of energy $\Delta\epsilon$ from the external bath, the electron will change its state from ϵ to $\epsilon+\Delta\epsilon$ only if the state with energy $\epsilon+\Delta\epsilon$ is not occupied, otherwise it must remain *frozen* in its state. Only electrons near the edge of the distribution, which are in number proportional to kT can contribute to the specific heat and this explains a specific heat going linearly with kT at low temperatures, i.e. Eq. (14.59).

14.4 Classical limit

Notice that for any kind of quantum non-interacting system considered insofar, in the classical limit in which $\langle n_j \rangle \ll 1$, so that there are much more states than *particles* (which can be realized by raising the temperature and/or lowering the density) one obtains

$$\langle n_j \rangle \simeq \ell e^{-\beta(\epsilon_j - \mu)}, \tag{14.60}$$

where $\ell = 1, 2, 3$ for bosonic particles, photons and fermionic particles, and phonons respectively. From $\langle N \rangle = \sum_j \langle n_j \rangle$ one obtains

$$e^{\beta\mu} = \frac{\langle N \rangle}{\ell \sum_j e^{-\beta\epsilon_j}}, \tag{14.61}$$

so that the classical result

$$\frac{\langle n_j \rangle}{\langle N \rangle} = \frac{e^{-\beta\epsilon_j}}{\sum_j e^{-\beta\epsilon_j}} \tag{14.62}$$

is obtained. What does this expression means? In the classical limit the energetic levels become a continuum. In this case in order to have a probability $\propto e^{-\beta E_r}$ for the system's states r it is sufficient to fill the single particle states in such a way that an average number $\propto e^{-\beta\epsilon_j}$ of particles occupy a level of energy ϵ_j. However, when the discrete nature of the levels becomes important this simple receipt does not work and the distributions (14.14,14.47) are found.

Appendix A

Binomial coefficient

We ask how many ways $C_N(n)$ there are to arrange N objects (say balls) of which n are of one type (say red) and the others are of a different type (say white), assuming that particles of the same color are indistinguishable. There are N ways to chose the first particle, $N-1$ to chose the second and so on. Then the number of possible choices is $N!$. However, many of these dispositions are equivalent, since particles are indistinguishable (this means that we do not want to count as different two dispositions which, e.g., can be obtained one from the other by exchanging two particles of the same color). Then we must divide $N!$ times the number of possible dispositions of the two kind of colored balls. Reasoning as before, there are $n!$ ways of exchanging the red balls, and $(N-n)!$ ways of exchanging the white ones. Hence the number of ways to arrange the N balls is

$$C_N(n) = \frac{N!}{n!(N-n)!}. \tag{A.1}$$

This number is also indicated as $\left(\begin{array}{c} N \\ n \end{array}\right)$, and is denoted as *binomial coefficient*. The name comes from the fact that the same quantity appears also in the binomial expansion

$$(p+q)^N = \sum_{n=0}^{N} \left(\begin{array}{c} N \\ n \end{array}\right) p^n q^{N-n}. \tag{A.2}$$

Appendix B

Gaussian integrals

In one dimension:

$$\frac{1}{(2\pi\sigma)^{1/2}}\int_{-\infty}^{\infty} dx\, e^{-\frac{x^2}{2\sigma}} = 1 \tag{B.1}$$

$$\frac{1}{(2\pi\sigma)^{1/2}}\int_{-\infty}^{\infty} dx\, x^2 e^{-\frac{x^2}{2\sigma}} = \sigma^2 \tag{B.2}$$

In d dimensions ($\vec{r} \equiv (x_1, \ldots, x_d)$):

$$\frac{1}{(2\pi\sigma)^{d/2}}\int_{-\infty}^{\infty} d\vec{r}\, e^{-\frac{r^2}{2\sigma}} = 1 \tag{B.3}$$

$$\frac{1}{(2\pi\sigma)^{d/2}}\int_{-\infty}^{\infty} d\vec{r}\, r^2 e^{-\frac{r^2}{2\sigma}} = d\,\sigma^2 \tag{B.4}$$

$$\int_{-\infty}^{\infty} d\vec{r}\, e^{-\frac{r^2}{2\sigma}+i\vec{r}\cdot\vec{y}} = e^{-\frac{\sigma y^2}{2}}\,(2\pi\sigma)^{\frac{d}{2}}\,. \tag{B.5}$$

This integral can be done by writing the exponent as $-r^2/(2\sigma) + i\vec{r}\cdot\vec{y} = -\{\vec{r} - [i/(2a)]\vec{y}\}^2/(2\sigma) - \sigma y^2/2$ which transforms the integral (B.5) into a standard Gaussian integral of the type (B.3).

