ELEMENTARY COURSE IN STATISTICAL MECHANICS

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April 2, 2008

Chapter 1

Thermodynamics

Thermodynamics is the study of macroscopic systems independent of their microscopic constituents. Statistical mechanics is the study of macroscopic systems that takes into account 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. 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. So also statistical mechanics encompasses thermodynamics in the case of 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 thermodynamics, the state of a system is defined by fixing some macroscopic variables 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.

A thermodynamic system is in *equilibrium* if the thermodynamic variables do not change over time. An isolated system that is not in equilibrium transforms or evolves over time until equilibrium is reached. In such a process, the transformation is *irreversible* since the system does not spontaneously evolve in the reverse direction. In general a transformation is called reversible if (a) it consists of a succession of equilibrium states and (b) it is such that the system passes through the same states when the external parameters change sign. An irreversible transformation is any transformation that is not reversible.

1.1 Laws of Thermodynamics

1.1.1 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 as the temperature of system A.

1.1.2 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 $\vec{r}_i \dots \vec{r}_n$ is given by

$$\Delta W \equiv \sum_i \vec{F}_i \cdot \Delta \vec{r}_i, \tag{1.1}$$

where $\vec{F}_i$ is the force acting on object i and $\Delta \vec{r}_i$ the displacement caused by the force. 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 specific heat is defined by

$$C \equiv \frac{\Delta Q}{\Delta T}. \tag{1.2}$$

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

$$\Delta U = \Delta Q - \Delta W, \tag{1.3}$$

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

For an infinitesimal transformation Eq. (1.3) becomes

$$dU = \delta Q - \delta W, \tag{1.4}$$

where δQ and δW are infinitesimal amounts of heat and work. The content of the first law is that dU is an exact differential, while δQ and δW are not. By integrating (1.4) from an initial state A to a final state B, we have

$$U_B - U_A = Q - W, \tag{1.5}$$

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),

$$Q_1 - W_1 = Q_2 - W_2, \tag{1.6}$$

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.

1.1.3 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

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

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

$$Q_1 - Q_2 = W. \tag{1.7}$$

The efficiency of any engine can be defined as

$$\eta \equiv \frac{Q_1 - Q_2}{Q_1}. \tag{1.8}$$

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

$$\eta_{\text{rev}} \geq \eta. \tag{1.9}$$

As a corollary of (1.9), 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 tranformation made of two isothermal and two adiabatic transformations (Fig. 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

$$\eta_{\text{rev}} = \frac{T_1 - T_2}{T_1}. \tag{1.10}$$

Therefore all reversible engines working between temperatures T_1 and T_2 have an efficiency given by (1.10). Using inequality (1.9) and definition (1.8), it follows that any engine working between two temperatures T_1 and T_2 satisfies the inequality

$$\frac{Q_1 - Q_2}{Q_1} \leq \frac{T_1 - T_2}{T_1}, \tag{1.11}$$

namely

$$\frac{Q_1}{T_1} - \frac{Q_2}{T_2} \leq 0, \tag{1.12}$$

the equality being valid for a reversible engine.

The relation (1.12) 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 (1.12) becomes

$$\sum_i \frac{\Delta Q_i}{T_i} \leq 0. \tag{1.13}$$

In the ideal limit in which the number of reservoirs becomes infinite and the heat exchanged with a reservoir is infinitesimal, relation (1.13) becomes

$$\oint \frac{\delta Q}{T} \leq 0. \tag{1.14}$$

Namely, in any cyclic transformation in which the engine exchanges an infinitesimal amount of heat δQ with a reservoir at temperature T, relation (1.14) holds. The equality holds for reversible cyclic transformations.

1.1.4 Entropy

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

$$dS \equiv \frac{\delta Q}{T}, \tag{1.15}$$

where δQ is the heat exchanged in a reversible transformation with a reservoir at temperature T. The function S whose differential is given by (1.15) is called the entropy, and it depends only on the thermodynamic state. From (1.15) we have

$$S_A - S_B = (\text{rev}) \int_B^A \frac{\delta Q}{T}, \tag{1.16}$$

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 can be defined as

$$S = (\text{rev}) \int_O^A \frac{\delta Q}{T}. \tag{1.17}$$

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 (1.14) to the entire cycle

$$\oint \frac{\delta Q}{T} = (\mathrm{irr}) \int_A^B \frac{\delta Q}{T} + (\mathrm{rev}) \int_B^A \frac{\delta Q}{T} \leq 0. \tag{1.18}$$

It follows from (1.16) that

$$(\mathrm{irr}) \int_A^B \frac{\delta Q}{T} \leq S_B - S_A. \tag{1.19}$$

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

$$S_B - S_A \geq 0. \tag{1.20}$$

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). Thus an adiabatic system evolves naturally towards states with higher entropy.

Equation (1.19) and its corollary (1.20) are a direct consequence of the second law of thermodynamics as stated by Clausius and Kelvin. Equation (1.20) in particular 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.

1.2 Thermodynamic Potentials

From Eqs. (1.14) and (1.15) the first law of thermodynamics for an infinitesimal reversible transformation of a fixed number of particles can be written

$$dU = TdS - PdV, \tag{1.21}$$

where P is the prssure, V the volume, and $\delta W = PdV$ the mechanical work done by the system on the external world. Since from (1.21) $U = U(S,V)$ is a function of S and V, and dU is a perfect differential, it follows that

$$\left(\frac{\partial U}{\partial S}\right)_V = T \qquad \left(\frac{\partial U}{\partial V}\right)_S = -P. \tag{1.22}$$

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. Accordingly, we introduce the Helmholtz potential A, obtained from U by subtracting the product of the conjugate variables TS

$$A = U - TS. \tag{1.23}$$

By differentiating $dA = dU - TdS - SdT$ and from (1.21), we find

$$dA = -PdV - SdT. \tag{1.24}$$

We note that the free energy is a function of V and T and that

$$\left(\frac{\partial A}{\partial T}\right)_V = -S \qquad \left(\frac{\partial A}{\partial V}\right)_T = -P. \tag{1.25}$$

Similarly, we can define the enthalpy

$$H = U + PV. \tag{1.26}$$

By differentiating (1.26) and taking (1.21) into account we find

$$dH = TdS + VdP, \tag{1.27}$$

from which

$$\left(\frac{\partial H}{\partial S}\right)_P = T \qquad \left(\frac{\partial H}{\partial P}\right)_S = V. \tag{1.28}$$

Finally, the Gibbs free energy

$$G = A + PV. \tag{1.29}$$

By differentiating (1.29) and taking (1.24) into account

$$dG = VdP - SdT, \tag{1.30}$$

with

$$\left(\frac{\partial G}{\partial P}\right)_T = V \qquad \left(\frac{\partial G}{\partial T}\right)_P = -S. \tag{1.31}$$

Relations (1.22), (1.25), (1.28) and (1.31) can be reproduced using the Born diagram:

$$\begin{array}{ccc} V & A & T \\ U & & G \\ S & H & P. \end{array}$$

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.,

$$\left(\frac{\partial A}{\partial T}\right)_V = -S. \tag{1.32}$$

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

$$df = udx \qquad \text{with} \qquad u \equiv \frac{df}{dx}, \tag{1.33}$$

the Legendre transform of f is

$$g \equiv f - xu, \tag{1.34}$$

where x and u are conjugate variables. By differentiating (1.34)

$$dg = df - xdu - udx = -xdu, \tag{1.35}$$

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 (1.33), and substitute in (1.34).

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 (1.21) is then written

$$dU = TdS - PdV + \mu dN. \tag{1.36}$$

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 (1.36).

From (1.36) it follows that $U = U(S, V, N)$ is a function of the variables S, V, N and that

$$(\frac{\partial U}{\partial S}\Big)_{V,N} = T, \qquad \left(\frac{\partial U}{\partial V}\right)_{S,N} = -P, \qquad \left(\frac{\partial U}{\partial N}\right)_{S,V} = \mu. \tag{1.37}$$

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

$$U(\lambda S, \lambda V, \lambda N) = \lambda U(S, V, N), \tag{1.38}$$

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

$$U = \left(\frac{\partial U}{\partial S}\right)_{V,N} S + \left(\frac{\partial U}{\partial V}\right)_{S,N} V + \left(\frac{\partial U}{\partial N}\right)_{S,V} N. \tag{1.39}$$

Taking (1.37) into account,

$$U = TS - PV + \mu N, \tag{1.40}$$

from which we obtain an expression for the Gibbs potential (1.29)

$$G \equiv U - TS + PV = \mu N. \tag{1.41}$$

It is also useful to consider the grand potential

$$\Phi \equiv A - \mu N, \tag{1.42}$$

which is a Legendre transform of the Helmholtz potential. From (1.42) and (1.23), we have

$$\Phi = -PV. \tag{1.43}$$

1.2.1 Physical Meaning of the Thermodynamic Potentials

Consider an isolated system made of two subsystems #1 and #2 in thermal contact, where U_1 and U_2 are the energies of the two subsystems and $U_{\rm tot} = U_1 + U_2$ the total energy. Since the entropy is additive, the total entropy is

$$S_{\rm tot} = S_1(U_1) + S_2(U_2). \tag{1.44}$$

If the system is not in equilibrium, the two subsystems will exchange energy until a state of maximum entropy is reached, i.e.,

$$\left(\frac{\partial S_{\rm tot}}{\partial U_1}\right)_V = \left(\frac{\partial S_1}{\partial U_1}\right)_V + \left(\frac{\partial S_2}{\partial U_2}\right)_V \frac{\partial U_2}{\partial U_1} = 0. \tag{1.45}$$

Since

$$\frac{\partial U_2}{\partial U_1} = -1, \tag{1.46}$$

then

$$\left(\frac{\partial S}{\partial U_1}\right)_V = \left(\frac{\partial S}{\partial U_2}\right)_V. \tag{1.47}$$

From the first part of (1.22)

$$T_1 = T_2. \tag{1.48}$$

If subsystem #2 is much larger than subsystem #1, then it can be considered a reservoir at a fixed temperature T (Fig. 7). The maximum of the total entropy will then correspond to the minimum of the free energy of subsystem #1. In fact, from (1.45) and using the fact that

$$\left(\frac{\partial S_2}{\partial U_2}\right)_V = \frac{1}{T} \tag{1.49}$$

we have

$$\left(\frac{\partial S_{\rm tot}}{\partial U_1}\right)_V = \frac{\partial S_1}{\partial U_1} - \frac{1}{T} = 0. \tag{1.50}$$

This equation corresponds to minimize the free energy of subsystem #1

$$A = U_1 - TS_1(U_1). \tag{1.51}$$

Chapter 2

Introduction to Statistical Mechanics

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 behavior. 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 behavior 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 10^{24} 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.

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. From such 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 frequently 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.

2.1 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—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. 1). Assume the particle begins at the origin and, at each interval of time τ, takes a step of length a_0 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. 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, and called the drunkard's walk.

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 $t = N\tau$ (after N steps), where a_0 is the lattice constant and 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) $P_4(3) = 4p^3q$.

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

$$N \equiv n_1 + n_2,$$

and

$$C_N(n_1) \equiv \binom{N}{n_1} = \frac{N!}{n_1!(N-n_1)!} \tag{2.4}$$

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

$$m = n_1 - n_2. \tag{2.5}$$

First we calculate the mean displacement

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

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.,

$$\langle n_1 \rangle = \sum_{n_1} n_1 P_N(n_1) = \sum_{n} n_1 C_N(n_1) p^{n_1} q^{n_2}. \tag{2.7}$$

To evaluate (2.7), we introduce the "generating function"

$$Z(x,y) \equiv \sum_{n_1=0}^{N} C_N(n_1) x^{n_1} y^{n_2}. \tag{2.8}$$

From (2.8) we get

$$x \frac{\partial Z}{\partial x}\bigg|_{\substack{x=p \\ y=q}} = \sum_{n_1=0}^{N} n_1 C_N(n_1) x^{n_1} y^{n_2}\Bigg|_{\substack{x=p \\ y=q}}, \tag{2.9}$$

which coincides with $\langle n_1 \rangle$. Using the binomial expansion, the sum in (2.8) is simply

$$Z(x,y) = (x+y)^N, \tag{2.10}$$

so

$$x\frac{\partial Z}{\partial x}\bigg|_{\substack{x=p\\y=q}} = Nx(x+y)^{N-1}\Big|_{\substack{x=p\\y=q}} = Np. \tag{2.11}$$

Therefore

$$\langle n_1 \rangle = Np. \tag{2.12}$$

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

$$\langle n_2 \rangle = y\,\frac{\partial Z}{\partial y}\bigg|_{\substack{x=p\\y=q}} = Nq. \tag{2.13}$$

Substituting (2.12) and (2.13) into (2.6), we find the mean value for m after N steps,

$$\langle m \rangle = N(p-q). \tag{2.14}$$

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

$$\langle (\Delta m)^2 \rangle = \langle (m - \langle m \rangle)^2 \rangle = \langle m^2 \rangle - \langle m \rangle^2. \tag{2.15}$$

From (2.5), $n_1 = (m+N)/2$ and

$$\langle (\Delta m)^2 \rangle = 4(\langle n_1^2 \rangle - \langle n_1 \rangle^2). \tag{2.16}$$

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

$$\langle n_1^2 \rangle = \left[x\frac{\partial}{\partial x}\left(x\frac{\partial Z}{\partial x}\right)\right]_{\substack{x=p\\y=q}}. \tag{2.17}$$

Straightforward calculation gives

$$\langle n_1^2 \rangle = (Np)^2 + Npq = \langle n_1 \rangle^2 + Npq. \tag{2.18}$$

Finally, from (2.16)

$$\langle (\Delta m)^2 \rangle = 4Npq. \tag{2.19}$$

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

$$w \equiv [\langle \Delta m^2 \rangle]^{1/2} = \sqrt{4pqN}. \tag{2.20}$$

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

$$\langle m \rangle - w \le m^* \le \langle m \rangle + w. \tag{2.21}$$

Equation (2.21) places different bound on m^* depending if $p = q$ or $p \neq q$. If $p = q$, then $\langle m \rangle = 0$ from (2.14), and $-w \le m^* \le w$. However if $p \neq q$, $\langle m \rangle \sim N$ while $w \sim \sqrt{N}$, so $\langle m \rangle \le m^* \le \langle m \rangle$. Hence

$$m^* \sim \begin{cases} \sqrt{N} & p = q \\ N & p \neq q \end{cases}. \tag{2.22}$$

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 (2.22),

$$m^* a_0 \sim \begin{cases} \sqrt{Dt} & p = q \\ Vt & p \neq q \end{cases}, \tag{2.23}$$

where $D = a_0^2/\tau$ is the diffusion constant and $V = (p - q)/a_0$ is the drift velocity.

2.1.1 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 $n_1 = \bar{n}_1$

$$\ln P_N(n_1) = \ln P_N(\bar{n}_1) + \frac{1}{2} \frac{\partial^2 \ln P_N(n_1)}{\partial n_1^2}\bigg|_{n_1 = \bar{n}_1} (n_1 - \bar{n}_1)^2 + \cdots \tag{2.24}$$

where we omit the first derivative term since

$$\frac{\partial \ln P_N(n_1)}{\partial n_1}\bigg|_{n_1 = \bar{n}_1} = 0. \tag{2.25}$$

Ignoring higher order terms, we immediately find the Gaussian distribution

$$P_N(n_1) = P_N(\bar{n}_1) e^{-(1/2)\lambda(n_1 - \bar{n}_1)^2}, \tag{2.26}$$

with

$$\lambda = -\left.\frac{\partial^2 \ln P_N(n_1)}{\partial n_1^2}\right|_{n_1=\bar{n}_1}. \tag{2.27}$$

We must calculate $\bar{n}_1, \lambda$ and show that higher order terms in (2.24) can be neglected.

From expressions (2.3) and (2.4) it follows that

$$\ln P_N(n_1) = \ln N! - \ln(N-n_1)! - \ln(n_1)! + n_1 \ln p + (N-n_1)\ln q. \tag{2.28}$$

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

$$\ln n! = n \ln n - n + \mathcal{O}\left(\frac{1}{\sqrt{n}}\right). \tag{2.29}$$

Rewriting (2.28) in this approximation, and requiring that its first derivative be zero, we find that the value $\bar{n}_1$ is given by

$$\bar{n}_1 = Np, \tag{2.30}$$

which shows that $\bar{n}_1$ is the exact average value $\langle n_1 \rangle$ of (2.12). The second derivative is given by

$$\lambda = -\left.\frac{\partial^2 \ln P_N(n_1)}{\partial n_1^2}\right|_{n_1=\bar{n}_1} = (Npq)^{-1}, \tag{2.31}$$

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

$$\left.\frac{\partial^k \ln P_N(n_1)}{\partial n_1^k}\right|_{n_1=\bar{n}_1} \sim \frac{1}{(Npq)^{k-1}}. \tag{2.32}$$

Hence higher order terms in (2.24) can be neglected, and the Gaussian approximation (2.26) is valid, provided that

$$|n_1 - \bar{n}_1| \ll Npq. \tag{2.33}$$

On the other hand, if

$$\frac{(n_1 - \bar{n}_1)^2}{Npq} \gg 1, \tag{2.34}$$

then $P_N(n_1)$ and its Gaussian approximation is much smaller than $P_N(\bar{n}_1)$. Therefore when (2.33) starts to be unsatisfied, namely $|n - \bar{n}_1| \sim Npq$, Eq. (2.34) is satisfied, provided that

$$Npq \gg 1. \tag{2.35}$$

Therefore condition (2.35) 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 (2.35) is no more satisfied, a different approximation is more appropriate, leading to the Poisson distribution.

Finally, the value of $P_N(\bar{n}_1)$ can be obtained by using the constraint that the sum over all probabilities is unity. Replacing the sum with an integral we have

$$\sum_{n_1=0}^{N} P_N(n_1) = \sum_{n_1=0}^{\infty} P_N(n_1)\Delta n_1 = 1, \tag{2.36}$$

where $\Delta n_1 = 1$, changing variables

$$x = \frac{n_1 - \bar{n}_1}{\sqrt{N}}; \qquad \Delta x = \frac{\Delta n_1}{\sqrt{N}} = \frac{1}{\sqrt{N}}. \tag{2.37}$$

The sum in the limit of large N can be replaced by an integral and the limits of integration go from $x = -\infty$ to $x = +\infty$. Using (2.26) and (2.31)

$$\sum_{n_1=0}^{N} P_N(n_1)\Delta n_1 = P(\bar{n}_1)\sqrt{N} \int_{-\infty}^{\infty} e^{-x^2/2pq} dx = 1. \tag{2.38}$$

Evaluating the Gaussian integral, from (2.38) we have

$$P_N(\bar{n}_1) = \frac{1}{\sqrt{2\pi Npq}}. \tag{2.39}$$

Finally from (2.26), (2.31), and (2.39) the distribution $P_N(n_1)$ is given by

$$P_N(n_1) = \frac{1}{\sqrt{2\pi Npq}} \exp\left[-\frac{(n_1 - \bar{n}_1)^2}{2Npq}\right], \tag{2.40}$$

which is a Gaussian distribution centered around $\bar{n}_1 \equiv pN$ of width $w = \langle (n_1 - \bar{n}_1)^2 \rangle^{1/2} = \sqrt{Npq}$. Expressing (2.40) in terms of the displacement $m = 2n_1 - N$, we obtain the probability $\bar{P_N}(m) = \frac{1}{2} P_N(\frac{(m+N)}{2})$ that after N steps the net displacement is m

$$\bar{P_N}(m) = \frac{1}{2} \cdot \frac{1}{\sqrt{2\pi Npq}} \exp\left[-\frac{1}{8Npq}(m - \bar{m})^2\right], \tag{2.41}$$

which is also a Gaussian, with a different mean

$$\bar{m} = N(p - q), \tag{2.42}$$

and twice the width,

$$\langle (\Delta m)^2 \rangle = 4Npq. \tag{2.43}$$

Note that these results agree with (2.14) and (2.19).

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

$$\ln f(x) = \ln f(x_0) + \frac{1}{2}\frac{\partial^2}{\partial x^2} \ln f(x)\bigg|_{x=x_0} (x - x_0)^2 \cdots \tag{2.44}$$

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

$$f(x) = f(x_0) \exp\left[-\frac{1}{2}\lambda(x - x_0)^2\right], \tag{2.45}$$

with λ given by

$$\lambda \equiv \left| \left(\frac{\partial^2}{\partial x^2} \ln f(x) \right)_{x=x_0} \right|. \tag{2.46}$$

An example is

$$f(x) = [g(x)]^N, \tag{2.47}$$

with

$$g(x) = xe^{-x/x_0}. \tag{2.48}$$

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 N large.

2.2 Distribution of Particles in a Box

Consider a box with N weakly-interacting particles divided into two equal parts. Imagine an ideal experiment to take W consecutive pictures in a time interval τ. Each picture represents a microscopic configuration. A macroscopic variable associated with the system is the average number of particles in the left half of the box. 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 given the initial conditions, positions and velocities of the particles. Once the coordinates of the particles are calculated as functions of time, one would have to value the average number of particles in the left part of the box. Statistical mechanics takes a probabilistic approach to this problem.

As in the random walk problem, we assume the probability that a given particle will be on the left side of the box to be $p = 1/2$ and on the right to be $q = 1 - p = 1/2$, given the symmetry between left and right. 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

$$p(1,1) = 2\cdot\frac{1}{4} = \frac{1}{2}. \tag{2.49}$$

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

In general, if we have N distinguishable particles, the probability of finding n_1 particles on the left and $n_2 = N - n_1$ on the right is given by

$$P_N(n_1) = \binom{N}{n_1} p^{n_1} q^{n_2}, \tag{2.50}$$

where

$$\binom{N}{n_1} = \frac{N!}{n_1!(N-n_1)!} \tag{2.51}$$

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. The probability that one particle will be on the left is p, and that one particle will be on the right $q = 1 - p$. In the case considered, $p = q = 1/2$, but if the box is divided into two unequal volumes V_1 and V_2, then

$$p = \frac{V_1}{V_1 + V_2} \qquad q = \frac{V_2}{V_1 + V_2}. \tag{2.52}$$

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 macroscopic configuration. For large values of N, the probability distribution becomes

$$P_N(n_1) = \frac{1}{\sqrt{2\pi Npq}} \exp\left[-\frac{1}{2Npq}(n_1 - \bar{n}_1)^2\right] \tag{2.53}$$

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

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

$$\frac{N}{2} - \sqrt{N} \leq n_1 \leq \frac{N}{2} + \sqrt{N}. \tag{2.54}$$

Let us introduce the intensive quantity

$$x \equiv \frac{n_1}{N}, \tag{2.55}$$

where x is the fraction of particles on the left of the box. From (2.54)

$$\frac{1}{2} - \frac{\sqrt{N}}{N} \leq x \leq \frac{1}{2} + \frac{\sqrt{N}}{N}. \tag{2.56}$$

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

To study the fluctuations in x about $1/2$ 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 (2.53),

$$P_N(n_1)dn_1 = \mathcal{P}_N(x)dx, \tag{2.57}$$

where, from (2.55),

$$dn_1 = Ndx. \tag{2.58}$$

From (2.52), (2.53), and (2.57) we find for the equivolume case, $p = 1 = 1/2$,

$$\mathcal{P}_N(x) = \frac{\sqrt{N}}{\sqrt{\pi/2}} \exp\left[-2N\left(x - \frac{1}{2}\right)^2\right]. \tag{2.59}$$

Distribution (2.59) 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 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 $x \neq 1$ have zero probability of occurring.

This example teaches 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 is based on some reasonable assumptions about *a priori* probability. 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; the fraction of configurations tends to 1 in the limit $N \to \infty$. All the other macroscopic states have zero probability of occurring.

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

Chapter 3

The Postulates of Statistical Mechanics

3.1 Statistical Ensembles

As already stated above, statistical mechanics studies macroscopic systems by examining their microscopic elements, elements that obey the laws of classical or quantum mechanics. To describe an isolated system in complete detail we can use either classical mechanics 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

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

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 $\{q_1 \dots q_{3N}\}$ and its conjugate momenta $\{p_1 \dots p_{3N}\}$. The evolution of the system is found solving the Hamiltonian equation

$$\begin{cases} \dot{q}_i(t) = \partial\mathcal{H}/\partial p_i \\ \dot{p}_i(t) = -\partial\mathcal{H}/\partial q_i \end{cases} \qquad i = 1 \dots 3N. \tag{3.2}$$

For fixed initial conditions

$$\begin{cases} q(t_0) = q_0 \\ p(t_0) = p_0 \end{cases}, \tag{3.3}$$

there is only one solution

$$\begin{cases} q(t) \equiv \{q_1(t) \dots q_{3N}(t)\} \\ p(t) \equiv \{p_1(t) \dots p_{3N}(t)\} \end{cases}, \tag{3.4}$$

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

Any macroscopic variable A is a function of the $6N$ coordinate $A = A[q(t), p(t)]$. Any measure of the macroscopic variable A corresponds to doing an average A_{obs} over a suitable interval of time τ

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

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. To measure the temperature, a thermometer gives the average value of the kinetic energy. 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). For a macroscopic system of 10^{24} particles, this task is impossible not only for the intrinsic difficulty of solving 6×10^{24} coupled differential equations, but also because it would be impossible to know exactly the initial coordinates of the particles.

How, then, does one calculate $\bar{A}$? We first must renounce any notion that we can know 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 the same value of the time average but in a much simpler way.

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

$$\langle A \rangle_{\text{ens}} = \frac{1}{\mathcal{N}} \sum_{k=1}^{\mathcal{N}} A_k, \tag{3.6}$$

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. We do this by considering the microscopic configuration of any system of the ensemble to be characterized by the value of the coordinates

$$\{q, p\} \equiv \{q_1 \dots q_{3N}, p_1 \dots p_{3N}\}. \tag{3.7}$$

This microstate can be considered as the coordinates of a point in a hyperspace in $6N$ dimensions called the phase space. Therefore 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

$$d\mathcal{N} = \rho(q, p) dq dp, \tag{3.8}$$

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

$$\langle A \rangle_{\text{ens}} = \frac{\int A(q, p) \rho(q, p) dq dp}{\int \rho(q, p) dq dp}, \tag{3.9}$$

where

$$\int \rho(q, p) dq dp = \mathcal{N}. \tag{3.10}$$

We now must choose an ensemble which has the property that 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.

We make the hypothesis that the correct ensemble, to describe a system in equilibrium, 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 $\rho(q, p)$ 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 $E \leq \mathcal{H}(p, q) \leq E + \delta E$, namely

$$\rho(q, p) \equiv \begin{cases} \text{const} & \text{in the region of allowed phase space} \\ 0 & \text{otherwise.} \end{cases} \tag{3.11}$$

Note that since the given system is never completely isolated, the allowed energy lies in a range; however we will show that the calculations based on distribution (3.11) 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 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 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.

If the given system is not in equilibrium, we cannot make the assumption (**??**). 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.

