Statistical Physics– a second course

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Chapter 1

Summary of Thermodynamics

Equation of state The dynamics of particles and their interactions were understood at the classical level by the establishment of Newton's laws. Later, these had to be slightly modified with the introduction of Einstein's theory of relativity. A complete reformulation of mechanics became necessary when quantum effects were discovered.

In the middle of last century steam engines were invented and physicists were trying to establish the connection between thermal heat and mechanical work. This effort led to the fundamental laws of thermodynamics. In contrast to the laws of mechanics which had to be modified, these turned out to have a much larger range of validity. In fact, today we know that they can be used to describe all systems from classical gases and liquids, through quantum systems like superconductors and nuclear matter, to black holes and the elementary particles in the early Universe in exactly the same form as they were originally established. In this way thermodynamics is one of the most fundamental parts of modern science.

1.1 Equations of state

Equation of state

We will now in the beginning consider classical systems like gases and liquids. When these are in equilibrium, they can be assigned state variables like temperature T, pressure P and total volume V. These can not take arbitrary values when the system is in equilibrium since they will be related by an equation of state. Usually it has the form

$$P = P(V, T) .\tag{1.1}$$

Only values for two state variables can be independently assigned to the system. The third state variable is then fixed.

The equations of state for physical systems cannot be obtained from thermodynamics but must be established experimentally. But using the methods of statistical mechanics and knowing the fundamental interactions between and the properties of the atoms and molecules in the system, it can in principle be obtained.

An ideal gas of N particles obeys the equation of state

$$P = \frac{NkT}{V} \tag{1.2}$$

where k is Boltzmann's fundamental constant $k = 1.381 \times 10^{-23}\, J\, K^{-1}$. For one mole of the gas the number of particles equals Avogadro's number $N_A = 6.023 \times 10^{23}\, mol^{-1}$ and $R = N_A k = 8.314\, J\, K^{-1}\, mol^{-1} = 1.987\, cal\, K^{-1}\, mol^{-1}$. Since $\rho = N/V$ is the density of particles, the ideal gas law (1.2) can also be
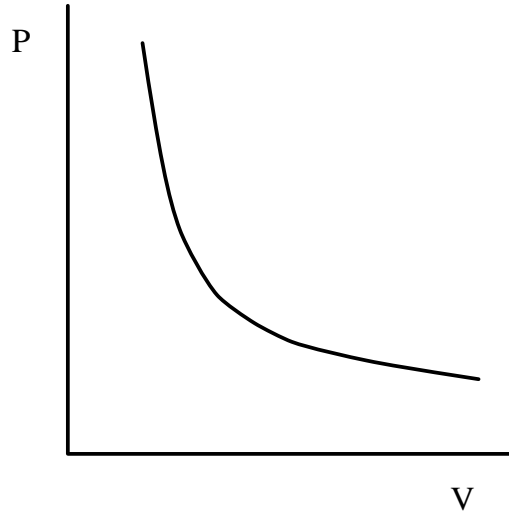
Figure 1.1: Equation of state for an ideal gas at constant temperature.

written as $P = kT\rho$. The pressure in the gas increases with temperature for constant density.

In an ideal gas there are no interactions between the particles. Including these in a simple and approximative way gives the more realistic van der Waals equation of state

$$P = \frac{NkT}{V - Nb} - \frac{aN^2}{V^2} \ . \tag{1.3}$$

It is useful for understanding in an elementary way the transition of the gas to a liquid phase.

Later in these lectures we will derive the general equation of state for gases

with two-body interactions. It will have the general form

$$P = kT \sum_{n=1}^{\infty} \rho^n B_n(T) \ . \tag{1.4}$$

The functions $B_n(T)$ are called virial coefficients with $B_1 = 1$. They can all be calculated in principle, but only the first few are usually obtained. We see that the van der Waal's equation (1.3) can be expanded to give this form of the virial expansion.

A real gas-liquid system has a phase diagram which can be obtained from the equation of state. When it is projected onto the PT and PV planes, it has the general form shown in Fig.1.2. For low pressures there is a gas phase g. It condenses into a liquid phase ℓ at higher pressures and eventually goes into
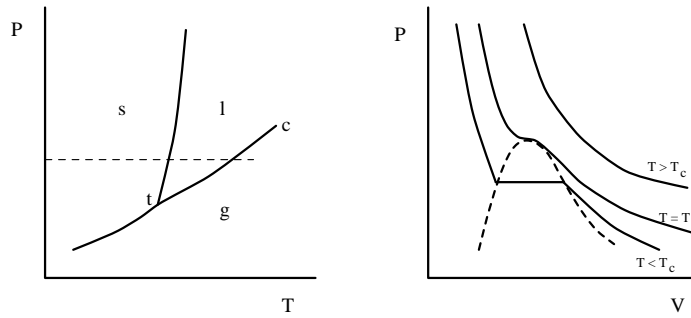
Figure 1.2: Phase diagram of a real liquid-gas system. The dotted line in the left figure indicates the two phase transitions it undergoes while being heated up at constant pressure.

the sold phase s at the highest pressures. At low temperatures, the gas can go directly into the solid phase. At the triple point t all three phases are in equilibrium. The gas-liquid co-existence curve terminates at the critical point c.

In other thermodynamic systems like magnets and superconductors, there will be other state variables needed to specify the equilibrium states. But they will again all be related by an equation of state. These systems are in many ways more important and interesting today than the physics of gases and liquids. But the general thermodynamics will be very similar. We will come back to these systems later in the lectures.

1.2   Laws of thermodynamics

Laws of thermodynamics

When we add an small amount of heat ΔQ to a system, its internal energy U will change at the same time as the system can perform some work ΔW. These changes are related by energy conservation,

$$\Delta Q = \Delta U + \Delta W \ . \tag{1.5}$$

For a system with fixed number of particles, the work done is given by the change of volume ΔV and the pressure in the gas as

$$\Delta W = P\,\Delta V \;. \tag{1.6}$$

It is positive when the volume of the system increases. The internal energy U depends only on the state of the system in contrast to the heat added and work done. These quantities depend on the way they have changed. U is therefore called a state function.

Experiments also revealed that the system can be assigned another, very important state function which is the entropy S. It is related to the heat added by the fundamental inequality

$$\Delta S \geq \frac{\Delta Q}{T} \tag{1.7}$$

where T is the temperature of the system. Reversible processes are defined to be those for which this is an equality.

In the limit where the heat is added infinitely slowly, the process becomes reversible and (1.5) and (1.7) combined give

$$T\Delta S = \Delta U + P\,\Delta V \tag{1.8}$$

for such a gas-liquid system. This equation is a mathematical statement of the First Law of thermodynamics. When we later consider magnets, it will involve other variables, but still basically express energy conservation.

The Second Law of thermodynamics is already given in (1.7). For an isolated system, $\Delta Q = 0$, it then follows that the entropy has to remain constant or increase, $\Delta S \geq 0$. Combining (1.7) with energy conservation from (1.5), we obtain

$$T\Delta S \geq \Delta U + P\,\Delta V \;. \tag{1.9}$$

This important inequality contains information about the allowed changes in the system.

As an illustration of the Second Law, consider the melting of ice. At normal pressure it takes place at 0 $^\circ C$ degrees with the latent or melting heat $\Lambda = 1440\ cal\,mol^{-1}$ taken from the surroundings. Water is more disordered than ice and its entropy is higher by the amount $\Delta S = \Lambda/273K = 5.27\ cal\,K^{-1}\,mol^{-1}$ since the process is reversible at this temperature. But why doesn't ice melt at $-10\ ^\circ C$ since it would then increase its entropy? The answer is given by (1.7) which in this case is violated, $5.27 < 1440/263$. However, it will melt spontaneously at $+10\ ^\circ C$ as we all know since $5.27 > 1440/283$. We have here made the reasonable approximation that the latent heat doesn't vary significantly in this temperature range.

The two laws of thermodynamics were formulated more than a hundred years ago by the German physicist Rudolf Clausius. In his words they were

1. Die Energi der Welt ist konstant.

2. Die Entropi der Welt strebt einem Maximum zu.

Sometimes (1.9) is also called Clausius' Inequality. It is the Second Law and the fundamental concept of entropy which contains the key to the connection between thermodynamics and statistical mechanics.

1.3 Maxwell relations and thermodynamic derivatives

Maxwell relations

We have already stated that the internal energy U is a state function. The first law (1.8) can be written on the form

$$dU = T\,dS - P\,dV \tag{1.10}$$

which shows that the natural variables for U are the entropy S and volume V, i.e. $U = U(S, V)$. Taking the differential,

$$dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV$$

and comparing, we find the partial derivatives

$$\left(\frac{\partial U}{\partial S}\right)_V = T \tag{1.11}$$

and

$$\left(\frac{\partial U}{\partial V}\right)_S = -P\ . \tag{1.12}$$

Since the second derivatives satisfy $\partial^2 U/\partial S\partial V = \partial^2 U/\partial V\partial S$, it follows that we must have the Maxwell relation

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V\ . \tag{1.13}$$

We can derive others when we have introduced new thermodynamic potentials in addition to the internal energy.

When using partial derivatives of this kind in thermodynamics, we will often need a few special properties they share. Consider the internal energy which is a function of the two natural state variables S and V, i.e. $U = U(S, V)$. But the entropy S is also a function of two such variables, say T and V which implies that that U can be considered as an implicit function of T and V. But this could just as well be two other state variables which will call X and Y to be general. A third state variable Z is then no longer independent because of the equation

of state and we must have $Z = Z(X, Y)$. We could also have taken Y and Z as independent and then we would have had $X = X(Y, Z)$. Taking the differentials of these two equations we obtain $dZ = (\partial Z/\partial X)_Y \, dX + (\partial Z/\partial Y)_X \, dY$ and $dX = (\partial X/\partial Y)_Z \, dY + (\partial X/\partial Z)_Y \, dZ$. Eliminating dY between them now gives

$$\left[\left(\frac{\partial X}{\partial Y}\right)_Z \left(\frac{\partial Y}{\partial X}\right)_Z - 1\right] dX + \left[\left(\frac{\partial X}{\partial Y}\right)_Z \left(\frac{\partial Y}{\partial Z}\right)_X + \left(\frac{\partial X}{\partial Z}\right)_Y\right] dZ = 0 \ .$$

Since the differentials dX and dZ are independent, their coefficients must separately be zero. It results in the two important relations

$$\left(\frac{\partial X}{\partial Y}\right)_Z = \left(\frac{\partial Y}{\partial X}\right)_Z^{-1} \tag{1.14}$$

and

$$\left(\frac{\partial X}{\partial Y}\right)_Z \left(\frac{\partial Y}{\partial Z}\right)_X \left(\frac{\partial Z}{\partial X}\right)_Y = -1 \ . \tag{1.15}$$

We can now take the internal energy to be a function of the two independent variables X and Y. Then

$$dU = \left(\frac{\partial U}{\partial X}\right)_Y dX + \left(\frac{\partial U}{\partial Y}\right)_X dY \ .$$

Dividing this by dZ and taking the resultant expression at constant Y, i.e. $dY = 0$, we are left with

$$\left(\frac{\partial U}{\partial Z}\right)_Y = \left(\frac{\partial U}{\partial X}\right)_Y \left(\frac{\partial X}{\partial Z}\right)_Y \tag{1.16}$$

which is just the ordinary chain rule for differentiation. On the other hand, dividing the previous expression by dX on both sides and taking the resultant equation at constant Z, we find

$$\left(\frac{\partial U}{\partial X}\right)_Z = \left(\frac{\partial U}{\partial X}\right)_Y + \left(\frac{\partial U}{\partial Y}\right)_X \left(\frac{\partial Y}{\partial X}\right)_Z \tag{1.17}$$

which also is a very useful relation.

1.4   Specific heats and compressibilities

When we add a small amount of heat ΔQ to the system holding the state variable X constant, the temperature will in general rise by a corresponding amount ΔT. The specific heat C_X is then defined by

$$C_X = \lim_{\Delta T \to 0} \left(\frac{\Delta Q}{\Delta T}\right)_X = T\left(\frac{\partial S}{\partial T}\right)_X \tag{1.18}$$

from (1.7) since in this limit the process is reversible. The derivative of entropy can be found from the First Law (1.8) where we can consider $U = U(T, V)$,

$$TdS = \left(\frac{\partial U}{\partial T}\right)_V dT + \left[P + \left(\frac{\partial U}{\partial V}\right)_T\right] dV \ . \tag{1.19}$$

Now taking this change under constant volume, we see that the specific heat C_V is given by the partial derivative

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V \ . \tag{1.20}$$

We can therefore always obtain this specific heat directly from knowing how the internal energy varies with the temperature.

Had we taken the heat addition above under constant pressure, we see that the specific heat C_P is related to C_V by

$$C_P = C_V + \left[P + \left(\frac{\partial U}{\partial V}\right)_T\right]\left(\frac{\partial V}{\partial T}\right)_P \ . \tag{1.21}$$

In (1.19) we could have considered instead $U = U(P, T)$ and would then have obtained directly that

$$C_P = \left(\frac{\partial H}{\partial T}\right)_P \ . \tag{1.22}$$

where

$$H(S, P) = U + PV \tag{1.23}$$

is the enthalpy. It plays a similar role as the internal energy, but now at constant pressure.

As an example, consider boiling of water. When it takes place at normal pressure $P = 1\,atm$, an amount of heat $\Delta Q = 539\,cal$ is required to transform $1g$ of water into vapor. But the vapor has a much larger volume, $\Delta V = (1671 - 1)\,cm^3$ and in the process must also do work $\Delta W = P\,\Delta V = 41\,cal$ against the atmospheric pressure. The change in enthalpy for this process is now $\Delta H = \Delta U + P\,\Delta V = \Delta Q = 539\,cal$ from the First Law, while the change in internal energy is $\Delta U = \Delta H - P\,\Delta V = 498\,cal$.

The specific heats (1.18) measures the change in temperature as a result of the added heat. Other such response functions are the compressibilities

$$K_X = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_X \tag{1.24}$$

and the thermal expansion coefficient

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P .$$ (1.25)

All these repose functions are related and one can show that for example

$$C_P - C_V = \frac{TV}{K_T} \alpha^2$$ (1.26)

$$K_T - K_S = \frac{TV}{C_P} \alpha^2$$ (1.27)

and

$$\frac{C_P}{C_V} = \frac{K_T}{K_S} .$$ (1.28)

Later we will see that for magnetic systems the susceptibilities play the same role as the compressibilities do in gas-liquid systems. They are important in characterizing the properties of these systems at the critical point.

1.5   Thermodynamic potentials

Until now we have considered closed systems which can not exchange particles with the surroundings. For an open system there will be an extra contribution to the work (1.6) done by the system when ΔN particles is transferred,

$$\Delta W = P \, \Delta V - \mu \, \Delta N$$ (1.29)

where μ is the chemical potential. The First Law is therefore changed into

$$dU = T \, dS - P \, dV + \mu \, dN .$$ (1.30)

Equations like (1.11) and (1.12) must now be taken also at constant particle number N.

In the differential (1.30) T, P and μ are intensive variables, while S, V and N are extensive variables, i.e. proportional to the number of particles in the system. Since the internal energy is also extensive, we must have

$$U(\lambda S, \lambda V, \lambda N) = \lambda U(S, V, N)$$ (1.31)

where λ is some scale parameter. Taking the derivative with respect to λ on both sides, we get

$$
\begin{aligned}
U(S, V, N) &= \frac{\partial}{\partial \lambda} U(\lambda S, \lambda V, \lambda N) \\
&= \left(S \frac{\partial}{\partial(\lambda S)} + V \frac{\partial}{\partial(\lambda V)} + N \frac{\partial}{\partial(\lambda N)} \right) U(\lambda S, \lambda V, \lambda N) \\
&= TS - PV + \mu N
\end{aligned}
$$ (1.32)

where we use that all the partial derivatives gives intensive variables which are independent of λ. If we take the differential of U and again use (1.30), it follows that

$$S\,dT - V\,dP + N\,d\mu = 0 \tag{1.33}$$

which is the Gibbs-Duhem relation.