Appendix C

Stirling's approximation

Stirling's approximation formula states that

$$\ln N! \simeq N \ln N - N, \tag{C.1}$$

for large N. In order to prove it is sufficient to observe that

$$\begin{aligned} \ln N! &= \ln 1 + \ln 2 + \cdots + \ln N \simeq \int_1^N \ln x dx = [x \ln x - x]_1^N = \\ &= N \ln N - N + 1, \end{aligned} \tag{C.2}$$

where the passage from the sum to the integral is the trapezium rule approximation. The approximation is good for large N since the integral is dominated from the region around the upper extreme where, for large N, the logarithm varies so slowly to allow an unitary integration step. The rough derivation presented above correctly reproduces the first two term in the large-N expansion (the +1, as we will see, is not correct), the so called *weak form* of the Stirling approximation, Eq. (C.1), which is sufficient for most purposes. Evaluating with different techniques also the next subleading term leads to the *strong form* of Stirling approximation

$$\ln N! \simeq N \ln N - N + \ln \sqrt{2\pi N}. \tag{C.3}$$

Appendix D

Lagrangian multipliers

Suppose we have a function $f(\{x_i\})$ of the n variables x_i $(i = 1, n)$. We want to maximize f with a certain constraint $g(\{x_i\}) = 0$. Let us consider the loci

$$f(\{x_i\}) = d \tag{D.1}$$

and

$$g(\{x_i\}) = 0 \tag{D.2}$$

for various values of the constant d. Suppose $n = 2$, so that these loci are contour lines. Imagine to walk along the contour line of g. In general the contour lines of g and f are distinct, so moving along the contour line for g while g remains constant (by definition of contour line) the value of f vary. Only when the contour line for g meets the contour line of f tangentially also f does not change, which means that it is at stationarity point (maximum, minimum, or saddle point). The contour lines of f and g are tangent when the tangent vectors of the contour lines are parallel. Since the gradient of a function is perpendicular to the contour lines, this is the same as saying that the gradients of f and g are parallel. Thus we want points where (D.2) is satisfied and

$$\nabla f(\{x_i\}) = -\lambda \nabla g(\{x_i\}), \tag{D.3}$$

To incorporate these conditions into one equation, we introduce an auxiliary function, the Lagrangian, as

$$\Lambda(\{x_i\}, \lambda) = f(\{x_i\}) + \lambda g(\{x_i\}) \tag{D.4}$$

and solve

$$\nabla \Lambda(\{x_i\}, \lambda) = 0, \tag{D.5}$$

where now the gradient is taken with respect to all the $n+1$ variables of $\Lambda(\{x_i\}, \lambda)$, or equivalently

$$\begin{cases} \dfrac{\partial \Lambda(\{x_i\}, \lambda)}{\partial x_i} = 0\,, \quad i = 1, \dots n \\ \dfrac{\partial \Lambda(\{x_i\}, \lambda)}{\partial \lambda} = 0. \end{cases} \tag{D.6}$$

This is the method of Lagrange multipliers. Note that the second of Eqs. (D.6) implies Eq. (D.2). The method can be easily generalized to the case of m constraints

$$g_k(\{x_i\}) = 0\,, \quad k = 1, \dots, m, \tag{D.7}$$

by introducing the Lagrangian

$$\Lambda(\{x_i\}, \{\lambda_k\}) = f(\{x_i\}) + \sum_{k=1}^{m} \lambda_k g_k(\{x_i\}) \tag{D.8}$$

and requiring

$$\nabla \Lambda(\{x_i\}, \{\lambda_k\}) = 0, \tag{D.9}$$

where now the gradient is taken with respect to all the $n+m$ variables of $\Lambda(\{x_i\}, \{\lambda_k\})$, or equivalently

$$\begin{cases} \dfrac{\partial \Lambda(\{x_i\}, \{\lambda_k\})}{\partial x_i} = 0\,, \quad i = 1, \dots n \\ \dfrac{\partial \Lambda(\{x_i\}, \{\lambda_k\})}{\partial \lambda_k} = 0\,, \quad k = 1, \dots m \end{cases} . \tag{D.10}$$

Appendix E

General solution of first order linear differential equations

Let us write consider the equation

$$\frac{d\vec{v}}{dt} = -\frac{\vec{v}}{\tau} + \vec{a}(t). \tag{E.1}$$

Multiplying both members of (E.1) by $e^{(t-t_0)/\tau}$, where $t_0 < t$ is a generic time, it follows that

$$\frac{d}{dt}\left[\vec{v}e^{(t-t_0)/\tau}\right] = \vec{a}(t)e^{(t-t_0)/\tau}. \tag{E.2}$$

Changing symbol $t \to t_1$ and integrating on t_1 between t_0 and t we obtain

$$\vec{v}e^{(t-t_0)/\tau} = \vec{v}(t_0) + \int_{t_0}^{t} \vec{a}(t_1)e^{(t_1-t_0)/\tau}dt_1, \tag{E.3}$$

from which the general solution reads

$$\vec{v} = \vec{v}(t_0)e^{-(t-t_0)/\tau} + e^{-t/\tau}\int_{t_0}^{t} \vec{a}(t_1)e^{t_1/\tau}dt_1. \tag{E.4}$$

Appendix F

Solution of inhomogeneous second order linear differential equations

Let us consider the equation

$$\frac{d^2y}{dt^2} + \frac{1}{\tau}\frac{dy}{dt} = f \tag{F.1}$$

The homogeneous equation (with $f = 0$) has general solution

$$y_{hom}(t) = y_1 e^{-t/\tau}, \tag{F.2}$$

where y_1 is a constant. A particular solution of Eq. (F.1) is

$$y_p(t) = f\tau t + y_2, \tag{F.3}$$

with f_2 another constant. The general solution of Eq. (F.1) is obtained as

$$y(t) = y_{hom}(t) + y_p(t). \tag{F.4}$$

The two constant are fixed by the initial conditions $y(0) = y_0$ and $dy/dt|_{t=0} = \dot{y}_0$, yielding

$$\begin{cases} y_1 = f\tau^2 - \dot{y}_0\tau \\ y_2 = y_0 - f\tau^2 - \dot{y}_0\tau. \end{cases} \tag{F.5}$$