3.2 Liouville Theorem

The distribution of points in phase space at time t_0 is characterized by the distribution $\rho(q,p) \equiv \rho(q,p,t_0)$. 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 (3.11) 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 $\rho(q,p,t)$. However, we will show that such a distribution is time-independent as a consequence of Liouville's Theorem, namely

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

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 $\rho(q,p;t)$. 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 $\vec{v} = \vec{v}(q,p)$ the phase space velocity of the point (q,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 (3.17) 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),

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

From (3.2) we can write (3.18) in the form

$$\frac{\partial \rho}{\partial t} + \sum_{i=1}^{3N}\left(\frac{\partial \rho}{\partial q_i}\frac{\partial \mathcal{H}}{\partial p_i} - \frac{\partial \rho}{\partial p_i}\frac{\partial \mathcal{H}}{\partial q_i}\right) = 0, \tag{3.19}$$

where the sum is called the Poisson bracket $\{\rho, \mathcal{H}\}$. Equations (3.18) or (3.19) are equivalent statements of Liouville's 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 $\rho(q, p; t_0) = \rho(q, p)$ is the only solution. The distribution $\rho(q, p; t) =$ const with respect to both the variable $\{q, p\}$ and the time t is a solution of (3.18) and coincides at $t = t_0$ with the initial condition $\rho(q, p; t_0) =$ const. Therefore a uniform distribution in phase space at time t_0 will remain uniform for all t,

$$\rho(q, p; t) = \rho(q, p; t_0). \tag{3.20}$$

Hence the hypothesis that the equal *a priori* distribution describes a system in equilibrium is consistent with Liouville's theorem.

Since the Liouville theorem is independent of our hypothesis of equal *a priori* probability, it is interesting to examine the consequences of Liouville theorem *without* assuming a priori $\rho(q, p) =$ const (the equal *a priori* probability hypothesis). Using only Liouville's theorem, let us see what what are the necessary conditions that must be satisfied by $\rho(q, p; t)$ in order to describe an equilibrium distribution. If $\rho(q, p, t)$ must describe an equilibrium distribution, then

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

so $\rho(q, p, t) = \rho(q, p)$. 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 $\rho(p, q)$ must be necessarily a constant of motion.

A function of a constant of motion is also a constant of motion. In particular, if ρ is chosen to be a function solely of the energy, i.e., $\rho(p, q) = \tilde{\rho}[\mathcal{H}(p, q)]$, then it satisfies (3.22) If we require also that the distribution must be equal to zero in the region of phase space not allowed, it follows

$$\tilde{\rho}[\mathcal{H}(q, p)] = \begin{cases} \text{const} & \text{if } E \le \mathcal{H}(p, q) \le E + \delta E \\ 0 & \text{otherwise,} \end{cases} \tag{3.23}$$

then this solution coincides for any t with the equal *a priori* probability distribution $\rho(q, p)$ given by (3.11). Note that a necessary consequence of (3.21) and Liouville's theorem is that $\rho(q, p)$ must be a constant of motion.

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. Thus we see that this assumption is equivalent to the assumption that the ensemble distribution must satisfy the equal *a priori* probability distribution.

3.3 Ergodic Hypothesis

The basic assumption of equilibrium statistical mechanics is that we can substitute time averages with ensemble averages, and that the ensemble averages must be performed with the equal *a priori* probability distribution; moreover the time average is limited to the characteristic time involved in the experiment. This assumption is equivalent to 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 the accessible phase space. Clearly if the ergodic hypothesis is valid the average over time will coincide with the average over an ensemble uniformly distributed and therefore the equal a priori probability hypothesis is valid.

There have been many efforts to prove the ergodic hypothesis. Limited cases where the ergodic hypothesis can be proved involve time averages over infinite time periods, and therefore do not apply to real experiments in which finite time is involved.

Therefore we must accept the postulate of equal *a priori* probability as a working hypothesis and verify *a posteriori* the validity of this postulate by comparing its consequences with experiments (see, e.g., the book Grandi, *Foundation of Statistical Mechanics*).

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, 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. 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 how this quantity behaves as a function of the number of degrees of freedom f. We define $\Omega(E)$ as the number of states between E and $E + \delta E$. 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

$$\epsilon = \frac{\hbar^2 \pi^2}{2mL^2}(n_1^2 + n_2^2 + n_3^3), \tag{4.2}$$

where $n_1, n_2, n_3 = 0, 1, 2\ldots$ are quantum numbers referring to the three degrees of freedom of a free particle. For N particles, the energy E is the sum of the energy of $3N$ degrees of freedom, each having an energy

$$\epsilon = \frac{\hbar^2\pi^2}{2mL^2}n^2. \tag{4.3}$$

with $n = 0, 1, 2\ldots$. Therefore for a single degree of freedom, the number of states $\varphi(\epsilon)$ between 0 and ϵ grows as $n \propto \sqrt{\epsilon}$, and

$$\varphi(\epsilon) \sim \sqrt{\epsilon}. \tag{4.4}$$

For each degree of freedom there is a factor as in (4.4). Therefore, for an $f = 3N$ degrees of freedom,

$$\phi(E) \sim [\varphi(\epsilon)]^f \sim \left(\frac{E}{f}\right)^{f/2}, \tag{4.5}$$

with $E = f\epsilon$.

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

$$\phi(E) \sim (E - E_0)^{\alpha f}, \tag{4.6}$$

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

$$\Omega(E) = \alpha f (E - E_0)^{\alpha f - 1}\delta E. \tag{4.7}$$

To better estimate the contribution of the single terms, from the logarithm

$$\ln\Omega(E) = \ln\alpha f + (\alpha f - 1)\ln(E - E_0) + \ln\delta E, \tag{4.8}$$

for large f, taking into account that δE cannot be larger than $E \sim f$

$$\frac{\ln\Omega(E)}{f} = \frac{\ln\alpha f}{f} + \frac{(\alpha f - 1)\ln(E - E_0)}{f} + \frac{\ln\delta E}{f} \simeq \ln(E - E_0). \tag{4.9}$$

Therefore

$$\Omega(E) \sim (E - E_0)^{\alpha f}, \tag{4.10}$$

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 f, we write

$$\Omega(E) \sim (E - E_0)^f. \tag{4.11}$$

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 A and A' separated by a barrier that does not allow the exchange of energy. If E_i is the energy of system A and E'_i the energy of system A', the total number of configurations allowed for the combined system $A_0 = A + A'$ is

$$\Omega_i^0 = \Omega(E_i)\Omega'(E'_i), \tag{4.12}$$

where $\Omega(E_i)$ is the number of configurations relative to system A compatible with energy E_i and $\Omega'(E'_i)$ the number of configurations relative to system A' compatible with energy E'_i.

What happens if the barrier between A and A' is removed so that the two systems can exchange energy, keeping first 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 A and A' can exchange energy, the full system A_0 can also be in microscopic states that correspond to configurations in which the initial energy could be different provided the total energy is kept constant. If we call Ω_f^0 the total number of states accessible to the total system, then

$$\Omega_f^0 \geq \Omega_i^0. \tag{4.13}$$

Immediately after removing the barrier the system is not equally distributed in all of the Ω_f^0 states but will only occupy a fraction Ω_i^0/Ω_f^0. If the system is not distributed in all its possible states, it is not in equilibrium. We will see when we study 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 A at equilibrium? What is the energy probability distribution $P(E)$?

The subsystems A and A' can be considered to be weakly interacting. In fact, the two subsystems usually interact through their common surface. Therefore the interaction energy E_{int} is proportional to the surface and can be neglected compared to the bulk energies E and E', which are proportional to the volume. If A has energy E, then A' must assume an energy E' such that

$$E + E' = E_{\text{tot}}, \tag{4.14}$$

where E_{tot} is the total energy of the combined system $A_0 = A + A'$. The number of configurations accessible to the combined system A_0 when the subsystems A and A' has energies E and E‘ is given by

$$\Omega^{(0)}(E) = \Omega(E)\Omega'(E'), \tag{4.15}$$

where $\Omega(E)$ and $\Omega'(E')$ are the number of configurations accessible to subsystems A and A' when they have energies E and E'. Since $\Omega(E)$ and $\Omega'(E')$ are the degeneracies of the two subsystems, Eq. (4.15) follows from the fact that for each macroscopic state corresponding to an energy E there are $\Omega'(E')$ states corresponding to an energy E'.

If system A_0 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 $P(E)$ that system A_0 is in a macroscopic state such that the subsystem is in a state of energy E and A' in a state of energy E' is given by the number of configurations $\Omega^0(E)$ which realize this event, divided by the total number of configurations Ω_{tot} accessible to A_0,

$$P(E) = \frac{\Omega(E)\Omega'(E')}{\Omega_{\text{tot}}}. \tag{4.16}$$

Since $P(E)$ is the product of a rapidly increasing function $[\Omega(E) \sim (E - E_0)^f]$ and a rapidly decreasing function $[\Omega'(E_{\text{tot}} - E) \sim (E_{\text{tot}} - E - E_0')^{f'}]$ of E, $P(E)$ has an extremely pronounced maximum around a value $\bar{E}$.

We will later see that the distribution becomes a Gaussian extremely peaked around the maximum value $\bar{E}$ if the degrees of freedom of the two subsystems f and f' are both large. Therefore the $\bar{E}$ coincides with the average energy, which for the postulate of statistical mechanics also coincides with the value of the measurement.

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

$$\left.\frac{\partial \ln P(E)}{\partial E}\right|_{E=\bar{E}} = 0. \tag{4.17}$$

Using the fact that $\partial E'/\partial E = -1$, (4.17) leads to

$$\left.\frac{\partial \ln \Omega(E)}{\partial E}\right|_{E=\bar{E}} = \left.\frac{\partial \ln \Omega'(E')}{\partial E'}\right|_{E'=\bar{E}'}. \tag{4.18}$$

Let us define

$$\beta(E) \equiv \frac{\partial \ln \Omega(E)}{\partial E}. \tag{4.19}$$

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

$$\beta(E) = \beta'(E'), \tag{4.20}$$

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

$$\beta^{-1} = kT, \tag{4.21}$$

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

(i) 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).

(ii) Two systems separately in equilibrium and characterized by *different* values of β, will not be in equilibrium if put in thermal contact.

(iii) Three systems A, B, and C such that if A and C and B and C are *separately* in thermal equilibrium, then $\beta_A = \beta_C$ and $\beta_B = \beta_C$ and hence $\beta_A = \beta_C$, so A and B will also be in thermal equilibrium.

4.3 A Quantitative Study of $P(E)$

We now show that $P(E)$ becomes a Gaussian distribution when the degrees of freedom f and f' respectively of A and A' are large. We expand $\ln P(E)$ around the maximum (as we did in Chapter 3 for the distribution of particles in a box)

$$\ln P(E) = \ln P(\bar{E}) + \frac{1}{2}\frac{\partial^2 \ln P(E)}{\partial E^2}\bigg|_{E=\bar{E}} (E-\bar{E})^2 + \cdots \tag{4.22}$$

Neglecting higher order terms we have

$$P(E) = P(\bar{E}) \exp\left[-\frac{1}{2}\alpha(E-\bar{E})^2\right], \tag{4.23}$$

where

$$\alpha \equiv -\left(\frac{\partial^2 \ln P(E)}{\partial E^2}\right)_{E=\bar{E}} \tag{4.24}$$

is positive since $\bar{E}$ is a maximum for $P(E)$. For simplicity we set $E_0 = E'_0 = 0$, so

$$\Omega(E) \sim E^f \qquad \Omega'(E') \sim E'^{f'}. \tag{4.25}$$

Hence from (4.11)

$$\frac{1}{2}\frac{\partial^2 \ln P(E)}{\partial E^2}\bigg|_{E=\bar{E}} \simeq -\left(\frac{f}{\bar{E}^2} + \frac{f'}{\bar{E}'^2}\right). \tag{4.26}$$

If both systems are macroscopic, we can for simplicity consider the case $f \approx f'$. Then

$$\bar{E} \sim \bar{E}' \qquad \text{and} \qquad \alpha \sim f^{-1} \tag{4.27}$$

and the width of the Gaussian $w = \frac{1}{\sqrt{\alpha}} \sim \sqrt{f}$, hence

$$\frac{w}{\bar{E}} \sim \frac{1}{\sqrt{f}}. \tag{4.28}$$

Thus the relative fluctuation approaches zero for f very large, and the n^{th} order derivative of P goes as $f/\bar{E}^n \sim f^{1-n}$. Therefore, using the argument of Chapter 2, we can neglect all the terms in the expansion (4.22) with powers larger than 2.

4.4 Definition of Entropy in Statistical Mechanics

Note that if one allows an isolated system to evolve naturally by removing a constraint, the total number of allowed configurations increases and therefore $\ln \Omega$ increases. We now demonstrate that the function S, defined as

$$S \equiv k \ln \Omega, \tag{4.29}$$

coincides with the entropy defined in thermodynamics.

Let us consider a system characterized by an energy E in equilibrium with a reservoir at temperature T, where a reservoir is a very large system, practically infinite, at constant temperature. If the system is in thermal contact with the reservoir and exchanges an amount of energy δE, the logarithm of the number of states will change by an amount

$$d(\ln \Omega) = \frac{\partial \ln \Omega}{\partial E}\delta E. \tag{4.30}$$

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 (4.19)

$$d(\ln \Omega) = \frac{\delta Q}{kT}. \tag{4.31}$$

Since $d \ln \Omega$ is an exact differential, 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. Therefore T in (4.31) must coincide, apart from a multiplicative constant, with the absolute temperature—which in thermodynamics is the integral factor of δQ.

Now we know from the second law of thermodynamics that

$$dS = \frac{\delta Q}{T}, \tag{4.32}$$

where dS is an exact differential and defines the entropy in thermodynamics. Therefore the quantity T that appears in (4.31) coincides with the absolute temperature T which appears in (4.32) (we will see that the multiplicative constant is equal to unity). Hence, from (4.31) and (4.32) we have

$$dS = kd(\ln \Omega). \tag{4.33}$$

If we postulate that at zero temperature there is no degeneracy ($\Omega = 1$), then by integrating (4.33) from a state at zero temperature to any other macroscopic state, we obtain the desired result (4.29). 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 $T \to 0$.

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

$$\Omega(E,x) = \sum_r f(E_r(x) - E), \tag{4.34}$$

where

$$f(E_r(x) - E) = \begin{cases} 1 & \text{if } 0 \leq E_r(x) - E \leq \delta E \\ 0 & \text{otherwise,} \end{cases} \tag{4.35}$$

Taking the derivative of (4.34) with respect to x we obtain:

$$\frac{\partial\Omega(E,x)}{\partial x} = -\sum_r \frac{\partial f(z_r)}{\partial E}\frac{\partial E_r}{\partial x}. \tag{4.36}$$

Here we have used the relations

$$\frac{\partial f}{\partial z_r} = -\frac{\partial f}{\partial E} \qquad \frac{\partial z_r}{\partial x} = \frac{\partial E_r}{\partial x}. \tag{4.37}$$

with $z_r = E_r(x) - E$

From (4.36), it follows that

$$\frac{\partial\Omega(E,x)}{\partial x} = \frac{\partial}{\partial E}[\Omega(E,x)\bar{X}] = \left(\bar{X}\frac{\partial\Omega(E,x)}{\partial E} + \Omega(E,x)\frac{\partial\bar{X}}{\partial E}\right). \tag{4.38}$$

where $\bar{X}$ is the average value of $-\frac{\partial E_r}{\partial x}$

$$\bar{X} \equiv \frac{-1}{\Omega(E,x)}\sum_r f(E_r(x) - E)\frac{\partial E_r}{\partial x}. \tag{4.39}$$

Hence

$$\bar{X}dx = \delta W, \tag{4.40}$$

where $-\bar{X}dx$ is the internal variation of the energy, due to the change from x to $x+dx$, $\bar{X}dx$ is therefore the work done from the system on the external world δW. For this reason $\bar{X}$ is denoted the generalized force.

From (4.38)dividing by $\Omega(E,x)$,

$$\frac{\partial \ln\Omega}{\partial x} = \bar{X}\frac{\partial\ln\Omega}{\partial E} + \frac{\partial\bar{X}}{\partial E}, \tag{4.41}$$

For large values of the degree of freedom f, the order of magnitude of the two terms on the right side of (4.41) gives

$$\bar{X}\frac{\partial \ln \Omega}{\partial E} \sim f\frac{\bar{X}}{E}, \tag{4.42}$$

where we have used (4.11); moreover,

$$\frac{\partial \bar{X}}{\partial E} \sim \frac{\bar{X}}{E}. \tag{4.43}$$

In conclusion, in the limit of extremely large f,

$$\frac{\partial \ln \Omega}{\partial x} = \beta \bar{X}. \tag{4.44}$$

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

$$\bar{X} dV = \delta W, \tag{4.45}$$

therefore $\bar{X} \equiv P$ is the pressure.

If x is the number of particles N, then

$$\bar{X} dN = \delta W, \tag{4.46}$$

and

$$\bar{X} = -\mu \tag{4.47}$$

is the chemical potential. If there are x_α ($\alpha = 1 \dots k$) different parameters, (4.44) can be generalized

$$\frac{\partial \ln \Omega(E, x_\alpha)}{\partial x_\alpha} = \beta \bar{X}_\alpha. \tag{4.48}$$

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

$$\frac{\partial \ln \Omega(E, x)}{\partial E} = \beta, \tag{4.49}$$

and the generalized force

$$\frac{\partial \ln \Omega(E, x)}{\partial x} = \beta \bar{X}. \tag{4.50}$$

Here, for simplicity, we have considered only one external parameter.

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 (4.43), 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

$$\beta = \beta' \qquad \text{and} \qquad \bar{X} = \bar{X}', \tag{4.51}$$

where $\bar{X}$ and $\bar{X}'$ are the pressures of the two systems.

If the system can also exchange particles, then x and x' denote the numbers of particles, while $\bar{X}$ and $\bar{X}'$ 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 $\beta = \beta'$ and $X_\alpha = X'_\alpha$. 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

$$d \ln \Omega(E, x) = \frac{\partial \ln \Omega}{\partial E} dE + \frac{\partial \ln \Omega}{\partial x} dx = \beta dE + \beta \bar{X} dx, \tag{4.52}$$

from which

$$dE = \beta^{-1} d(\ln \Omega) - \bar{X} dx = KT d(\ln \Omega) - \bar{X} dx, \tag{4.53}$$

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

$$k d(\ln \Omega) = \frac{\delta Q}{T}. \tag{4.54}$$

In conclusion, we find that $dS = k d(\ln \Omega)$ 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.

Chapter 5

Ideal Gas

5.1 Classical Ideal Gas

The definition of entropy given in the previous chapter 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 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

$$\omega_0^N = (\Delta q \Delta p)^{3N}. \tag{5.1}$$

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

$$S = k \ln \frac{\Delta\Gamma}{\omega_0^N}. \tag{5.2}$$

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 this chapter we will discuss in detail how to choose ω_0 using a technique that compares the entropy of a classical ideal gas with that of a quantum ideal gas, $\omega_0 = h^3$ where h is the Planck constant.

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

$$\mathcal{H}(p,q)=\sum_{i=1}^{3N}\frac{p_i^2}{2m}. \tag{5.3}$$

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

$$\Delta\Gamma=\int dq_1dq_2\dots dq_{3N}\int_{E\leq\mathcal{H}(p,q)\leq E+\delta E}dp_1dp_2\dots dp_{3N}. \tag{5.4}$$

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 $0\leq\mathcal{H}(p,q)\leq E$

$$\Gamma=V^N\int_{0\leq\mathcal{H}(p,q)\leq E}dp_1\dots dp_{3N}, \tag{5.5}$$

and then differentiate to get

$$\Delta\Gamma=\frac{d\Gamma}{dE}\delta E. \tag{5.6}$$

Given the form of the Hamiltonian (5.3), the integral over the momentum in (5.4) is given by the hypervolume in momentum space such that

$$\sum_{i=1}^{3N}\frac{p_i^2}{2m}\leq E. \tag{5.7}$$

For a fixed value of E, Eq. (5.7) describes a hypersphere of radius $R(E)$ in a $3N$ coordinate space, with

$$R(E)=(2mE)^{1/2}. \tag{5.8}$$

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

$$\int_{0\leq\mathcal{H}(p,q)\leq E}dp_1dp_2\dots dp_{3N}=B_NR^{3N}, \tag{5.9}$$

where B_N is the unit sphere volume, which depends only on N and not on R (see Appendix A)

$$B_N=\frac{(\pi)^{(3/2)N}}{\left(\frac{3}{2}N\right)!}. \tag{5.10}$$

Thus

$$\frac{\Gamma}{\omega_0^N} = \left(\frac{V}{\omega_0}\right)^N B_N (2mE)^{3N/2}. \tag{5.11}$$

Differentiating with respect to E, we find

$$\frac{\Delta\Gamma}{\omega_0^N} = \frac{3}{2}\left(\frac{V}{\omega_0}\right)^N B_N (2mE)^{3N/2} \frac{N\delta E}{E} = \frac{3}{2}\frac{\Gamma}{\omega_0^N}\frac{N\delta E}{E}. \tag{5.12}$$

Taking the logarithm of (5.12), and using Stirling's approximation for B_N (5.10), we find for $\Omega = \Delta\Gamma/\omega_0^N$

$$\ln \Omega = N \ln \left[\frac{V}{\omega_0}\left(\frac{4\pi m E}{3N}\right)^{3/2}\right] + \frac{3}{2}N, \tag{5.13}$$

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. (5.11) and (5.12), $\ln \Delta\Gamma$ 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.

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

$$\beta = \frac{\partial \ln \Omega}{\partial E} \tag{5.14}$$

and

$$\beta P = \frac{\partial \ln \Omega}{\partial V}, \tag{5.15}$$

we obtain from Eq. (5.13)

$$E = \frac{3}{2}NkT \tag{5.16}$$

and

$$PV = NkT. \tag{5.17}$$

Relation (5.17) shows that the temperature $T = 1/k\beta$ defined through (5.14) coincides with the absolute temperature of the ideal gas.

5.2 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

$$\epsilon = \frac{\hbar^2 \pi^2}{2m} \frac{1}{L^2}(n_1^2 + n_2^2 + n_3^2), \tag{5.18}$$

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

$$\epsilon = \frac{\hbar^2 \pi^2}{2m} \frac{1}{V^{2/3}} \sum_{i=1}^{3N} n_i^2. \tag{5.19}$$

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

$$0 \leq \sum_{i=1}^{3N} n_i^2 \leq \frac{2m}{\hbar^2} \frac{L^2}{\pi^2} E = R^2, \tag{5.20}$$

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 neglect the discrepancy which comes when counting the states near the surface (see Fig. 1.5). This effect 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 divided by $\frac{1}{2^{3N}}$, since $3N$ is the dimension of the space.

In conclusion repeating the calculation points along the same lines as done in the classical case, we obtain for the number of configurations Ω with energy between E and $E + \delta E$

$$\ln \Omega = N \ln \left[\frac{V}{h^3} \left(\frac{4\pi m E}{3N} \right)^{3/2} \right] + \frac{3}{2} N. \tag{5.21}$$

This expression coincides with the classical result (5.13)provided that the volume of the elementary cell is $\omega_0 = h^3$.

5.3 Gibbs Paradox

From the expressions (5.13) and (5.21) 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

$$V \to \lambda V \qquad E \to \lambda E \qquad N \to \lambda N. \tag{5.22}$$

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 (5.13), unlike the energy which appears divided by N.

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

$$\Omega_{\text{corr}} = \frac{\Omega}{N!}. \tag{5.23}$$

By using the expression for Ω (5.13) and applying Stirling's approximation, one finds

$$\ln\Omega_{\text{corr}} = N\ln\left[\frac{V}{h^3N}\left(\frac{4\pi mE}{3N}\right)^{3/2}\right] + \frac{5}{2}N, \tag{5.24}$$

which now has the correct property, since the volume V now is divided by N. 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 (**??**) and (**??**).

In conclusion, to treat a classical system, then 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 6

Canonical Ensemble

6.1 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 or given 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' 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 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 $E_{\rm tot}$. Hence the configurations of A' compatible with r are those corresponding to an energy E' such that $E' + E_r = E_{\rm tot}$.

Thus

$$P_r = \frac{\Omega'(E')}{\Omega_{\rm tot}} = \frac{\Omega'(E_{\rm tot} - E')}{\Omega_{\rm tot}}, \tag{6.1}$$

where $\Omega'(E')$ is the number of configurations of subsystem A' corresponding to an energy $E' = E_{\rm tot} - E_r$, and $\Omega_{\rm tot}$ is the total number of configurations in which system $A + A'$ can be.[1] If we take the log of P_r in (6.1) and expand around $E_r = 0$, we find

$$\ln P_r = C - \left(\frac{\partial \ln \Omega'}{\partial E'}\right)_{E'=E_{\rm tot}} E_r + \cdots, \tag{6.2}$$

where C is a constant that does not depend on r. Since E_r is very small compared to $E_{\rm tot}$, higher order terms can be neglected.

$$\left(\text{In fact:} \qquad \Omega' \sim E'^f \qquad \left.\frac{\partial^k \ln \Omega'}{\partial E'^k}\right|_{E'=E_{\rm tot}} \sim \frac{f}{E_{\rm tot}^k}\right).$$

From (6.2)

$$P_r = \frac{1}{Z} e^{-\beta E_r}, \tag{6.3}$$

where

$$\beta = \left(\frac{\partial \ln \Omega'}{\partial E'}\right)_{E'=E_{\rm tot}}, \tag{6.4}$$

and T is the temperature of system A' when its energy $E' = E_{\rm tot}$. Since system A' is much larger than system A, the energy of A'—when in equilibrium with A—practically coincides with energy $E_{\rm tot}$.

The normalization factor Z is obtained by imposing $\sum_r P_r = 1$, so from (6.3)

$$Z = \sum_r e^{-\beta E_r}. \tag{6.5}$$

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 (6.3) is called a *canonical ensemble.*

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[1] Note the similarity between (6.1) here and (4.16) in Chapter 4. The difference here is that $\Omega(E_r) = 1$, since there is only one configuration that realizes the microscopic configuration r.

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

$$\langle E\rangle \equiv \sum_r E_r P_r = \sum_r \frac{E_r e^{-\beta E_r}}{Z}. \tag{6.6}$$

Therefore, from (6.5),

$$-\frac{\partial \ln Z}{\partial \beta} = -\frac{1}{Z}\frac{\partial Z}{\partial \beta} = \langle E\rangle. \tag{6.7}$$

Similarly, the mean square fluctuation is defined as

$$\langle \Delta E^2\rangle \equiv \langle E^2\rangle - \langle E\rangle^2 = \sum_r \frac{E_r^2 e^{-\beta E_r}}{Z} - \left(\sum_r \frac{E_r e^{-\beta E_r}}{Z}\right)^2. \tag{6.8}$$

Therefore,

$$\frac{\partial^2 \ln Z}{\partial \beta^2} = -\frac{\partial \langle E\rangle}{\partial \beta} = \langle E^2\rangle - \langle E\rangle^2. \tag{6.9}$$

Moreover,

$$\frac{\partial \langle E\rangle}{\partial \beta} = -T^2 \frac{\partial \langle E\rangle}{\partial T}. \tag{6.10}$$

Since the variation of the energy is done at fixed external parameters, the variation of the energy is due only to the exchange of heat and not to any mechanical work. Therefore, from Eq. (1.3) of Chapter 1, C_V, the specific heat at constant volume, is

$$C_V \equiv \frac{\partial \langle E\rangle}{\partial T}. \tag{6.11}$$

From (6.9)–(6.11) we have

$$kT^2 C_V = \langle E^2\rangle - \langle E\rangle^2. \tag{6.12}$$

Equation (6.12) 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 (6.12) 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

$$\bar{X} \equiv -\sum_r \frac{\partial E_r}{\partial x} P_r, \tag{6.13}$$

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

$$\delta W = \bar{X}\delta x. \tag{6.14}$$

From (6.13) we see that

$$\bar{X} = \frac{1}{\beta}\frac{\partial \ln Z}{\partial x}. \tag{6.15}$$

In the particular case in which x is the volume V, $\bar{X}$ is the pressure p, (6.15) becomes

$$p = \frac{1}{\beta}\frac{\partial \ln Z}{\partial V}. \tag{6.16}$$

6.2 Energy Distribution

The distribution probability (6.3) 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 $E+\delta E$,

$$P(E) = \sum_{E \le E_r \le E+\delta E} P_r = \frac{\Omega(E)e^{-\beta E}}{Z}, \tag{6.17}$$

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

We can write (6.17) as

$$P(E) = \frac{e^{-F(E)/kT}}{Z}, \tag{6.18}$$

where

$$F(E) = E - TS(E), \tag{6.19}$$

and

$$S(E) = k \ln \Omega(E). \tag{6.20}$$

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

$$F(E) = F(\bar{E}) + \frac{1}{2} \frac{\partial^2 F}{\partial E^2}\bigg|_{E=\bar{E}} (E - \bar{E})^2 + \cdots, \tag{6.21}$$

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

$$\frac{\partial F(E)}{\partial E}\bigg|_{E=\bar{E}} = 0. \tag{6.22}$$

Hence, from (6.19),

$$\frac{\partial S(E)}{\partial E}\bigg|_{E=\bar{E}} = \frac{1}{T}, \tag{6.23}$$

where T is the temperature of the reservoir.