When a system is isolated, the energy, particle number and volume is fixed and the entropy will be maximized in a spontaneous process. But sometimes other experimental parameters are fixed, like the temperature in stead of the energy. This can be achieved by putting the system in contact with a big reservoir at constant temperature T_0. If it is big enough the system can absorb energy from it without changing its temperature. Then, the total entropy of the system and the reservoir combined will be maximized, provided the total system is isolated. We will denote the energy and the entropy of the reservoir by primed quantities S' and U'. We are free to assume that the reservoir exchanges energy through a reversible process so that $T_0 \Delta S' = \Delta U'$. By energy conservation $\Delta U' = -\Delta U$, so that the total entropy change in a spontaneous process is

$$0 \leq T_0(\Delta S + \Delta S') = T_0 \Delta S - \Delta U. \tag{1.34}$$

Defining the Helmholtz free energy as

$$F = U - T_0 S \tag{1.35}$$

this may be written as

$$(\Delta F)_{T,V,N} \leq 0 \tag{1.36}$$

since T_0 is a constant during the spontaneous process. Note that F is defined entirely in terms of system quantities, the only external parameter being T_0.

Equation (1.36) describes processes that happen by them selves at fixed (V, N, T_0). The system could for instance be a rigid bottle water with an ice cube melting in a warm room. At equilibrium, when the ice has melted, the actual value of F depends on the variable set (V, N, T_0). To determine how, we must consider these variables as free and take the differential of equation (1.35). Setting $T = T_0$ this gives

$$dF = dU - dT\,S - T\,dS \tag{1.37}$$

Using equation (1.30), which holds for reversible processes, we get

$$dF = -S\,dT - P\,dV + \mu\,dN. \tag{1.38}$$

This result is of course general, and not limited to the bottle of ice and water. It shows that the natural, or canonical, variables of F is indeed the ones that are fixed for the system. It is seen from equation (1.38) that at equilibrium $F = F(T, V, N)$, and once this function is known S, p and μ may be obtained as the derivatives of F. Note that when (T, V, N) are fixed, equation (1.38) gives

$dF = 0$, which is the reversible case. For spontaneous, irreversible processes $\Delta F \geq 0$, and in this case the actual change in F can be determined if the process goes from one equilibrium state to another. For instance if the bottle of ice is placed in a warm room, it will change to a bottle of water and vapor, and ΔF is the difference between the initial equilibrium value in the frozen state, and the final equilibrium value in the melted state.

From a mathematical point of view U and F are related by a so-called Legendre transformation. Adding TS changes the S-dependence of U to a T-dependence in F. In general, if some quantity $F = F(X,Y)$ where $Z = (\partial F/\partial X)_Y$, then $G = F - XZ$ will be a function of Y and Z only, $G = G(Y,Z)$. This follows from $dG = (\partial F/\partial Y)_X\, dY - X\, dZ$. We can use this transformation to construct other important thermodynamic potentials. With the help of equation (1.38)

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N} \qquad P = -\left(\frac{\partial F}{\partial V}\right)_{T,N} \qquad \mu = \left(\frac{\partial F}{\partial N}\right)_{T,V} . \qquad (1.39)$$

These derivatives can be used to establish new Maxwell relations.

In addition to eliminating S as a variable in the internal energy U in favor of T to arrive at the Helmholtz free energy, we could also add PV to replace V by P. The Legendre transformation is then

$$\begin{aligned} G(T,P,N) &= U - TS + PV \\ &= N\mu(T,P) \end{aligned} \qquad (1.40)$$

which is the Gibbs free energy. From (1.30) it follows that

$$dG = -S\, dT + V\, dP + \mu\, dN \qquad (1.41)$$

which implies

$$S = -\left(\frac{\partial G}{\partial T}\right)_{P,N} \qquad V = \left(\frac{\partial G}{\partial P}\right)_{T,N} \qquad \mu = \left(\frac{\partial G}{\partial N}\right)_{T,P} \qquad (1.42)$$

in analogy with (1.39).

If the pressure is held at constant pressure instead of volume, the Gibbs free energy will spontaneously decrease or be minimal,

$$(\Delta G)_{T,P,N} \leq 0 . \qquad (1.43)$$

These thermodynamic potentials have many important applications and specially in physical chemistry in connection with phase equilibria and in chemical reactions.

In condensed matter physics one often also considers systems with fixed volume, temperature and constant chemical potential μ instead of particle number N. For such systems one needs the corresponding thermodynamic potential

which can be derived from Helmholtz free energy by another Legendre transformation. It gives

$$
\begin{aligned}
\Omega(T, V, \mu) &= F(T, V, N) - \mu N \\
&= -PV
\end{aligned}
\tag{1.44}
$$

which is usually called the Landau free energy. From (1.30) it follows that the differential

$$
d\Omega = -S\, dT - P\, dV - N\, d\mu \; .
\tag{1.45}
$$

This new thermodynamic potential will be extensively used when we later consider quantum systems of indistinguishable particles.

The free energies so far depend on canonical variables that may be fixed experimentally. This is true for the variable sets (T, V, N), (T, P, N) and (T, μ, V) corresponding to the free energies F, G and Ω. It does not matter if the systems in question evolve spontaneously and change. In contrast, there is no simple and general experimental procedure to fix (S, V, N), the variables corresponding to U. In order to fix S one must remove heat from the system after a spontaneous process, that increases S, has taken place.

Assuming such a procedure one can imagine processes at constant S. From (1.9) it then follows that a system that is kept at constant entropy and volume, can only change spontaneously such that

$$
(\Delta U)_{S,V} \le 0
\tag{1.46}
$$

i.e. by lowering its internal energy. When the system is in equilibrium, it cannot change spontaneously and hence its internal energy must be a minimum at constant volume and entropy.

Finally, we can write (1.9) in terms of the enthalpy (1.23) as

$$
T\Delta S \ge \Delta H + V\,\Delta P \; .
\tag{1.47}
$$

For a system which is kept at constant pressure and entropy, the enthalpy will therefore be a minimum when it is at equilibrium,

$$
(\Delta H)_{S,P} \le 0 \; .
\tag{1.48}
$$

Like the internal energy U, H is also a thermodynamic potential. From the First Law (1.8) we now have

$$
dH = T\, dS + V\, dP
\tag{1.49}
$$

so that entropy and pressure are the natural variables for the enthalpy. From this we can derive the Maxwell relation

$$
\left(\frac{\partial T}{\partial P} \right)_S = \left(\frac{\partial V}{\partial S} \right)_P
\tag{1.50}
$$

in the same way as we derived (1.13).

1.6   Fluctuations and thermodynamic stability

The infinitesimal variations ΔS, ΔV and ΔU in Clausius Inequality (1.9) represent spontaneous changes in the system. When it is in equilibrium, its probability is at a maximum. As we shall see more in detail later, there can still be statistical fluctuations away from equilibrium, $S \to S + \delta S$, $V \to V + \delta V$ and $U \to U + \delta U$. These will then take the system to a state with less probability. But the process back to equilibrium will be spontaneous and satisfy Clausius Inequality. We therefore have that $\Delta = -\delta$ and get the condition

$$T\delta S \le \delta U + P\,\delta V \tag{1.51}$$

which has to be satisfied by all thermodynamic fluctuations.

As an application of this, consider again the internal energy $U(S,V)$. Then

$$
\begin{aligned}
\delta U \;=\;& \left(\frac{\partial U}{\partial S}\right)_V \delta S + \left(\frac{\partial U}{\partial V}\right)_S \delta V \\
+\;& \frac{1}{2}\left[\left(\frac{\partial^2 U}{\partial S^2}\right)\delta S^2 + 2\left(\frac{\partial^2 U}{\partial S \partial V}\right)\delta S\delta V + \left(\frac{\partial^2 U}{\partial V^2}\right)\delta V^2\right]
\end{aligned}
$$

Now since $P = -\left(\partial U/\partial V\right)_S$ and $T = \left(\partial U/\partial S\right)_V$, it follows from (1.51) that

$$\left[\left(\frac{\partial^2 U}{\partial S^2}\right)\delta S^2 + 2\left(\frac{\partial^2 U}{\partial S \partial V}\right)\delta S\delta V + \left(\frac{\partial^2 U}{\partial V^2}\right)\delta V^2\right] \ge 0\,.$$

Since the fluctuations δS and δV are independent, this is satisfied when the two quadratic terms have positive coefficients, i.e.

$$\left(\frac{\partial^2 U}{\partial V^2}\right) = -\left(\frac{\partial P}{\partial V}\right)_S = \frac{1}{VK_S} \ge 0 \tag{1.52}$$

and

$$\left(\frac{\partial^2 U}{\partial S^2}\right) = \left(\frac{\partial T}{\partial S}\right)_V = \frac{T}{C_V} \ge 0\,. \tag{1.53}$$

In addition, the coefficient matrix must be positive definite so the determinant must be positive,

$$\left(\frac{\partial^2 U}{\partial S^2}\right)\left(\frac{\partial^2 U}{\partial V^2}\right) - \left(\frac{\partial^2 U}{\partial S \partial V}\right)^2 \ge 0$$

which requires

$$\left(\frac{\partial T}{\partial V}\right)_S^2 \le \frac{T}{VK_S C_V}\,. \tag{1.54}$$

We see that the most important result from these conditions for thermodynamic stability, is that specific heats and compressibilities are positive.

1.7 Phase transitions

Let us consider an isolated system consisting of two phases in thermodynamic equilibrium with each other. This happens due to exchange of particles and energies between them until the entropy $S(U, V, N) = S_1(U_1, V_1, N_1) + S_2(U_2, V_2, N_2)$ of the combined system is maximal. We must therefore have

$$
\begin{aligned}
dS &= \left[\left(\frac{\partial S_1}{\partial U_1} \right)_{V_1, N_1} - \left(\frac{\partial S_2}{\partial U_2} \right)_{V_2, N_2} \right] dU_1 + \left[\left(\frac{\partial S_1}{\partial V_1} \right)_{U_1, N_1} - \left(\frac{\partial S_2}{\partial V_2} \right)_{U_2, N_2} \right] dV_1 \\
&+ \left[\left(\frac{\partial S_1}{\partial N_1} \right)_{U_1, V_1} - \left(\frac{\partial S_2}{\partial N_2} \right)_{U_2, V_2} \right] dN_1 = 0
\end{aligned}
$$

where we have used that $dU_1 = -dU_2$ etc. for such an isolated system. Since these three infinitesimal changes are all independent, their coefficients must all be zero. From (1.30) we have the important derivatives

$$
\left(\frac{\partial S}{\partial U} \right)_{V,N} = \frac{1}{T} \qquad \left(\frac{\partial S}{\partial V} \right)_{U,N} = \frac{P}{T} \qquad \left(\frac{\partial S}{\partial N} \right)_{U,V} = -\frac{\mu}{T} \qquad (1.55)
$$

which immediately give the equilibrium conditions

$$
T_1 = T_2 \qquad P_1 = P_2 \qquad \mu_1 = \mu_2 \ . \qquad (1.56)
$$

These are just what we intuitively had expected.

We will now make a little use of these conditions. Consider two points T, P and $T + dT, P + dP$ along the co-existence curve in the phase diagram Fig.1.2 between gas and liquid. Phase equilibrium at the first point requires that $\mu_g(T, P) = \mu_\ell(T, P)$ and $\mu_g(T + dT, P + dP) = \mu_\ell(T + dT, P + dP)$ at the second point. These two conditions give together that $d\mu_g(T, P) = d\mu_\ell(T, P)$. But from the Gibbs-Duhem relation (1.33) we have $d\mu = -sdT + vdP$ where $s = S/N$ is the molecular entropy and $v = V/N$ is the molecular volume. The equilibrium conditions thus lead to the relation

$$
-s_g dT + v_g dP = -s_\ell dT + v_\ell dP
$$

or

$$
\left(\frac{dP}{dT} \right)_{coex} = \frac{s_g - s_\ell}{v_g - v_\ell} = \frac{\lambda}{T(v_g - v_\ell)} \qquad (1.57)
$$

where $\lambda = T(s_g - s_\ell)$ is the latent heat per particle in the transition. This is the Clausius-Clapeyron equation.

If we furthermore assume that the latent heat along the co-existence curve is constant and $v_\ell << v_g \approx kT/P$, we can integrate the Clausius-Clapeyron equation to give the vapor pressure formula

$$
P(T) = Ce^{-\frac{\lambda}{RT}} \qquad (1.58)
$$

where C is some constant and $\Lambda = N_A \lambda$ is the latent heat per mole. Knowing the equations of state for the liquid and solid states, we can also similarly find the pressure along their co-existence line.

When we change the temperature, pressure or volume of a substance so that we cross a co-existence line in the phase diagram, it will absorb or release some latent heat Λ. Since entropy is the first derivative of one of the free energies and it changes discontinuously by the amount $\Delta S = \Lambda / T$ in the transition across the co-existence line, this is called a first order phase transition. They all involve some latent heat like in melting or condensation.

Accurate measurements reveal that the latent heat Λ actually varies with temperature along the liquid-gas co-existence curve. The nearer one gets to the critical temperature T_c, the smaller it gets as shown in Fig.1.3. At the critical point the two phases become identical and $\Lambda(T_c) = 0$ so that the entropy changes continuously. But its first derivative, i.e. the second derivative of the free energy, will be discontinuous. At the critical point we therefore say that we
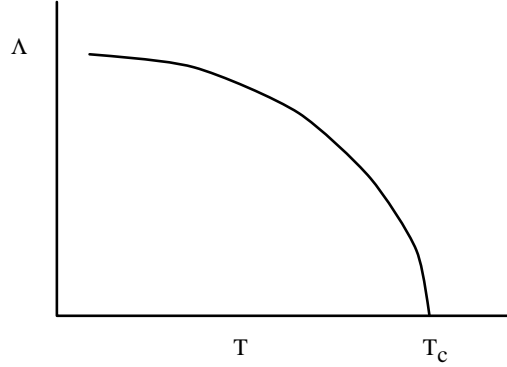
Figure 1.3: The latent heat in a first order phase transition decreases as the temperature approaches the critical temperature T_c.

have a second order phase transition. It is in many ways the most interesting from a theoretical point of view and will later be discussed in greater detail.

When the equation of state is projected into the PV plane, it has the typical form shown in Fig.1.2. We see that the critical point is an inflexion point determined by the two conditions

$$\left(\frac{\partial P}{\partial V} \right)_{T_c} = 0 \qquad\qquad \left(\frac{\partial^2 P}{\partial V^2} \right)_{T_c} = 0 \qquad\qquad (1.59)$$

They can be used to find the critical values T_c, P_c and V_c from a given equation of state.

1.8   Entropy

The state variable which provides the bridge between thermodynamics and statistical mechanics, is the entropy. It is given by Boltzmann's famous formula

$$S = k \log W \tag{1.60}$$

where W is the number of microscopic or quantum states it can be in. When the temperature goes to zero, most systems end up in a non-degenerate ground state of lowest energy, i.e. $W = 1$ and the zero-temperature entropy $S_0 = 0$.

   This very general result is called Nernst's Theorem and sometimes also promoted to new, third law of thermodynamics. But it is not always true and hence does not deserve this status. When the ground state is degenerate, $W > 1$ and $S_0 > 0$. For instance, a substance of N linear molecules which can line up in two equivalent directions, will have $W = 2^N$ and a zero-temperature entropy $S_0 = R \log 2$ per mol. Another example is ice which has $S_0 = R \log 3/2$ as first explained by Linus Pauling.

   For substances with $S_0 = 0$ we can determine the entropy from the measurements of the specific heat using formula (1.18). The specific heat at constant pressure C_P is experimentally most accessible over a wide range of temperatures for gas-liquid systems. We must then have

$$\lim_{T \to 0} C_P(T) = 0 \tag{1.61}$$

so that

$$S(T) = \int_0^T dT \, \frac{C_P(T)}{T} \tag{1.62}$$

is well-defined in this limit.

   When these measurements are done, one finds an entropy which typically varies with temperature as in Fig.1.4. It makes finite jumps at the melting temperature T_m and at the boiling temperature T_b. Denoting the corresponding latent heats by Λ_m and Λ_b, the entropy just above the boiling temperature is given by four contributions:

$$S(T_b) = S_s(0 \to T_m) + \frac{\Lambda_m}{T_m} + S_\ell(T_m \to T_b) + \frac{\Lambda_b}{T_b}$$

where the entropies of the solid phase S_s and liquid phases S_ℓ can be experimentally determined from (1.62).

   Such data have been established for very many substances in physical chemistry. As an example, let us consider $1 mol$ of the noble gas Kr at constant pressure $P_0 = 1 \, atm$:

$$
\begin{array}{ll}
T_m = 115.9 \; K & T_b = 119.9 \; K \\
\Lambda_m = 390.9 \; cal \, mol^{-1} & \Lambda_b = 2158 \; cal \, mol^{-1} \\
S_s = 12.75 \; cal \, K^{-1} \, mol^{-1} & S_\ell = 0.36 \; cal \, K^{-1} \, mol^{-1}
\end{array}
$$
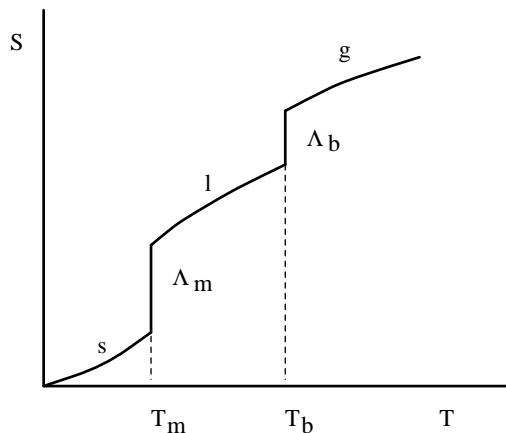
Figure 1.4: When the solid s is heated up, it melts at the temperature T_m, goes into a liquid phase l, boils at the temperature T_b and goes into the gas phase g.

Adding the four contributions together, we find the entropy $S(T = 119.9)/R = 17.35$ for krypton at the boiling point.

The entropy of a gas can not be calculated from thermodynamics alone. From the First Law (1.8) we have

$$dS = \frac{1}{T}dU + \frac{P}{T}dV$$

Assuming the gas to be ideal, the pressure is $P = NkT/V$ and the internal energy $U = \frac{3}{2}NkT$. We can then integrate up the entropy differential to get

$$S = Nk(\log V + \frac{3}{2}\log T + \sigma_0) \tag{1.63}$$

where σ_0 is an unknown integration constant. It is called the entropy constant. This constant can not be determined from the thermodynamic formulation, but requires calculations based on the counting of states, and, in order to do this correctly, quantum mechanics.

When calculating the entropy from Boltzmanns formula by counting microstates the following observation, first made by Gibbs, is crucial. Gibbs pointed out that even in the classical limit the particles in the gas are really identical, and when we calculate the entropy from Boltzmann's formula (1.60) we should divide the number of microstates W by $N!$ corresponding to the number of permutations of the N indistinguishable particles in the gas.

As mentioned, one of the big problems in physical chemistry before the advent of quantum mechanics was the origin of the entropy constants. Without them, one could not calculate absolute values of the entropy. They could be obtained by measurements for different substances, but it was first with the advent of quantum mechanics one were able to understand the physics behind

them and actually calculate some of them. This was first done in 1912 by Sackur and Tetrode using the new quantum physics still in its infancy. They found for an ideal gas

$$\sigma_0 = \frac{3}{2} \log \frac{2\pi e m k}{h^2} \tag{1.64}$$

where m is the mass of the particles, $e = 2.718\ldots$ and h is Planck's constant. We will derive this result in the next chapter.

For practical calculations of entropy, it is convenient to rewrite (**??**) slightly in terms of a reference temperature T_0 and a reference pressure P_0. It then takes the form

$$S = Nk \left[\frac{5}{2} \log \frac{T}{T_0} - \log \frac{P}{P_0} + C(T_0, P_0) \right] \tag{1.65}$$

where now

$$C(T_0, P_0) = \log \left[\left(\frac{2\pi m}{h^2} \right)^{\frac{3}{2}} \frac{(ekT_0)^{\frac{5}{2}}}{P_0} \right] \tag{1.66}$$

For the krypton gas we considered we take $T_0 = 1\,K$ and $P_0 = 1\,atm$ and obtain $C = 5.38$. This should be compared with the measured value which is

$$C = 17.35 - (\frac{5}{2} \log 119.9) = 5.36$$

in almost too good agreement with the measured value. Remember that the ideal gas approximation has been used for krypton vapour just above the boiling point.

This was a big triumph for modern physics, relating a fundamental quantum constant having to do with light and energy levels in atoms to the thermodynamic properties of substances. From then on it was clear that statistical mechanics must be based on quantum mechanics.

1.9 Free particles and multi-dimensional spheres

One of the simplest example of the practical use of the microcanonical ensemble is again provided by the ideal gas. If it contains N free particles, it is described by the Hamiltonian

$$H = \sum_{i=1}^{3N} \frac{p_i^2}{2m} . \tag{1.67}$$

The constant energy surface in phase space is therefore a multi-dimensional cylinder with a spherical base of dimension $n - 1 = 3N - 1$ and radius $R = \sqrt{2mE}$. We will need the area S_{n-1} and volume V_n of such a sphere in n dimensions. They both follow from the integral

$$V_n = \int_{x^2 \leq R^2} d^n x . \tag{1.68}$$

For dimensional reasons we must have $V_n = C_n R^n$ where C_n is some constant depending only on the dimension n. Since the differential volume element

$$dV_n = S_{n-1} dR = n C_n R^{n-1} dR$$

we also have $S_{n-1} = n C_n R^{n-1}$. The main task is therefore to calculate C_n.

It can be obtained most directly from the product of Gaussian integrals

$$\prod_{i=1}^{n} \int_{-\infty}^{+\infty} dx_i \, e^{-x_i^2} = \pi^{\frac{n}{2}} = \int dV_n \, e^{-R^2} \ .$$

In the last integral we use our expression for dV_n and obtain

$$\pi^{\frac{n}{2}} = n C_n \int_0^{\infty} dR R^{n-1} e^{-R^2}$$

which is given by the gamma function. We then have for the constant

$$C_n = \frac{\pi^{\frac{n}{2}}}{\left(\frac{n}{2}\right)!} \tag{1.69}$$

and for the surface area of the n-dimensional sphere

$$S_{n-1} = \frac{2\pi^{\frac{n}{2}}}{\left(\frac{n}{2} - 1\right)!} R^{n-1} \ . \tag{1.70}$$

As a check, it is seen to give the standard results $S_1 = 2\pi R$ and $S_2 = 4\pi R^2$ using $\left(\frac{1}{2}\right)! = \frac{1}{2}\sqrt{\pi}$. Furthermore, it gives $S_0 = 2$ which is the surface of a 1-dimensional sphere. i.e. the two endpoints of the straight line $(-R/2, R/2)$, while $S_3 = 2\pi^2 R^3$ is the 3-dimensional volume of the Universe in Einstein's cosmological model where it is closed with constant, positive curvature.

The volume in phase space inside the constant energy surface is now

$$\Omega = \frac{V^N}{(2\pi\hbar)^{3N}} \frac{\pi^{\frac{3N}{2}}}{\left(\frac{3N}{2}\right)!} (2mE)^{\frac{3N}{2}} \tag{1.71}$$

and the density of states

$$\Sigma = \frac{\partial \Omega}{\partial E} = \frac{V^N}{(2\pi\hbar)^{3N}} \frac{2m\pi^{\frac{3N}{2}}}{\left(\frac{3N}{2} - 1\right)!} (2mE)^{\frac{3N}{2} - 1} \tag{1.72}$$

where $V = \int d^3q$ is the physical volume of the gas. Since the particles in the gas are indistinguishable, the number of microstates is $W = \Omega/N!$. When calculating the entropy $S = k \log W$, we use Stirling's formula since $N \gg 1$ and obtain

$$S = Nk \left\{ \frac{5}{2} + \log \left[\frac{V}{N} \left(\frac{mE}{3\pi N\hbar^2} \right)^{\frac{3}{2}} \right] \right\} \ . \tag{1.73}$$

Without the division by $N!$ we would not have found the entropy to be extensive, i.e. proportional with N. It should be clear that we would have obtained exactly the same answer had we used the density of states (1.72) instead of the volume (1.71) as long as $N \gg 1$.

The remaining thermodynamic quantities now follow directly as before. Making use of $1/T = (\partial S/\partial E)_{N,V}$ we immediately obtain the internal energy $E = \frac{3}{2}NkT$. Using this result in the entropy expression (1.73) we get the Sackur-Tetrode formula. The pressure follows from $P/T = (\partial S/\partial V)_{N,E}$ which gives the ideal gas law $PV = NkT$. The ideal gas chemical potential follows from $\mu = -T\partial S/\partial N$ as

$$\mu = -kT \ln \left[\frac{V}{N} \left(\frac{mE}{3\pi N\hbar^2} \right)^{3/2} \right]. \qquad (1.74)$$
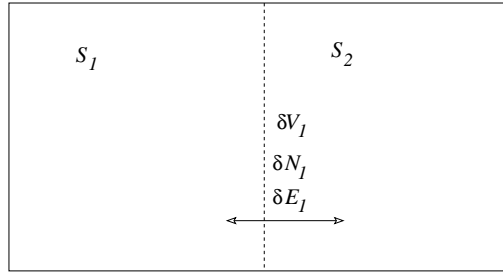
Figure 1.5: A system with entropy S_2 that is free to interchange energy, particles or volume with an ideal gas of entropy S_1.

Equation (1.73) may be used to show that the Boltzmann formula (1.60) is a valid definition of entropy for *any* system, and that the resulting pressure, temperature and chemical potential for such a system agrees with those of an ideal gas.

Assume that we use an ideal gas to probe the state of an arbitrary system by bringing the gas and the system in contact, as shown in figure 1.5. The system is described by the extensive quantities S_1, E_1, N_1, V_1 and the ideal gas by S_2, E_2, N_2, V_2, and each system has a number of available microstates W_1 and W_2. If the systems are not too strongly coupled we may write the total number of microstates as the product $W = W_1 W_2$, which means that the total entropy is additive:

$$S_{tot} = k \ln W_1 W_2 = k \ln W_1 + k \ln W_2 = S_1 + S_2. \qquad (1.75)$$

It follows by the maximization of S_{tot} in equilibrium that any exchangable quantity will adjust so as to give $dS_{tot} = 0$, or, if all extensive quantities are exchangable

$$0 = dS_1 + dS_2$$

$$\begin{aligned} = \quad & \frac{dE_1}{T_1} + \frac{p_1 dV_1}{T_1} - \frac{\mu_1 dN_1}{T_1} \\ + \quad & \frac{dE_2}{T_2} + \frac{p_2 dV_2}{T_2} - \frac{\mu_2 dN_2}{T_2}. \end{aligned} \tag{1.76}$$

Since the total energy, volume and particle number are conserved $dE_1 = -dE_2$, $dV_1 = -dV_2$, and $dN_1 = -dN_2$ and we may write

$$0 \quad = \quad \left(\frac{1}{T_1} - \frac{1}{T_2}\right) dE_1 + \left(\frac{p_1}{T_1} - \frac{p_2}{T_2}\right) dV_1 - \left(\frac{\mu_1}{T_1} - \frac{\mu_2}{T_2}\right) dN_1. \tag{1.77}$$

Since the differentials are independent

$$T_1 = T_2 \ , p_1 = p_2 \ \text{ and } \mu_1 = \mu_2 \tag{1.78}$$

where T_2, p_2 and μ_2 are given by the above ideal gas expressions. The above derivation also shows that the basic relation equation (1.30) holds when the entropy is defined by the Boltzmann formula, and that the intensive quantities T, p, μ are those that may be measured experimentally via an ideal gas.

Instead of a gas of free particles, we can also consider the system of free, 3-dimensional oscillators in the microcanonical ensemble. We can think of the oscillators as the vibrating ions in a crystal lattice. The mathematics becomes very similar as seen from the Hamiltonian

$$H = \sum_{i=1}^{3N} \left(\frac{p_i^2}{2m} + \frac{1}{2}m\omega^2 q_i^2\right) \tag{1.79}$$

when we assume that all have the same frequency. The phase space volume Ω is again a sphere but now with twice the dimension, $n = 6N$:

$$\Omega = \frac{1}{(2\pi\hbar)^{3N}} \frac{\pi^{3N}}{(3N)!} \left(\frac{2mE}{m\omega}\right)^{3N} . \tag{1.80}$$

Since the oscillator are localized and therefore distinguishable, the number of microstates is just $W = \Omega$ and the entropy becomes

$$S = 3Nk(1 + \log\frac{E}{3N\hbar\omega}) . \tag{1.81}$$

It is again extensive as it should be. The internal energy is now $U = 3NkT$ as follows directly from the Hamiltonian (1.79) and the equipartition theorem.

Chapter 2

Non-Interacting Particles

When the thermodynamics of simple systems is developed, one very often starts with the ideal gas. The reasons for this are many. First of all the ideal gas is a quite good approximation to real gases with interactions as long as one stays away from questions having to do with the liquid phase and phase transitions. Secondly, the mathematics is transparent and one can introduce in a simple way concepts and methods which will be useful when one later starts to treat more realistic systems.

Free spin-1/2 magnetic moments in an external field constitutes an even simpler system than the ideal gas. Although being an idealized system, it is also physically important in many instances. This example will introduce the basic properties of the microcanonical and canonical ensembles. After developing Maxwell-Boltzmann statistics for independent particles, we will treat the ideal gas and derive its equation of state and the Sackur-Tetrode result for the entropy. When the particles are quantum mechanically indistinguishable, the counting of states will be different and we arrive at Bose-Einstein and Fermi-Dirac statistics.

2.1 Spin-$\frac{1}{2}$ particles in a magnetic field

We will here consider N particles in an external magnetic field B which is taken along the z-axis. The particles are assumed to be localized, i.e. cannot move. One can for instance consider them to be sitting at the lattice sites of a regular crystal as a simple model of a magnetic material. They have all the same spin $S = \frac{1}{2}$. Each of them will have an energy in the field given by

$$\epsilon = -\mathbf{m} \cdot \mathbf{B} = -m_z B \tag{2.1}$$

where $\mathbf{m} = 2\mu \mathbf{S}$ is the magnetic moment and μ is a Bohr magneton. Since the quantum mechanical spin along the z-axis can only take the values $S_z = \pm\frac{1}{2}$, we see that a particle can only have the energy $\epsilon_\uparrow = -\mu B$ if its spin points up along the B-field, and $\epsilon_\downarrow = +\mu B$ if it points down.