As discussed in Chapter 4, the value $\bar{E}$ that maximizes the probability corresponds to the value of the energy at equilibrium. Equation (6.23) states that at equilibrium the entropy of system A satisfies the thermodynamical relation. Using (6.20), we can express the second derivative of $F(E)$ in (6.19). Since T is the temperature of the reservoir and does not depend on E, we have

$$\left(\frac{\partial^2 F(E)}{\partial E^2}\right)_{E=\bar{E}} = -T \left(\frac{\partial^2 S(E)}{\partial E^2}\right)_{E=\bar{E}}, \tag{6.24}$$

and

$$\left(\frac{\partial^2 S(E)}{\partial E^2}\right)_{E=\bar{E}} = \left(\frac{\partial}{\partial E} \frac{1}{T(E)}\right)_{E=\bar{E}} = -\frac{1}{T^2(\bar{E})} \left(\frac{\partial T(E)}{\partial E}\right)_{E=\bar{E}}, \tag{6.25}$$

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

$$T(\bar{E}) = T \quad ; \qquad \left(\frac{\partial T(E)}{\partial E}\right)_{E=\bar{E}} = \frac{1}{C_V}, \tag{6.26}$$

where C_V is the specific heat at constant volume. Therefore from (6.25) and (6.26), (6.24) gives

$$\left(\frac{\partial^2 F}{\partial E^2}\right)_{E=\bar{E}} = \frac{1}{TC_V}. \tag{6.27}$$

Finally, using the argument of Chapter 4, for very large N (the thermodynamic limit of system A) we can neglect higher order terms in (6.21), and, from (6.18) and (6.27),

$$P(E) = A \exp[-(E-\bar{E})^2/2kT^2C_V], \tag{6.28}$$

where the factor $A = e^{-F(\bar{E})/kT}/Z$ does not depend on E. We find that the distribution $P(E)$ is a Gaussian centered around the average value $\bar{E} = \langle E\rangle$ with variance $\langle E^2\rangle - \langle E\rangle^2 = kT^2C_V$ in agreement with Eq. (6.12). We note that the equilibrium is reached for $E = \bar{E}$ where $P(E)$ is maximum. This value in turn corresponds to the value which minimizes $F(E)$,

$$F(E) = E - TS(E), \tag{6.29}$$

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. (6.29).

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 (6.28) (i.e., the root mean square energy fluctuation) divided by the average value gives, since $\bar{E} = \langle E\rangle$

$$\frac{\sqrt{\langle E^2\rangle - \langle E\rangle^2}}{\langle E\rangle} \sim \frac{\sqrt{C_V}}{\langle E\rangle} \sim \frac{1}{\sqrt{N}}, \tag{6.30}$$

where we have taken into account that C_V and $\langle E\rangle$ are proportional to the number of particles N. From (6.30), 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.

6.3 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 $\bar{X}$. We now show that in the thermodynamic limit the free energy defined thermodynamically coincides with the quantity

$$F = -kT\ln Z, \tag{6.31}$$

where Z is the partition function (6.5). First we note that

$$Z = \sum_r e^{-\beta E_r} = \sum_E \Omega(E)e^{-\beta E} = \sum_E g(E)e^{-\beta E}\delta E, \tag{6.32}$$

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

$$\ln g(E) = \ln\Omega(E), \tag{6.33}$$

since $\ln(\Delta E)$ is at most of the order of $\ln N$, and is negligible compared with $\ln\Omega \sim N$. Since in (6.32) the energy interval δE is small compared to E, we can substitute an integral for the sum

$$Z = \int e^{-F(E)}dE, \tag{6.34}$$

where $F(E) = E - TS(E)$. Using the Gaussian approximation (6.28) for $P(E)$, we find

$$Z = e^{-\beta F(\bar{E})}\int_0^\infty e^{-(E-\bar{E})^2/2kT^2C_V}dE. \tag{6.35}$$

The Gaussian integral is evaluated in Appendix A, so

$$\int_{-\infty}^{+\infty} e^{-\alpha x^2} dx = \sqrt{\frac{\pi}{\alpha}}, \tag{6.36}$$

it follows from (6.35) that

$$-kT \ln Z = F(\bar{E}) - kT \ln \sqrt{2\pi k T^2 C_V}. \tag{6.37}$$

In the limit of infinite N, the last term in (6.37) can be neglected since C_V is of the order of N, so

$$-kT \ln Z = \bar{E} - TS. \tag{6.38}$$

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

$$d(\ln Z) = \frac{\partial \ln Z}{\partial x} dx + \frac{\partial \ln Z}{\partial \beta} d\beta, \tag{6.39}$$

where x is an external parameter (such as V). From (6.35) and (6.37)

$$d(\ln Z) = \beta \bar{X} dx - \bar{E} d\beta = \beta \delta W - d(\beta \bar{E}) + \beta d\bar{E} = \beta(\delta W + d\bar{E}) - d(\beta \bar{E}), \tag{6.40}$$

where δW is the work done by the system from Eq. (6.14), and $d\bar{E}$ the variation of the internal energy. Therefore $\delta W + \delta \bar{E} = \delta Q$, where δQ is the heat absorbed by the system.

In conclusion, from (6.40)

$$d(\ln Z + \beta \bar{E}) = \beta \delta Q = dS, \tag{6.41}$$

and on integrating, we find

$$-kT \ln Z = \bar{E} - TS. \tag{6.42}$$

Comparing (6.42) with (6.29) shows that $F = -kT \ln Z$ is the free energy.

From (6.42) we can derive a useful expression for the entropy in the canonical ensemble. Substituting (6.6) into (6.42), we find

$$S = \sum_s P_s \left(\frac{E_s}{T} + k \ln Z \right), \tag{6.43}$$

where we have used $\sum_s P_s = 1$. From (6.3) follows

$$\frac{E_s}{T} = -k \ln P_s - k \ln Z. \tag{6.44}$$

Hence substituting (6.44) into (6.43), the expression for the entropy in the canonical ensemble can be written in the form

$$S = -k \sum_s P_s \ln P_s = -k \langle \ln P_s \rangle . \tag{6.45}$$

The form of Eq. (6.45) is familiar in information theory. If P_s denotes the probability of finding the system in a given state s, then (6.45) is a measrue 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 (6.45) $S = -k \sum_s P_s \ln P_s$ 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

$$S = k \ln \Omega \tag{6.46}$$

assumes its maximum value, corresponding to minimum information.

Note that definition (6.45) applies also to the microcanonical ensemble where $P_s = 1/\Omega$ and the entropy (6.45) gives (6.46), which is the expression used in the microcanonical ensemble.

6.4 First Law of Thermodynamics

Let us write the variation of energy for a reversible transformation

$$\bar{E} = \sum_r E_r P_r , \tag{6.47}$$

so that

$$d\bar{E} = \sum_r E_r dP_r + \sum_r P_r dE_r . \tag{6.48}$$

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. The first term can be written as

$$\sum_r E_r dP_r = -kTd \left(\sum_r P_r \ln P_r \right) = -TdS , \tag{6.49}$$

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.

6.5 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

$$P(q, p)dqdp = \frac{e^{-\beta\mathcal{H}(q,p)}}{Z}\frac{dqdp}{N!h^{3N}}. \tag{6.50}$$

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

$$Z = \frac{1}{N!h^{3N}}\int e^{-\beta\mathcal{H}(q,p)}dqdp, \tag{6.51}$$

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

$$\langle A\rangle = \frac{\int A(q, p)e^{-\beta\mathcal{H}(q,p)}dqdp}{\int e^{-\beta\mathcal{H}(q,p)}dqdp}. \tag{6.52}$$

6.6 Energy Equipartition Theorem

Consider a classical system of N particles with Hamiltonian

$$\mathcal{H}(q, p) = \sum_{i=1}^{3N}\frac{p_i^2}{2m} + V(q_1 \dots q_{3N}) + \sum_i U(q_i). \tag{6.53}$$

Here $V(q_1, \cdots q_N)$ 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,

$$\left\langle x_i \frac{\partial H}{\partial x_j} \right\rangle = kT\delta_{i\jmath}, \tag{6.54}$$

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

$$\left\langle x_i \frac{\partial \mathcal{H}}{\partial x_j} \right\rangle = \int x_i \left(\frac{\partial \mathcal{H}}{\partial x_j} \right) e^{-\beta\mathcal{H}} d\omega \bigg/ \int e^{-\beta\mathcal{H}} d\omega, \tag{6.55}$$

where for simplicity we have put

$$d\omega \equiv dx_1 \ldots dx_{6N}. \tag{6.56}$$

Note that

$$\frac{\partial e^{-\beta\mathcal{H}}}{\partial x_j} = -\beta \left(\frac{\partial \mathcal{H}}{\partial x_j} \right) e^{-\beta\mathcal{H}}, \tag{6.57}$$

so (6.55) can be written as

$$\left\langle x_i \frac{\partial \mathcal{H}}{\partial x_j} \right\rangle = -\frac{1}{\beta} \int x_i \left(\frac{\partial e^{-\beta\mathcal{H}}}{\partial x_j} \right) d\omega \bigg/ \int e^{-\beta\mathcal{H}} d\omega. \tag{6.58}$$

Integrating the numerator by parts, we find

$$-\frac{1}{\beta} \int x_i \frac{\partial e^{-\beta\mathcal{H}}}{\partial x_j} d\omega = -\frac{1}{\beta} \left\{ \int \left[x_i e^{-\beta\mathcal{H}} \right]_{x_j^{\min}}^{x_j^{\max}} d\omega_j - \int \frac{\partial x_i}{\partial x_j} e^{-\beta\mathcal{H}} d\omega \right\}. \tag{6.59}$$

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

$$\left[x_i e^{-\beta\mathcal{H}} \right]_{x_j^{\min}}^{x_j^{\max}} = 0, \tag{6.60}$$

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 (6.53) 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 (6.59) is nonzero, and (6.58) becomes

$$\left\langle x_i \frac{\partial H}{\partial x_j} \right\rangle = kT \int \frac{\partial x_i}{\partial x_j} e^{-\beta \mathcal{H}} d\omega \Big/ \int e^{-\beta \mathcal{H}} d\omega, \tag{6.61}$$

Since $\partial x_i / \partial x_j = \delta_{ij}$ from (6.61) follows the relation (6.54), which proves the theorem.

Next we demonstrate an interesting consequence of this theorem. From the Hamiltonian (6.53),

$$p_i \frac{\partial \mathcal{H}}{\partial p_i} = \frac{p_i^2}{m}. \tag{6.62}$$

From (6.54) for $x_i = x_j = p_i$,

$$\left\langle p_i \frac{\partial \mathcal{H}}{\partial p_i} \right\rangle = kT. \tag{6.63}$$

Therefore from (6.62) and (6.63),

$$\left\langle \frac{p_i^2}{2m} \right\rangle = \frac{1}{2} kT. \tag{6.64}$$

Equation (6.64) 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

$$\sum_{i=1}^{3N} \left\langle \frac{p_i^2}{2m} \right\rangle = \frac{3}{2} NkT. \tag{6.65}$$

Relations (6.64) and (6.65) are quite general and hold for almost any potential and hence for many systems in nature. Moreover, (6.65) 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

$$\mathcal{H} = \sum_{i=1}^{3N} (a_i p_i^2 + b_i q_i^2). \tag{6.66}$$

The reader may demonstrate that

$$\langle \mathcal{H} \rangle = 3NkT, \tag{6.67}$$

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

6.7 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 $(p_i, p_i + dp_i)$ $i = 1, 2, 3$ 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

$$f(\vec{p}) = \frac{\int e^{-\beta\mathcal{H}} dp^{3N-3} d^{3N}q}{\int e^{-\beta\mathcal{H}} d^{3N}p d^{3N}q}. \tag{6.68}$$

For a general Hamiltonian of the form

$$\mathcal{H} = \sum_{i=1}^{3N} \frac{p_i^2}{2m} + V(q_1 \cdots q_{3N}), \tag{6.69}$$

the integral in (6.68) can be performed, and we find

$$f(\vec{p}) = \frac{e^{-\beta p^2/2m}}{(2\pi mkT)^{3/2}}. \tag{6.70}$$

The prefactor in the denominator ensures the normalization

$$\int f(\vec{p}) d^3p = 1. \tag{6.71}$$

Expression (6.70) for $f(\vec{p})$ is the Maxwell-Boltzmann distribution and is rather general.

We leave as an exercise for the reader to show that the average kinetic energy for each component is given by

$$\frac{\langle p_i^2 \rangle}{2m} = \frac{1}{2}kT, \tag{6.72}$$

which is another way of obtaining one of the consequences, (6.64), of the energy equipartition theorem.

6.8 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 (6.69) the Hamiltonian is the sum of all the kinetic energies of each particle

$$\mathcal{H} = \sum_{i=1}^{3N} \frac{p_i^2}{2m}. \tag{6.73}$$

The partition function is, from (6.51),

$$Z = \frac{1}{h^{3N} N!} \int \exp\left(-\beta \sum_i \frac{p_i^2}{2m}\right) d^{3N}q d^{3N}p. \tag{6.74}$$

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

$$Z = \frac{V^N}{h^{3N} N!} \left[\int_{-\infty}^{+\infty} e^{-\beta p_i^2/2m} dp_i\right]^{3N}. \tag{6.75}$$

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

$$Z = \frac{1}{N!} Z_1^N, \tag{6.76}$$

where

$$Z_1 \equiv \frac{V}{h^3} \left(\int e^{-\beta p_i^2/2m} dp_i\right)^3. \tag{6.77}$$

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

$$Z_1 = \frac{V}{h^3} (2\pi m k T)^{3/2}. \tag{6.78}$$

Hence from (6.76),

$$Z = \frac{V^N}{h^{3N}} \frac{1}{N!} (2\pi m k T)^{3N/2}. \tag{6.79}$$

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

$$F = -kT \ln Z = NkT \left[\ln \left\{\frac{N}{V} \left(\frac{h^2}{2\pi m k T}\right)^{3/2}\right\} - 1\right]. \tag{6.80}$$

From (6.16)

$$p = -\frac{\partial F}{\partial V} = \frac{NkT}{V}, \tag{6.81}$$

which gives the equation of state of the ideal gas

$$pV = NkT. \tag{6.82}$$

From (6.7) the average energy is given by,

$$\langle E \rangle = -\frac{\partial \ln Z}{\partial \beta} = \frac{3}{2}NkT, \tag{6.83}$$

in agreement with the equipartition theorem (6.65).

The entropy S can be obtained using the relation

$$S = \frac{\langle E \rangle - F}{T}, \tag{6.84}$$

where F is given by (6.80). If from (6.83) we express T as function of $\langle E \rangle = \bar{E}$, S can be written as a function of $\bar{E}$, N and V. It is left as an exercise to show that $S(\bar{E})$ coincides with the entropy calculated in the microcanonical ensemble. The results, however, have in both cases been obtained in the thermodynamic limit $N \to \infty$.

6.9 Harmonic Oscillators

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

6.9.1 Classic treatment

The Hamiltonian of a one-dimensional harmonic oscillator is

$$\mathcal{H}_i = \frac{1}{2}m\omega^2 q_i^2 + \frac{p_i^2}{2m}. \tag{6.85}$$

The total for N Hamiltonian oscillators is

$$\mathcal{H} = \sum_{i=1}^{N} \mathcal{H}_i. \tag{6.86}$$

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,

$$Z_1 = \frac{1}{h}\int e^{-\beta(\frac{1}{2}m\omega^2 q_1^2)}dq_1 \int e^{-\beta p_1^2/2m}dp_1 = \frac{1}{\beta\hbar\omega}. \tag{6.87}$$

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

$$Z = Z_1^N = (\beta\hbar\omega)^{-N}. \tag{6.88}$$

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, $\bar{E}$, and S. Thus from the relation $F = -kT\ln Z$,

$$F = NkT\ln\frac{\hbar\omega}{kT}, \tag{6.89}$$

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

$$\bar{E} = NkT, \tag{6.90}$$

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

$$S = Nk\left(\ln\frac{kT}{\hbar\omega} + 1\right). \tag{6.91}$$

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. (6.89) and the specific heat at constant volume is $C_V = Nk$. 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.

6.9.2 Quantum mechanical treatment

The eigenvalues for a simple harmonic oscillator are given by

$$\epsilon_{n_i} = \left(n_i + \frac{1}{2}\right)\hbar\omega. \tag{6.92}$$

The partition function is

$$Z = \sum e^{-\beta E} = \sum_{\{n_i\}} e^{-\beta(\epsilon_{n_1}+\ldots+\epsilon_{n_N})} = \left(\sum_{n_1} e^{-\beta\epsilon_{n_1}}\right)\cdots\left(\sum_{n_N} e^{-\beta\epsilon_{n_N}}\right) = Z_1^N. \tag{6.93}$$

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

$$Z_1 = \sum_{n_1} e^{-\beta\epsilon_{n_1}} = e^{-\beta\hbar\omega/2}\sum_{n_1} e^{-\beta\hbar\omega n_1} = \frac{e^{-\beta\hbar\omega/2}}{1-e^{-\beta\hbar\omega}}. \tag{6.94}$$

The average energy is then given by

$$\langle E\rangle = -\frac{\partial \ln Z}{\partial\beta} = N\left[\frac{\hbar\omega}{2} + \frac{\hbar\omega}{e^{\beta\hbar\omega}-1}\right]. \tag{6.95}$$

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

$$C_V = \begin{cases} Nk(\beta\hbar\omega)^2 e^{-\beta\hbar\omega} & \text{for } T\to 0 \\ Nk & \text{for } T\to\infty \end{cases}. \tag{6.96}$$

Note that as $T \to \infty$, (6.95) and (6.96) are consistent with the classical result (6.90).

6.10 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 μ. According to quantum mechanics, the component of the magnetic moment along the field can assume only the values $\pm\mu$.[2] If the system is in an external field H and in

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[2] 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 $-S, -S+1, \cdots S$. The value of S can be integer (bosons) or half integer (fermions). For $S = 1/2$, $m_s = \pm 1/2$.

contact with a reservoir at temperature T, we ask what is the magnetization along H. If the magnetic moments of one atom do not interact with those of other atoms, then we can focus on one single atom in contact with an energy reservoir made of all the other atoms plus the reservoir with which the entire system is in contact.

The Hamiltonian for one atom is

$$\mathcal{H} = -\vec{\mu}\cdot\vec{H} = -\mu_z H, \tag{6.97}$$

where we have chosen the axis z along the direction of the field $\vec{H}$, and μ_z can assume only two values $\mu_z = \pm\mu_o$ where we have put $\mu_o = \frac{1}{2}\mu_B$. For convenience, let us introduce a "spin" variable that can assume two values $S = \pm 1$. The Hamiltonian (6.97) can then be written as

$$\mathcal{H} = -S\mu_0 H. \tag{6.98}$$

where $S = \pm 1$ corresponds respectively to the spin up or down. Using the canonical ensemble, the corresponding probabilities are

$$P(+1) = \frac{e^{-\beta\mathcal{H}(S=+1)}}{Z} = \frac{e^{\beta\mu_0 H}}{Z}, \tag{6.99}$$

and

$$P(-1) = \frac{e^{-\beta\mathcal{H}(S=-1)}}{Z} = \frac{e^{-\beta\mu_0 H}}{Z}. \tag{6.100}$$

Since the states of the system are given by $S = \pm 1$, the partition function is given by

$$Z = e^{\beta\mu_0 H} + e^{-\beta\mu_0 H}. \tag{6.101}$$

The average magnetization is

$$m = \mu_0\langle S\rangle = \mu_0\frac{e^{\beta\mu_0 H} - e^{-\beta\mu_0 H}}{e^{\beta\mu_0 H} + e^{-\beta\mu_0 H}} = \tanh(\beta\mu_0 H). \tag{6.102}$$

In general, given a Hamiltonian which contains a term xX,

$$\mathcal{H} = \mathcal{H}_0 - xX, \tag{6.103}$$

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

$$\langle X\rangle = \frac{\partial \ln Z}{\partial(\beta x)}. \tag{6.104}$$

In our case, $x = H$ and $X = \mu_0 S$, and (6.102) is obtained directly from the partition function (6.101) by taking the derivative with respect to βH.

Consider now the entire system of N spins. Since the spins are not interacting, the Hamiltonian can be written as

$$\mathcal{H} = -\mu_0 H \sum_{i=1}^{N} S_i, \tag{6.105}$$

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

$$Z = \sum_{\{S_i\}} \exp[-\beta\mathcal{H}(S_1 \ldots S_N)] = \sum_{\{S_i\}} \exp[+\beta\mu_0 H \sum_i S_i], \tag{6.106}$$

where the sum is over the configurations of spins $S_1 = \pm 1, S_2 = \pm 1, \cdots S_N = \pm 1$. From (6.106), we have

$$Z = \sum_{\{S_i\}} e^{\beta\mu_0 H \sum S_i} = \left(\sum_{\{S_1=\pm 1\}} e^{\beta\mu_0 H S_1} \right) \left(\sum_{\{S_2=\pm 1\}} e^{\beta\mu_0 H S_2} \right) \cdots \left(\sum_{\{S_N=\pm 1\}} e^{\beta\mu_0 H S_N} \right). \tag{6.107}$$

Hence

$$Z = Z_1^N = \left(e^{\beta\mu_0 H} + e^{-\beta\mu_0 H} \right)^N, \tag{6.108}$$

where Z_1 is the partition function of one single particle.

Similarly, the average magnetization is given by

$$M = \mu_0 \left\langle \sum_{i=1}^{N} S_i \right\rangle = \mu_0 \sum_{i=1}^{N} \langle S_i \rangle = \mu_0 N \frac{e^{\beta\mu_0 H} - e^{-\beta\mu_0 H}}{e^{\beta\mu_0 H} + e^{-\beta\mu_0 H}}. \tag{6.109}$$

Therefore the total magnetization is Nm where m is the magnetization of a single spin. Moreover, since the spins do not interact, the magnetization of one species equals the magnetization of that spin—as if it were alone in contact with a reservoir.

Figure xx shows the magnetization as a function of the dimensionless field variable $h \equiv \mu H/kT$. For $h \gg 1$, the magnetization asymptotically reaches its saturation value $m = \mu_o$. Physically, this means that for a fixed temperature for values of the field such that $\mu_o H \gg kT$, the thermal energy is much less than the magnetic energy and almost all the spins are aligned with the magnetic field. For $x \ll 1$, 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 $\mu_o H \ll kT$, 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.

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

$$\chi_T \equiv \left(\frac{\partial M}{\partial H}\right)_T . \tag{6.110}$$

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

$$\chi_T \delta H = \delta M. \tag{6.111}$$

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 (6.109),

$$\chi_T = \left(\frac{\partial M}{\partial H}\right)_T = N\frac{\mu_0^2}{kT}. \tag{6.112}$$

Note that as T decreases, χ increases and diverges as $T \to 0$. In fact, from Fig. xx 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.

6.11 Negative Temperature

Consider a system of N non-interacting particles, in which each particle can be in two possible energetic states, with energies $\epsilon_1 < \epsilon_2$ (Fig. XX). The paramagnetic system is a particular example. The average energy per particle is given by

$$\bar{\epsilon} = \frac{\epsilon_1 + \epsilon_2 e^{-\beta\epsilon_2+\beta\epsilon_1}}{1 + e^{-\beta\epsilon_2+\beta\epsilon_1}}. \tag{6.113}$$

Note that

$$\bar{\epsilon} = \begin{cases} \epsilon_1 & \text{for } T \to 0 \\ (\epsilon_1+\epsilon_2)/2 & \text{for } T \to \infty \end{cases} . \tag{6.114}$$

One might have expected that the energy as $T \to \infty$ approaches ϵ_2, not $(\epsilon_1 + \epsilon_2)/2$. To resolve this apparent paradox, consider, for a fixed value of T, the free energy of the system

$$F = E - TS(E) \tag{6.115}$$

The average energy $E = \bar{E} = N\bar{\epsilon}$ corresponds to the minimum of the Free energy. The energy E is given by:

$$E = N_1\epsilon_1 + N_2\epsilon_2 = N_2(\epsilon_2 - \epsilon_1) + N\epsilon_1. \tag{6.116}$$

Here N_2 is the number of particles with energy ϵ_2 and $N_1 = N - N_2$ is the number of particles with energy ϵ_1,

The entropy corresponding to the macroscopic state of energy E, $S(E) = k \ln \Omega(E)$ where Ω is the number of microscopic states that can be obtained by placing N_1 particles in the state of energy ϵ_1 and N_2 particles in the state of energy ϵ_2,

$$\Omega[E(N_2)] = \binom{N}{N_2} = \frac{N!}{N_2!N_1!}. \tag{6.117}$$

Ω (Fig. XX) takes its lowest value $\Omega = 1$ for $N_2 = 0$ and $N_2 = N$, and its maximum for $N_2 = N/2$. Therefore for $T \to 0$, the term which dominates in (6.115) is the energy, and the free energy is minimum if the particles are all in the state of minimum energy $\bar{E}/N = \epsilon_1$. On the other hand, if $T \to \infty$, then the term which dominates in (6.115) is the entropy. Therefore the minimum of the free energy corresponds to the maximum of Ω which occurs at $N_1 = N/2$ so from (6.116), $\bar{E}/N = (\epsilon_1 + \epsilon_2)/2$.

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 $\Omega(E)$ 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 (Fig. xx), is that the entropy for energy above the maximum becomes a decreasing function of the energy, which implies for these values of the energy a *negative* absolute temperature,

$$\beta = \frac{\partial \ln \Omega}{\partial E} < 0 \tag{6.118}$$

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.

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 very large, corresponding to negative temperature. Usually after a relaxation time, the spins will release energy to the environment or to the crystal 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 7

Entropy Maximization Approach to the Canonical Ensemble

In Chapter 6, we obtained the canonical ensemble for a system A 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, since all have the same number of particles N and exchange energy with all the others, which act as a reservoir for that particular subsystem. The only constraint is that the total energy E_{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 and an associated energy E_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

$$\sum_r n_r = \mathcal{N} \tag{7.1}$$

and

$$\sum_r E_r n_r = E_{\text{tot}} = \mathcal{N}U \tag{7.2}$$

The first condition implies that the total number of subsystems $\mathcal{N}$ is fixed, and the second condition implies that the total energy $\mathcal{N}U$ is fixed. Every distribution n_r which satisfies (7.1) and (7.2) 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

$$\mathcal{W}\{n_r\} = \frac{\mathcal{N}!}{n_1! n_2! \cdots n_r! \cdots} \tag{7.3}$$

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 $\mathcal{W}\{n_r\}$.