The quantum states of the whole system with for example $N = 5$ spins are given by corresponding spin sequences like $\uparrow\uparrow\downarrow\downarrow\uparrow$. If we denote the number of up-spins by $n_\uparrow$ and the number of down-spins by $n_\downarrow$ in such a state, the energy of the system will be

$$E = -\mu(n_\uparrow - n_\downarrow)B \tag{2.2}$$

with total number of particles or spins

$$N = n_\uparrow + n_\downarrow \; . \tag{2.3}$$

The difference

$$M = \mu(n_\uparrow - n_\downarrow) \tag{2.4}$$

is the total magnetic moment of the system.

Now let us assume first that the system is isolated so that its total energy is constant. Obviously, there are many states with the same energy, i.e. with the same numbers $n_\uparrow$ and $n_\downarrow$. As an example, consider again $N = 5$ spins with $n_\uparrow = 3$ and $n_\downarrow = 2$. Then all the possible states shown in Fig.2.1 They are said

$$\uparrow\ \uparrow\ \uparrow\ \downarrow\ \downarrow \qquad\qquad \downarrow\ \uparrow\ \uparrow\ \uparrow\ \downarrow$$

$$\uparrow\ \uparrow\ \downarrow\ \uparrow\ \downarrow \qquad\qquad \downarrow\ \uparrow\ \uparrow\ \downarrow\ \uparrow$$

$$\uparrow\ \uparrow\ \downarrow\ \downarrow\ \uparrow \qquad\qquad \downarrow\ \uparrow\ \downarrow\ \uparrow\ \uparrow$$

$$\uparrow\ \downarrow\ \uparrow\ \downarrow\ \uparrow \qquad\qquad \downarrow\ \downarrow\ \uparrow\ \uparrow\ \uparrow$$

$$\uparrow\ \downarrow\ \downarrow\ \uparrow\ \uparrow \qquad\qquad \uparrow\ \downarrow\ \uparrow\ \uparrow\ \downarrow$$
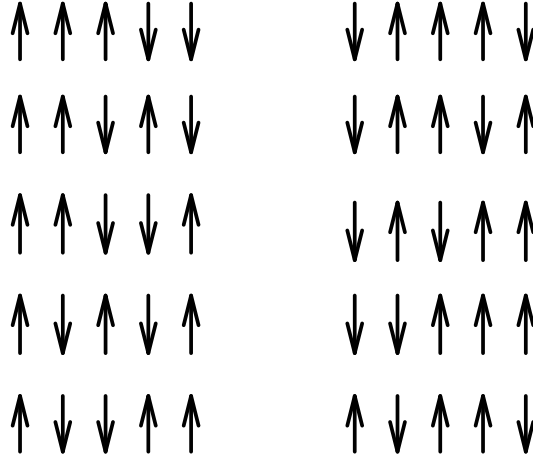
Figure 2.1: Ensemble of 5 spins with magnetization $M/\mu = +1$.

to form an ensemble of states. Since it consists of states with given energy, it is called a microcanonical ensemble. In this example it contains 10 states. In general the number will be

$$W = \frac{N!}{n_\uparrow!\, n_\downarrow!} \; . \tag{2.5}$$

Notice that the numbers $n_\uparrow$ and $n_\downarrow$ are fixed by the energy (2.2) and total number of particles (2.3).

In the microcanonical ensemble each state is assumed to occur with the same probability in the ensemble. This is a fundamental assumption in statistical mechanics and cannot be proven in general. But it can be made plausible by many different arguments. For the spin system we consider, it follows almost from symmetry alone since there is nothing which *a priori* makes any state in the ensemble more probable than others. The number of states (2.5) is then directly proportional to the probability of finding the system in the thermodynamic state specified by E and N and represented by the different quantum states in the ensemble.

In order to find the most probable state, we must take the derivative of (2.5). Since the number of particles is assumed to be large, we can make use of Stirling's formula $\log n! \approx n \log n - n$. It follows directly from

$$
\begin{aligned}
\log n! \quad &= \quad \sum_{k=1}^{n} \log k \approx \int_1^n dk \log k \\
&= \quad k \log k|_1^n - \int_1^n dk = n \log n - n + 1
\end{aligned}
$$

A more accurate result valid for smaller values of n can be obtained in the saddle point approximation for the integral

$$
I = \int_a^b dx \, e^{-f(x)} \ .
$$

If the function $f(x)$ has a pronounced minimum in the interval (a, b) at the point x_0, the dominant part to the integral will come from the region around the minimum because the integrand is exponentially small outside it. Expanding the function to second order

$$
f(x) = f(x_0) + f'(x_0) + \frac{1}{2} f''(x_0)(x - x_0)^2 + \ldots
$$

with $f'(x_0) = 0$, we obtain for the integral

$$
\begin{aligned}
I \quad &\approx \quad e^{-f(x_0)} \int_{-\infty}^{\infty} dx e^{-\frac{1}{2} f''(x_0)(x - x_0)^2} \\
&= \quad e^{-f(x_0)} \sqrt{\frac{2\pi}{f''(x_0)}}
\end{aligned}
\tag{2.6}
$$

where we have expanded the integration interval from (a, b) to $(-\infty, +\infty)$.

Stirling's formula now follows from writing

$$
n! = \int_0^{\infty} dx \, x^n e^{-x} = \int_0^{\infty} dx \, e^{-(x - n \log x)} \ .
$$

The function $f(x) = x - n \log x$ has a minimum for $x = x_0 = n$ where $f''(x_0) = 1/n$. We then get from the saddle point approximation

$$
n! \approx e^{-(n - n \log n)} \sqrt{2\pi n} = \sqrt{2\pi n} \, n^n e^{-n} \ .
\tag{2.7}
$$

Keeping the next higher term in the approximation, one finds

$$
n! \approx \sqrt{2\pi n} \, n^n e^{-n} (1 + \frac{1}{12n}) \ .
$$

To the same order in $1/n$ it can be written as

$$
n! \approx \sqrt{2\pi(n + \frac{1}{6})} \, n^n e^{-n}
\tag{2.8}
$$

which is the Mermin formula for $n!$. It is very accurate down to $n = 1$ and even gives $0! = 1.023\ldots$

Knowing the number of states in the ensemble, we can from Boltzmann's formula (1.60) find the entropy of the system. Using Stirling's approximation for $n!$, it gives

$$S = k \left(N \log N - n_\uparrow \log n_\uparrow - n_\downarrow \log n_\downarrow \right) . \tag{2.9}$$

It is a function of the system energy E via the constraints (2.2) and (2.3). The distribution of particles is now given by (1.55) or

$$\left(\frac{\partial S}{\partial E} \right)_N = \frac{1}{T} \tag{2.10}$$

when the system is at thermodynamic equilibrium with temperature T. Taking the derivative

$$\left(\frac{\partial S}{\partial E} \right)_N = \frac{\partial S}{\partial n_\uparrow} \left(\frac{\partial n_\uparrow}{\partial E} \right)_N + \frac{\partial S}{\partial n_\downarrow} \left(\frac{\partial n_\downarrow}{\partial E} \right)_N , \tag{2.11}$$

using (2.2) and rearranging the result, we obtain

$$\frac{n_\uparrow}{n_\downarrow} = e^{\frac{2\mu B}{kT}} \; . \; . \tag{2.12}$$

We see that the lower the temperature of the system, the more particles have spin up, i.e. are in the lowest one-particle energy state. The total energy of the system is $E = -MB$ where the magnetization now follows from the above result as

$$M = N\mu \tanh \frac{\mu B}{kT} . \tag{2.13}$$

When the temperature $T \to 0$, all the spins point up along the external field and the magnetization $M = N\mu$. At very high temperatures it goes to zero with just as many spins pointing up as down.

The magnetization also varies with the external field. This dependence is measured by the susceptibility defined by

$$\chi = \left(\frac{\partial M}{\partial B} \right)_T \tag{2.14}$$

in analogy with the compressibility (1.24) in a gas. From (2.13) we find

$$\chi = \frac{N\mu^2}{kT} \frac{1}{\cosh^2 (\mu B / kT)} \tag{2.15}$$

and it is seen to diverge when the temperature goes to zero.

Instead of using the microcanonical ensemble where the energy is fixed and the temperature is a derived property, we can use the canonical ensemble. Then the system is at a fixed temperature and the energy will be a derived quantity. In fact, we will find an average value for the energy and the measured energy will fluctuate around this mean. Now many more states will be included in the ensemble since they no longer need to have a given energy. They will no longer have the same probability, but will have a distribution in energy as we will now derive.

Again we start with Boltzmann's relation for the entropy, $S = k \log W$, with W from (2.5). But now $n_\uparrow$ and $n_\downarrow$ are not known, but have to be determined from the requirement that the system is in thermal equilibrium at temperature T. To achieve this in practice, our system of spins must be in thermal contact with a large, surrounding system or heat bath at the same temperature. By the exchange of energy, these two systems will then be in thermal equilibrium.

Let now the spin system receive an energy $\Delta U = 2\mu B$ which turns a spin from being up to being down, i.e. $n_\uparrow \rightarrow n_\uparrow - 1$ and $n_\downarrow \rightarrow n_\downarrow + 1$. The corresponding change in entropy is then

$$
\begin{aligned}
\Delta S &= k \left[\log \frac{N!}{(n_\uparrow - 1)! \, (n_\downarrow + 1)!} - \log \frac{N!}{n_\uparrow! \, n_\downarrow!} \right] \\
&= k \log \frac{n_\uparrow}{n_\downarrow + 1}
\end{aligned}
$$

so that

$$
\frac{\Delta S}{\Delta E} = \frac{k}{2\mu B} \log \frac{n_\uparrow}{n_\downarrow} \tag{2.16}
$$

where we have written $n_\downarrow + 1 \approx n_\downarrow$ to a very good approximation when the number of particles is macroscopic. Since the spin system is in thermal equilibrium, this ratio is just the inverse temperature and we are back to the result (2.12) from the microcanonical ensemble.

We can write the above result for the distribution of particles at thermodynamic equilibrium as

$$
n_\sigma = \frac{N}{Z_1} e^{-\beta \epsilon_\sigma} \tag{2.17}
$$

where $\beta = 1/kT$ and the sum over energy levels

$$
\begin{aligned}
Z_1 &= \sum_{\sigma=\uparrow,\downarrow} e^{-\beta \epsilon_\sigma} \tag{2.18} \\
&= e^{\beta \mu B} + e^{-\beta \mu B} = 2 \cosh \frac{\mu B}{kT} \tag{2.19}
\end{aligned}
$$

is called the one-particle partition function. It contains essentially all the thermodynamic information about the system. The average energy of one particle is

$$
\langle \epsilon \rangle = \frac{1}{Z_1} \sum_{\sigma=\uparrow,\downarrow} \epsilon_\sigma \, e^{-\beta \epsilon_\sigma} = -\mu B \tanh \frac{\mu B}{kT} \tag{2.20}
$$

so that the total energy $U = N\langle\epsilon\rangle$ is the same as before. But now there will be fluctuations around this average energy which was fixed at the value $U = E$ in the microcanonical ensemble.

2.2   Maxwell-Boltzmann statistics

We will first consider a system of free particles which can be taken to be atoms or molecules localized at the sites of a lattice as a simple model of a crystal. They are all assumed to be identical, but since they are localized, they can be distinguished from each other. At the end of this section we will drop this assumption and consider the same particles in a gas where they can move freely around. They will then be indistinguishable. But they will in both cases be independent of each other since there will be no interactions between them. These will be included in the following chapter.

The possible energy levels ϵ_i for each atom or particle in the system are given by the eigenvalues of some quantum mechanical Hamiltonian operator. Let us denote the degeneracy of the level ϵ_i by g_i. If the number of particles in this level is n_i, the total number of particles in the system is

$$N = \sum_i n_i \tag{2.21}$$

which is here assumed to be held constant. We can pick out such a set $\{n_i\}$ of occupation numbers in

$$C = N! \prod_i \frac{1}{n_i!} \tag{2.22}$$

different ways when the particles are distinguishable. But the n_i particles at level ϵ_i can be distributed in $g_i^{n_i}$ different ways over the different quantum states with that energy. The total number of microstates for a given set $\{n_i\}$ of occupation numbers is then

$$W = N! \prod_i \frac{g_i^{n_i}}{n_i!} \tag{2.23}$$

The equilibrium distribution of particles is the one which makes this number maximal for a given total energy $E = \sum_i n_i \epsilon_i$ of the system.

It is simplest to use the canonical ensemble in order to derive the equilibrium distribution of particles. Let the system be in thermal contact with a heat bath so that the two systems can exchange energy. If some energy $\Delta U = \epsilon_i - \epsilon_j$ is then transferred to the particles, the occupation numbers will change in (2.23), $n_i \to n_i + 1$ and $n_j \to n_j - 1$, and there will be a corresponding change in the entropy,

$$
\begin{aligned}
\Delta S &= k\left[\log\frac{g_i^{n_i+1}}{(n_i+1)!}\frac{g_j^{n_j-1}}{(n_j-1)!} - \log\frac{g_i^{n_i}}{n_i!}\frac{g_j^{n_j}}{n_j!}\right] \\
&= k\log\frac{g_i n_j}{g_j(n_i+1)}
\end{aligned}
\tag{2.24}
$$

Again we use that at equilibrium $\Delta U = T \Delta S$ which gives

$$\frac{g_i n_j}{g_j (n_i + 1)} = e^{\beta(\epsilon_i - \epsilon_j)} \ . \tag{2.25}$$

Similar constraints must be satisfied by other pairs of occupation numbers also. Taking $n_i + 1 \approx n_i$, we see immediately that they are all satisfied together with (2.21) if

$$n_i = \frac{N}{Z_1} g_i \, e^{-\beta \epsilon_i} \tag{2.26}$$

where

$$Z_1 = \sum_i g_i \, e^{-\beta \epsilon_i} \tag{2.27}$$

is the one-particle partition function. It will again give all the thermodynamics.

This method has two attractive features. First of all we do not need Stirling's formula for $n!$. Secondly, we have to assume that only one occupation number satisfies $n_i \gg 1$, all the other will be connected to it and can have any value as n_j did above.

The result (2.26) is the Boltzmann distribution for the occupation numbers. It says that the probability to find a particle in the gas at temperature T with energy ϵ_i is

$$p_i = \frac{n_i}{N} = \frac{1}{Z_1} g_i \, e^{-\beta \epsilon_i} \tag{2.28}$$

with $\sum_i p_i = 1$ according to (2.21). The average one-particle energy is therefore

$$\langle \epsilon \rangle = \sum_i \epsilon_i \, p_i = \frac{1}{Z_1} \sum_i \epsilon_i g_i \, e^{-\beta \epsilon_i} \tag{2.29}$$

Other averages over this distribution are calculated in the same way. In this particular case we do not have to perform a new summation since the result is seen to be simply given by

$$\langle \epsilon \rangle = -\frac{\partial}{\partial \beta} \log Z_1 \tag{2.30}$$

Similar simplifications can very often be done when calculating such averages.

Writing the total internal energy of the system $U = N \langle \epsilon \rangle$ as $U = \sum_i n_i \epsilon_i$ and taking the differential, we have

$$dU = \sum_i \epsilon_i dn_i + \sum_i n_i d\epsilon_i \ . \tag{2.31}$$

This is the statistical mechanical version of the Third Law of thermodynamics, (1.8). In the first term the occupation numbers n_i change and must be identified

with the change in entropy $T\,dS$. The second term is therefore the mechanical work $P\,dV$.

The entropy of the gas can now be obtained from (2.23). Using Stirling's formula, we obtain

$$
\begin{aligned}
\frac{S}{k} &= \log W = N \log N - N + \sum_i \left(n_i \log g_i - n_i \log n_i + n_i\right) \\
&= N \log N - \sum_i n_i \log \frac{n_i}{g_i} = N \log N - \sum_i n_i \left(\log \frac{N}{Z_1} - \beta \epsilon_i\right) \\
&= N \log Z_1 + \frac{U}{kT} = \log Z_1^N + \frac{U}{kT} \tag{2.32}
\end{aligned}
$$

Exactly this combination of entropy and internal energy occurs in the Helmholtz free energy (**??**). Defining it now by

$$
F = -kT \log Z_1^N \tag{2.33}
$$

we see that we indeed have $F = U - TS$.

We will later see that the free energy is in general related to the full partition function Z of the gas as $F = -kT \log Z$. For non-interacting and distinguishable particles we therefore have

$$
Z = e^{-\beta F} = Z_1^N \ . \tag{2.34}
$$

This relation provides a bridge between the physics at the microscopic, atomic level and the macroscopic, thermodynamic level.

As a simple example, take the Einstein model for the vibrations of the N ions in a crystal lattice. They are then described by N free and distinguishable harmonic oscillators, all with the same frequency ω. The energy level of each harmonic oscillator is $\epsilon_n = \hbar\omega(n + \frac{1}{2})$ and the one-particle partition function becomes

$$
Z_1 = \sum_{n=0}^{\infty} e^{-\beta \epsilon_n} = \frac{e^{-\frac{1}{2}\beta\hbar\omega}}{1 - e^{-\beta\hbar\omega}} = \frac{1}{2 \sinh\left(\beta\hbar\omega/2\right)} \ . \tag{2.35}
$$

The free energy of one such oscillator is therefore

$$
F = \frac{1}{2}\hbar\omega + kT \log\left(1 - e^{-\beta\hbar\omega}\right) \tag{2.36}
$$

while the internal energy is

$$
\langle\epsilon\rangle = \frac{1}{2}\hbar\omega + \frac{1}{e^{\beta\hbar\omega} - 1} \tag{2.37}
$$

which follows directly from (2.30). The same result also applies to one mode of the electromagnetic field in blackbody radiation.

In the one-particle partition function (2.27) we sum over the different energy levels of the particle, each with degeneracy g_i. But this is equivalent to

$$
Z_1 = \sum_s e^{-\beta \epsilon_s} \tag{2.38}
$$

where now the sum extends over all the one-particle quantum states, including the degenerate ones. The average number of particles in the quantum state s is then

$$n_s = \frac{N}{Z_1} e^{-\beta\epsilon_s} \tag{2.39}$$

which would follow from maximizing the number of microstates

$$W = N! \prod_s \frac{1}{n_s!} \ . \tag{2.40}$$

The entropy $S = k \log W$ is then simply

$$
\begin{aligned}
S &= k(N \log N - \sum_s n_s \log n_s) \\
&= -Nk \sum_s p_s \log p_s
\end{aligned} \tag{2.41}
$$

where now $p_s = n_s/N$ is the probability to find the particle in the quantum state s. This formula for the entropy which is also due to Boltzmann, turns out to be quite general and useful. We will meet it again when we discuss entropy from the point of view of information theory.

Until now we have assumed the particles to be identical, but distinguishable. If they are no more localized, we have to give up this assumption. Permuting the N particles among themselves cannot make any observable difference and the number W of quantum states must be reduced by the factor $N!$. The only place where this factor shows up in the previous results, is in the expression (2.32) for the entropy which now becomes instead

$$S = k \log \frac{Z_1^N}{N!} + \frac{U}{T} \ . \tag{2.42}$$

Again we can write the Helmholtz free energy of the whole system as $F = -kT \log Z$ where now the full partition function is

$$Z = \frac{Z_1^N}{N!} \tag{2.43}$$

instead of (2.34). The entropy (2.32) will be reduced by the logarithm of this permutation factor. It can be written as

$$S = -k \sum_i g_i(f_i \log f_i - f_i) \tag{2.44}$$

where $f_i = n_i/g_i$ is the filling fraction of energy level ϵ_i. These numbers are very small in classical systems so that the entropy will be positive.

2.3   Ideal gas

A free particle of mass m has the Hamiltonian $\widehat{H} = \widehat{\mathbf{p}}^2/2m$. The quantized energy levels $\epsilon_{\mathbf{n}}$ are the eigenvalues of the Schrödinger equation

$$\widehat{H}\psi_{\mathbf{n}}(\mathbf{x}) = \epsilon_{\mathbf{n}}\psi_{\mathbf{n}}(\mathbf{x}) . \tag{2.45}$$

In a cubic box with sides of length L we can require that the wave functions must vanish on the walls $x = 0, y + 0$ and $z = 0$. Then they they have the form

$$\psi_{\mathbf{n}}(\mathbf{x}) = \sin(k_x x) \sin(k_y y) \sin(k_z z) .$$

Since we also have $\psi_{\mathbf{n}}(\mathbf{x} + L\mathbf{e}_i) = 0$ where $\mathbf{e}_i$ are the unit vectors in the three directions, we find the wave numbers $k_i = n_i \pi/L$ where the quantum numbers $n_i = 1, 2, 3, \ldots$. This gives the energy eigenvalues

$$\epsilon_{\mathbf{n}} = \frac{\hbar^2 \pi^2}{2mL^2}(n_x^2 + n_y^2 + n_z^2) . \tag{2.46}$$

All the thermodynamic properties of the ideal gas follow now from the one-particle partition function

$$Z_1 = \sum_{\mathbf{n}} e^{-\beta\epsilon_{\mathbf{n}}} . \tag{2.47}$$

This sum can only be performed numerically. But when the volume $V = L^3$ in which the particle moves, becomes very large, the spacing between the different terms in the sum becomes so small that we can replace it with an integral. Since the spacings between the allowed quantum numbers are $\Delta n_i = 1$, we can write

$$
\begin{aligned}
Z_1 &= \sum_{\{n_i=1\}}^{\infty} \Delta n_x \Delta n_y \Delta n_z \, e^{-\frac{\beta\hbar^2\pi^2}{2mL^2}(n_x^2+n_y^2+n_z^2)} \\
&= \frac{1}{8}\int d^3n \, e^{-\frac{\beta\hbar^2\pi^2}{2mL^2}n^2} = \frac{1}{8}\left(\int_{-\infty}^{\infty} dn_x \, e^{-\frac{\beta\hbar^2\pi^2}{2mL^2}n_x^2}\right)^3 \\
&= \frac{V}{(2\pi\hbar)^3}\left(\frac{2\pi m}{\beta}\right)^{\frac{3}{2}} = \frac{V}{\Lambda^3}
\end{aligned}
\tag{2.48}
$$

Here the box volume $V = L^3$ and

$$\Lambda = \left(\frac{2\pi\beta\hbar^2}{m}\right)^{\frac{1}{2}} = \frac{h}{\sqrt{2\pi mkT}} \tag{2.49}$$

is called the thermal wavelength of the particle. We will discuss its significance at the end of this section.

Instead of the above box boundary conditions, we could have used periodic boundary conditions $\psi_{\mathbf{p}}(\mathbf{x} + L\mathbf{e}_i) = \psi_{\mathbf{p}}(\mathbf{x})$ in open space. The wave functions are then plane wave, momentum eigenstates of the form $\psi_{\mathbf{p}}(\mathbf{x}) = \exp\left(\frac{i}{\hbar}\mathbf{p}\cdot\mathbf{x}\right)$ with momentum eigenvalues $\mathbf{p} = \frac{2\pi\hbar}{L}(n_x\mathbf{e}_x + n_y\mathbf{e}_y + n_z\mathbf{e}_z)$. With the energies $\epsilon_{\mathbf{n}} = \frac{\hbar^2}{2m}\left(\frac{2\pi}{L}\right)^2\mathbf{n}^2$ in the partition function we see that we get the same result as above since the quantum numbers n_i now take the values $n_i = 0, \pm 1, \pm 2, \ldots$. Periodic boundary conditions are very often used since the eigenstates can then be labeled by the momentum eigenvalues $\mathbf{p}$.

Irrespective of the boundary conditions we use, we see that we can always write the partition function as

$$Z_1 = V \int \frac{d^3 p}{(2\pi\hbar)^3}\, e^{-\beta\frac{\mathbf{p}^2}{2m}}\ . \tag{2.50}$$

The continuous energy eigenvalues are now $\epsilon = \mathbf{p}^2/2m$. Expressing the momentum by the energy, $p = \sqrt{2m\epsilon}$, we can rewrite the above integral as

$$Z_1 = \frac{V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}}\int_0^\infty d\epsilon\, \epsilon^{\frac{1}{2}} e^{-\beta\epsilon}\ . \tag{2.51}$$

The integration measure

$$D(\epsilon) = \frac{1}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}}\epsilon^{\frac{1}{2}} \tag{2.52}$$

is called the density of states for one particle. Its name is derived from the property that there is exactly one quantum state in the phase space volume $(2\pi\hbar)^3 = h^3$ as follows from (2.50). In 3-dimensional space it varies as the square root of the energy. A similar calculation shows that in two dimensions it is independent of the energy for non-relativistic particles. This has many important, physical consequences.

The thermodynamic properties of a gas of such particles can now be derived from the free energy

$$F = -kT \log \frac{Z_1^N}{N!}\ .$$

Most easily follows the pressure

$$P = -\left(\frac{\partial F}{\partial V}\right)_{T,N} = \frac{NkT}{V} \tag{2.53}$$

which is just the equation of state for the ideal gas. Similarly, we obtain the chemical potential

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{T,V} = -kT\log\frac{Z_1}{N} = kT\log\frac{P\Lambda^3}{kT} \tag{2.54}$$

and the internal energy from (2.39),

$$U = -\frac{\partial}{\partial \beta} \log Z = \frac{3}{2} N k T \ . \tag{2.55}$$

The specific heat is therefore

$$C_V = \frac{3}{2} N k \ . \tag{2.56}$$

Finally, we find for the entropy

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N} = k \log \frac{Z_1^N}{N!} + \frac{U}{T} \tag{2.57}$$

which is just equation (2.42). Substituting (2.48), we obtain

$$S = N k \left[\frac{5}{2} - \log \rho \Lambda^3\right] \tag{2.58}$$

where $\rho = N/V$ is the density of particles. Since $\rho = P/kT$, we recover exactly the Sackur-Tetrode equation (1.65) for the ideal gas entropy. It is also seen that there is no Gibb's paradox for the mixing of identical gases. Without the permutation factor $N!$ divided out of the partition function to account for the indistinguishability of the particles, we would have ended up with a different result for the entropy which would not agree with experiments.

The specific heat (2.56) is constant and therefore does not go to zero as the temperature goes to zero. As discussed in connection with the so-called Third Law of thermodynamics in the previous chapter, this property is required of experimental heat capacities in order to have well-defined entropies in this limit. So something is wrong with our results for the ideal gas at low temperatures. One might first think that it is related to the approximation we did in arriving at the partition function (2.48) where we replaced the sum with an integral. But this is not the cause of the difficulties.

From quantum mechanics we know that particles at the atomic level have wave properties which make them very different from classical particles. Their de Broglie wavelength is given by the momentum as $\lambda = h/p$. From (2.55) we find the average momentum $\langle p^2 \rangle = 2m \langle \epsilon \rangle = 3mkT$. We see that λ depends on the temperature and equals the quantity Λ in (2.49) except for a numerical factor of order one. It is therefore the thermal wavelength. Putting in numbers, we find that

$$\Lambda = \frac{20 \mathring{A}}{\sqrt{MT}} \tag{2.59}$$

when M is the molar mass of the particle. In order for the classical picture of particles to be valid, the thermal wavelength should be smaller than the typical distance $\ell = (V/N)^{\frac{1}{3}}$ between the particles. In terms of the particle density $\rho = N/V$, we get the criterium

$$\rho \Lambda^3 << 1 \tag{2.60}$$

for Maxwell-Boltzmann statistics to be applicable. When this is not the case, the corresponding wave functions will overlap and we can no longer separate the individual particles. At low enough temperatures this always happens. The smaller the mass of the particles is, the easier it will be to see the quantum effects. For He^4 at room temperature, we find $\Lambda \approx 1 \mathring{A}$ and is therefore smaller than the average distance between atoms at normal densities. But when $T = 1\,K$ the thermal wavelength will be more than ten times larger and quantum effects will start to dominate. On the other hand, electrons in metals have much smaller masses and we conclude from (2.59) that even at room temperatures they must be described by quantum statistics.

2.4 Fermi-Dirac statistics

In the counting of available microstates that led to Maxwell-Boltzmann statistics we assumed that the particles were identical but could be distinguished in principle. Even if they are very small, we could for example assume that they could be painted in different colors or assigned numbered labels. This classical assumption was then tried compensated for by dividing the obtained number of microstates by the number of particle permutations. The net result is still not quantum statistics, but classical Maxwell-Boltzmann statistics of identical particles. In quantum statistics one can not distinguish identical particles and the counting of microstates must be done differently.

When the particles in the system have half-integer spin, they are fermions. As such, they will obey the Pauli principle saying that not more than one particle can be in each quantum state. We have to incorporate this quantum requirement in the counting of available microstates for system of identical fermions.

The particles will again be assumed to have no mutual interactions. Each of them can be in a quantized energy level ϵ_i with degeneracy g_i as before. For the first particle in this level there are therefore g_i available states. The next particle in the same level can then be in one of the $g_i - 1$ unoccupied states so not to violate the Pauli principle. Since the particles are indistinguishable, there are therefore $g_i(g_i-1)/2$ available states for two fermions. For n_i fermions this number will be $g_i!/n_i!\,(g_i - n_i)!$. A typical state is shown in Fig. 2.2. The

Figure 2.2: Energy level with degeneracy $g_i = 14$ occupied by $n_i = 8$ fermions.

total number of available states for fermions in all energy levels is then

$$W = \prod_i \frac{g_i!}{n_i!\,(g_i - n_i)!} \; . \tag{2.61}$$

We see that this result is much different from the classical result in (2.23), even when dividing out the factor $N!$. The entropy is again given by Boltzmann's

formula $S = k \log W$.

The equilibrium distribution n_i of particles over the different energy levels is now most easily found in the canonical ensemble where the fermion system is in thermal and material contact with a heat bath at fixed temperature T and chemical potential μ containing the same kind of particles. If a particle of energy ϵ_i is transferred from the heat bath to the system, only the occupation number $n_i \rightarrow n_i + 1$ is changed. The corresponding change in entropy is then from (2.61) found to be

$$
\begin{aligned}
\Delta S &= k \log \frac{g_i!}{(n_i + 1)! \, (g_i - n_i - 1)!} - k \log \frac{g_i!}{n_i! \, (g_i - n_i)!} \\
&= k \log \frac{g_i - n_i}{n_i + 1} \ .
\end{aligned}
$$

In the denominator we can drop replace $n_1 + 1$ by n_i when we assume that the number of particles in each energy level is very large. This entropy change is now related to the energy change $\Delta U = \epsilon_i$ and number change $\Delta N = 1$ by the First Law which gives $T\Delta S = \Delta U - \mu \Delta N = \epsilon_i - \mu$. Substituting for ΔS we obtain

$$
\frac{g_i}{n_i} - 1 = e^{\beta(\epsilon_i - \mu)} \tag{2.62}
$$

which gives the equilibrium number of particles in energy level ϵ_i as

$$
n_i = \frac{g_i}{e^{\beta(\epsilon_i - \mu)} + 1} \ . \tag{2.63}
$$

This is the Fermi-Dirac distribution. The chemical potential is determined from the constraint

$$
N = \sum_i n_i = \sum_i \frac{1}{e^{\beta(\epsilon_i - \mu)} + 1} \tag{2.64}
$$

where N is the total number of particles in the systems. Similarly, one obtains the internal energy of the system of particles from

$$
U = \sum_i \epsilon_i \, n_i = \sum_i \frac{\epsilon_i}{e^{\beta(\epsilon_i - \mu)} + 1} \ . \tag{2.65}
$$

In a later chapter we will come back to discuss in more detail the new physics which follows.