The most probable distribution $\{n_r^*\}$ is the distribution that maximizes $\mathcal{W}\{n_r\}$—or, equivalently, the distribution that maximizes $\ln \mathcal{W}\{n_r\}$, subject to the conditions (7.1) and (7.2). Using the method of Lagrange multipliers (Appendix A), we calculate the maximum of

$$\ln \tilde{\mathcal{W}}\{n_r\} = \ln \mathcal{W}\{n_r\} - \alpha \left(\sum_r n_r - \mathcal{N} \right) - \beta \left(\sum_r E_r n_r - \mathcal{N}U \right), \tag{7.4}$$

where α and β are the Lagrange parameters that will be fixed to satisfy conditions (7.1) and (7.2).

Using Stirling's approximation in (7.3) and the condition (7.1), we find

$$\ln \mathcal{W} = \mathcal{N} \ln \mathcal{N} - \sum_r n_r \ln n_r. \tag{7.5}$$

Substituting (7.5) into (7.4) and maximizing with respect to the quantity n_s, we have

$$\frac{\partial \ln \tilde{\mathcal{W}}}{\partial n_s} = -\ln n_s - 1 - \alpha - \beta E_s = 0, \tag{7.6}$$

from which we find

$$n_s^* = C e^{-\beta E_s}. \tag{7.7}$$

The constant $C = e^{-(1+\alpha)}$ can be fixed by requiring condition (7.1),

$$C = \frac{\mathcal{N}}{\sum_s e^{-\beta E_s}}. \tag{7.8}$$

Hence we finally find

$$\frac{n_s^*}{\mathcal{N}} = \frac{e^{-\beta E_s}}{\sum_s e^{-\beta E_s}}, \tag{7.9}$$

where β is fixed by requiring the condition (7.2).

We next show that the most probable distribution $\{n_r^*\}$, 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 (7.4) around the value n_r^*,

$$\ln \tilde{\mathcal{W}}\{n_r\} = \ln \tilde{\mathcal{W}}\{n_r^*\} + \frac{1}{2}\sum_r \left(\frac{\partial^2 \ln \tilde{\mathcal{W}}}{\partial n_r^2}\right)_{n_r = n_r^*} (n_r - n_r^*)^2 \cdots \tag{7.10}$$

The first derivative is zero, while the second derivative is given by

$$\frac{\partial^2 \ln \tilde{\mathcal{W}}}{\partial n_r^2} = \frac{\partial^2 \ln \mathcal{W}}{\partial n_r^2} = -\frac{1}{n_r}. \tag{7.11}$$

Moreover, due to the conditions (7.1) and (7.2), $\ln \tilde{\mathcal{W}}\{n_r\} = \ln \mathcal{W}\{n_r\}$. Therefore from (7.10) and (7.11), we find a Gaussian distribution

$$\mathcal{W}\{n_r\} = \mathcal{W}\{n_r^*\} \exp\left[-\frac{1}{2}\sum \frac{(n_r - n_r^*)^2}{n_r^*}\right], \tag{7.12}$$

with average value $\langle n_r \rangle = n_r^*$, and width (a measure of the rms fluctuations)

$$\Delta n_r^* = \left(\langle (n_r - n_r^*)^2 \rangle\right)^{1/2} = \sqrt{n_r^*}. \tag{7.13}$$

Therefore, considering that $n_r^* \sim \mathcal{N}$, we have in the $\mathcal{N} \to \infty$ limit

$$\frac{\Delta n_r^*}{n_r^*} \sim \frac{1}{\sqrt{\mathcal{N}}} \to 0. \tag{7.14}$$

Hence if we consider the normalized distribution

$$p_r^* = \frac{n_r^*}{\mathcal{N}} = \frac{e^{-\beta E_r}}{A}, \tag{7.15}$$

we find that the probability $\mathcal{P}(\{p_r\})$ to find a distribution $\{p_r\}$ given by $\mathcal{P}(\{p_r\}) = \mathcal{W}(\{\mathcal{N} p_r\})$ is extremely peaked around the canonical distribution p_r^* and becomes a delta function in the limit $\mathcal{N} \to \infty$.

Thus from the postulate of equal *a priori* probability we have found that the equilibrium distribution coincides with the canonical distribution. Next we want to show that the formalism so far developed allows us to find an alternative postulate that is equivalent to the postulate of equal *a priori* probability. Let us express $\ln \mathcal{W}(n_r)$ in terms of the normalized distribution $p_r = n_r/\mathcal{N}$,

$$\ln \mathcal{W} = \mathcal{N} \ln \mathcal{N} - \sum_r n_r \ln n_r = -\mathcal{N} \sum_r p_r \ln p_r. \tag{7.16}$$

Here $\mathcal{W}$ is the number of configurations associated with the distribution p_r and $k \ln \mathcal{W}$ is therefore by definnition the entropy corresponding to that distribution. 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* (7.16). In fact, if the system is isolated, then p_r must satisfy the condition of being zero for all the configurations that are not allowed—i.e., for those configurations that correspond to the fixed energy. This implies that the sum in (7.16) is restricted to only the allowed configurations. The maximization of (7.16) and the normalization condition gives then

$$p_r = \frac{1}{\Omega} \tag{7.17}$$

where Ω is the number of allowed configurations. The distribution (7.17) coincides with the postulate of equal probability. If the system A can exchange energy with the other systems of ensemble, then the formalism that we have developed shows that the distribution that maximizes the entropy of the entire system under the conditions (7.1) and (7.2) is given by (7.15), which coincides with the canonical distribution. Note also that the maximization of (7.16) under conditions (7.1) and (7.2) is equivalent to the maximization of the quantity

$$\ln \mathcal{W} - \mathcal{N}\beta \sum p_r E_r = -\mathcal{N} \left(\sum_r p_r \ln p_r + \beta \sum_r p_r E_r \right), \tag{7.18}$$

which is equivalent to the minimization of the quantity $\sum p_r \ln p_r + \beta \sum_r p_r E_r$, which coincides with the free energy of a single system without further requirements. Namely, maximization of the total entropy under the condition (7.1) and (7.2) is equivalent to the minimization of the free energy of the system without conditions.

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

$$E_{\text{tot}} = E + E' \tag{8.1}$$

and number of particles

$$N_{\text{tot}} = N + N' \tag{8.2}$$

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

$$P(E,N) = \frac{\Omega(E,N)\Omega'(E',N')}{\Omega_{\rm tot}}, \tag{8.3}$$

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 $\bar{E}$ and $\bar{N}$ 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 $\bar{E}$ and $\bar{N}$. Since $P(E,N)$ is the equilibrium distribution, $\bar{E}$ and $\bar{N}$ are the mean values for the system A when in equilibrium.

The conditions that $\bar{E}$ and $\bar{N}$ 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),

$$\left.\frac{\partial \ln \Omega(E,N)}{\partial E}\right|_N = \left.\frac{\partial \ln \Omega'(E',N)}{\partial E'}\right|_{N'}. \tag{8.6}$$

Condition (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

$$\beta(E,N) = \left.\frac{\partial \ln \Omega(E,N)}{\partial E}\right|_N. \tag{8.8}$$

Condition (8.5) gives

$$\left.\frac{\partial \ln \Omega(E,N)}{\partial N}\right|_{E} = \left.\frac{\partial \ln \Omega'(E',N')}{\partial N'}\right|_{E'}. \tag{8.9}$$

Condition (8.9) 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. 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 6), we find

$$P_r = \frac{\Omega'(E',N')}{\Omega_{\text{tot}}}, \tag{8.13}$$

where

$$E_{\text{tot}} = E' + E_r \tag{8.14}$$

and

$$N_{\text{tot}} = N' + N_r. \tag{8.15}$$

Note the similarity between (8.13) and (8.3), with the difference being that here $\Omega(E_r, N_r) = 1$ since there is only one configuration that realizes configuration r.

For $E_r \ll E_{\text{tot}}$ and $N_r \ll N_{\text{tot}}$, we can epand $\ln P_r$ around $E_r = 0$ and $N_r = 0$,

$$\ln P_r = -\ln \Omega_{\text{tot}} + \ln \Omega'(E_{\text{tot}}, N_{\text{tot}}) - \beta' E_r + \mu'\beta' N_r + \cdots \tag{8.16}$$

where

$$\beta' = \left.\frac{\partial \ln \Omega'(E',N')}{\partial E'}\right|_{\substack{N'=N_{\rm tot}\\ E'=E_{\rm tot}}} \qquad -\mu'\beta' = \left.\frac{\partial \ln \Omega'(E',N')}{\partial N'}\right|_{\substack{N'=N_{\rm tot}\\ E'=E_{\rm tot}}} . \tag{8.17}$$

Since system A' is a reservoir, at equilibrium the number of particles N' and the energy E' will essentially coincide with $N_{\rm tot}$ and $E_{\rm tot}$. 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.,

$$\beta' = \beta \qquad \text{and} \qquad \mu' = \mu.$$

Following the arguments of Chapter 6 for the canonical distribution, we can neglect higher order terms in (8.13) and write

$$P_r = \frac{e^{-\beta E_r + \beta\mu N_r}}{\mathcal{Z}}, \tag{8.18}$$

where $\mathcal{Z}$ is a normalization constant called the grand canonical partition function. Imposing $\sum_r P_r = 1$, we find

$$\mathcal{Z} = \sum_N e^{\beta\mu N} \sum_r{}' e^{-\beta E_r}, \tag{8.19}$$

where the the first sum runs over all possible values of N and the second sum runs over all microscopic states r such that $N_r = N$.

Now $\mathcal{Z}$ can be written as

$$\mathcal{Z} = \sum_N e^{\beta\mu N} Z_N, \tag{8.20}$$

where

$$Z_N = \sum_r{}' e^{-\beta E_r}, \tag{8.21}$$

is the partition function of the canonical ensemble for N particles.

The grand canonical partition function has the properties that

$$\left(\frac{\partial \ln \mathcal{Z}}{\partial \beta\mu}\right)_\beta = \frac{\sum_r N_r e^{-\beta E_r + \beta\mu N_r}}{\mathcal{Z}} = \langle N \rangle, \tag{8.22}$$

and

$$\left(\frac{\partial^2 \ln \mathcal{Z}}{\partial(\beta\mu)^2}\right)_\beta = kT\left(\frac{\partial\langle N\rangle}{\partial\mu}\right)_T = \langle N^2\rangle - \langle N\rangle^2 \equiv \langle(\Delta N)^2\rangle, \tag{8.23}$$

where

$$\langle N^2\rangle = \sum_r \frac{N_r^2 e^{-\beta E_r + \beta\mu N_r}}{\mathcal{Z}}. \tag{8.24}$$

Thus the grand cononical partition function (8.20) can be used to calculate fluctuations. Equation (8.23) 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

$$\left(\frac{\partial\langle N\rangle}{\partial\mu}\right)_{V,T} = -\frac{\langle N^2\rangle}{V^2}\left(\frac{\partial V}{\partial P}\right)_{N,T}. \tag{8.25}$$

From (8.23) and (8.25),

$$\frac{\langle(\Delta N)^2\rangle}{\langle N\rangle^2} = -kT\frac{1}{V^2}\left(\frac{\partial V}{\partial P}\right)_{N,T}. \tag{8.26}$$

from which

$$\frac{\langle(\Delta\rho)^2\rangle}{\langle\rho\rangle^2} = \frac{kT}{\langle N\rangle}\left(\frac{\partial\langle\rho\rangle}{\partial P}\right)_{N,T}. \tag{8.27}$$

Here $\langle\rho\rangle \equiv \langle N\rangle/V$ and $\langle(\Delta\rho)^2\rangle$ is the density fluctuation.

Equation (8.27) 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 $(\partial\langle\rho\rangle/\partial P)_T$ represents the response function. Physically it gives the density variation due to an infinitessimal variation of the external pressure. Relation (8.27) 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 (8.25).

Differentiating the thermodynamic relation $G = N\mu$, we obtain

$$dG = \mu dN + N d\mu. \tag{8.28}$$

From (1.41) and (1.36) we also have

$$dG = \mu dN - SdT + VdP. \tag{8.29}$$

Combining (8.28) and (8.29)

$$Nd\mu = -SdT + VdP, \tag{8.30}$$

which gives

$$d\mu = vdP - sdT, \tag{8.31}$$

in which we have introduced the intensive variables $v \equiv V/N$ and $s \equiv S/N$. From (8.31)

$$\left(\frac{\partial \mu}{\partial P}\right)_T = v. \tag{8.32}$$

Using the mathematical relation (Appendix A)

$$\left(\frac{\partial \mu}{\partial P}\right)_T = \left(\frac{\partial \mu}{\partial v}\right)_T \left(\frac{\partial v}{\partial P}\right)_T, \tag{8.33}$$

it follows that

$$\left(\frac{\partial \mu}{\partial v}\right)_T = v \left(\frac{\partial P}{\partial v}\right)_T, \tag{8.34}$$

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 (8.34) can be written as

$$\left(\frac{\partial \mu}{\partial v}\right)_T = -\frac{N^2}{V} \left(\frac{\partial \mu}{\partial N}\right)_{T,V}. \tag{8.35}$$

Therefore

$$v \left(\frac{\partial P}{\partial v}\right)_T = -\frac{N^2}{V} \left(\frac{\partial \mu}{\partial N}\right)_{T,V}. \tag{8.36}$$

Since the left-hand side of (8.36) can be written as

$$v \left(\frac{\partial P}{\partial v}\right)_T = V \left(\frac{\partial P}{\partial V}\right)_{T,N}, \tag{8.37}$$

then (8.36) becomes

$$-\frac{N^2}{V} \left(\frac{\partial \mu}{\partial N}\right)_{T,V} = V \left(\frac{\partial P}{\partial V}\right)_{T,N}, \tag{8.38}$$

and

$$\left(\frac{\partial N}{\partial \mu}\right)_{T,V} = -\frac{N^2}{V^2} \left(\frac{\partial V}{\partial P}\right)_{T,N}, \tag{8.39}$$

which coincides with (8.25) 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 (8.20),

$$\mathcal{Z} = \sum_N e^{\beta\mu N - \beta A(N,\beta)}, \tag{8.40}$$

where

$$A(N,\beta) = -kT \ln Z(N,\beta) \tag{8.41}$$

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 (1.43).

We first will show that the particle number distribution P_N is extremely peaked around its most probable value $\bar{N}$, and becomes a delta function in the thermodynamic limit

$$P_N = \frac{e^{-\beta[-\mu N + A(N,\beta)]}}{\mathcal{Z}}. \tag{8.42}$$

We can expand $\ln P_N$ around its maximum value $\bar{N}$ or, equivalently, expand the exponent $-\mu N + A(N,\beta)$ around its minimum

$$-\mu N + A(N,\beta) = -\mu\bar{N} + A(\bar{N},\beta) + \frac{1}{2}\left(\frac{\partial^2 A}{\partial N^2}\right)_{N=\bar{N}} (N-\bar{N})^2 + \cdots. \tag{8.43}$$

The condition for the minimum gives

$$\left(\frac{\partial A}{\partial N}\right)_{N=\bar{N}} = \mu, \tag{8.44}$$

which gives the thermodynamic relation between free energy and chemical potential. The second derivative of F gives

$$\left(\frac{\partial^2 A}{\partial N^2}\right)_{N=\bar{N}} = \left(\frac{\partial \mu}{\partial N}\right)_{N=\bar{N}}. \tag{8.45}$$

Therefore the particle number probability distribution is

$$P_N = \frac{e^{-\beta[-\mu\bar{N} + A(\bar{N},\beta)]}}{\mathcal{Z}} e^{(N-\bar{N})^2/2\Delta^2} \tag{8.46}$$

where, from (8.39), the particle number fluctuation is

$$\Delta^2 = \frac{\bar{N}^2}{V^2} \left(\frac{\partial V}{\partial P} \right)_{T,\bar{N}} . \tag{8.47}$$

Now Δ^2 is proportional to volume V in the thermodynamic limit,

$$\frac{\Delta}{\langle \bar{N} \rangle} \propto \frac{1}{\sqrt{\bar{N}}}. \tag{8.48}$$

Therefore the probability distribution becomes a delta function in the density variable $\rho \equiv N/V$, when N and $V \to \infty$. Hence, in the thermodynamic limit, the only macroscopic state that is realized is the one with density $\rho = \bar{\rho}$, and the grand canonical ensemble becomes equivalent to the canonical ensemble.

Finally, the grand partition function is

$$\mathcal{Z} = \exp[\beta(\mu \bar{N} - A(\bar{N}, \beta))] \sum_N \exp \left[-\frac{1}{2} \beta \left(\frac{\partial^2 A}{\partial N^2} \right)_{N=\bar{N}} (N - \bar{N})^2 \right], \tag{8.49}$$

from which we find (see Chapter 6)

$$\ln \mathcal{Z} = \beta[\mu \bar{N} - A(\bar{N}, \beta)] \tag{8.50}$$

when we neglect terms of $\mathcal{O}(\ln N)$. Finally, recalling that

$$A(\bar{N}, \beta) = \bar{E} - TS, \tag{8.51}$$

and that

$$G = \mu \bar{N} = \bar{E} - TS + PV, \tag{8.52}$$

we find from (8.50),

$$-kT \ln \mathcal{Z} = -PV, \tag{8.53}$$

which is the desired relation.

Chapter 9

Critical Phenomena

Thus far we have considered only those phenomena that do not show smooth behavior as a function of thermodynamic variables. In this chapter we consider phenomena that exhibit sharp changes as a function of thermodynamic variables, e.g., the sudden density change that occurs when 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. 9), starting with the equation of state, which indicates that, at equilibrium, the pressure P, the density ρ, and the temperature T of a one-component homogeneous system satisfies the functional relation $f(P, \rho, T) = 0$. This equation of state defines a surface in a three-dimensional space with coordinates P, ρ, and T. Projecting the equation onto a plane P, T 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, ρ_c, and T_c are called critical pressure, critical density, and critical temperature. This means that it is possible to change the liquid into

Figure 9.1: This is Fig. 9.1.

Figure 9.2: This is Fig. 9.2.

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, ρ (Fig. 9). At a sufficiently high temperature, we expect the fluid to follow the equation of state for ideal gases, $P = k_B \rho T$, which, for any fixed T, is characterized by a straight line. As the temperature decreases, the effect of the attractive interaction is felt and the curve shows a departure from the straight line until, for $T = T_c$, the curve exhibits an inflection point at $\rho = \rho_c$. For T below T_c there is a phase separation between the gas and the liquid. For any value of the pressure there are two possible density values, ρ_G and ρ_L, corresponding to the coexistence of the gas and the liquid. As function of T, ρ_G and ρ_L define a curve that joins at ρ_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,

$$\rho_L - \rho_G \to 0 \qquad \text{as} \qquad T \to T_c^-, \tag{9.1}$$

so the two phases become indistinguishable. Phenomenologically, we discover that for $T = T_c$ the curve at ρ_c has a flex. This imples that the compressibility

$$\chi_T \equiv \left(\frac{\partial \rho}{\partial P}\right)_T \to \infty \qquad \text{as} \qquad T \to T_c^+, \tag{9.2}$$

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 we can relate the density fluctuation to the compressibility,

$$\frac{\langle \rho^2 \rangle - \langle \rho \rangle^2}{\langle \rho \rangle^2} = \frac{k_B T}{N} \chi_T. \tag{9.3}$$

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 beaker 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.

The intensity of the light scattered can be related to the density-density correlation function $g(\vec{x}-\vec{x}')$, defined as

$$g(\vec{x}-\vec{x}') \equiv \langle (\rho(\vec{x}) - \langle \rho(\vec{x}) \rangle)(\rho(\vec{x}') - \langle \rho(\vec{x}') \rangle) \rangle, \tag{9.4}$$

where $\rho(\vec{x})$ is the particle density at position $\vec{x}$. 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 sytem is translationally invariant: $\rho(x)$ does not depend on the position $\vec{x}$ and $\langle \rho(\vec{x}) \rangle = \rho$ (the average density). For the same reason $g(\vec{x}-\vec{x}')$ depends only on the distance between $\vec{x}$ and $\vec{x}'$.

The density-density pair correlation function measures the correlation between the density fluctuation at x and 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 x is independent of the density at point x', namely

$$g(\vec{x}-\vec{x}') \equiv \langle (\rho(x) - \rho)(\rho(x') - \rho) \rangle \simeq \langle \rho(x) - \rho \rangle \langle \rho(x') - \rho \rangle = 0, \tag{9.5}$$

since $\langle \rho(x) \rangle = \langle \rho(x') \rangle = \rho$. For lower temperatures one cannot neglect interparticle interactions and the factorization in (9.5) is not allowed. The more $g(\vec{x}-\vec{x}')$ differs from zero, the larger the correlation between the density fluctuations at $\vec{x}$ and $\vec{x}'$. The distance ξ within which $g(\vec{r})$ differs from zero represents the linear dimension of the droplet (fluctuation). More precisely, ξ can be defined as

$$\xi^2 \equiv \frac{\int g(\vec{r}) r^2 d\vec{r}}{\int g(\vec{r}) d\vec{r}}, \tag{9.6}$$

where the integral extends over the entire volume of the system.

Note that $g(\vec{r})$ is related to the density fluctuation and therefore diverges as $T \to T_c$. In fact,

$$\int\int g(\vec{x}-\vec{x}')dxdx' = V\int g(\vec{r})d\vec{r} = \langle (N-\langle N\rangle)^2\rangle = \langle N^2\rangle - \langle N\rangle^2. \quad (9.7)$$

Therefore, in view of (9.3),

$$\int g(\vec{r})d\vec{r} = V(\langle\rho^2\rangle - \langle\rho\rangle^2) = k_BT\langle\rho\rangle\chi_T. \quad (9.8)$$

Since χ_T diverges, $\int g(\vec{r})d\vec{r}$ also diverges.

Experimental it is also found that ξ diverges as T approaches T_c. How can ξ be measured experimentally? The standard theory of scattering relates the scattered intensity of a monoatom beam to the Fourier transform of $g(\vec{r})$,

$$\tilde{g}(\vec{q}) = \int g(\vec{r})e^{i\vec{q}\cdot\vec{r}}d\vec{r}. \quad (9.9)$$

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 $\tilde{g}(\vec{q})$ 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},

$$\xi^{-2} \propto \frac{\int I(\vec{q})q^2d\vec{q}}{\int I(\vec{q})d\vec{q}}. \quad (9.10)$$

It is usually found that for large r

$$g(r) \sim \frac{e^{-r/\xi}}{r^\mu}, \quad (9.11)$$

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.

Let us mention for completeness the behavior of the specific heat near the critical point. Is is found experimentally that the specific heat at constant volume C_V also exhibiits 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 the energy fluctuations are very large, although smaller than the density fluctuations.

Ferromagnetic Transition

Other systems exhibit a phenomenology very similar to the liquid-gas transition. A ferromagnetic system has the property that at high temperatures it behaves as a ferromagnet, i.e., under the influence of an external magnetic field it exhibits a macroscopic magnetization. When this external field approaches zero, the magnetization per particle m also goes to zero (see Chapter IV). However, below a critical temperature T_c (called the Curie temperature), even when there is no external magnetic field present, the system exhibits 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. 3) 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. 4), we have H as a function of m for a fixed temperature T. For high temperatures the system behaves as a non-interacting spin system. From Eq. XX of Chapter X we expect $m = \tan(\beta H)$, 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 $\chi_T = (\partial m / \partial H)$. The specific heat at constant H, C_H diverges at the critical point.

From the fluctuation dissipation relation, $\chi_T \propto \langle m^2 \rangle - \langle m \rangle^2$. 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

$$g_{ij} \equiv \langle (\vec{s}_i - \langle \vec{s}_i \rangle)(\vec{s}_j - \langle \vec{s}_j \rangle) \rangle, \tag{9.12}$$

where $\vec{s}_i$ is the value of the spin at site i. The data share a phenomenology similar to the liquid-gas transition, namely that the correlation length, roughly the size of the droplets, diverges as the critical point is approached. In analogy with (9.7), it follows from (9.12) that

$$\sum_{i,j} g_{ij} = \langle \vec{M}^2 \rangle - \langle \vec{M} \rangle^2, \tag{9.13}$$

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. The same is true for other systems near their respective critical points. Two other examples are

- the transition from a normal fluid with a finite viscosity to a superfluid with zero viscosity, which occurs in liquid helium at extremely low temperatures, and
- the transition from a normal conductor with a finite resistivity to a superconductor with zero resistivity, which occurs in some systems at low temperatures.

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 $C_V \to \infty$, 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.

9.1 Critical Exponents

In the previous section we saw 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

$$m = A\epsilon^{\beta}(1 + B\epsilon^{\Delta_1} + C\epsilon^{\Delta_2} + \cdots), \tag{9.14}$$

where

$$\epsilon \equiv \left| \frac{T - T_c}{T_c} \right|, \tag{9.15}$$

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 ϵ. Very close to the critical point ($\epsilon \ll 1$) the term in parenthesis can be well-approximated by 1 and the magnetization behaves asymptotically as

$$m \simeq A\epsilon^{\beta}. \tag{9.16}$$

More generally, if a function $f(\epsilon)$ vanishes or diverges in $\epsilon = 0$, we define the critical exponent λ as

$$\lambda \equiv \lim_{\epsilon \to 0} \frac{\ln f(\epsilon)}{\ln \epsilon}. \tag{9.17}$$

Equation (9.17) implies that, close to $\epsilon = 0$, $f(\epsilon)$ can be well-approximated by $f(\epsilon) \sim A\epsilon^{\lambda}$. If $\lambda > 0$, $f(\epsilon)$ vanishes, while if $\lambda < 0$, $f(\epsilon)$ diverges. For a function of the form in Eq. (9.14), the critical exponent, defined using definition (9.17), 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 left and right. Therefore close to the critical point we write simply

$$M \sim A\epsilon^{\beta}, \qquad \chi \sim B_{\pm}\epsilon^{-\gamma}, \qquad C_V \sim D_{\pm}\epsilon^{-\alpha}, \qquad \xi \sim E_{\pm}\epsilon^{-\nu}, \tag{9.18}$$

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, at T_c for large values of r,

$$g(r) \sim \frac{1}{r^{d-2+\eta}}, \tag{9.19}$$

where d is the dimensionality of the system and η a 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.

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 the next section we will study such a model as it is applied to the paramagnet-ferromagnet transition.

9.2 Ising Model

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

$$\mathcal{H} = -\mu H \sum_{i=1}^{N} S_i, \tag{9.20}$$

where $S_i = \pm 1$ are the components of the spin i along the direction of the field. It was shown in Chapter XX 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 (9.20) neglects all the interactions among the spins. In the ferromagnetic Ising model, an interaction term $\mathcal{H}_{\text{int}}$ is added to Hamiltonian (9.20), i.e.,

$$\mathcal{H}_{\text{int}} = -J \sum_{\langle ij \rangle} S_i S_j, \tag{9.21}$$

where $J > 0$ is the strength of the interaction and the sum extends over all nearest neighbors. 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 (9.21) may favor the alignment of the spins and therefore may induce the phenomenon of spontaneous magnetization.