2.5   Bose-Einstein statistics

When bosons occupy an energy level ϵ_i consisting of g_i degenerate one-particle quantum states, there can be an arbitrary number of particles in each state as shown in Fig.2.3. Here the different states are separated by vertical walls. Of the $g_i + 1$ such walls only $g_i - 1$ gan be used to generate different separations of the identical bosons since two of the walls always have to be fixed at the ends.

Figure 2.3: Energy level with degeneracy $g_i = 11$ occupied by $n_i = 10$ bosons.

The number of such separations is therefore given by the different groupings of n_i bosons and $g_i - 1$ walls. In this way we obtain $(n_i + g_i - 1)!/n_i!\,(g_i - 1)!$ microstates for the n_i bosons in this level. The total number of states for the whole system is then

$$W = \prod_i \frac{(n_i + g_i - 1)!}{n_i!\,(g_i - 1)!} \tag{2.66}$$

which can be used to find the entropy.

We can now proceed as in the previous derivations of Fermi-Dirac statistics to derive the equilibrium distribution of bosons. The system is kept in contact with a heat bath at temperature T and chemical potential μ. Taking one particle with energy ϵ_i from the bath to the system of bosons induces now the entropy change

$$\Delta S = k \log \frac{g_i + n_i}{n_i + 1} \; . \tag{2.67}$$

Again using the First Law $T\Delta S = \Delta U - \mu \Delta N = \epsilon_i - \mu$ and assuming $n_i \gg 1$, we obtain at once the Bose-Einstein distribution

$$n_i = \frac{g_i}{e^{\beta(\epsilon_i - \mu)} - 1} \; . \tag{2.68}$$

The chemical potential and internal energy can then be obtained as for fermions. We will later use this result to derive the thermodynamics of photons, phonons and other bosonic systems.

All the thermodynamics of these quantum systems is seen to be determined by the filling fractions

$$f_i = \frac{n_i}{g_i} = \frac{1}{e^{\beta(\epsilon_i - \mu)} \pm 1} \; . \tag{2.69}$$

The entropy follows from Boltzmann's formula applied to the equilibrium values of (2.61) for fermions and (2.66) for bosons. In both cases one finds that the result takes essentially the same form

$$S = -k \sum_i g_i[f_i \log f_i \pm (1 \mp f_i) \log (1 \mp f_i)] \tag{2.70}$$

where the upper signs hold for fermions and the lower ones for bosons.

In the classical limit the particles are spread out over very many energy levels so that it is characterized by $n_i \ll g_i$. Since the number (2.61) of microstates for fermions can be written as

$$W = \prod_i \frac{1}{n_i!} \left[g_i(g_i - 1)(g_i - 2)\ldots(g_i - n_i + 1)\right],$$

we see that it gives the Maxwell-Boltzmann result

$$W = \prod_i \frac{g_i^{n_i}}{n_i!}$$

in this classical limit. Similarly, the number of microstates for bosons (2.66) can be written as

$$W = \prod_i \frac{1}{n_i!} \left[(g_i + n_i - 1)(g_i + n_i - 2) \ldots (g_i + 1)g_i \right]$$

which also gives the same result in the classical limit. We see that the factor $N!$ which we previously had to remove by fiat in deriving the Maxwell-Boltzmann distribution, is now automatically absent. The quantum entropy (2.70) also becomes equal to the classical result (2.44).

When the gas becomes classical, the chemical potential is large and negative. Both of the quantum distributions (2.69) then approach the classical result

$$f_i = e^{\beta \mu} e^{-\beta \epsilon_i} \ .$$

Comparing this expression with (2.28), we see that we have the relation $e^{\beta \mu} = N/Z_1$ or

$$\mu = -kT \log \frac{Z_1}{N} \tag{2.71}$$

between the one-particle partition function and the chemical potential. This result was previously obtained for the ideal gas in (2.54). It is seen to be generally valid for non-interacting systems in the classical limit.

Chapter 3

Statistical Ensembles

We saw in the preceding chapter that a system of particles could be in a number of different of microstates or quantum states. When the system is in thermodynamic equilibrium, we envisage that it passes with time through all these states. A thermodynamic average is then in some sense an average over all these states it will eventually be in. But instead of taking this system average over time, we can equivalently average over an imagined ensemble of identical copies of the system where the different members of the ensemble are to be found in the available microstates of the system. This method based on ensembles was invented by Gibbs and is far superior.

For a closed system with given energy, it was necessary to assume that the probability to find the system in any of the available microstates was the same. Only this *a priori* assumption made it possible to extract thermodynamic properties which agree with experiments. Obviously, it would be of interest to derive this assumption from more fundamental principles. In the following section we will see that it may be justified from the laws of classical mechanics for classical systems and from quantum mechanics for quantum systems.

3.1   Ensembles in phase space

We will now consider more general and physically more realistic systems where the particles have mutual interactions. The simplest Hamiltonian of such a system is

$$H = \sum_i^f \frac{p_i^2}{2m} + U(q_1, q_2, \cdots, q_f) \qquad (3.1)$$

where $f = 3N$ for N identical particles in 3-dimensional space. They have position coordinates q_i and momenta p_i. We can easily imagine more complex systems where for instance the interaction energy also depends on the momenta, where the masses are position-dependent or the motion is relativistic. This

will not matter for what we will derive in the following and we will just write $H = H(q,p)$ where q stands for the set of coordinates $\{q_i\}$ and p the set of momenta $\{p_i\}$.

The classical dynamics of the system is determined by Hamilton's equations

$$\dot{q}_i = \frac{\partial H}{\partial p_i}, \qquad \dot{p}_i = -\frac{\partial H}{\partial q_i} \tag{3.2}$$

which is a generalization of Newton's laws for classical mechanics. If we could solve all these coupled, first order differential equations, we could write the solutions on the general form

$$q_i = q_i(t, q_0, p_0), \qquad p_i = p_i(t, q_0, p_0) \tag{3.3}$$

where (q_0, p_0) specify the initial set of values for these variables. It gives the classical state of the system as it changes with time and can be represented by a moving point in a $2f$-dimensional phase space with coordinates (q, p).

As an example, consider the 1-dimensional harmonic oscillator with with mass m and frequency ω so that the Hamiltonian is

$$H = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 q^2 \ . \tag{3.4}$$

The equations of motion (3.2) now become $\dot{q} = p/m$ and $\dot{p} = -m\omega^2 q$ of which the first is just the ordinary relation between momentum and velocity. Using it in the second, we obtain the standard oscillator equation $\ddot{q} + \omega^2 q = 0$. Its general solution can be written as

$$
\begin{aligned}
q &= A\cos(\omega t + \phi) \\
p &= -Am\omega\sin(\omega t + \phi)
\end{aligned}
$$

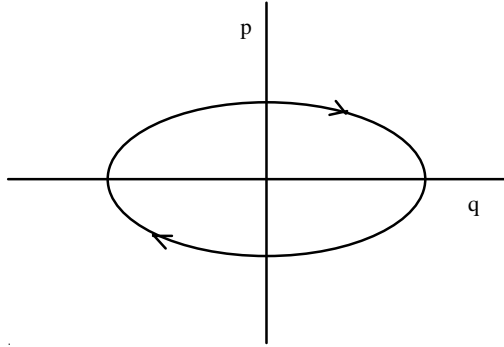where the integration constants A and ϕ can be expressed in terms of the position q_0

Figure 3.1: Particle in 1-dimensional harmonic oscillator potential moves in phase space on an ellipse where the energy is constant.

and momentum p_0 at time $t = 0$. We see that this oscillatory motion in 1-dimensional

space corresponds to a cyclic motion on the ellipse

$$q^2 + \frac{p^2}{m^2\omega^2} = A^2$$

in the 2-dimensional phase space as shown in Fig.3.1. From (3.4) we find that A is directly given in terms of the oscillator energy, $E = \frac{1}{2}m\omega^2 A^2$.

Exact solutions of Hamilton's equations can only be obtained for few, special systems. In most cases one has to use numerical methods to investigate the motion in phase space. Until a few years ago most physicists believed that this could be done to any desired accuracy by just letting bigger and faster computers work for longer periods. But these investigations have revealed that most realistic systems of interacting particles which have non-linear equations of motion, are basically chaotic. This means that the motion in phase space is extremely sensitive to the initial conditions (q_0, p_0) in the general solutions (3.3). The smallest change in any of these variables can result in a completely different trajectory after a finite time. And since numerical methods today make use of computers which all have finite word lengths, there will always be some inaccuracy in the initial conditions and we cannot in practice predict the motion of the system for all later times. This insight is still new and one does still not really understand what implications it has for classical, statistical mechanics.

Even if we cannot calculate the trajectory in phase space, we can still discuss it. For a system with very many particles in thermodynamic equilibrium, we would not be interested in the details of the motion. Only average properties over long time intervals will be related to the thermodynamic state variables. Such a time average of the function $A = A(q, p)$ is

$$\overline{A} = \lim_{T\to\infty} \frac{1}{T} \int_0^T dt\, A(q(t), p(t)) \tag{3.5}$$

where one includes states of the system corresponding to all the different regions in phase space it visits. The problem is to actually calculate this average since it requires knowledge of the system trajectory for all times. And that we don't have, especially not if the motion is chaotic.

Gibbs proposed instead to use an average over a huge ensemble of the same systems, but having different initial conditions so that they to any time fills the available phase space as a liquid fills a container. If we denote the density in phase space of these system points in the ensemble by $\rho = \rho(q, p)$, the number of systems in a volume element $\Delta q \Delta p$ near the phase space point (q, p) is $\rho(q, p)\, \Delta q \Delta p$. The greater the density is in a certain region of phase space, the greater the probability is to find the system under consideration with the corresponding values for the dynamical variables.

As we saw in the previous chapter, it is necessary to invoke quantum mechanics in the counting of microstates. The reason is that due to Heisenberg's uncertainty principle, it is impossible to specify simultaneously both the position and momentum of a particle to an accuracy smaller than Planck's constant. From the result (2.50) for the density of states of one particle in a large, 3-dimensional

box, we know that the volume in phase space corresponding to one microstate is $h^3 = (2\pi\hbar)^3$. In our multi-dimensional phase space with dimension $2f$ it is therefore natural to introduce the dimensionless differential volume element

$$d\omega = \frac{d^f q \, d^f p}{(2\pi\hbar)^f} \tag{3.6}$$

already here in the connection with classical statistical mechanics. This volume element will arise automatically when we later derive quantum statistical mechanics of many-particle systems.

It is now convenient to choose the normalization of phase space density $\rho(q, p)$ such that

$$\int d\omega \, \rho(q, p) = 1 \ . \tag{3.7}$$

Then the ensemble average of the same quantity $A(q, p)$ we considered above, is

$$\langle A \rangle = \int d\omega \, \rho(q, p) A(q, p) \ . \tag{3.8}$$

Instead of finding the average from the full trajectory of one system as the solution of an enormous set of coupled differential equations, we now only have to find the function $\rho(q, p)$ and obtain the average by a multiple integration.

Actual measurements are obviously given by the time average (3.5). It is not at all obvious that it equal to the ensemble average (3.8). The ergodic hypothesis says that they are the same. It can only be proven for a few special systems. A general proof will probably involve a better understanding than we have today of chaos in Hamiltonian systems.

3.2   Liouville's theorem

The density ρ in phase space is governed by Hamilton's equations for each point in this abstract liquid. Since systems cannot spontaneously be created or destroyed, the number of points in a given volume can only change by currents flowing in and out. As in ordinary hydrodynamics or electrodynamics, this gives rise to the equation of continuity

$$\frac{\partial \rho}{\partial t} + \boldsymbol{\nabla} \cdot \mathbf{J} = 0 \tag{3.9}$$

for the most general case when ρ varies explicitly with time. The current of system points is $\mathbf{J} = \rho \mathbf{V}$ where the velocity vector $\mathbf{V} = (\dot{q}_i, \dot{p}_i)$ has $2f$ components. Similarly, the nabla operator in phase space is $\boldsymbol{\nabla} = (\partial/\partial q_i, \partial/\partial p_i)$. It gives the current divergence

$$
\begin{aligned}
\boldsymbol{\nabla} \cdot \mathbf{J} &= \sum_{i=1}^{f} \left(\frac{\partial \rho}{\partial q_i} \dot{q}_i + \frac{\partial \rho}{\partial p_i} \dot{p}_i \right) \\
&= \sum_i \left(\frac{\partial \rho}{\partial q_i} \frac{\partial H}{\partial p_i} - \frac{\partial H}{\partial q_i} \frac{\partial \rho}{\partial p_i} \right)
\end{aligned}
$$

when we use Hamilton's equations (3.2). Note that $\partial \dot{q}_i / \partial q_j = (d/dt)\partial q_i / \partial q_j = d\delta_{ij}/dt = 0$, and, likewise, $\partial \dot{p}_i / \partial q_j$. The special combination of partial derivatives in equation (3.10) is called the Poisson bracket in classical mechanics. For two general variables $A = A(q,p)$ and $B = B(q,p)$ it is denoted by the symbol

$$\{A, B\} = \sum_i \left(\frac{\partial A}{\partial q_i} \frac{\partial B}{\partial p_i} - \frac{\partial B}{\partial q_i} \frac{\partial A}{\partial p_i} \right) \; . \tag{3.10}$$

It plays the same role in classical mechanics as the commutator does in quantum mechanics. The fundamental Poisson brackets are $\{q_i, q_j\} = 0$, $\{q_i, p_j\} = \delta_{ij}$ and $\{p_i, p_j\} = 0$. Hamilton's equations can then be written as $\dot{q}_i = \{q_i, H\}$ and $\dot{p}_i = \{p_i, H\}$.