To calculate thermodynamic properties, we first calculate the partition function,

$$Z = \sum_{\{S_1\}} \exp \left[\beta H \sum_i S_i + \beta J \sum_{\langle ij \rangle} S_i S_j \right], \tag{9.22}$$

where the sum is over all spin configurations, and for simplicity we have chosen $\mu = 1$.

One of the features of the Ising model is that it is extremely versatile, e.g., it can be mapped onto the lattice gas model that describes the liquid-gas transition. To see this, we begin with a Hamiltonian for a simple fluid of the form

$$\mathcal{H} = \sum_{i=1}^{3N} \frac{p_i^2}{2m} + \sum_{i<j} U(|\vec{r}_i - \vec{r}_j|), \tag{9.23}$$

where the particles interact via a two-body potential. In the grand canonical ensemble, the grand partition function is

$$\mathcal{Z} = \sum_N e^{\beta\mu N} Z_N, \tag{9.24}$$

where Z_N is the partition function with N particles fixed. By integrating the momentum variables in Z_N and considering that

$$\lambda \equiv \int e^{-\beta(p^2/2m)} d\vec{p} = (2\pi mkT)^{3/2}, \tag{9.25}$$

we can write

$$\mathcal{Z} = \sum_N e^{\beta\mu_{\text{eff}}N} \frac{1}{N!} \int \exp\left[-\beta \sum_{1<j} U(|\vec{r}_i - \vec{r}_j|)\right] d\vec{r}_1 \ldots d\vec{r}_N, \tag{9.26}$$

where $\mu_{\text{eff}} = \mu + kT \ln \lambda$.

Now we consider a simplification of (9.26) 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, (Fig. xx)

$$U(\vec{r}_i - \vec{r}_j) = \begin{cases} \infty & \text{if } \vec{r}_i = \vec{r}_j \\ -\epsilon & \text{if } \vec{r}_i \text{ and } \vec{r}_j \text{ are nearest neighbors} \\ 0 & \text{otherwise.} \end{cases} \tag{9.27}$$

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. Since the particles are indistinguishable, two configurations that differ by the exchange of two particles are considered indistinguishable and therefore counted only once.

Because of the hard core repulsion, two particles cannot occupy the same cell. The energy of a given configuration can be written $-\epsilon \sum_{\langle ij \rangle} n_i n_j$ and the integral in (9.25) is therefore replaced by

$$\frac{1}{N!} \int \exp\left[-\beta \sum_{\langle ij \rangle} U(|\vec{r}_i - \vec{r}_j|)\right] d\vec{r}_1 \cdots d\vec{r}_N = \sum_{\{n_i\}}{}^{\star} \exp\left[\beta\epsilon \sum_{\langle ij \rangle} n_i n_j\right]. \tag{9.28}$$

The sum is over all configurations and the asterisk indicates that the configuration must satisfy the condition $\sum_i n_i = N$, so $\sum_N \sum_{\{n_i\}}{}^{\star} = \sum_{\{n_i\}}$.

Thus from (9.26) and (9.28) follows

$$Z = \sum_{\{n_i\}} \exp\left[\beta\mu_{\text{eff}} \sum_i n_i + \beta\epsilon \sum_{\langle ij\rangle} n_i n_j\right], \tag{9.29}$$

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

$$S_i = 2n_i - 1, \tag{9.30}$$

where $n_i = 0, 1$ for $S_i = +1, -1$. If we use (9.30) in (9.22), the Ising partition function Z_I becomes

$$Z_I\left(\frac{J}{kT}, \frac{H}{kT}\right) = \sum_{\{n_i\}} \exp\left[\beta\mu_{\text{eff}} \sum_i n_i + \beta\epsilon \sum_{\langle ij\rangle} n_i n_j + W_0\right], \tag{9.31}$$

where

$$\begin{aligned} \mu_{\text{eff}} &= 2H - 2Jz \\ \epsilon &= 4J \\ W_0 &= \beta(JN\frac{z}{2} - HN), \end{aligned} \tag{9.32}$$

and z is the coordination number, namely the number of nearest-neighbor sites to a given site.

From (9.31) we see that the Ising and lattice gas models are equivalent,

$$Z_I\left(\frac{J}{kT}, \frac{H}{kT}\right) = Z_{\text{LG}}\left(\frac{\epsilon}{kT}, \frac{\mu_{\text{eff}}}{kT}\right) e^{W_0}, \tag{9.33}$$

where ϵ, μ_{eff}, and W_0 are related to J and H through (9.32).

9.3 Broken Symmetry

Now we will show, using a symmetry argument, that when the external field is zero the average magnetization is also zero. 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 mangetization below a critical temperature. In fact, 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. In fact, most thermodynamic states we observe contain a symmetry not contained in the microscopic Hamiltonian that describes the system. When this happens, it is usually said that the system exhibits a *spontaneous broken symmetry.* Illustrating the origin of this spontaneous broken symmetry using the Ising model, helps us understand the mechanism behind the general occurrence of spontaneous broken symmetry.

The Hamiltonian of the Ising model in a zero field is given by (9.21), 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

$$m \equiv \frac{1}{N} \sum_i m_i, \tag{9.34}$$

with

$$m_i \equiv \frac{1}{Z} \sum_{\{S_i\}} S_i e^{-\beta \mathcal{H}\{S_i\}}. \tag{9.35}$$

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 (9.35) and using the symmetry of the Hamiltonian

$$m_i = -\frac{1}{Z} \sum_{\{S'_i\}} S'_i e^{-\beta \mathcal{H}\{S'_i\}} = -\frac{1}{Z} \sum_{\{S_i\}} S_i e^{-\beta \mathcal{H}\{S_i\}} = -m_i. \tag{9.36}$$

In conclusion, $m_i = -m_i$ implies $m_i = 0$.

In order to find a value for $m \neq 0$ we must break the symmetry by introducing a field H in the hamiltonian and calculate the magnetization $m(H, T, N)$. By taking first the thermodynamic limit $N \to \infty$ and then the $H \to 0$ limit it may happen that $\lim_{H \to 0} \lim_{N \to \infty} m(H, T, N) \neq 0$. If we take $H \to 0$ first and then $N \to \infty$ the result will be always zero, i.e.

$$\lim_{N \to \infty} \lim_{H \to 0} m(H, T, N) = 0. \tag{9.37}$$

This result follows from the consideration that $m(H, N)$ for finite N is an analytic function given by a finite sum of analytic functions; in Eq. (9.35) the number of terms is finite. Therefore the limit $H \to 0$ is equal to the function calculated at $H = 0$, i.e.,

$$\lim_{H\to 0} m(H,T,N) = m(0,T,N) = 0.$$

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 nonanalytic below some temperature and therefore the second limit $H \to 0$ does not necessarily coincide with the value calculated at $H = 0$.

Thus we say that there is a spontaneous broken symmetry if it happens that

$$\lim_{H\to 0}\lim_{N\to\infty} m(H,T,N) \neq 0 \tag{9.38}$$

for some range of the temperature.

Now let us see in more detail the mechanism that gives rise to a spontaneous broken symmetry (9.38). To fix the ideas, we will consider the Ising model, but the considerations are rather general and their validity is also 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.,

$$P(M,H,T,N) = \frac{1}{Z}\sum_{\{S_i\}}^{*} e^{-\beta\mathcal{H}} = \frac{1}{Z}e^{\beta HM-\beta A(M,T)}, \tag{9.39}$$

where the star means that the sum is over all configurations such that $\sum_{i=1}^{N} S_i = M$ and

$$\exp[-\beta A(M,T)] = \sum_{\{S_i\}}^{*} \exp\left[\beta J\sum_{\langle ij\rangle} S_i S_j\right]. \tag{9.40}$$

The partition function can be written as

$$Z = \sum_{M} \exp[\beta HM - \beta A(M,T)]. \tag{9.41}$$

Following the standard procedure in the canonical ensemble, the sum is dominated by the maximum of $HM - A(M,T)$ which satisfies the equation $H = (\partial A/\partial M)_T$. This value is a maximum for the probability (9.39) and a minimum for the free energy $A(M,T) - HM$.

Consider first the case $H = 0$. Due to the symmetry $A(M,T) = A(-M,T)$, 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, the free energy is dominated by the energy that has two minima, one at $+\overline{M}$ and one at $-\overline{M}$. Therefore we expect two minima in the free energy (Fig. xx) 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, in the limit $N \to \infty$, the probability distribution $P(m, T)$ in the magnetization per spin m, tends to the sum of two delta functions for $T < T_c$

$$P(m, T) = \frac{1}{2}[\delta(m - \overline{m}(T)) + \delta(m + \overline{m}(T))], \tag{9.42}$$

and to a single delta function for $T > T_c$

$$P(m, T) = \delta(m). \tag{9.43}$$

When we add a magnetic field, the free energy $\tilde{F} \equiv F(M, T) - HM$ 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 delta function that peaks around a value of $\overline{m}(H, T)$ for high T, while for low T (no matter how small H is) the distribution approaches a delta function peaked around the largest maximum and the other relative maximum is suppressed (see Appendix B). For high T the magnetization approaches zero as $H \to 0$, while for low T the magnetization approaches $\overline{m}(0, T) > 0$, 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 $P(m, T)$, and (ii) because even a very small field gives rise to only one delta function in the limit $N \to \infty$.

[DISCUSS THE CASE IN WHICH $H \to 0$ FIRST AND THEN $N \to \infty$.]

On the other hand, if N is fixed in the limit $H \to 0^+$, the distribution does not become an exact delta 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 $-\overline{m}$ and $+\overline{m}$; however the system is trapped for a long time in a state corresponding to a magnetization $\overline{m}$. If we evaluate the time τ in which the system is trapped, we realize that the system, to pass from the state with magnetization $\overline{m}$ to the state with magnetization $-\overline{m}$, 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 $\sim e^{-R^{d-1}}$. 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's 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 $\overline{m}$.

Next we show that in the limit $N \to \infty$ the distribution $P(m, H, T, N)$ gives rise to a delta function peaked in the highest maximum. Let us consider H fixed and T fixed and let us drop the explicit dependence on these variables

$$P(m, N) = \frac{e^{-Nf(m)}}{\int e^{-Nf(m)} dm}. \tag{9.44}$$

Here we have substituted an integral for the sum (see Chapter XX). If $f(m)$ has only one minimum at $\overline{m}$ (high T) we can expand $f(m)$ around such a minimum

$$\exp[-Nf(m)] = \exp\left[-Nf(\overline{m}) - \frac{1}{2}N\lambda(m-\overline{m})^2\right], \tag{9.45}$$

where

$$\lambda = -\left(\frac{\partial^2 f}{\partial m^2}\right)_{m=\overline{m}} .$$

Therefore, from (9.44),

$$P(m,N) = e^{-(1/2)N\lambda(m-\overline{m})^2} \Big/ \int e^{-(1/2)N\lambda(m-\overline{m})^2} dm \ , \tag{9.46}$$

which in the limit $N \to \infty$ tends to a delta 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 develop around the two minima and write

$$\exp[-Nf(m)] = \exp\left[-Nf(m_1) - \frac{N}{2}\lambda_1(m-m_1)^2\right] + \exp\left[-Nf(m_2) - \frac{N}{2}\lambda_2(m-m_2)^2\right], \tag{9.47}$$

with

$$\lambda_i = \left|\left(\frac{\partial^2 f}{\partial m^2}\right)_{m=m_i}\right| \qquad i = 1, 2.$$

Using (9.47), we can evaluate the integral

$$\int e^{-Nf(m)} dm = \sqrt{\frac{\pi}{N\lambda_1}} e^{-Nf(m_1)} + \sqrt{\frac{\pi}{N\lambda_2}} e^{-Nf(m_2)} \tag{9.48}$$

Since $f(m_1) < f(m_2)$, in the limit $N \to \infty$ the second term can be neglected. From (9.44), (9.47) and (9.48)

$$P(m,N) = \frac{\sqrt{N\lambda_1} e^{-(1/2)N\lambda_1(m-m_1)^2}}{\sqrt{\pi}} + \frac{\sqrt{N\lambda_1} e^{-N[f(m_2)-f(m_1)]} e^{-(1/2)N\lambda_2(m-m_2)^2}}{\sqrt{\pi}} \tag{9.49}$$

In the limit $N \to \infty$, the second term can be neglected and the distribution tends to a delta function centered at m_1.

9.4 Mean-Field Theories

Mean-field theories offer a very simple and powerful theory of phase transitions. Requiring minimal assumptions they explain the origin of the two minima introduced in the previous section.

We have shown how the partition function can be written for an Ising model,

$$Z = \int e^{-\beta N[f(m,T)-Hm]} dm, \tag{9.50}$$

where $\tilde{f} = f(m,T) - Hm$ is the free energy, which has the symmetry property $f(m,T) = f(-m,T)$. The partition function of any system that has the same symmetry properties can be written in the form (9.50), 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 $\tilde{f}$ for small values of m and to stop at the 4th order,

$$\tilde{f} = f(0,t) + a(T)m^2 + b(T)m^4 - Hm, \tag{9.51}$$

where we have used the fact that $f(m,T)$ is even in m—therefore 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 $T - T_c$

$$a(T) = a_0(T - T_c) \qquad\qquad b(T) = b_0, \tag{9.52}$$

with $a(T)$ and $b(T)$ constants that we assume to be positive. Inserting these values in (9.51), and plotting the free energy $\tilde{f}$ as a function of m, we find one minimum for $T > T_c$ and two minima for $T < T_c$ (Fig. xx). The minimum of the free energy gives the mean value. From (9.51), equating the first derivative to zero gives

$$m[2a_0(T - T_c) + 4b_0 m^2] = H, \tag{9.53}$$

which represents the equation of state relating H, m, and T. For $H = 0$, (9.53) gives

$$m = \begin{cases} 0 & \text{if } T > T_c \\ \\ \pm\sqrt{\frac{1}{2}\frac{a_0}{b_0}(T_c - T)} & \text{if } T < T_c. \end{cases} \tag{9.54}$$

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 an exponent $\beta = 1/2$.

The susceptibility $\chi_T = (\partial m/\partial H)_T$ can also be calculated from the equation of state (9.53)

$$\chi^{-1} = \left(\frac{\partial H}{\partial m}\right)_T = 2a_0(T - T_c) + 12b_0 m^2, \tag{9.55}$$

where m is also obtained from the equation of state. In the particular case $H = 0$, substituting solution (9.54) for m for $T > T_c$ and $T < T_c$ one has

$$\chi = \begin{cases} (1/2a_0)[1/(T - T_c)] & \text{if } T > T_c \\ \\ (1/4a_0)[1/(T_c - T)] & \text{if } T < T_c, \end{cases} \tag{9.56}$$

which predicts an exponent $\gamma = 1$. Note that the critical exponents above and below T_c are equal. Further, we see $A_+ = 2A_-$.

The specific heat C_H can easily be calculated from the free energy. The result for $H = 0$ gives a jump $C_H(T_c^+) - C_H(T_c^-) = a_0^2/2b_0$ with exponents $\alpha = \alpha' = 0$.

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.

While the exponents for 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. If we assume only that the free energy is analytic, then we get results that are not even qualitatively correct. This warns us that it is important in every physical problem to assume analyticity in the right quantities. 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, and 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.

9.5 Mean-Field Theory: The Weiss Approximation

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-consitent field due to the presence of the other $N-1$ electrons.

We apply the Weiss theory to the Ising model in a field

$$\mathcal{H} = -J \sum_{\langle ij \rangle} S_i S_j - h \sum_i S_i. \tag{9.57}$$

The key idea is to substitute the variable S_j with the average value $\langle S_j \rangle$. Substituting in (9.57), we find

$$\mathcal{H} = -(mJz + H) \sum_i S_i, \tag{9.58}$$

where z is the coordination number—the number of nearest-neighbor spins of spin i. Here $m \equiv \langle S_i \rangle$ needs to be self-consistently calculated using the Hamiltonian (9.58). Note that, because the Hamiltonian is invariant under translation, m does not depend on site i. To go from (9.57) to (9.58), we add and subtract the average magnetization $\langle s_i \rangle = m$ to each spin variable s_i in (9.57),

$$s_i = s_i - m + m. \tag{9.59}$$

Hamiltonian (9.57) can then be written

$$\mathcal{H} = -(Jmz + H) \sum_i s_i + Jm^2 \frac{Nz}{2} - J \sum_{\langle ij \rangle} (s_i - m)(s_j - m). \tag{9.60}$$

Hamiltonian (9.60) is identical to Hamiltonian (9.57). However, if we neglect the last term, which represents the short-range fluctuation, we obtain the mean-field approximation

$$\mathcal{H} = -H_{\text{eff}} \sum_i s_i + W_1, \tag{9.61}$$

where $H_{\text{eff}} = mzJ + H$ and $W_1 \equiv Jm^2N(z/2)$.

If we disregard the constant W_1, which is irrelevant to the calculation of average quantities, Hamiltonian (9.61) is identical to Hamiltonian (9.57). We note that the mean-field approximation has replaced the original Hamiltonian (9.57) of N interacting spins by a new Hamiltonian (9.61) of N independent spins interacting with an effective external field H_{eff} that depends on m, which must be self-consistently calculated. To do this we can use the result in Chapter 4 that applies an external field to a system of non-interacting spins in an external field, i.e.,

$$m = \tan \beta H_{\text{eff}} = \tan \beta (Jzm + H). \tag{9.62}$$

For $H = 0$, (9.62) becomes

$$m = \tan(\beta Jzm), \tag{9.63}$$

which 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 $y = \tan \beta zm$ has at the origin a slope

$$\left.\frac{dy}{dm}\right|_{m=0} = \beta Jz. \tag{9.64}$$

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

$$kT_c = Jz. \tag{9.65}$$

We are now able to calculate the critical exponents. We start by rewriting (9.62) as

$$m = \tanh(\beta H_{\text{eff}}) = \frac{e^{\beta H_{\text{eff}}} - e^{-\beta H_{\text{eff}}}}{e^{\beta H_{\text{eff}}} + e^{-\beta H_{\text{eff}}}}, \tag{9.66}$$

from which

$$\beta H_{\text{eff}} = \tanh^{-1} m = \frac{1}{2} \ln \frac{1+m}{1-m}. \tag{9.67}$$

Expanding near $m = 0$ up to the third order in m and rearranging, we find

$$H = m\left[(kT - Jz)\, m + \frac{kT}{3} m^3\right]. \tag{9.68}$$

This is the same equation found in Landau's theory, but now the coefficients are explicitly known:

$$a(T) = 1 - \frac{Jz}{kT} \qquad \text{and} \qquad b(T) = \frac{1}{3}\left(\frac{zJ}{kT}\right)^3 . \tag{9.69}$$

Consistent with Landau's theory, $a(T)$ is zero at $T_c = Jz/k$. To lowest order in $T - T_c$,

$$a(T) = \frac{(T - T_c)}{T_c} \qquad \text{and} \qquad b(T_c) = \frac{1}{3}. \tag{9.70}$$

The critical exponents are therefore the same as in the Landau theory, i.e., $\beta = 1/2$, $\gamma = 1$, and $\alpha = 0$.

Finally, the free energy can be calculated as

$$f = -\frac{1}{2}kTJzm^2 - kT \ln\left(e^{\beta H_{\text{eff}}} + e^{-\beta H_{\text{eff}}}\right), \tag{9.71}$$

where m is given by the self-consistent equation (9.66). Alternatively, one could have derived the self-consistent equation by minimizing the free energy (9.71) with respect to m, as can be easily checked. Note that the free energy (9.71) is an analytic function at $m = 0$. Consequently, Landau's theory can be applied to the approximated model (9.61). That is why the Weiss approximation gives the same critical exponents as the Landau theory.

There are many way to improve the Weiss mean-field result. 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.

Improving the theory so that it can predict exponents other than the mean-field exponent proved to be a difficult problem. Significant breakthroughs were made at the beginning of the 1970s, when K. Wilson formulated renormalization group theory.

[Problem: show that an Ising model in which all the spins interact equally well with one another,

$$H = -\frac{1}{N}\sum_{ij} s_i s_j - H\sum_i s_i, \tag{9.72}$$

can be solved exactly and that the solution coincides with the Weiss mean-field solution.]

9.6 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 $g(r)$ for a fluid, but the procedure will also be valid for spin systems. Remember that $g(r)$ measures the correlation between two points at a distance 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 distance r. The range within which the effect is felt, i.e., the range within which $g(r) \neq 0$, is called the correlation length ξ and has been precisely defined in Eq. (xx). 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 [see Eq. (xx)]. Therefore if we consider the Fourier transform, $\tilde{g}(\vec{k}) = \int g(\vec{r})e^{\vec{k}\cdot\vec{r}}d\vec{r}$, for $k = 0$, $\tilde{g}(0) = \int g(\vec{r})d\vec{r}$ diverges at T_c. Therefore $\tilde{g}(k)$ is not an analytic functin at $T = T_c$ and $k = 0$. We can never develop a theory that assumes $\tilde{g}(k)$ is an analytic function, and thus this cannot help us find the desired divergence, even qualitatively.

We introduce another quantity, the direct pair correlation function, which is defined by

$$g(\vec{r}) \equiv C(\vec{r}) + \int C(\vec{r} - \vec{r}')g(\vec{r}')d\vec{r}'. \tag{9.73}$$

Taking the Fourier transform of (9.73), we have

$$\tilde{g}(\vec{k}) = \tilde{C}(\vec{k}) + C(\vec{k})\tilde{g}(\vec{k}), \tag{9.74}$$

from which

$$\tilde{C}(\vec{k}) = \frac{\tilde{g}(\vec{k})}{1 + \tilde{g}(\vec{k})}. \tag{9.75}$$

So given the pair correlation function $\tilde{g}(\vec{k})$, the direct pair correlation function $\tilde{C}(\vec{k})$ is uniquely defined by (9.75). From (9.74) we can also express $\tilde{g}(\vec{k})$ as a function of $\tilde{C}(\vec{k})$,

$$\tilde{g}(\vec{k}) = \frac{\tilde{C}(\vec{k})}{1 - \tilde{C}(\vec{k})}. \tag{9.76}$$

From (9.76) we note that if $\tilde{C}(0)$ at T_c equals 1, $\tilde{g}(0)$ diverges and $k = 0$. Therefore $\tilde{C}(\vec{k})$ can be a well-behaved function at $T = T_c$, even if $\tilde{g}(\vec{k})$ is not.

Before we proceed to the evaluation of $\tilde{g}(k)$, we give a physical interpretation to the direct pair correlation function $C(\vec{r})$. From (9.73) we can perturbatively solve the integral equation as

$$g(\vec{r}) = C(\vec{r}) + \int C(\vec{r}_1)C(\vec{r} - \vec{r}_1)d\vec{r}_1 + \int C(\vec{r}_1)C(\vec{r}_2 - \vec{r}_1)C(\vec{r} - r_2)d\vec{r}_2 d\vec{r}_1 + \cdots. \tag{9.77}$$

Graphically, this series can be expressed as

The first term $C(\vec{r})$ can be interpreted as the contribution to $C(\vec{r})$ 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 $\vec{0}, \vec{r}$ are corelated by a direct correlation that propagates from 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 correlation.

We now proceed as in the Landau theory and expand $\tilde{C}(k)$ as a power of k^2 (since $g(r)$ 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,

$$\tilde{C}(\vec{k}, T) = \tilde{C}(0, T) + B(T)k^2 + \cdots, \tag{9.78}$$

where we have explicitely introduced the dependence on the temperature. From (9.76) it follows at T_c that $\tilde{C}(0, T_c) = 1$. We assume analyticity near T_c, so

$$\tilde{C}(0, T) = 1 + A_0(T - T_c) \qquad \text{and} \qquad B(T) = B_0. \tag{9.79}$$

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 (9.78).

In conclusion, from (9.76), (9.78), and (9.79) we can write to the lowest order in k^2 and $T - T_c$,

$$\tilde{g}(k, T) = \frac{D}{\xi^{-2} + k^2}, \tag{9.80}$$

where

$$D = -B_0^{-1}, \qquad \xi^{-2} = \xi_0^{-2}\frac{(T - T_c)}{T_c} \qquad \text{and} \qquad \xi_0^{-2} = T_c A_0 D. \tag{9.81}$$

For $k = 0$, we have

$$\tilde{g}(0, T) = \frac{1}{A(T - T_c)}. \tag{9.82}$$

Since $\tilde{g}(0, T)$ is the square of the density fluctuation, it must be positive. Therefore $A > 0$. From (9.82) we also find the compressibility diverges with an exponent $\gamma = 1$, as found in the Landau theory.

Since the only divergence of $g(k, T)$ is at $k = 0$, B_0 also is negative. The form of (9.80), which is called a Lorentzian, is valid near $T = T_c$ and when k is small. By performing a Fourier transform (9.80), we obtain $g(r)$ for large values of r

$$g(r) \propto \frac{e^{-r/\xi}}{r^{d-2}}, \tag{9.83}$$

where d is the space dimension.

From (9.83), it follows that ξ coincides with the correlation length of (9.82), for which

$$\xi \simeq \xi_0 \left(\frac{T - T_c}{T_c} \right)^{-\nu} \tag{9.84}$$

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,

$$g(r) = \frac{1}{r^{d-2+\eta}}, \tag{9.85}$$

with $\eta = 0$.

As stated earlier, the Ornstein-Zernike theory does not begin with a particular model. It only assumes the analyticity of $\tilde{C}(\vec{k}, T)$ 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 require of $\tilde{C}(\vec{k}, T)$. To perform an explicit calculation including T_c and the amplitudes, we can calculate $\tilde{c}(\vec{k}, T)$. This can be done starting from definition (9.75). By doing a series expansion in β, to the first order, it is possible to show (see Problem) that

$$\tilde{C}(\vec{k}) = \frac{\tilde{V}(\vec{k})}{kT}, \tag{9.86}$$

where

$$\tilde{V}(\vec{k}) = \int V(\vec{r}) e^{i\vec{k}\cdot\vec{r}} d\vec{r}, \tag{9.87}$$

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 (9.87). The critical temperature is therefore given by condition (9.80)

$$\frac{\tilde{V}(0)}{kT_c} = 1. \tag{9.88}$$

In the case of the Ising model $\tilde{V}(0) = zJ$, which gives the Weiss result $KT_c = zJ$. Other quantitites such as ξ can be obtained by calculating (9.87) to the order k^2.

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
$C \sim \epsilon^{-\alpha}$	$\alpha = 0$	Specific heat of constant volume or constant field
$g(r) \sim e^{-r/\xi}/r^{d-2+\eta}$	$\eta = 0$	Pair correlation function
$\xi \sim \epsilon^{-\nu}$	$\nu = 1/2$	Correlation length
$\epsilon = \lvert (T-T_c)/T_c \rvert$		

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.

9.7 Exact Solution of the One-Dimensional Ising Model

We next solve the one-dimensional Ising model and compare the result with mean-field results. The one-dimensional Ising model in the zero field has Hamiltonian

$$\mathcal{H} = -J \sum_{i=1}^{N} S_i S_{i+1}. \tag{9.89}$$

The partition function can be written as

$$Z = \sum_{\{s_i\}} \prod_{i=1}^{N} e^{K S_i S_{i+1}}, \tag{9.90}$$

where $K \equiv \beta J$. Using the identity

$$e^{K S_i S_{i+1}} = \cosh K + \sinh K S_i S_{i+1}. \tag{9.91}$$

From (9.90) we have

$$\begin{aligned} Z &= [\cosh K]^N \sum_{\{s_i\}} \prod_i [1 + s_i s_{i+1} \tan K] \qquad (9.92) \\ &= [\cosh K]^N \left[\sum_{\{s_i\}} [1 + \sum_i s_i s_{i+1} \tan K + \cdots] \right]. \end{aligned}$$

Since the sum is over all values of spins, all the terms except 1 are zero; therefore

$$Z = 2^N [\cosh K]^{N-1}. \tag{9.93}$$

The free energy is

$$f(K) = -kT \lim_{N\to\infty} \frac{\ln Z}{N} = \ln 2 + \cosh K. \tag{9.94}$$

The extension to the presence of a magnetic field H gives (see problem)

$$f(K,h) = K + \ln\{\cosh h + [\sinh^2 h + e^{-4K}]^{1/2}\}, \tag{9.95}$$

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

$$g_{ij} \equiv \langle s_i s_j \rangle. \tag{9.96}$$

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

$$\begin{aligned} g_{ij} &= \frac{1}{Z} \sum_{\{s_i\}} s_i s_{i+1} e^{K \sum_i s_i s_{i+1}} \qquad (9.97) \\ &= \frac{1}{Z} [\cosh K]^{N-1} \sum_{\{s_i\}} s_i s_j \prod_{\ell=1}^{N-1} (1 + s_\ell s_{\ell+1} \tan K) \\ &= \frac{1}{Z} [\cosh K]^{N-1} (\tan K)^{|i-j|} 2^N. \end{aligned}$$

From (9.95) we finally obtain

$$g_{ij} = [\tan K]^{|i-j|}, \tag{9.98}$$

which can be written in the form

$$g_{ij} = \exp\left[\frac{-r_{ij}}{\xi}\right], \tag{9.99}$$

where $r_{ij} = a|i-j|$, with a being the lattice spacing and

$$\xi = \frac{a}{|\ln \tan K|}, \tag{9.100}$$

which shows that as $T \to 0$, the correlation length diverges as

$$\xi = a \exp\left[\frac{2J}{k_B T}\right]. \tag{9.101}$$

Although the one-dimensional Ising model does not show any spontaneousl 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.

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 $T = T_c = 2.269$ J/k$_B$. 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 $\eta = 1/4$.

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).

Table I: Critical exponents.

	β	γ	α	ν	η
2d	1	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

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 I 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. How can we understand this result? The pair correlation function between two points at a distance of n lattice spacing is

$$[\tan \beta J]^n = \exp[-n \ln |\tan \beta J|]. \tag{9.102}$$

Because the correlation decays by a factor $\tan\beta J$ 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.

Note that at infinite temperature the correlation drops to zero after only one step and the correlation length is zero. On the other hand, at zero temperature the corelation does not decay at all, $\tan(\beta J) = 1$ and the correlation length is therefore infinite.

9.8 Critical Exponents in Higher Dimensions

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, $g_n = [\lambda \tan(\beta J)]^n$.

When these two effects compensate, the correlation length becomes infinite. Therefore the critical temperature is given by

$$\lambda \tan\left(\frac{J}{k_B T_c}\right) = 1. \tag{9.103}$$

The pair correlation function between two points separated by a distance r is related to g_n by $4\pi g(\vec{r}) r^{d-1} dr = g(n) dn$. If we assume that the relation between r and n is

$$n^\nu = r, \tag{9.104}$$

we obtain

$$g(r) = \exp\left[-\left(\frac{r}{\xi}\right)^{1/\nu}\right] \frac{1}{r^{d-2+\eta}}, \tag{9.105}$$

with

$$\eta = \frac{2\nu - 1}{\nu}, \tag{9.106}$$

and

$$\xi = \frac{1}{[\ln \lambda \tan \beta J]^\nu} \sim (T - T_c)^{-\nu}. \tag{9.107}$$

Therefore ν corresponds to the correlation length exponent. Finally we can speculate that the paths along which correlations propagate are non-intersecting 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.,

$$\nu = \begin{cases} 3/(d+2) & \text{if } d \leq 4 \\ 1/2 & \text{if } d \geq 4 \end{cases}, \tag{9.108}$$

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 (9.103) T_c is large and, if we expand the hyperbolic tangent to first order,

$$\frac{zJ}{KT_c} = 1. \tag{9.109}$$

From (9.106) and (9.108) 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.

9.9 Scaling Laws and Universality

As we mentioned in the previous section, 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.,

$$\alpha + 2\beta + \gamma \geq 2 \qquad \text{and} \qquad d\nu \geq 2 - \alpha. \tag{9.110}$$

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 hypothesis, a second hypothesis, “universality,” was proposed. This hypothesis—clearly stated by Kadanoff—is bsed on the empirical fact that all system 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.

Many different phenomenological approaches were developed to derive such relations. We will follow one approach developed mainly by Kadanoff, which has the virtue of paving the way toward the renormalization group theory. 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. Let us see how this idea can be implemented to make predictions.

To fix the ideas, let us 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. We can further suppose that if the original spin Hamiltonian has the form

$$-\beta\mathcal{H} = K \sum_{\langle ij \rangle} s_i s_j + h \sum_i s_i, \tag{9.111}$$

with $K = J/K_B T$ and $h = H/KT$. 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 $W_0(K, h)$,

$$-\beta\mathcal{H}' = K' \sum_{\langle \alpha\beta \rangle} s_\alpha s_\beta + h' \sum_\alpha s_\alpha + W_0(K, h), \tag{9.112}$$

where the sum is over all nearest-neighbor cells, and K' and h' are the renormalized coupling constant and the magnetic field, respectively.

We first consider the case in which $h = h' = 0$. The renormalized coupling constant depends on K and ℓ, i.e.,

$$K' = f(K, \ell). \tag{9.113}$$

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 (9.113) to the first order near the critical point

$$K' = f(K_c, \ell) + \left(\frac{\partial f}{\partial K}\right)_{K=K_c} (K - K_c) + \cdots \tag{9.114}$$

We now evaluate $f(K_c, \ell)$. Given that the Hamiltonian of the cells is the same as that of the spin system, the correlation length of the cells $\xi'(K')$ has the same functional form as the spin system. Therefore $\xi'(K') = \xi(K')$. Moreover, since cell systems and spin systems are identical (apart from a rescaling of the lengths by a factor ℓ), we have

$$\xi(K') = \frac{\xi(K)}{\ell}. \tag{9.115}$$

From (9.113) and (9.115), it follows that at K_c

$$\xi[f(K_c, \ell)] = \frac{\xi(K_c)}{\ell} = \infty. \tag{9.116}$$

If $\xi[f(K_c, \ell)] = \infty$, it follows that $f(K_c, \ell) = K_c$. Therefore (9.114) can be written

$$\epsilon' = a(\ell)\epsilon, \tag{9.117}$$

where $\epsilon = (K - K_c)/K_c$, $\epsilon' = (K' - K_c)/K_c$, and $a(\ell) = (\partial f/\partial K)_{K=K_c}$. The transformation from ϵ to ϵ' must obey group properties, i.e., if we rescale the spin system by a factor ℓ_1 and then rescale again the cells by a factor ℓ_2, we obtain the same result as we would if we scaled the spin system by a factor $\ell_1\ell_2$. If $\epsilon_1 = a(\ell_1)\epsilon$ and $\epsilon_2 = a(\ell_2)\epsilon_1$, then $\epsilon_2 = a(\ell_1\ell_2) = \epsilon$, i.e.,

$$a(\ell_1\ell_2) = a(\ell_1)a(\ell_2). \tag{9.118}$$

This functional form has the only solution

$$a(\ell) = \ell^x. \tag{9.119}$$

Therefore (9.117) becomes

$$\epsilon' = \ell^x\epsilon, \tag{9.120}$$

where ϵ is the scaling field and x the scaling exponent; $(K = K_c)$ is a fixed point in the transformation, and under rescaling it does not change.

We relate now x to the correlation exponent ν. Close to K_c we have $\xi(K) = \xi_0\epsilon^{-\nu}$ and $\xi(K') = \xi_0\epsilon'^{-\nu}$. From (9.115) and (9.120) it follows

$$x = \frac{1}{\nu}, \tag{9.121}$$

and from (9.120) $x = \ln a(\ell)/\ln \ell$. Similarly, in the presence of a small field, the renormalized field is

$$h' = \ell^y h. \tag{9.122}$$

We now relate the free energy of the system of spins to the system of cells. The partition function for the spin system $Z_N(K, h)$ can be written

$$Z_N(K, h) = \sum_{\{s_i\}} e^{-\beta\mathcal{H}} = \sum_{\{s_\alpha\}} \sum_{\text{internal}} e^{-\beta\mathcal{H}} = \sum_{\{s_\alpha\}} e^{-\beta\mathcal{H}'} = Z_{N'}(K', h')e^{W_0(K,h)}, \tag{9.123}$$

where we have partitioned the sum over the spin variables into the sum over the internal degree of freedom of the cells $\sum_{\text{internal}}$ and the sum over the degree of freedom of the cells $\sum_{\{s_\alpha\}}$. We have used also the relation

$$\sum_{\text{internal}} e^{-\beta\mathcal{H}} = e^{-\beta\mathcal{H}'} \tag{9.124}$$

which is the way to define $\mathcal{H}'$. $N' = \ell^{-d}N$ is the number of cells. From (9.123) we have

$$-KT\frac{\ln Z_N(K,H)}{N} = -KT\frac{\ln Z_{N'}(K',H')}{N'}\frac{N'}{N} - K_BT\frac{A(K,h)}{N}. \tag{9.125}$$

Taking the limit $N \to \infty$, we obtain the relation btween the free energy for spin $f(K,h)$ and the free energy per cell $f(K',h')$

$$f(K,h) = \ell^{-d}f(K',h') + B(K,h), \tag{9.126}$$

where $B(K,T) = -KT\ln[A(K,T)/N]$. 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 $g(\epsilon,h) = f_{\text{sing}}(K,h)$ as the singular part of $f(K,h)$, from (9.126) we have

$$g(\epsilon,h) = \ell^{-d}g(\ell^x\epsilon,\ell^y h). \tag{9.127}$$

A function that satisfies the function relation (9.127) is called a generalized homogeneous function. In conclusion, from the scaling arguments it follows that the singular part of the free energy is a generalized homogeneous function.

We now examine the consequences of (9.127). Since (9.127) is valid for any ℓ, for any ϵ we can chose an ℓ such that $\ell^x\epsilon = 1$. From (9.127) immediately follows

$$g(\epsilon,h) = \epsilon^{d/x}\varphi\left(\frac{h}{\epsilon^{y/x}}\right), \tag{9.128}$$

where $\varphi(z) = g(1,z)$ is a function of only one variable. Taking into account that

$$\begin{aligned} C_H &\sim \left(\frac{\partial^2 g}{\partial\tau^2}\right)_{h=0} \sim \tau^{-\alpha}; \\ M &\sim \left(\frac{\partial g}{\partial h}\right)_{h=0} \sim \epsilon^{\beta}; \\ \chi &\sim \left(\frac{\partial^2 g}{\partial h^2}\right)_{h=0} \sim \tau^{-\gamma}, \end{aligned} \tag{9.129}$$

from (9.128) it follows

$$-\alpha = \frac{d}{x} - 2, \qquad \beta = \frac{d}{x} - \frac{y}{x}, \qquad \text{and} \qquad -\gamma = \frac{d}{x} - \frac{2y}{x}. \tag{9.130}$$

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

$$\alpha = 2\beta + \gamma = 2, \tag{9.131}$$

which is the Rushbrooke relation with an equality sign. Note that from (9.121) and (9.130) it also follows that

$$d\nu = 2 - \alpha, \tag{9.132}$$

which reproduces the second scaling relation.

The scaling hypothesis not only predicts relations among critical exponents, but also predicts a kind of "data collapse," which can be explained in terms of the simple example of a uniaxial ferromagnet. From (9.123) we can calculate the magnetization $m = \partial g/\partial h$, we find

$$m = \epsilon^{\beta}\varphi'(h\epsilon^{-y/x}). \tag{9.133}$$

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 $m - \epsilon$ 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 (9.128) 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.

9.10 Renormalization Group

The scaling approach followed in the previous section was historically developed 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 (9.113) and consequently of the critical exponent through relation

(9.120). What was missing that was needed to develop the renormalization group theory, was an implementation of (9.124), i.e., it was necessary to define the cell variables and the internal degree of freedom in terms of the spin variables . Then using (9.124) we can calculate the renormalization coupling constant. The definition of the cell variables is not unique. To illustrate how the renormalization group works, we consider first a very simple case: the 1d Ising model, which exhibits the property that for $H = 0$ the correlation length diverges as

$$\xi \sim \left(e^{+2J/KT}\right)^{-1}, \tag{9.134}$$

as T approaches 0, which can therefore be considered a critical point. The partition function for the 1d Ising model in a zero field can be written

$$Z = \sum_{\{s_i\}} e^{K(s_1 s_2 + s_2 s_3 + s_3 s_4 + \cdots)}, \tag{9.135}$$

which can also be written as

$$Z = \sum_{\{s_i, s_3, \cdots\}} \sum_{\{s_2, s_4, \cdots\}} e^{K(s_1 s_2 + s_2 s_3)} e^{K(s_3 s_4 + s_4 s_5)} \cdots. \tag{9.136}$$

We consider the system divided into cells of size $\ell = 2$ made of spins $(1,2)(3,4)(5,6)\ldots$ For convenience we consider the first spin in cell 1,3,5 the cell variable and spin 2,4,6 the internal variable. In (9.136) the second sum is over the internal degree of freedom of the cell. Therefore, using (9.124), the renormalized Hamiltonian is given by

$$\sum_{s, s_4, \cdots} e^{K(s_1 s_2 + s_2 s_3)} e^{K(s_3 s_4 + s_4 s_5)} \cdots = e^{K'[s_1 s_3 + s_3 s_5 + s_5 s_7 + \cdots] + (N/2) W_0}, \tag{9.137}$$

where K' and W_0 can be easily calculated from

$$\sum_{s_2 = \pm 1} e^{K(s_1 s_2 + s_2 s_3)} = e^{K' s_1 s_3 + W_0}. \tag{9.138}$$

From (9.138) we have

$$e^{K(s_1 s_3)} + e^{-K(s_1 s_3)} = e^{K' s_1 s_3 + W_0}. \tag{9.139}$$

By fixing first $s_1 = s_3 = \pm 1$ and then $s_1 = -s_3 = \pm 1$, we obtain two equations,

$$e^{W_0} = 2(u + u^{-1}) \tag{9.140}$$

and

$$u' = \frac{2}{u + u^{-1}}, \qquad (9.141)$$

where, for convenience, we have using 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 (9.141). These are given by solving

$$u^* = \frac{2}{u^* + u^{-1^*}}. \qquad (9.142)$$

Equation (9.142) can be solved graphically by locating the intersection of $u'(u)$ given by (9.141) and $u' = u$. From Fig. XX and (9.142) we see that there are two fixed points: $u^* = 0(T = 0)$ and $u^* = \infty(T = \infty)$. 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 (9.139)

$$\xi(u^*) = \frac{\xi(u^*)}{\ell}. \qquad (9.143)$$

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?

Following the argument of the previous section, expanding the renormalized coupling constant near the fixed point

$$u' - u^* = a(u - u^*), \qquad (9.144)$$

we can associate the scaling exponent $x = \ln a / \ln \ell$ with the behavior of the correlation length at the fixed point. 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 (9.144) we find

$$u_n - u^* = a^n(u_0 - u^*). \tag{9.145}$$

If $a > 1$ (unstable fixed point), after many interations the 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 corrsponds 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

$$u' = 2u, \tag{9.146}$$

therefore $a = 2$. Taking into account that the rescaling factor $\ell = 2$, we find the critical exponent ν given by

$$\nu = \frac{\ln \ell}{\ln a} = 1. \tag{9.147}$$

Therefore the correlation length close to $u = 0$ ($T = 0$) behaves as

$$\xi \sim u^{-1} = e^{2J/KT}, \tag{9.148}$$

which coincides with the analytic result obtained from the exact solution.

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 $l = 2$, one removes all the interactions coming out from the central spin A (see Fig. XX) and adds these interactions to the other interactions in the cell. In this way, the interactions along the perimetr of the cells are doubled . This is done uniformly in the entire lattice. The approximation consists in replacing the old Hamiltonian with an interaction K with a new one obtained via the bond-moving procedure with interaction $2K$.

The central spins in the A positions now do not interact with any other spins and can be ignored. The B spins interact with two neighbor spins only as in the one-dimensional chain. The second step consists in applying the decimation procedure to the B spins. The end results is that that spin in position C interacts 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

$$u' = \frac{2}{u^2 + u^{-2}}. \tag{9.149}$$

Figure XX shows the presence of 3 fixed points

$$\begin{array}{lrcll} (1) & u^* & = & 0 & (T = 0) \\ (2) & u^* & = & 1 & (T = \infty) \\ (3) & u^* & = & u_c & (T = T_c). \end{array} \tag{9.150}$$

The first two fixed points are stable. The third one $u_c =$ ...is unstable. In fact, the critical exponent

$$\nu = \frac{\ln 2}{\ln a_c} \simeq 0.6, \tag{9.151}$$

where

$$a_c = \left.\frac{du'}{du}\right|_{u=u_c}. \tag{9.152}$$

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 $u = 1$ ($T = 0$). 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. When under repeated renormaliation 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 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.

In the approximation involved in the Magdal-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, more coupling constants are involved. Suppose, for simplicity, that within certain approximations an Ising model with a nearest-neighbor coupling interaction K_1 plus a next-nearest-neighbor coupling interaction K_2 is mapped onto a renormalized Hamiltonian with the same form as coupling constants K_1' and K_2'. The recursion relation will have the form

$$\begin{aligned} K_1' &= f_1(K_1, K_2, \ell) \\ K_2' &= f_2(K_1, K_2, \ell). \end{aligned} \tag{9.153}$$

The fixed points are now points in a larger space. Let us suppose K_1^* and K_2^* are the unstable fixed points. Expanding (9.153) around the fixed point leads to

$$\begin{aligned} \epsilon_1' &= a_{11}\epsilon_1 + a_{12}\epsilon_2 \\ \epsilon_2' &= a_{21}\epsilon_1 + a_{22}\epsilon_2. \end{aligned} \tag{9.154}$$

in which

$$a_{ij} = \left(\frac{\partial f_i}{\partial K_j}\right)_{\substack{K_1 = K_1^* \\ K_2 = K_2^*}} \qquad i,j = 1,2, \tag{9.155}$$

which can be put in a matricial form

$$\begin{pmatrix} \epsilon_1' \\ \epsilon_2' \end{pmatrix} = \begin{pmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{pmatrix} \begin{pmatrix} \epsilon_1 \\ \epsilon_2 \end{pmatrix} \tag{9.156}$$

We can chose a linear combination of ϵ_1 and ϵ_2

$$\begin{aligned} u_1 &= c_{11}\epsilon_1 + c_{12}\epsilon_2 \\ u_2 &= c_{21}\epsilon_1 + c_{22}\epsilon_2, \end{aligned} \tag{9.157}$$

such that

$$\begin{aligned} u_1' &= \lambda_1 u_1 = \ell^{x_1} u_1 \\ u_2' &= \lambda_2 u_2 = \ell^{x_2} u_2, \end{aligned} \tag{9.158}$$

namely

$$\begin{pmatrix} u_1' \\ u_2' \end{pmatrix} = \begin{pmatrix} \lambda_1 & 0 \\ 0 & \lambda_2 \end{pmatrix} \begin{pmatrix} u_1 \\ u_2 \end{pmatrix} \tag{9.159}$$

Here u_1 and u_2 are the scaling fields and x_1 and x_2 the scaling exponents. The scaling fields are relevant if $x_1 > 0$, irrelevant if $x_1 < 0$, and marginal if $x = 0$. The case in which both are relevant corresponds to the case in which ϵ_1 is the coupling constant and ϵ_2 the magnetic field. Suppose $x_1 > 0$ and $x_2 < 0$. In this case if one is on the curve defined as $u_1 = 0$, i.e., $c_{11}\epsilon_1 + c_{12}\epsilon_2 = 0$, under renormalization u_2 will approach zero. Therefore any point on the curve will approach the fixed point $u_1 = 0, u_2 = 0$.

The line defined by $u_1 = 0$, $c_1\epsilon_1 + c_2\epsilon_2 = 0$ gives in the plane K_1, K_2 the line of critical points. Each critical point is attracted by the fixed point and is described by the same critical exponent $\nu = 1/x_1$.

To see this, consider the correlation length near the fixed point

$$\xi(u_1', u_2') = \frac{\xi(u_1 u_2)}{\ell} \tag{9.160}$$

which, from (9.158) can be written

$$\ell\xi(\ell^{x_1}u_1, \ell^{x_2}u_2) = \xi(u_1, u_2). \tag{9.161}$$

Fixing $\ell^{x_1} u_1 = 1$ and $\ell = u^{-1/x_1}$ we have

$$\xi(u_1, u_2) = u_1^{-1/x_1} \psi(u_2 u_1^{|x_2|/x_1}), \tag{9.162}$$

where $\psi(s) = \xi(1, s)$. We have also taken into account that $x_2 < 0$. From (9.162) it follows that $\xi \to \infty$ whenever $u_1 \to 0$ with a universal exponent $\nu = 1/x$. This shows how renormalization theory can predict the universal behavior of an entire family of model systems.

Chapter 10

Nonequilibrium Statistical Mechanics

Thus far we have only considered systems that are at equilibrium. The question we ask now is how can we generalize the equilibrium distribution given by the microcanonical, canonical, and grand canonical ensembles to describe systems out of equilibrium?

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 approach. To illustrate the idea, we use a simple approach based on the "random walk model." This model, which has been developed in Chapter 3, 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. (XX)]. The same result can be obtained using the hydrodynamic approach which is based on Fick's law

$$\vec{J}(\vec{r}, t) = -D\nabla\rho(\vec{r}, t). \tag{10.1}$$

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. (10.1) 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,

$$\nabla\cdot\vec{J} + \frac{\partial \rho}{\partial t} = 0. \tag{10.2}$$

From (10.1) and (10.2) the "diffusion equation" follows,

$$\frac{\partial \rho}{\partial t} = D\nabla^2 \rho(\vec{r}, t). \tag{10.3}$$

Equation (10.3) 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

$$\rho(\vec{r}, t) = \frac{N}{(4\pi Dt)^{3/2}} \exp\left(-\frac{r^2}{4Dt}\right), \tag{10.4}$$

where

$$N = \int \rho(\vec{r}, t) d\vec{r} \tag{10.5}$$

is the number of particles. Note that for $t = 0$, Eq. (10.4) gives a delta function, reproducing the initial conditions. 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 $\vec{F}(t)$. In this approach, which is due to Langevin , the equation of motion can be written as

$$m\frac{d\vec{v}}{dt} = \vec{F}(t), \tag{10.6}$$

where m and $\vec{v}$ are the mass and velocity of the diffusion particle, respectively.

Next it is assumed that the force can be composed of two terms: $\vec{F}_1(t)$ and $\vec{F}_2(t)$. The first, due to the viscosity, is proportional to the velocity of the particle $\vec{F}_1 = -(1/B)\vec{v}$, where B is the mobility coefficient. The second, $\vec{F}_2$, has the property of having a zero time average over short intervals of time, namely

$$m\frac{d\vec{v}}{dt} = \frac{\vec{v}}{B} + \vec{F}_2(t), \tag{10.7}$$

with

$$\langle \vec{F}_2(t) \rangle = 0, \tag{10.8}$$

where the $\langle \ldots \rangle$ stands for a time average or, equivalently, an ensemble average. For convenience we will only consider the ensemble average.

By taking the ensemble average over (10.7) and considering the property (10.8), the following equation is obtained for the average velocity $\langle \vec{V} \rangle$

$$m\frac{d\langle \vec{v} \rangle}{dt} = -\frac{\langle v \rangle}{B}, \tag{10.9}$$

from which

$$\langle \vec{v} \rangle = \vec{v}_0 e^{-t/\tau}, \tag{10.10}$$

with $\tau = mB$. Equation (10.10) 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, (10.7) we can derive an equation for $\langle r^2 \rangle$. Taking the scalar product of both member of (10.7) with $\vec{r}$, we obtain

$$\vec{r}\cdot\frac{d\vec{v}}{dt} = -\frac{\vec{r}\cdot\vec{v}}{\tau} + \frac{\vec{r}\cdot\vec{F}_2}{m}. \tag{10.11}$$

Using the identities

$$\frac{dr^2}{dt} = \frac{d}{dt}(\vec{r}\cdot\vec{r}) = 2\vec{r}\cdot\vec{v} \tag{10.12}$$

and

$$\frac{d^2r^2}{dt^2} = 2\frac{d}{dt}(\vec{r}\cdot\vec{v}) = 2v^2 + 2\vec{r}\cdot\frac{d\vec{v}}{dt}. \tag{10.13}$$

From (10.11) it follows

$$\frac{d^2r^2}{dt^2} + \frac{1}{\tau}\frac{d}{dt}r^2 = 2v^2 + \frac{2\vec{r}\cdot\vec{F}_2}{m}. \tag{10.14}$$

Taking the ensemble average from (10.14), we have

$$\frac{d^2\langle r^2 \rangle}{dt^2} + \frac{1}{\tau}\frac{d}{dt}\langle r^2 \rangle = 2\langle v^2 \rangle, \tag{10.15}$$

where we have used the properties that $\langle \vec{r}\cdot\vec{F}_2 \rangle = 0$. To solve (10.15), 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

$$\frac{1}{2}m\langle v^2\rangle = \frac{3}{2}kT. \tag{10.16}$$

Substituting (10.16) in (10.15),

$$\frac{d^2\langle r^2\rangle}{dt^2} + \frac{1}{\tau}\frac{d}{dt}\langle r^2\rangle = \frac{6kT}{m}. \tag{10.17}$$

The solution of (10.6) under the initial condition that $\langle r^2\rangle = 0$ and $(d\langle r^2\rangle/dt)\langle r^2\rangle =$ 0 is given by

$$\langle r^2\rangle = \frac{6kT}{m}\tau^2\left\{\frac{t}{\tau} - \left(1 - e^{-t/\tau}\right)\right\}. \tag{10.18}$$

In the limit $t \ll \tau$, using the expansion $e^{-x} = 1 - x + (x^2/x) + \cdots$ from (10.18) we have

$$\langle r^2\rangle = \frac{3kT}{m}t^2 = \langle v^2\rangle t^2, \tag{10.19}$$

while for $t \gg \tau$

$$\langle r^2\rangle = 6kTBt. \tag{10.20}$$

Equation (10.19) 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 (10.16). Equation (10.20) gives a time-dependence identical to the one obtained in the random walk or hydrodynamic approach. In fact, from (10.4),

$$\langle r^2\rangle = \frac{1}{N}\int \rho(\vec{r},t)r^2 d\vec{r} = 6Dt, \tag{10.21}$$

which, compared with (10.20), gives a relation between the diffusion coefficient D and the mobility B,

$$kTB = D, \tag{10.22}$$

which is known as Einstein's relation.

10.1 Fluctuation Dissipation Relation

In the previous section the term $\langle v^2\rangle$ was evaluated only in the long time regime. We want to evaluate it for any time. We wil see that as a byproduct we will find an important relation that will connect B to the fluctuaing force $\vec{F}_2$.