We can now write the continuity equation (3.9) as

$$\frac{\partial \rho}{\partial t} + \{\rho, H\} = 0 \; . \tag{3.11}$$

In order to see the physical content of this expression, we calculate the change in the density near a system point as it moves with the phase space liquid. It is given by the total derivative

$$\begin{aligned} \frac{d\rho}{dt} &= \frac{\partial \rho}{\partial t} + \sum_{i=1}^{f} \left(\frac{\partial \rho}{\partial q_i} \dot{q}_i + \frac{\partial \rho}{\partial p_i} \dot{p}_i \right) \\ &= \frac{\partial \rho}{\partial t} + (\mathbf{V} \cdot \nabla)\rho = \frac{\partial \rho}{\partial t} + \{\rho, H\} \end{aligned} \tag{3.12}$$

where the first term gives the change in density at a fixed point in phase space while the second term gives the change due to the flow of the liquid. Comparing
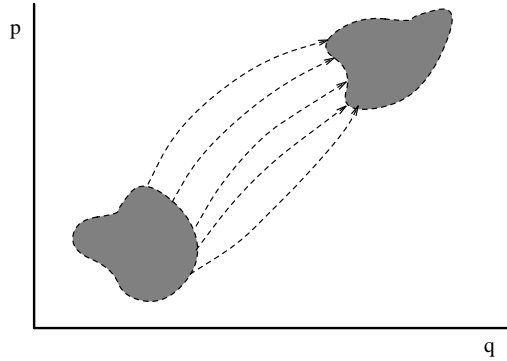

Figure 3.2: The size of a volume of particles moving in phase space is constant but changes in shape.

this with (3.11), we see that the derivative is zero,

$$\frac{d\rho}{dt} = 0 \tag{3.13}$$

and the local density remains constant as seen by an observer moving with a system point. This is Liouville's theorem. If we follow an initial volume element in phase space defined by the system particles within it, it will remain constant but in general change its form as shown in Fig.3.2. Since the motion is most probably chaotic, its very difficult to picture of how this theorem is actually satisfied at all times. However, if ρ is initially constant throughout phase space, it will remain so in time. This is equivalent to saying that an initial phase-space state, where all microstates are equally probable, will stay that way over the course of time. This is nothing else than the previously assumed postulate of *a priori probabilities*, i.e. any microstate has the same probability. Remember that a given system needs to ergodic in order to be represented by an ensemble of system. Ergodicity means that the system will eventually visit all of the phase space that is covered by the ensemble, and for ergodic systems Liouvilles theorem implies that every microstate is equally likely to be visited with time.

For a system in equilibrium all averages are constant in time. They must therefore have an ensemble density which is independent of time, i.e. $\partial\rho/\partial t = 0$. From (3.11) then follows that it must satisfy the condition

$$\{\rho, H\} = 0 \; . \tag{3.14}$$

Writing out the Poisson bracket, we see that this is in general a very complex differential equation which has to be satisfied by the ensemble density. It has many different solutions of which we know very little.

The obviously simplest solution is just $\rho = const$ and the corresponding ensemble is called the microcanonical ensemble. It is of fundamental importance in statistical mechanics and we will investigate it in the following section. Almost just as easily one sees that (3.14) has solutions of the form $\rho = \rho(H)$. If there are additional classical constants of motion $C = C(q, p)$ defined by $dC/dt = \{C, H\} = 0$, we can also have a density distribution $\rho = \rho(H, C)$ which satisfy (3.14). The corresponding system of points in phase space is then called the canonical ensemble. It is used in most practical calculations in statistical mechanics.

For both the microcanonical and canonical ensemble the density distributions are constant in time. On a truly microscopic level this cannot be the case since then we will see the individual system points and their chaotic motion. It is only when we consider the motion in phase space at a slightly larger scale when this continuum description holds and the density appears to be smooth and constant in time. This coarse-grained scale is necessary for the statistical description to be valid and is set by quantum mechanics via Planck's constant. In terms of classical mechanics we can say that the chaotic motion of the individual phase space points have effectively stirred the liquid so much that it assumes a stationary and smooth density.

These two general solutions for the ensemble density, seem almost trivial and one is inclined to think that they have very little physical content. But we will see that these are the density distributions Nature actually makes use of. It is surprising that we can describe and understand these extremely complex

interacting many-particle systems with the absolutely simplest solutions of the differential equation (3.14). The physics is so complex that it gets simple.

3.3 Microcanonical ensembles

In the microcanonical ensemble the probability density is independent of (q, p). The system points are therefore uniformly distributed over the available phase space. If ergodicity holds a and we follow a particular point in the system as it moves with time, it will eventually be in any region of phase space with equal probability. This is again the previously assumed postulate of a priori probabilities, i.e. any microstate has the same probability.

Let us now apply this ensemble to a closed system with given energy E, volume V and particle number N. Since the system is classical, it will move in phase space on the $(2f - 1)$-dimensional hypersurface $H(q, p) = E$. The probability to find it at any point on this surface is the same and can therefore be written as

$$\rho(q, p) = \frac{1}{\Sigma}\, \delta(E - H(q, p)) \tag{3.15}$$

where Σ is called the density of states for the system. In some sense it is a measure for the total area of the hypersurface and is given by the normalization (3.7) as

$$\Sigma = \int d\omega\, \delta(E - H(q, p)) \,. \tag{3.16}$$

Here $d\omega$ is the phase space volume element (3.6). We mentioned in that connection that in order to measure the phase space density correctly, we had to invoke quantum mechanics. But then q and p cannot be both specified simultaneously, and we must instead imagine that the system points in the ensemble move within a thin shell of finite thickness Δ. The probability density will then be

$$\rho = \begin{cases} 1/\Gamma & \text{if } E \leq H \leq E + \Delta \\ 0 & \text{otherwise} \end{cases}$$

where now $\Gamma = \int d\omega$ is the volume of the shell.

We will see that these two densities give the same thermodynamic results for systems with very large number of particles. Then the dimension of phase space is so large that if we we add in one extra dimension normal to the hypersurface, the extra number of states we include will be negligible compared to those in the surface. In fact, we can just as well include all the states in the volume of phase space $\Omega(E)$ with energies less than E. This volume naturally arises from the density of states (3.16) which can be written

$$\begin{aligned} \Sigma &= \frac{\partial}{\partial E} \int d\omega\, \theta(E - H(q, p)) \\ &\equiv \frac{\partial \Omega}{\partial E} \end{aligned} \tag{3.17}$$

when we make use of the identity $\delta(x) = \theta'(x)$. We can therefore write the volume as $\Omega = \int dE\,\Sigma$. But it is also given by an ordinary volume integration $\Omega = \int d\sigma\,dn$ where $d\sigma$ is a differential surface element and dn is a differential normal to the surface. Now $dE = |\nabla H|\,dn$ so the integral (3.17) can be transformed into

$$\Sigma = \int \frac{d\sigma}{|\nabla H|} \ .$$

(3.18)

We will shortly see an example of this for the harmonic oscillator. Since $|\nabla H|$ is a measure for the velocity of the points in phase space, we see that areas where the points move slowly contribute correspondingly more to the density of states.

Having obtained the surface area Σ, the number of microstates W is then

$$W = \frac{\Sigma}{N!}$$

(3.19)

for indistinguishable particles and the entropy can be again obtained from Boltzmann's equation $S = k \log W$. As said above, we can here just as well use the shell volume Γ or the full volume Ω instead of Σ when we have a system in the thermodynamic limit $N \to \infty$. We will see an example of why this is true when we next consider the ideal gas in the microcanonical ensemble. From the entropy we then get the temperature $1/T = \partial S/\partial E$ and the other thermodynamic variables.

If we calculate the entropy from the phase space volume Ω, the temperature follows from

$$\frac{1}{kT} = \frac{\partial}{\partial E} \log \Omega = \frac{1}{\Omega}\frac{\partial \Omega}{\partial E} \ .$$

But the derivative of Ω is (3.17) just the area of the bounding surface Σ so we obtain

$$kT = \frac{\Omega}{\Sigma} \ .$$

(3.20)

This simple result gives rise to a compact derivation of the equipartition theorem. It follows from the microcanonical average

$$\langle p_n \frac{\partial H}{\partial p_n} \rangle = \frac{1}{\Sigma} \int d\omega\, p_n \frac{\partial H}{\partial p_n} \delta(E - H)$$

where we write

$$\frac{\partial H}{\partial p_n} \delta(E - H) = -\frac{\partial}{\partial p_n} \theta(E - H)) \ .$$

(3.21)

Integrating over p_n, we then get

$$\langle p_n \frac{\partial H}{\partial p_n} \rangle = \frac{1}{\Sigma} \int \frac{d^f q}{(2\pi\hbar)^f} dp_1 \cdots dp_f \theta(E - H)$$

(3.22)

after a partial integration where the boundary term doesn't contribute. The remaining integral is now just the volume Ω. We then have

$$\langle p_n \frac{\partial H}{\partial p_n} \rangle = \frac{\Omega}{\Sigma} = kT \ .$$

(3.23)

Obviously, the same result applies also to the average with p_n replaced with q_n. Since the Hamiltonian (3.1) for an interacting system of particles is quadratic in the momenta, we can write the above result on the more well-known form

$$\langle \frac{p_n^2}{2m} \rangle = \frac{1}{2} kT \ . \tag{3.24}$$

Every quadratic term in the Hamiltonian is seen to carry an average energy of $\frac{1}{2} kT$. This is the equipartition theorem.

In the next chapter we will make use of the virial, defined by

$$\theta = - \sum_n q_n \dot{p}_n = \sum_n q_n \frac{\partial H}{\partial q_n} \ . \tag{3.25}$$

Taking the average of it and using (3.23), we find

$$\langle \theta \rangle = 3NkT \tag{3.26}$$

where we have used that the sum contains $f = 3N$ equal terms. This result is called the virial theorem and will be used in the next chapter when we investigate the equation of state for an interacting gas.

Some of this formalism can be illustrated in connection with the 1-dimensional harmonic oscillator we considered in the previous section. The Hamiltonian (3.4) gave rise to a 2-dimensional phase space. For a given energy E the system moves on an ellipse as shown in Fig.3.1. It has the minor axis $b = \sqrt{2mE}$ and the major axis $a = b/m\omega$. The area of the ellipse is $A = \pi ab = 2\pi E/\omega$ so that the phase space volume $\Omega = A/2\pi\hbar = E/\hbar\omega$. We then find the entropy $S = k \log(E/\hbar\omega)$ which gives the internal energy $E = kT$. This is correct and also in agreement with the equipartition theorem.

It is slightly more difficult to obtain the density of states Σ. Starting from (3.17), we must do the integration

$$2\pi\hbar\Sigma = \int dq dp \, \delta(E - \frac{p^2}{2m} - \frac{1}{2} m\omega^2 q^2) = m \int \frac{dq}{p} \tag{3.27}$$

where $p = \sqrt{2mE - m^2\omega^2 q^2}$ as follows from the δ-function. Integrating around the full ellipse, we then find

$$\begin{aligned} \Sigma &= \frac{1}{\pi\hbar} \sqrt{\frac{2m}{E}} \int_0^a \frac{dq}{\sqrt{1 - \frac{q^2}{a^2}}} \\ &= \frac{1}{\pi\hbar} \sqrt{\frac{2m}{E}} a \frac{\pi}{2} = \frac{1}{\hbar\omega} \end{aligned}$$

Had we instead started with (3.18), we would first need the line element $d\sigma = \sqrt{dq^2 + dp^2}$. Since $dp/dq = -m^2\omega^2 q/p$, it follows that

$$d\sigma = dq \sqrt{1 + \left(\frac{m^2\omega^2 q}{p} \right)^2} \ .$$

From $|\nabla H|^2 = \frac{p^2}{m^2} + m^2\omega^4 q^2$, we have

$$|\nabla H| = \frac{p}{m} \sqrt{1 + \left(\frac{m^2\omega^2 q}{p} \right)^2}$$

and we are back at the integral (3.27) for Σ.

We see that our results are consistent with the fundamental relation (3.17). But since this system only contains one particle so that the phase space is 2-dimensional, we can not use Σ instead of Ω in the calculation of the number of available microstates. The density of states Σ is even independent of energy and would have given zero internal energy at all temperatures.

3.4   Canonical ensembles

The systems in a statistical ensemble behave in many ways as an ideal gas in phase space. It is ideal since there can be no interactions between the system particles. We can therefore describe this abstract gas in statistical terms exactly as we did for an ideal gas in the previous chapter. We will make use of this correspondence here in the derivation of the canonical distribution. It describes a system in thermal equilibrium by allowing energy to be exchanged with the surroundings.

In order to be more general, we will now describe the system of particles by quantum mechanics. The classical Hamiltonian (3.1) is then replaced by the Hamiltonian operator

$$\widehat{H} = H(\widehat{q}, \widehat{p}) = \sum_i^f \frac{\widehat{p}_i^2}{2m} + U(\widehat{q}_1, \widehat{q}_2, \cdots, \widehat{q}_f) \; . \tag{3.28}$$

It gives the possible states of the system as the solution of the corresponding Schrödinger equation

$$\widehat{H}\Psi_s = E_s\Psi_s \tag{3.29}$$

where the energy eigenvalue E_s results when the system is in the quantum eigenstate $\Psi_s = \Psi_s(q_1, q_2, \cdots, q_f)$. Since the system is not thermally isolated, it will not remain in such an eigenstate, but all the time make transitions to other states. This corresponds in the classical picture to the motion of the system point through phase space.

When we now have an ensemble of a very large number A of such systems, there will at any time be a number A_s of these which are in the quantum state Ψ_s with energy E_s. These numbers characterize the ensemble and are constant in time although the individual systems always undergo transitions. The average or internal energy of each system in the ensemble is therefore

$$U = \langle\, E\,\rangle = \frac{1}{A} \sum_s E_s A_s = \sum_s E_s P_s \tag{3.30}$$

where $P_s = A_s/A$ is the probability to find a system in the state Ψ_s. They satisfy the obvious normalization

$$\sum_s P_s = 1 \; . \tag{3.31}$$

Note that when ergodicity holds, the ensemble represents a single system, and P_s is just the probablility of finding that system in state s.

Other averages are now defined in the same way. We can define the entropy of the full ensemble in exactly the same way as for a gas of free particles. As long as we concentrate on individual quantum states and not energy levels of each system, we don't have to worry about degeneracies. Also, there is no questions about the counting of states since the ensemble gas can be considered classical although the internal dynamics of each system is quantum mechanical. Since each configuration $\{A_s\}$ of the systems in the ensemble can be obtained in many different ways given by the multinomial formula, we can define the entropy per system as

$$S = \frac{1}{A} k \log \frac{A!}{\prod_s A_s!} \; .$$ (3.32)

The equilibrium probability distribution can now be obtained my maximizing this quantity with the average energy (3.30) held constant.

A more direct derivation of the canonical distribution is obtained by following the steps which led to the Maxwell-Boltzmann distribution for independent particles in Chapter 2. Assuming that one of the systems in the ensemble receives an energy increment $\Delta U = E_i - E_j$, it will jump from the quantum state Ψ_j to Ψ_i. The resulting change $A_i \to A_i + 1$ and $A_j \to A_j - 1$ in the ensemble distribution will induce the entropy change

$$\Delta S = \frac{1}{A} k \log \frac{A_j}{A_i + 1}$$ (3.33)

which follows from the analogous result (2.24). From the First Law $A\Delta S = \Delta U/T$ applied to the ensemble gas, follows now immediately that

$$\frac{A_i}{A_j} = e^{-\beta(E_i - E_j)}$$ (3.34)

when we assume that $A_i \gg 1$. As a result, we have the canonical probability

$$P_s = \frac{1}{Z} e^{-\beta E_s}$$ (3.35)

to find a system at temperature T with energy E_s. It is just Boltzmann's result for the energy distribution of the systems in the ensemble gas.

The equilibrium entropy follows from the general formula (3.32). Since the numbers A and A_s can be as large as we want, we can safely apply Stirling's formula for their factorials. We then easily obtain

$$S = -k \sum_s P_s \log P_s$$ (3.36)

which is Gibb's formula for the entropy.

In the microcanonical ensemble, all the systems have the same energy, $E_s = E$ and each state appears with the same probability. If there are W such allowed

quantum states for the system, then $P_s = 1/W$ and the entropy (3.36) simplifies to Boltzmann's formula $S = k \log W$.