Let us write the Langevin equation in the form

$$\frac{d\vec{v}}{dt} = -\frac{\vec{v}}{\tau} + \vec{a}(t), \tag{10.23}$$

where $\vec{a}(t) = \vec{F}_2(t)/m$. Multiplying both members of (10.23) by $e^{t/\tau}$, it follows that

$$\frac{d}{dt}\left[\vec{v}e^{t/\tau}\right] = \vec{a}e^{t/\tau}. \tag{10.24}$$

Integrating between 0 and t we obtain

$$\vec{v}e^{t/\tau} = \vec{v}(0) + \int_0^t \vec{a}(t_1)e^{t_1/\tau}dt. \tag{10.25}$$

Multiplying by $e^{-t/\tau}$ and taking the square, we obtain

$$\begin{aligned} v^2(t) &= v^2(0)e^{-2t/\tau} + e^{-2t/\tau}\int_0^t\int_0^t e^{(t_1+t_2)/\tau}\vec{a}(t_1)\cdot\vec{a}(t_2)dt_1dt_2 + \\ & \qquad 2e^{-2t/\tau}\left[\vec{v}(0)\cdot\int_0^t e^{t_1/\tau}\vec{a}(t_1)dt_1\right]. \end{aligned} \tag{10.26}$$

Taking the average from (10.24), we obtain

$$\langle v^2(t)\rangle = v^2(0)e^{-2t/\tau} + e^{-2t/\tau}\int_0^t\int_0^t \langle\vec{a}(t_1)\cdot\vec{a}(t_2)\rangle e^{(t_1+t_2)/\tau}dt_1dt_2, \tag{10.27}$$

since the last term in (10.26) gives zero contribution (if the average of $\vec{a}$ is zero over a very short time, also the average of the component along the direction of the vector, which can be considered fixed over such a short time, is zero).

To proceed further, we must know the quantity $K = \langle\vec{a}(t_1)\cdot\vec{a}(t_2)\rangle$, 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 autocorrelation function. In a stationary regime in which the fluid is stationary, the autocorrelation function depends only on the time difference $s = t_1 - t_2$

$$K(s) = \langle\vec{a}(t_1)\cdot\vec{a}(t_2)\rangle. \tag{10.28}$$

Next we assume that

$$K(s) = C\delta(s). \tag{10.29}$$

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^*,

$$K(s) = \langle \vec{a}(t_1)\cdot\vec{a}(t_1+s)\rangle = \langle \vec{a}(t_1)\rangle\cdot\langle \vec{a}(t_1+s)\rangle. \tag{10.30}$$

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 (10.29).

In conclusion, we assume that the force $\vec{F}_2$ appearing in the Langevin equation has zero mean and a delta correlation. Using (10.29), we can easily evaluate the integral in (10.27), giving

$$\langle v^2(t)\rangle = v^2(0)e^{-2t/\tau} + C\frac{\tau}{2}\left(1-e^{-2t/\tau}\right). \tag{10.31}$$

This is the desired expression, which still contains the quantity C, which is unknown. However, by taking the limit $t\to\infty$ we find

$$\langle v^2(t)\rangle = C\frac{\tau}{2}, \tag{10.32}$$

and using the equipartition theorem we obtain

$$C = \frac{6kT}{\tau m} = \frac{6kT}{Bm^2}. \tag{10.33}$$

Consequently,

$$\langle \vec{F}_1(t_1)\cdot\vec{F}_1(t_2)\rangle = \frac{6kT}{B}\delta(t_1-t_2). \tag{10.34}$$

This relation shows that the higher the strength of the fluctuating force, the higher the viscosity B^{-1}, showing that these two quantitites have the same orgin in the collisions of the fluid particles.

After some further elaboration we can obtain a new relation that turns out to be conceptually very important. We start with the following relation (see Problem XX)

$$\langle r^2\rangle = \int_0^t\int_0^t \langle \vec{v}(t_1)\cdot\vec{v}(t_2)\rangle dt_1dt_2 = t\int_{-\infty}^{\infty}\langle \vec{v}(0)\cdot\vec{v}(s)\rangle ds. \tag{10.35}$$

Comparing (10.35) with (XX), we find

$$\int_{-\infty}^{\infty}\langle \vec{v}(0)\cdot\vec{v}(s)\rangle ds = 6BkT. \tag{10.36}$$

On the other hand, if we apply an external force f to the particle, the Langevin equation can be written

$$m\frac{d\vec{v}}{dt} = -\frac{\vec{v}}{B} + \vec{f} + \vec{F}_2. \tag{10.37}$$

Therefore,

$$m\frac{d\langle\vec{v}\rangle}{dt} = -\frac{\langle\vec{v}\rangle}{B} + \vec{f}, \tag{10.38}$$

which gives

$$\langle\vec{v}\rangle = \left(\vec{v}_0 - B\vec{f}\right) e^{-t/\tau} + B\vec{f}, \tag{10.39}$$

and, for large t,

$$\langle v\rangle = Bf, \tag{10.40}$$

or

$$\frac{\delta\langle v\rangle}{\delta f} = B. \tag{10.41}$$

B can be consider the response function to an external force, namely the variation of the average velocity due to the unitary change of an external force.

From (10.37) and (10.36) on obtains

$$\frac{\delta\langle\vec{v}\rangle}{\delta f} = \frac{1}{6KT}\int_{-\infty}^{\infty}\langle\vec{v}(S)\cdot\vec{v}(0)\rangle ds. \tag{10.42}$$

This relation, which is one of the fluctuation dissipation relations, relates the integral over time of the fluctuations of the velocity at equlilibrium to the response to an external force, which in this case is linked to the dissipation due to the viscosity. This relation is analogous to those found for the static quantities.

10.2 Master Equation

In the Langevin approach we have considered the motin of a particle subject to random forces. Let us now write an equation for the distribution probability $f(x,t)$. For N particles diffusing in a medium in 1 dimension, where $f(x,t)dx$ is the probabiity of finding a particle between x and $x+dx$ at time t, $Nf(x,t)dx$ (the number of particles in the volume dx) satisfies

$$N\frac{\partial}{\partial t}f(x,t)dx = -\int Nf(x,t)dxW(x,x')dx' + \int Nf(x',t)dxW(x',x)dx', \tag{10.43}$$

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 (10.43) represents the variation per unit of time of the number of particles in the volume dx. The second and third terms are the outgoing and incoming particles, respectively, in the volume dx. By dividing Eq. (10.43) by Ndx, we obtain the master equation,

$$\frac{\partial}{\partial t} f(x,t) = -\int f(x,t) W(x,x')dx' + \int f(x',t) W(x',x)dx'. \qquad (10.44)$$

To see how (10.44) can give the decay to equilibrium, we make the assumption that

$$\int W(x,x')dx' \equiv \frac{1}{\tau} \qquad (10.45)$$

is a constant, and that

$$\int f(x',t) W(x',x)dx' \equiv \frac{1}{\tau} f_{\text{eq}}(x) \qquad (10.46)$$

is a function which depends only on x. Under these assumptions, Eq. (10.44) becomes

$$\frac{\partial}{\partial t} f(x,t) = -\frac{1}{\tau} f(x,t) + \frac{1}{\tau} f_{\text{eq}}. \qquad (10.47)$$

The solution of (10.47) under the initial condition $f(x,0)=f_0(x)$ gives

$$f(x,t) = f_{\text{eq}}(x) + (f_0(x) - f_{\text{eq}}(x)) \cdot e^{-t/\tau}, \qquad (10.48)$$

which shows how the system reaches equilibrium exponentially with a characteristic time τ.

10.3 Fokker-Planck Equation

From the master equation we can obtain a differential equation that is called the Fokker-Planck equation. It is reasonable to suppose that $W(x,x')$ is highly peaked around $x=x'$ and goes rapidly to zero for $x \neq x'$. Let us put $\xi = x' - x$. Equation (10.44) can then be written

$$\frac{\partial}{\partial t} f(x,t) = -\int f(x,t) W(x,x+\xi)d\xi + \int f(x+\xi,t) W(x+\xi,x)d\xi. \quad (10.49)$$

When we expand the integrand of (10.49) around $x_0 = x - \xi$, we get

$$f(x+\xi,t)W(x+\xi,x) = \sum_n \frac{1}{n!} \frac{\partial^n}{\partial x^n} \left(f(x+\xi,t) W(x+\xi,x) \right) \Bigg|_{x=x_0} \xi^n. \quad (10.50)$$

For small ξ, we can stop at the second order, so that

$$\begin{aligned} f(x+\xi,t)W(x+\xi,x) &= f(x,t)W(x,x-\xi) \\ &+ \frac{\partial}{\partial x}\left(f(x+\xi,t)W(x+\xi,t)\right)\Big|_{x=x_0}\xi \\ &+ \frac{1}{2}\frac{\partial^2}{\partial x^2}\left(f(x+\xi,t)W(x+\xi,t)\right)\Big|_{x=x_0}\xi^2. \end{aligned} \tag{10.51}$$

By putting $\xi = -\xi'$, it can easily be shown that

$$\begin{aligned} \int_{-\infty}^{\infty} f(x,t)W(x,x-\xi)d\xi &= -\int_{\infty}^{-\infty} f(x,t)W(x,x+\xi')d\xi' \\ &= \int_{-\infty}^{\infty} f(x,t)W(x,x+\xi')d\xi'. \end{aligned} \tag{10.52}$$

Therefore from (10.49), (10.50), and (10.52) we obtain the Fokker-Planck equation,

$$\frac{\partial}{\partial t}f(x,t) = -\frac{\partial}{\partial x}\left\{\mu_1(x)f(x,t)\right\} + \frac{1}{2}\frac{\partial^2}{\partial x^2}\left\{\mu_2(x)f(x,t)\right\}, \tag{10.53}$$

where

$$\mu_1(x) = \int_{-\infty}^{\infty} W(x,x+\xi)\xi d\xi, \tag{10.54}$$

and

$$\mu_2(x) = \int_{-\infty}^{\infty} W(x,x+\xi)\xi^2 d\xi. \tag{10.55}$$

Note that μ_1 and μ_2 can be written as

$$\mu_1 = \frac{\langle \delta x\rangle}{\delta t} \equiv \langle V\rangle, \tag{10.56}$$

and

$$\mu_2 = \frac{\langle (\delta x)^2\rangle}{\delta t}. \tag{10.57}$$

In the presence of an external force f_{ext}, the Langevin equation is written

$$m\frac{dV}{dt} = -\frac{V}{B} + F_1(t) + f_{\text{ext}}, \tag{10.58}$$

which in the limit $m \to 0$ gives

$$\langle V\rangle = Bf_{\text{ext}}. \tag{10.59}$$

Since $f_{\text{ext}} = -\partial\mathcal{H}/\partial x$ where $\mathcal{H}$ is the Hamiltonian, we find

$$\mu_1 = -B\frac{\partial\mathcal{H}}{\partial x}. \tag{10.60}$$

Moreover, from the Langevin equation in one dimension we find

$$\langle x^2\rangle = 2kTBt \qquad\qquad t \gg \tau. \tag{10.61}$$

Since we are considering the case $m \to 0$ ($\tau \to 0$), Eq. (10.61) is valid for any t. Therefore for a mean square displacement $\langle(\delta x)^2\rangle$ in a time δt we have

$$\mu_2 = \frac{\langle(\delta x)^2\rangle}{\delta t} = 2kTB. \tag{10.62}$$

In conclusion, the Fokker-Planck equation becomes

$$\frac{\partial f}{\partial t} = B\frac{\partial}{\partial x}\left[\frac{\partial\mathcal{H}}{\partial x}\cdot f\right] + kBT\frac{\partial^2}{\partial x^2}f. \tag{10.63}$$

The first term is a drift term due to external forces. The second is a diffusive term. In the absence of external forces, Eq. (10.52) coincides with the diffusive equation. In the stationary regime $t \to \infty$, we have

$$0 = \frac{\partial}{\partial x}\left[\frac{\partial\mathcal{H}}{\partial x}\cdot f\right] + kT\frac{\partial^2}{\partial x^2}f, \tag{10.64}$$

whose solution

$$f_{\text{eq}} = e^{-\beta\mathcal{H}}, \tag{10.65}$$

gives the Boltzmann distribution.

As an application, let us consider a particle in a viscous medium subject to an elastic potential $-(1/2)\lambda x^2$. The Fokker-Planck equation becomes

$$\frac{\partial f}{\partial t} = \lambda B\frac{\partial}{\partial x}[xf] + kBT\frac{\partial^2}{\partial x^2}f \tag{10.66}$$

under the initial condition that the particle is localized in x_0 at $t = 0$. The solution is given by (see problem XX)

$$f(x,t) = \left\{\frac{1}{2\pi KT(1-e^{-2\lambda Bt})}\right\}^{1/2} \exp\left[-\frac{\lambda(x - x_0e^{-\lambda Bt})^2}{2KT(1-e^{-2\lambda Bt})}\right]. \tag{10.67}$$

Equation (10.57) is a Gaussian distribution that becomes a delta function localized at x_0 for $t = 0$, while for $t \to \infty$ is a Gaussian centered in $x = 0$

with width $\sqrt{KT}/\lambda$. In other words, a particle originally in x_0 will diffuse moving on average towards the origin $x = 0$ with an equilibrium distribution $f_{\rm eq}$ given by

$$f_{\rm eq}(x) = \frac{1}{(2\pi kT)^{1/2}} \exp\left[-\frac{\lambda x^2}{2kT}\right], \tag{10.68}$$

which coincides with the Boltzmann distribution of a particle subject to an elastic potential $U(x) = (1/2)\lambda x^2$. The mean squre displacement in the equilibrium configuration is given by

$$\langle x^2\rangle = \int f_{\rm eq}(x)x^2dx = \frac{kT}{\lambda}, \tag{10.69}$$

which can be written as

$$\langle U(x)\rangle = \frac{1}{2}\lambda\langle x^2\rangle = \frac{1}{2}kT, \tag{10.70}$$

which gives the principle of equipartition of the energy.

10.4 H-Theorem

The master equation that we presented earlier 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 $f d\vec{r} d\vec{p}$, 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 equation without derivation is

$$\frac{\partial f_1}{\partial t} = \int d^3p_2 d^3p_1' d^3p_2' \delta^4(p_f - p_i)|t_{f_i}|^2[f_2'f_1' - f_1f_2], \tag{10.71}$$

where $|t_{f_i}|^2$ is the transition probability from the initial state i to the final state f in a collision process between two particles, particle 1 and particle 2. In the initial state i, the impulse is $\vec{p}_1$ and $\vec{p}_2$ and in the final state f, the impulse is p_1' and p_2'. The delta function in the integral imposes the conservation of energy and of the three components of the momentum. The notation $f_1 \equiv f(\vec{r}_1, \vec{p}_1, t)$ with the obvious notation for f'.

Equation (10.71) is the famous Boltzmann equation that gives the single particle probability distribution as a function of time. In the stationary case,

$\partial f_1/\partial t = 0$. It can be shown (see problem XX) that the solution f_{eq} has the form of the Boltzmann distribution $f_{\text{eq}}(p) = e^{-\beta(p^2/2m)}$.

A direct consequence of the Boltzmann equation is the famous Boltzmann H-theorem. If we define H as

$$H = \int d^3r d^3p f(\vec{r}, p, t) \ln f(\vec{r}, p.t), \tag{10.72}$$

it is possible to show (see Problem 4) that $dH/dt \leq 0$. If we associate the entropy with $-H$, 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? The second objection, mainly due to Poincaré, 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. (10.72) 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 partition function of single particles, namely

$$f_2(\vec{r}, \vec{p}, \vec{r}_2, \vec{r}_2; t) = f_1(\vec{r}_1 \vec{p}_1, t) f_1(\vec{r}_2 \vec{p}_2, t), \tag{10.73}$$

which is equivalent to saying that the particles are not correlated. The Boltzmann equation is valid only if (10.73) 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. $\sim 10^{10^{24}}$sec. The age of the universe is estimated to be of the order of 10^{10} years $\sim 10^{16}$sec. Therefore

$$\tau \simeq \frac{10^{10^{24}}}{10^{16}} \sim 10^{(10^{24}-16)} \sim 10^{10^{24}} \quad \text{ages of the universe.}$$

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 invarient, until 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 XXX).

10.5 General Master Equation

Here we want to generalize the master equation, discussed in the previous section, to an ensemble distribution. Given an ensemble of $\mathcal{N}$ equivalent system, the probability P_r of finding a system of the ensemble in a state r is given by $P_r = \mathcal{N}_r/\mathcal{N}$, where $\mathcal{N}_r$ is the number of systems in the state r and as $\mathcal{N}$ tends to infinity. Using the same argument as in the previous section, we can write a differential equation for P_r

$$\dot{P}_r = -\sum_s P_r W_{rs} + \sum_s P_s W_{sr}, \tag{10.74}$$

where W_{rs} is the probability per unit time that a system goes from the microscopic state r to the microscopic state s. If we multiply each term of (10.74) 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 given by the number of systems that in the unit time go from the state r to any state s. The second (with positive contribution) is given by 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 (10.74) at equilibrium where $\dot{P}_r = 0$. From (10.74) we have

$$\sum_s P_r^{(\mathrm{eq})} W_{rs} = \sum_s P_s^{(\mathrm{eq})} W_{sr}, \tag{10.75}$$

where $P_r^{(\mathrm{eq})}$ is the equilibrium distribution. This equation is certainly satisfied if

$$P_r^{(\mathrm{eq})} W_{rs} = P_s^{(\mathrm{eq})} W_{sr}. \tag{10.76}$$

Equation (10.76) is called the “detailed balance equation.”

For the microcanonical ensemble we have $P_r^{(\mathrm{eq})} = \text{const}$ for each accessible configuration r. This implies

$$W_{rs} = \text{const} \tag{10.77}$$

for the canonical ensemble $P_r^{(\mathrm{eq})} = \text{const } e^{-\beta E_r}$. Therefore, a solution of (10.76) is given by

$$W_{rs} = \text{const } e^{-\beta E_s}. \tag{10.78}$$

The constant in (10.77) and (10.78) fix the unit time. If the system satisfies ergodicity, namely that each state can be reached by any other state s, then Eq. (10.74) with W_{rs} given by (10.77) or (10.78) assure that, starting from any initial distribution, the ensemble evolves toward the equilibrium distribution.

For an isolated system for which the microcanonical ensemble applies, it can be shown that the H function

$$H = \sum P_r \ln P_r \tag{10.79}$$

satisfies (see problem XX)

$$\frac{dH}{dt} = -\frac{1}{2}\sum_{r,s} W_{rs}(P_r - P_s)(\ln P_r - \ln P_s) \leq 0. \tag{10.80}$$

Since $S = -kH$, (10.80) implies that the entropy in an isolated system decreases with the time and reaches the maximum value when $P_r =$ constant for each r, namely when the equilibrium distribution is reached.

10.6 Spectral Analysis

In the previous section 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

$$y(t) = a_0 + \sum_n a_n \cos 2\pi n f_0 t + \sum_n b_n \sin 2\pi n f_0 t. \tag{10.81}$$

The coefficients are given by

$$\begin{aligned} a_0 &= \frac{1}{T}\int_0^T y(t)dt, &(10.82)\\ a_n &= \frac{1}{T}\int_0^T y(t)\cos 2\pi n f_0 t dt, &(10.83)\\ b_n &= \frac{1}{T}\int_0^T y(t)\sin 2\pi n f_0 t dt. &(10.84)\end{aligned}$$

The time average of the signal is $\bar{y} = a_0$ 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 $\vec{x} = 0$). 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 $y_k(t)$

$$\langle y(t) \rangle = \frac{1}{\mathcal{N}} \sum_k y_k(t). \tag{10.85}$$

If $\mathcal{N}$ is large enough, the time average and ensemble average will coincide, $\bar{y} = \langle y(t) \rangle = 0$. We can take then the ensemble average of a_n and b_n from (10.83) and (10.84) and since $\langle y(t) \rangle = 0$ we find

$$\langle a_0 \rangle = 0 \tag{10.86}$$

$$\langle a_n \rangle = 0 \tag{10.87}$$

$$\langle b_n \rangle = 0. \tag{10.88}$$

Using the ortogonal properties of the trigonometric functions sine and cosine, the time average of $y^2(t)$,

$$\overline{y^2(t)} = \frac{1}{2} \sum_n (a_n^2 + b_n^2). \tag{10.89}$$

If we take the ensemble average of (10.89), we obtain

$$\langle y^2(t) \rangle = \frac{1}{2} \sum_n (\langle a_n^2 \rangle + \langle b_n^2 \rangle), \tag{10.90}$$

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 $\langle a_n^2 \rangle = \langle b_n^2 \rangle$. Therefore

$$\langle y^2(t) \rangle = \sum_n \langle a_n^2 \rangle. \tag{10.91}$$

From (10.83) we have

$$\langle a_n^2 \rangle = 4 f_0^2 \int_0^{1/f_0} \int_0^{1/f_0} \langle y(t_1) y(t_2) \rangle \cos 2\pi n f_0 t_1 \cos 2\pi n f_0 t_2 dt_1 dt_2. \tag{10.92}$$

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

$$K(s) = \langle y(t_1)y(t_2)\rangle, \tag{10.93}$$

where $K(s)$ is expected to be extremely peaked around $s = 0$. Using the properties of the trigonometric functions we can write (10.92) as

$$\langle a_n^2\rangle = 2f_0^2 \int_0^{1/f_0} dS \int_{-\infty}^{\infty} dsK(s)(\cos 2\pi n f_0 s + \cos 4\pi n f_0 S), \tag{10.94}$$

where we have made the following change

$$\begin{aligned} s &\equiv t_2 - t_1 \\ S &\equiv \frac{1}{2}(t_1 + t_2). \end{aligned} \tag{10.95}$$

Note that the integral internal in the variable s has been extended from minus infinity to plus infinity because $K(s)$ is extremely peaked around $s = 0$. The second term in the integral (10.94) gives zero contribution. Therefore from (10.94) we have

$$\langle a_n^2\rangle = 4f_0 \int_0^{\infty} K(s)\cos 2\pi n f_0 s ds. \tag{10.96}$$

In order to take the limit $t \to \infty$, we define

$$W(nf_0)\Delta(nf_0) = \langle a_n^2\rangle, \tag{10.97}$$

where $\Delta(nf_0) = (n+1)f_0 - nf_0 = f_0$. Defining $f = nf_0$ (10.96) becomes

$$W(f) = 4\int_0^{\infty} K(s)\cos(2\pi f s)ds. \tag{10.98}$$

In the limit $T = (1/f_0) \to \infty$, f becomes a continuous variable. In this limit, the antifourier transform of (10.98) gives

$$K(s) = \int_0^{\infty} W(f)\cos(2\pi f s)df. \tag{10.99}$$

Relations (10.98) and (10.99) are the Wiener-Khintchine relations. They relate the weight of the contributions of each frequency to the Fourier Transform of the autocorrelation functions. Given the signal, one can calculate the autocorrelation function and therefore the width $W(f)$ that characterizes the signal.

Let us look at the physical meaning of (10.99). For $s = 0$ we have

$$K(0) = \langle y^2 \rangle = \int_0^\infty W(f) df, \tag{10.100}$$

namely the width of the signal is the integral of the weights over all frequencies. Note that these signals with the same width (the same intensity) may differ completely from each other (Fig. XX). The fingerprint of a signal is $W(f)$. A signal that contains all frequencies is extremely noisy and is called white noise. In fact, from (10.99), if $W(f) = \text{const}$, $K(s) \propto \delta(s)$. 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. This can be realized only if the signal is very noisy. However, 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

$$W(f) \equiv \begin{cases} W_0 & 0 \le f \le f_c \\ 0 & f > f_c \end{cases} . \tag{10.101}$$

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 11

Quantum Statistical Mechanics

11.1 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 accordingto the Shroedinger equation

$$i\hbar \frac{\partial}{\partial t}\psi(x,t) = \hat{\mathcal{H}}\psi(x,t), \tag{11.1}$$

where $\hat{\mathcal{H}}$ is the Hamiltonian operator.

The mean value of any observable defined by an operator $\hat{A}$ at time t is

$$\langle \hat{A} \rangle \equiv A(t) = \int \psi^*(x,t)\hat{A}\psi(x,t)dx, \tag{11.2}$$

where the wave function is normalized to unity. The result of a measurement A_{obs} is time average over observable time,

$$A_{\text{obs}} \equiv \frac{1}{\tau}\int_0^\tau A(t)dt. \tag{11.3}$$

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

$$A_K(t) = \int \psi_K^*(x,t)\hat{A}\psi_K(x,t)dx, \tag{11.4}$$

$$\langle \hat{A} \rangle_{\text{ens}} \equiv \frac{1}{\mathcal{N}} \sum_K A_K(t). \tag{11.5}$$

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 $\phi_n(x)$

$$\psi_K(x,t) = \sum_n C_n^{(K)}(t)\phi_n(x), \tag{11.6}$$

where the coefficients $C_n^{(K)}(t)$ satisfy the normalization condition

$$\sum_n |C_n^{(K)}(t)|^2 = 1. \tag{11.7}$$

Consequently (11.4) can be written

$$A_K(t) \equiv \sum_{mn} C_m^{*(K)}(t) C_n^{(K)}(t) A_{mn}, \tag{11.8}$$

where

$$A_{mn} \equiv \int \phi_m^*(x)\hat{A}\phi_n(x)dx. \tag{11.9}$$

Consequently,

$$\langle \hat{A} \rangle_{\text{ens}} \equiv \frac{1}{\mathcal{N}} \sum_K A_K(t) = \sum_{mn} \left[\frac{1}{\mathcal{N}} \sum_K C_m^{*(K)} C_n^{(K)} \right] A_{mn}. \tag{11.10}$$

If we define

$$\rho_{nm} \equiv \frac{1}{\mathcal{N}} \sum_K C_m^{*(K)} C_n^{(K)}, \tag{11.11}$$

then (11.10) can be written in a more complete form,

$$\langle \hat{A} \rangle_{\text{ens}} = \sum_{n,m} \rho_{nm} A_{mn}. \tag{11.12}$$

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

$$\rho_{nm} = \int \phi_n^*(x)\hat{\rho}\phi_m(x)dx. \tag{11.13}$$

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 (11.12) can then be written as the trace of the product of $\hat{\rho}$ and $\hat{A}$

$$\langle \hat{A} \rangle_{\text{ens}} = \frac{\text{Tr}\hat{\rho}\hat{A}}{\text{Tr}\hat{\rho}}, \tag{11.14}$$

where we have also divided by Tr$\hat{\rho}$ in the general case in which the coefficients $C_m^{(K)}$ are not normalized to 1 [see Eq. (11.7). 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. 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 $\hat{\rho}$. To do so we must specify the elements of the matrix $\hat{\rho}$ in a particular base. We choose as a base the eigenfunction $\phi_n(x)$ of the Hamiltonian. We then postulate

$$\rho_{nn} = \frac{1}{\mathcal{N}} \sum_K |C_n^{(K)}|^2 = \begin{cases} 1 & \forall_n : E \leq E_n \leq E + \delta E \\ 0 & \text{otherwise} \end{cases}, \tag{11.15}$$

and

$$\rho_{mn} = 0 \qquad \text{for} \qquad m \neq n. \tag{11.16}$$

The matrix is then written

$$(\rho_{mn}) \equiv \begin{pmatrix} 1 & & & & & & 0 \\ & 1 & & & & & \\ & & \ddots & & & & \\ & & & 1 & & & \\ & & & & 0 & & \\ & & & & & \ddots & \\ 0 & & & & & & 0 \end{pmatrix}, \tag{11.17}$$

and the diagonal elements that are zero correspond to those eigenfunctions of the energy now accessible, namely outside the energy interval $(E, E+\delta E)$.

The first part of postulate (11.15) 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 accessiible state, every asseccible state is equally probable. The second part of the postulate does not have a correspondence in classical statistical mechanics and, for the following reason, it is called the postulate of the random phases.

If we write the coefficients $C_n^{(K)}$ as the product of the modulus times the phase

$$C_n^{(K)} \equiv |C_n^{(K)}| e^{i\varphi_n^{(K)}}, \tag{11.18}$$

then the non-diagonal elements are

$$\rho_{nm} = \frac{1}{\mathcal{N}} \sum_K |C_m^{(K)}||C_n^{(K)}| e^{i(\varphi_m^{(K)} - \varphi_n^{(K)})}. \tag{11.19}$$

Therefore, according to random phase postulate (11.16), (11.19) must be zero for any $m \neq n$. This can occur only if the phases in the ensemble (namely, as functions of K) are completely random.

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 (11.15) and (11.16).

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). Let us consider the time average by expanding the wave function in (11.2) in terms of the eigenfunctions of the energy,

$$\psi(x,t) = \sum_n C_n(t)\phi_n(x). \tag{11.20}$$

Therefore,

$$A(t) \equiv \int \psi^*(x,t)\hat{A}\psi(x,t)dx = \sum_{mn} C_m^*(t)C_n(t)A_{mn}. \tag{11.21}$$

Therefore the time average of $A(t)$ (11.3) is

$$A_{\text{obs}} \equiv \sum_{mn} \rho'_{nm} A_{mn}, \tag{11.22}$$

where

$$\rho'_{nm} \equiv \overline{C_m^*(t)C_n(t)}. \tag{11.23}$$

Here the bar indicates time average.

Now the postulate that the time average (11.22) and the ensemble average coincide implies

$$\rho_{mn} = \rho'_{mn} \tag{11.24}$$

if we write the coefficient as

$$C_n = |C_n| e^{i\varphi_n(t)}. \tag{11.25}$$

The postulate on the density matrix implies

$$|C_n|^2 = \begin{cases} \text{const.} & E \leq E_n \leq E + \delta E \\ 0 & \text{otherwise} \end{cases}, \tag{11.26}$$

and

$$\overline{C_m^*(t) C_n(t)} = |C_m||C_n| \overline{\exp\{-i[\varphi_m(t) - \varphi_n(t)]\}}. \tag{11.27}$$

Equation (11.26) implies that the probability of finding the system in any of the accessible states is the same as for all the states. Equation (11.27) implies that the phases $\varphi_m(t)$ are completely random and independent of each other. Physically this means that the state of the system is a superposition of incoherent states or in a mixture of states. The consequence is that all inteference terms vanish.

In conclusion, the postulates of quantum statistical mechanics are equivalent to, e.g., that the wave function of a macroscopic system is a superposition of incoherent states with coefficients satisfying (11.26) and (11.27).

The concept of coherent states is one used in optics. If $\vec{E}_1(t)$ and $\vec{E}_2(t)$ constitute an electrical field caused by two different light sources of constant intensity and located at a given point in space at time t, then the total field is $\vec{E}(t) = \vec{E}_1(t) + \vec{E}_2(t)$ and the light intensity at that given point is

$$|\vec{E}_1(t)|^2 = |\vec{E}_1|^2 + |\vec{E}_2|^2 + \vec{E}_1(t) \cdot \vec{E}_2^*(t) + \vec{E}_1(t)^* \cdot \vec{E}_2(t). \tag{11.28}$$

The component along the x direction can be written

$$E_{1x} = |E_{1x}| e^{i\varphi_1(t)}, \qquad E_{2x} = |E_{2x}| e^{i\varphi_2(t)}, \tag{11.29}$$

and similarly for the components in the y and z direction. If the sources are independent, the two phase are uncorrelated, therefore if we take the time average of the intensity (11.28) we obtain

$$|\vec{E}_1|^2 = |E_1|^2 + |E_2|^2, \tag{11.30}$$

since the interference term gives zero contribution. The only way to have constructive or destructive interference is when the contribution comes from the same source, in which case $\varphi_1(t) - \varphi_2(t) = \text{const.}$

11.2 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 (11.17) 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,

$$i\hbar\frac{\partial}{\partial t}\psi^{(K)}(x,t) = \hat{\mathcal{H}}\psi(K)(x,t). \tag{11.31}$$

Fixing a base $\phi_m(x)$ (not necessarily eigenfunctions of the Hamiltonian $\hat{\mathcal{H}}$),

$$\psi^{(K)}(x,t) = \sum_m C_m^{(K)}(t)\phi_m. \tag{11.32}$$

Substituting (11.32) into (11.31) we have

$$i\hbar\sum_m \dot{C}_m^{(K)}(t)\phi_m = \sum_m C_m^{(K)}(t)\mathcal{H}\phi_m. \tag{11.33}$$

Multiplying (11.33) by $\phi_n(x)$, integrating over x, and using the orthonormality conditions for $\phi_m(x)$, we have

$$i\hbar\dot{C}_n^{(K)}(t) = \sum_m C_m^{(K)}(t)\mathcal{H}_{nm}, \tag{11.34}$$

where

$$\mathcal{H}_{nm} \equiv \int \phi_n^*\mathcal{H}\phi_m. \tag{11.35}$$

Recalling the definition of the density matrix

$$\rho_{nm}(t) \equiv \frac{1}{\mathcal{N}}\sum_K C_m^{*(K)}(t)C_n^{(K)}(t), \tag{11.36}$$

from (11.34) we have

$$i\hbar\frac{\partial}{\partial t}\rho_{nm} = \frac{i\hbar}{\mathcal{N}}\sum_K\left(\dot{C}_m^{*(K)}C_n^{(K)} + C_m^{*(K)}\dot{C}_n^{(K)}\right) = \sum_\ell\left(H_{n\ell}\rho_{\ell m} - \rho_{n\ell}H_{\ell n}\right), \tag{11.37}$$

or, in terms of operators,

$$i\hbar\frac{\partial\hat{\rho}}{\partial t} = [\hat{H},\hat{\rho}]. \tag{11.38}$$

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 $\rho_{nm}(t)$ [see Eq. (XX)]

$$\rho_{nm}(t) = \int \phi_n^*(x)\hat{\rho}(t)\phi_m(x)dx. \tag{11.39}$$

Equation (11.39) 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

$$\rho_{nm}[t, \phi_n^*(t), \phi_m(t)] = \int \phi_n^*(x,t)\hat{\rho}(t)\phi_m(x,t)dx, \tag{11.40}$$

where we have indicated the time dependence through $\phi_n^*(x,t)$ and $\phi_m(t)$ explicitely.

The total derivation of (11.40) gives

$$\begin{aligned} i\hbar\frac{d}{dt}\rho_{nm}[t, \phi_n^*(t), \phi_m(t)] &= -\int \phi_n^*(x,t)[H, \hat{\rho}]\phi_m(x,t)dx \\ &+ i\hbar\int \phi_n^*(x,t)\frac{\partial\hat{\rho}(t)}{\partial t}\phi_m(x,t)dx, \end{aligned} \tag{11.41}$$

which can be written formally as

$$i\hbar\frac{d\hat{\rho}}{dt} = [\hat{\rho}H] + i\hbar\frac{\partial\rho}{\partial t}, \tag{11.42}$$

which together with (11.38) gives

$$i\hbar\frac{d\hat{\rho}}{dt} = 0, \tag{11.43}$$

which is the analog of Liouville's equation in classical statistical mechanics. Both Eq. (11.38) and Eq. (11.40) are general equations and can be satisfied by any ensemble distribution. In particular, 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 $\hat{\mathcal{H}}$. It follows from (11.38) 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.

11.3 Microcanonical and Canonical Ensemble

The statistical ensemble considered thus far is related to an isolated system and is called a microcanonical ensemble. In this case the density matrix can be related to thermodynamic functions. In fact, from (xx) it follows that

$$\mathrm{Tr}\hat{\rho} = \Omega, \tag{11.44}$$

where Ω is the number of accessible microstates. Therefore, using the arguments developed in classical statistical mechanics, the entropy is given by

$$S = K \ln(\mathrm{Tr}\hat{\rho}). \tag{11.45}$$

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 the diagonal elements are given by $\rho_{nn} = e^{-\beta E_n}$.

In terms of operators, we then have

$$\hat{\rho} = e^{-\beta \hat{H}}, \tag{11.46}$$

with the partition function given by

$$Z = \mathrm{Tr}\hat{\rho} = \sum_n e^{-\beta E_n}, \tag{11.47}$$

and the free energy F given by

$$F = -KT \ln Z. \tag{11.48}$$

Similarly, for the grand canonical ensemble the matrix density is given by

$$\hat{\rho} = e^{-\beta \hat{\mathcal{H}} + \beta \mu \hat{N}}, \tag{11.49}$$

where μ is the classical potential and $\hat{N}$ the operator relative to the number of particles. The grand partition function $\mathcal{Z}$ is therefore given by

$$\mathcal{Z} = \mathrm{Tr}\hat{\rho} = \sum_r e^{\beta \mu N_r - \beta E_r}, \tag{11.50}$$

which is related to pressure P and volume V by

$$PV = KT \ln \mathcal{Z}. \tag{11.51}$$

Problem. Consider a particle with a two-component spin in a thermal bath in an external magnetic field $\vec{H}$. The partition function and the average magnetization in the direction of the field. The Hamiltonian can be written

$$\hat{H} = -\vec{\mu}\cdot\vec{H} = -\hat{\mu}_z H, \tag{11.52}$$

where μ_2 is the component of the magnetic moment along the direction of the field (coincident with the z axis), and $\hat{\mu}_z$ is given by a Pauli matrix

$$\hat{\mu}_z = \mu_0 \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \tag{11.53}$$

with μ_0 being the magnetic component along the z direction. The partition function is given by

$$Z = \text{Tr}\hat{\rho} = e^{-\beta\mu_0 H} + e^{\beta\mu_0 H}. \tag{11.54}$$

The average magnetization is given by

$$\langle \hat{\mu}_z \rangle = \frac{\text{Tr}\hat{\rho}\hat{\mu}_z}{\text{Tr}\hat{\rho}} = \mu_0 \frac{e^{+\beta\mu_0 H} - e^{-\beta\mu_0 H}}{e^{+\beta\mu_0 H} + e^{-\beta\mu_0 H}}, \tag{11.55}$$

which coincides with the result obtained in classical statistical mechanics.

11.4 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 Gibbs correction 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 given by (xx) in the coordinates representation with the eigenvectors and eigenvalues given by

$$\hat{H}|K\rangle = \epsilon_K |K\rangle, \tag{11.56}$$

where

$$\epsilon_K = \frac{\hbar^2 K^2}{2m}. \tag{11.57}$$

Here we are using the Dirae notation where $|K\rangle$ is a vector corresponding to a microstate. In the representation of the coordinates, the wave function is

$$u_K(\vec{x}) = \langle x|K\rangle = \frac{1}{L^{3/2}}e^{i\vec{K}\cdot\vec{x}}, \tag{11.58}$$

where

$$\vec{K} = \frac{2\pi}{L}\vec{n}, \qquad \vec{n} \equiv \{n_x, n_y, n_z\}, \tag{11.59}$$

where n_x, n_y, and n_z are ± 1, ± 2, ± 3...

Let us calculate the matrix density $\hat{\rho} = e^{-\beta\hat{H}}$ in the base of the eigenfunction of the position

$$\langle\vec{x}|\hat{\rho}|\vec{x}'\rangle = \sum_K \langle x|K\rangle e^{-\beta\epsilon_K}\langle K|x'\rangle. \tag{11.60}$$

For $x = x'$ (11.60) is the probabiity of finding the particle in x. For $x \neq x'$ (11.60) is the average of the product of the amplitude of finding the particle in x and x', so it is a measure of the wave function. Since the particle is in a superposition of many states, it will be equally distributed everywhere in the box.

From (11.58) we have

$$\langle\vec{x}|\hat{\rho}|\vec{x}'\rangle = \sum_K \frac{1}{L^3}e^{-\beta\epsilon_K}e^{i\vec{K}\cdot(\vec{x}-\vec{x}')}. \tag{11.61}$$

In the limit Ł $\to \infty$, the sum can be transformed into an integral, namely

$$\vec{x}|\hat{\rho}|x'\rangle = \frac{1}{(2\pi)^3}\int e^{\frac{-\beta(\hbar^2K^2}{2m)}}e^{i\vec{K}\cdot(\vec{x}-\vec{x}')}d\vec{K}, \tag{11.62}$$

where we have used the property (11.59)

$$\frac{\Delta n_x \Delta n_y \Delta n_z}{L^3} = \frac{\Delta K_x \Delta K_y \Delta K_z}{(2\pi)^3}. \tag{11.63}$$

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 (11.62) is the Fourier transform of a Gaussian distribution. This integral can be expressed

$$\langle\vec{x}|\hat{\rho}|\vec{x}'\rangle = \left(\frac{m}{2\pi\beta\hbar^2}\right)^{3/2} e^{-(m/2\beta\hbar^2)(\vec{x}-\vec{x}')}, \tag{11.64}$$

and gives a Gaussian whose width,

$$\lambda = \frac{\hbar}{\sqrt{KTm}}, \tag{11.65}$$

is DeBroglie's wavelangth and is the inverse of the width of the original Gaussian in (11.62). Equation (11.64) is significant. For $x = x'$, (11.64) becomes

$$\vec{x}|\hat{\rho}|x\rangle = \left(\frac{m}{2\pi\beta\hbar^2}\right)^{3/2}, \tag{11.66}$$

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 (11.65) 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.

The partition function is given by

$$\mathrm{Tr}\hat{\rho} = \int \langle\vec{x}|\hat{\rho}|\vec{x}'\rangle dx = \left(\frac{m}{2\pi\beta\hbar^2}\right)^{3/2} V, \tag{11.67}$$

where V is the volume of the box. 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. We want to extend the result to the case of two particles and then to N particles.

We now consider two noninteracting particles and consider the matrix density

$$\langle\vec{x}_1\vec{x}_2|\hat{\rho}|\vec{x}'_1\vec{x}'_2\rangle. \tag{11.68}$$

The eigenvalues and eigenfunctions of the Hamiltonian $\hat{H}$ are now

$$H|\vec{K}_1\vec{K}_2\rangle = \epsilon(K_1, K_2)|\vec{K}_1\vec{K}_2\rangle, \tag{11.69}$$

where

$$\epsilon(K_1, K_2) = \frac{\hbar^2 K_1^2}{2m} + \frac{\hbar^2 K_2^2}{2m}. \tag{11.70}$$

The wave function for one particle is given by (11.58). 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

$$\psi_E(\vec{x}_1,\vec{x}_2)=\frac{1}{\sqrt{2}}\left[U_{K_1}(\vec{x}_1)U_{K_2}(\vec{x}_2)\pm U_{K_1}(\vec{x}_2)U_{K_2}(\vec{x}_1)\right], \qquad (11.71)$$

where the symmetric wave function (with plus sign) refers to bosons while the antisymmetric (with minus sign) refers to fermions.

Inserting twice the unit operator,

$$\sum_{\vec{K}_1\vec{K}_2}|\vec{K}_1\vec{K}_2\rangle\langle\vec{K}_1\vec{K}_2|=1, \qquad (11.72)$$

in (11.68) we have

$$\langle\vec{x}_1\vec{x}_2|\hat{\rho}|\vec{x}_1\vec{x}_2\rangle=\sum_{\vec{K}_1\vec{K}_2}{}^{'}\, e^{-\beta\epsilon(K_1K_2)}\psi_E^*(\vec{x}_1',\vec{x}_2')\psi_E(\vec{x}_1,\vec{x}_2), \qquad (11.73)$$

where the prime indicates the constraint that in the sum are excluded all the states obtained by exchanging K_1 and K_2, since this operation gives states which are not independent. Substituting (11.71) into (11.73), we note that each term in (11.63) 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 (11.73) becomes

$$\langle\vec{x}_1\vec{x}_2|\hat{\rho}|\vec{x}_1\vec{x}_2\rangle=\frac{1}{2}\sum_{K_1K_2}e^{-\beta(\hbar^2K_1^2/2m)}e^{-\beta(\hbar^2K_2^2/2m)}\,\cdot$$

$$\cdot\left[U_{K_1}(\vec{x}_1)U_{K_2}(\vec{x}_2)U^*_{K_1}(\vec{x}_1')U^*_{K_2}(\vec{x}_2')\pm U_{K_1}(\vec{x}_2)U_{K_2}(\vec{x}_1)U^*_{K_1}(\vec{x}_1')U^*_{K_2}(\vec{x}_2')\right]=$$

$$=\frac{1}{V^2}\frac{1}{2}\left[\sum_{K_1}e^{-\beta(\hbar^2K_1^2/2m)}e^{i\vec{K}_1(\vec{x}_1-\vec{x}_1')}\cdot\sum_{K_2}e^{-\beta(\hbar^2K_2^2/2m)}e^{i\vec{K}_2(\vec{x}_2-\vec{x}_2')}\pm\right.$$

$$\left.\pm\sum_{K_1}e^{-\beta(\hbar^2K_1^2/2m)}e^{i\vec{K}_1(\vec{x}_2-\vec{x}_1')}\cdot\sum_{K_2}e^{-\beta(\hbar^2K_2^2/2m)}e^{i\vec{K}_2(\vec{x}_1-\vec{x}_2')}\right], \qquad (11.74)$$

from which we can calculate the partition function

$$\begin{aligned} Z &= \int\langle\vec{x}_1\vec{x}_2|\hat{\rho}|\vec{x}_1\vec{x}_2\rangle d\vec{x}_1d\vec{x}_2 \\ &= \frac{1}{\lambda^6}\cdot\frac{1}{2}\int\left[1\pm e^{-2\pi(r_{12}^2/\lambda^2)}\right]d\vec{x}_1d\vec{x}_2, \qquad r_{12}\equiv|\vec{x}_1-\vec{x}_2|, \quad (11.75) \end{aligned}$$

where λ is the DeBroglie wavelength. The integral can be evaluated, giving

$$Z = \frac{1}{2}\left(\frac{V}{\lambda^3}\right)^2 \left[1 \pm \frac{1}{2^{5/2}}\left(\frac{2}{V}\lambda^3\right)\right]. \tag{11.76}$$

In (11.76) the term $n\lambda^3$ appears with $n = 2/V$ being the particle density.

Whenever

$$n\lambda^3 \ll 1, \tag{11.77}$$

we can neglect the second term and th partition function becomes the same for both fermions or bosons,

$$Z = \frac{1}{2}\left(\frac{V}{\lambda^3}\right)^2, \tag{11.78}$$

which means that qunatum mechanical effects can be neglected. This result can be generalized to N non-interacting particles. Under condidtions (11.77) where $n = N/V$ is the density, the partition function reduces to the classical limit

$$Z = \frac{1}{N!}\left(\frac{V}{\lambda^3}\right)^N, \tag{11.79}$$

which coincides with the classical derivation (XX).

What is the physical meaning of condition (11.77)? Since the mean interparticle distance $r \sim n^{1/3}$, (11.77) can be written as

$$\frac{\lambda}{r} \ll 1, \tag{11.80}$$

which 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 hte quantum effect can be neglected. Nevertheless it is interesting to note that (11.79) 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 $\hbar = 0$, 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.

11.5 Classical Descriptions of Quantum Particles

We consider here two noninteracting quantum particles in a box. The density probability distribution is given by

$$\rho(\vec{x}_1, \vec{x}_2) \propto \left(1 \pm e^{-2\pi(r_{12}^2/\lambda^2)}\right). \tag{11.81}$$

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 (11.81), 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 that two particles cannot be in the same state. On the contrary, bosons behave as if there were an effective attraction.

Problem: What is the effective potential between two classical particles when they have the same spatial distribution? If the effective potential is $V(r)$, then the density probability distribution for two classical particles is

$$\rho(\vec{x}_1, \vec{x}_2) \propto e^{-\beta V(r_{12})}. \tag{11.82}$$

Equating (11.82) with (11.81) gives

$$V(r_{12}) \propto -\beta^{-1} \ln \left(1 \pm e^{-2\pi(r_{12}^2/\lambda^2)}\right). \tag{11.83}$$

Plot the potential in the case of bosons and fermions.

Chapter 12

Statistics of Non-Interacting Particles

In this chapter we will calculate the energy distribution for non-interacting particles for bosons and 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

$$Z = \sum_r e^{-\beta(E_r - \mu N_r)}, \tag{12.1}$$

where r denotes a microstate and with N_r particles and energy E_r. 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 $r \equiv \{n_1, n_2, n_j \ldots\}$, which represents the number of particles in state 1, 3, $j, \ldots$ The energy E_r can then be written in terms of the energy of a single particle ϵ_K

$$E_r \equiv E_{n_1, n_2, \ldots} = \sum_j n_j \epsilon_j. \tag{12.2}$$

The paraticle number N_r is given by

$$N_r \equiv N_{n_1,n_2,\ldots} = \sum_j n_j. \tag{12.3}$$

The partition function (12.1) can therefore be written as

$$Z = \sum_{n_1,n_2,\ldots} e^{-\beta \sum_j (\epsilon_j - \mu) n_j}. \tag{12.4}$$

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 on to values $n_i = 0,\ 1$.

In (12.4) the exponential of the sum can be written s the product of exponentials, therefore

$$Z = \prod_j Z_j, \tag{12.5}$$

and

$$\beta PV = \ln Z = \sum_j \ln Z_j, \tag{12.6}$$

where

$$Z_j = \sum_{n_j} e^{-\beta(\epsilon_j - \mu) n_j}. \tag{12.7}$$

The average number of particles in state K is given by

$$\langle n_j \rangle = \frac{\sum_{n_1 n_2 \ldots} n_j e^{-\beta \sum_r (\epsilon_r - \mu) n_r}}{Z} = \frac{\sum_{n_j} n_j e^{-\beta(\epsilon_j - \mu) n_j}}{Z_j} \frac{\prod_{r \neq j} Z_r}{\prod_{r \neq j} Z_r}. \tag{12.8}$$

[[[→ LAST FRACTION IN EQUATION = 1.0 ???]]] Therefore

$$\langle n_j \rangle = \frac{\sum_{n_j} n_j e^{-\beta(\epsilon_j - \mu) n_j}}{Z_j} \frac{\partial \ln Z_j}{\partial \beta \mu}, \tag{12.9}$$

and taking into account (12.7),

$$\langle n_j \rangle = \frac{\partial \ln Z_j}{\partial \beta \mu}. \tag{12.10}$$

Now we must calculate explicitely Z_j for bosons and fermions.

Bosons: The sum in (12.7) is over all values $n_j = 0, 1, 2, \cdots$

$$Z_j = \sum_{n_j=0}^{\infty} e^{-\beta(\epsilon_j - \mu)n_j} = \frac{1}{1 - e^{\beta(\mu - \epsilon_j)}}. \tag{12.11}$$

From (12.10) we have

$$\langle n_j \rangle = \frac{1}{e^{\beta(\epsilon_j - \mu)} - 1}, \tag{12.12}$$

which is called the Bose-Einstein distribution, and from (12.6)

$$\beta PV = -\sum_j \ln \left[1 - e^{\beta(\mu - \epsilon_j)} \right]. \tag{12.13}$$

Fermions: The sum in (12.7) is limited only to values 0,1; therefore,

$$Z_j = 1 + e^{-\beta(\epsilon_j - \mu)}. \tag{12.14}$$

From (12.10) we have

$$\langle n_j \rangle = \frac{1}{e^{\beta(\epsilon_j - \mu)} + 1}, \tag{12.15}$$

which is called the Fermi-Dirac distribution, and from (12.6)

$$\beta PV = -\sum_j \ln \left[1 + e^{-\beta(\epsilon_j - \mu)} \right]. \tag{12.16}$$

The chemical potential can be fixed by fixing the average number of particles in the system

$$\sum_j \langle n_j \rangle = \langle N \rangle. \tag{12.17}$$

12.0.1 Bose-Einstein Condensation

One of the consequences of the Bose-Einstein distribution is that at sufficiently low temperature a finite fraction of the total number of particles condenses into a single state at $K = 0$. It has been suggested that this transition is the basic mechanism for the superfliud transition in liquid helium. There are two isotopes of helium: ^{4}He and ^{3}He. An atom of ^{4}He has two protons and two neutrons, has a spin, and therefore is a boson. ^{4}He below a critical temperature exhibits such unusual properties as an absence of viscosity when it flows through a capillary. That is why it is called a superfluid. Although the Bose condensation obtained for the distribution (x) applies to a noninteracting Bose gas, it has been suggestd 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 condenstation phenomenon. A confirmation of this suggestion came from the observation that liquid ^{3}He, which has spin 1/2 and is a fermion but chemically is the same as ^{4}He, does not possess the same superfluid properties as ^{4}He.

12.0.2 Specific Heat of Electrons in Metals

As an application of the Fermi distribution, we calculated how much electrons contribute to the specific heat in metals. To a good approximation, the electrons in the conduction bond—those that conduct electricity—can be considered free. Therefore we can apply the Fermi distribution where the energy spectrum $\epsilon(\vec{K}) = \hbar^2 K^2/2m$ is given by (12.2). Moreover, each state has a degeneracy of 2 due to two possible spin configurations. If N is the number of electrons, the chemical potential is given by

$$N = 2\sum_{\vec{k}} f[\epsilon(\vec{K})] = \frac{2V}{(2\pi)^3}\int f[\epsilon(\vec{K})]k\vec{K}, \tag{12.18}$$

where the factor 2 comes from the spin configurations; $f(\epsilon)$ is the Fermi distriubiton,

$$f(\epsilon) = \frac{1}{e^{\beta(\epsilon-\mu)}}, \tag{12.19}$$

and using (12.7) 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

$$N = \frac{V}{\pi^2}\int_0^\infty K^2 f[\epsilon(\vec{K})]dK = \frac{1}{2}\frac{V}{\pi^2}\frac{(2m)^{3/2}}{\hbar^3}\int_0^\infty \epsilon^{1/2} f(\epsilon)d\epsilon. \tag{12.20}$$

In the limit $T \to \infty$, the Fermi distribution becomes a step function. 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 (12.20) we have

$$N = \frac{1}{3}\frac{V}{\pi^2}\frac{(2m)^{3/2}}{\hbar^3}\epsilon_F^{3/2}, \tag{12.21}$$

which relates the density N/V to the Fermi level.

For higher temperature, the Fermi distribution becomes a smooth function going from 1.0 to zero around the Fermi energy in a range of energy of the order KT (see Fig. xx). We will see now that only the fraction of electrons in this range will contribute to the specific heat, since the others at lower energy behave as if frozen. 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. It si clear then why only electrons near the edge of the distribution can contribute to the specific heat (Fig. xx). Let us calculate explicitly the energy and the specific heat,

$$E = A \int_0^\infty \epsilon^{3/2} f(\epsilon) d\epsilon, \tag{12.22}$$

where

$$A = \frac{1}{2}\frac{V}{\pi^2}\frac{(2m)^{3/2}}{\hbar^3}. \tag{12.23}$$

The specific heat C_V is given by

$$C_V = \frac{\partial E}{\partial T} = A \int_0^\infty \epsilon^{3/2} \frac{\partial f}{\partial T} d\epsilon. \tag{12.24}$$

In the limit of small T, it can be shown that $C_V \propto KT$ (see problem).