We can also derive this canonical distribution (3.35) in a less abstract way. Consider just one system in thermal equilibrium with a heat bath at given temperature T. If the system and the heat bath are closed towards other systems, their total energy E_{tot} is constant and we can use the microcanonical ensemble to describe this combined system. Then all the microstates will have the same probability. If the system we consider has energy E_s, the heat bath will have an energy $E_B = E_{tot} - E_s$. At this energy, the heat bath can be in a great number of microstates W. The probability to find the system in the specific state s must then be proportional to this number, i.e. $P_s \propto W(E_{tot} - E_s)$. We now write

$$W(E_{tot} - E_s) = \exp \frac{1}{k} S(E_{tot} - E_s) \ .$$

Using that $E_s \ll E_{tot}$, we can expand the exponential to get

$$S(E_{tot} - E_s) = S(E_{tot}) - E_s \left(\frac{\partial S}{\partial E} \right)_{V,N} = S(E_{tot}) - E_s/T$$

since we can keep only the leading terms in the limit where the heat bath is infinite. This gives again the result (3.35).

The unknown normalization constant Z in the canonical distribution (3.35) can depend on the temperature and other thermodynamic quantities necessary to define the system. From the normalization condition (3.31) we get

$$Z = \sum_s e^{-\beta E_s} \ . \tag{3.37}$$

This sum is the canonical partition function for the system and can be used to calculate essentially all the different thermodynamic properties of the system. The internal energy (3.30) can now be written as

$$U = \frac{1}{Z} \sum_s E_s e^{-\beta E_s} \ . \tag{3.38}$$

Taking the derivative of (3.37) with respect to β, we see that we can also obtain the internal energy more directly from

$$U = -\frac{\partial}{\partial \beta} \log Z \tag{3.39}$$

which is very useful in practical calculations. We can find the thermodynamic content of Z from the Gibbs formula (3.36) in which we insert our result for the equilibrium probability P_s to obtain

$$
\begin{aligned}
S &= k \sum_s (P_s \log Z + \beta P_s E_s) \\
&= k \log Z + U/T
\end{aligned}
$$

We see that $Z = e^{-\beta F}$ where $F = U - TS$ is the Helmholtz free energy.

For a system of N non-interacting, distinguishable particles, we can express the system energy E_s in terms of the one-particle energies ϵ_{s_i} state s_i as $E_s = \sum_i \epsilon_{s_i}$. The sum over all system states (3.37) will be the sum over

$$Z = \sum_{\{s_i\}} \prod_i e^{-\beta \epsilon_{s_i}} = \prod_i \sum_{s_i} e^{-\beta \epsilon_{s_i}} = Z_1^N \;.\; . \tag{3.40}$$

When the particles are indistinguishable, we must again divide this result with $N!$.

We have here assumed that phase space can be divided up into regions with discrete values for the possible energies of the system. So our results for the canonical ensemble will automatically be valid for quantum systems. The state of a classical system is on the other hand given by the continuous phase space coordinates (q, p) and the probability to be in this state is proportional to the ensemble density $\rho(q, p)$. Comparing the formula (3.8) for the ensemble average with our result (3.38) in the canonical ensemble, we have the obvious connection

$$P_s = \frac{1}{Z} e^{-\beta E_s} \qquad \Longleftrightarrow \qquad \rho(q, p) = \frac{1}{Z} e^{-\beta H(q,p)} \tag{3.41}$$

between the probabilities in the two descriptions.

We can also obtain the exponential form of the classical density distribution by taking two independent systems with Hamiltonians H_1 and H_2 and combining them into one system with Hamiltonian $H = H_1 + H_2$. Then the combined phase space density must satisfy $\rho(H_1 + H_2) \propto \rho(H_1)\rho(H_2)$. This equation for the unknown function $\rho(H)$ has the solution $\rho(H) \propto \exp(-\beta H)$ where we must show that the unknown parameter β is in fact $1/kT$.

From the normalizations of these two probability distributions follow the corresponding partition functions

$$Z = \sum_s e^{-\beta E_s} \qquad \Longleftrightarrow \qquad Z = \int d\omega \, e^{-\beta H(q,p)} \;. \tag{3.42}$$

The Helmholtz free energy is in both cases given by $F = -kT \log Z$. If the system consists of indistinguishable particles, the classical expression on the right hand side must be reduced by the standard factor $N!$.

When the discrete expression on the left describes a quantum system and the quantum states are correctly defined for identical particles, being symmetric for bosons and antisymmetric for fermions, there should be no $N!$ in the quantum partition function. It will come out automatically when we take the quantum result into the classical regime. Finally, the averages in the two cases also have the same form,

$$\langle A \rangle = \frac{1}{Z} \sum_s A_s \, e^{-\beta E_s} \qquad \Longleftrightarrow \qquad \langle A \rangle = \frac{1}{Z} \int d\omega A(q, p) \, e^{-\beta H(q,p)} \;. \tag{3.43}$$

When we in the following use the discrete description, its mostly because of notational simplicity. With the above correspondences we can always take the results over into the classical and continuous phase space.

In the canonical ensemble the temperature is fixed by the external heat bath. This is achieved by the freedom the system has to exchange energy with the bath. Its energy will therefore fluctuate around its average value (3.38) which is different from the square root of

$$\langle E^2 \rangle = \frac{1}{Z} \sum_s E_s^2 \, e^{-\beta E_s} = \frac{1}{Z} \frac{\partial^2}{\partial \beta^2} \sum_s e^{-\beta E_s}$$

The deviation from the average energy is given by the difference

$$
\begin{aligned}
(\Delta E)^2 &= \langle E^2 \rangle - \langle E \rangle^2 \\
&= \frac{1}{Z} \frac{\partial^2 Z}{\partial \beta^2} - \left(\frac{1}{Z} \frac{\partial Z}{\partial \beta} \right)^2 = \frac{\partial}{\partial \beta} \left(\frac{1}{Z} \frac{\partial Z}{\partial \beta} \right) \\
&= -\frac{\partial U}{\partial \beta} = kT^2 C_V
\end{aligned}
\tag{3.44}
$$

where C_V is the constant volume heat capacity. Since the left hand side goes like the square of the number of particles N in the system and C_V like N, we see that the magnitude of the fluctuation goes like $1/\sqrt{N}$ and is negligible for a macroscopic system.

3.5   Grand canonical ensembles

The canonical ensemble describes systems in thermal contact with a heat bath or the surroundings. It can then exchange energy, but the number of particles remains the same. However, many system in chemistry and physics allow process which will change the number of particles. In order to have thermodynamic equilibrium, we must then let the system also to be in material contact with the surroundings in addition to being in thermal contact. These more general systems with variable particle number are described by the grand canonical ensemble.

Again we will consider a very large ensemble of A such systems. When it is in equilibrium, it contains A_{Ns} systems with exactly N particles and is in the quantum state Ψ_s for this number of particles. Summing up, we then obviously have

$$\sum_{Ns} A_{Ns} = A \ . \tag{3.45}$$

The entropy of the system will then be given by the formula

$$S = \frac{1}{A} k \log \frac{A!}{\prod_{Ns} A_{Ns}!} \tag{3.46}$$

analogous to (3.32). We can find the equilibrium distribution by considering $\Delta N = N' - N$ particles added to the system with the simultaneous change in energy $\Delta U = E_{N's'} - E_{Ns}$. This will make the change $A_{N's'} \to A_{N's'} + 1$ and $A_{Ns} \to A_{Ns} - 1$ in the distribution of systems in the ensemble. From (3.46) now follows the corresponding change in the entropy

$$\Delta S = \frac{1}{A} k \log \frac{A_{Ns}}{A_{N's'} + 1} \ . \tag{3.47}$$

Using the First Law $AT\Delta S = \Delta U - \mu \Delta N$ applied to ensemble where μ is the chemical potential of the surrounding heat bath, we now get

$$\frac{A_{N's'}}{A_{Ns}} = e^{\beta \mu (N' - N) - \beta (E_{N's'} - E_{Ns})} \tag{3.48}$$

where we again have assumed that $A_{Ns} \gg 1$. As a result, we have the probability

$$P_{Ns} = \frac{A_{Ns}}{A} = \frac{1}{\Xi} e^{\beta(\mu N - E_{Ns})} \tag{3.49}$$

to find a system with N particles and with energy E_{Ns}. The unknown constant Ξ follows from the normalization (3.45) which gives

$$\Xi = \sum_{N=0}^{\infty} \sum_s e^{\beta(\mu N - E_{Ns})} \ . \tag{3.50}$$

It is the grand canonical partition function. We can now calculate the average energy of the system

$$U = \sum_{Ns} E_{Ns} P_{Ns} = \frac{1}{\Xi} \sum_{N=0}^{\infty} \sum_s E_{Ns} \, e^{\beta(\mu N - E_{Ns})} \ . \tag{3.51}$$

Other averages are defined the same way.

The entropy can be obtained from (3.46) and is obviously again given by the Gibbs formula

$$S = -k \sum_{Ns} P_{Ns} \log P_{Ns} \ . \tag{3.52}$$

Inserting the equilibrium probabilities (3.49), it gives

$$\begin{aligned} S &= -k \sum_{Ns} P_{Ns} [\beta(\mu N - E_{Ns}) - \log \Xi] \\ &= -k \left[\beta(\mu \bar{N} - U) - \log \Xi \right] \end{aligned}$$

where $\bar{N} = \sum_{Ns} N P_{Ns}$ is the average number of particles in the system. Defining the free energy

$$\Omega = -kT \log \Xi \tag{3.53}$$

we find that it is

$$\begin{aligned}
\Omega &= U - TS - \mu\bar{N} = G - PV - \mu\bar{N} \\
&= -PV
\end{aligned} \tag{3.54}$$

since the Gibbs free energy $G = \mu\bar{N}$. The thermodynamic potential $\Omega = \Omega(T, V, \mu)$ is thus the Landau free energy.

In the classical case we must envisage a phase space with systems with all possible number of particles. The systems with N particles will then have the probability density

$$\rho_N(q,p) = \frac{1}{\Xi}\, e^{-\beta(H_N(q,p)-\mu N)} \tag{3.55}$$

with the partition function

$$\Xi = \sum_{N=0}^{\infty} \int d\omega\, e^{-\beta(H_N(q,p)-\mu N)}\ . \tag{3.56}$$

It should be divided by $N!$ for indistinguishable particles.

It is possible to get to this conclusion along a different route. We will see that for a macroscopic system the fluctuations ΔN in the particle number around the mean number $\bar{N}$ is negligible. In the sum (3.50) for the grand partition function we then expect terms with $N \approx \bar{N}$ to dominate. We will then approximately have

$$\Xi(T, V, \mu) \approx \Delta N e^{\beta\mu\bar{N}} Z_{\bar{N}}(T, V)$$

where $Z_{\bar{N}}(T, V) = \exp(-\beta F)$ is the ordinary, fixed-volume partition function for $\bar{N}$ particles. Taking logarithms on both sides now gives $\Omega = F - \bar{N}\mu - \log\Delta N$. Since $\Delta N/\bar{N} \to 0$ as $\bar{N} \to \infty$, we can safely neglect the ΔN in the thermodynamic limit and we are back to the result $\Omega = -PV$ for the Landau free energy.

From (3.49) we can find the probability P_N that the system contains exactly N particles. It is obtained from P_{Ns} by summing over all possible states s at this particle number,

$$P_N = \sum_s P_{Ns} = \frac{Z_N}{\Xi}\, e^{\beta\mu N} \tag{3.57}$$

where Z_N is the canonical partition function for the system with exactly N particles,

$$Z_N = \sum_s e^{-\beta E_{Ns}}\ . \tag{3.58}$$

The average number $\langle N \rangle = \bar{N}$ of particles in the system is then

$$
\begin{aligned}
\bar{N} &= \sum_{N=0}^{\infty} N P_N = \frac{1}{\Xi} \sum_{N=0}^{\infty} N Z_N e^{\beta \mu N} \\
&= \frac{kT}{\Xi} \frac{\partial \Xi}{\partial \mu} = -\left(\frac{\partial \Omega}{\partial \mu} \right)_{T,V}
\end{aligned}
\tag{3.59}
$$

This is consistent with Ω being the Legendre transformed of the Helmholtz free energy $F(T, V, N)$ from where the chemical potential follows as $\mu = (\partial F / \partial N)_{T,V}$. Then $\Omega = F - N\mu$ as we found above.

The fluctuations in the particle number around this average value can now be obtained in the same way as the energy fluctuations (3.44) in the canonical ensemble. We obtain

$$
\langle N^2 \rangle = \sum_{N=0}^{\infty} N^2 P_N = \frac{(kT)^2}{\Xi} \frac{\partial^2 \Xi}{\partial \mu^2}
$$

so that the deviation away from the mean is

$$
\begin{aligned}
(\Delta N)^2 &= \langle N^2 \rangle - \langle N \rangle^2 \\
&= (kT)^2 \frac{\partial^2 \log \Xi}{\partial \mu^2} = -kT \left(\frac{\partial^2 \Omega}{\partial \mu^2} \right)_{T,V}
\end{aligned}
\tag{3.60}
$$

From (3.59) we have that

$$
\left(\frac{\partial P}{\partial \mu} \right)_T = \frac{\bar{N}}{V} = \rho
\tag{3.61}
$$

so that the fluctuations are given by

$$
\langle N^2 \rangle - \langle N \rangle^2 = kTV \left(\frac{\partial \rho}{\partial \mu} \right)_T .
$$

But using the chain rule

$$
\left(\frac{\partial \rho}{\partial \mu} \right)_T = \left(\frac{\partial \rho}{\partial P} \right)_T \left(\frac{\partial P}{\partial \mu} \right)_T
$$

we find that the result can be expressed by the isothermal compressibility (1.24),

$$
\langle N^2 \rangle - \langle N \rangle^2 = kTN\rho K_T .
\tag{3.62}
$$

Again we see that this statistical fluctuation can be related to a thermodynamic response function. Both this result and (3.44) for the energy fluctuation in the canonical ensemble are examples of what is more generally called the fluctuation-dissipation theorem.

Away from any second order phase transitions, the right hand side of (3.62) is of the order N so that $\Delta N/N \propto 1/\sqrt{N}$ and therefore completely negligible in macroscopic systems.

Let us now treat the ideal gas in the grand canonical ensemble. The N-particle canonical partition function can be obtained from the one-particle partition function Z_1 in (2.48). For indistinguishable particles we then have

$$Z_N = \frac{Z_1}{N!} = \frac{1}{N!} \left(\frac{V}{\Lambda^3} \right)^N . \tag{3.63}$$

We first find the grand canonical partition function (3.50)

$$\Xi = \sum_{N=0}^{\infty} e^{\beta \mu N} Z_N = \exp \left(\frac{V}{\Lambda^3} e^{\beta \mu} \right) \tag{3.64}$$

Introducing the fugacity $z = e^{\beta \mu}/\Lambda^3$ we therefore have the simple result $\Xi = \exp zV$. The average number of particles (3.59) is then $\bar{N} = zV$. But since the Landau free energy $\Omega = -kT \log \Xi = -kT\bar{N}$ we immediately also have the equation of state $PV = \bar{N}kT$ in this ensemble.

The probability that the ideal gas contains exactly N particles is

$$P_N = \frac{e^{-\bar{N}}}{N!} \left(\frac{V}{\Lambda^3} \right)^N e^{\beta \mu N} = \frac{\bar{N}^N}{N!} e^{-\bar{N}} \tag{3.65}$$

which is just the Poisson probability distribution. It gives rise to a fluctuation (3.60) in the particle number which is found to be exactly $\Delta N = \sqrt{N}$.

3.6   Information theory

There is a close relation between the concepts entropy and information. If a thermodynamic system is at a low temperature, it can only be in a few states and it has low entropy. One can then describe the state of the whole system by using a few words or just a couple of lines with equations. It requires little information. On the other hand, at high temperatures the system is much more disordered and it has large entropy. Then one needs to provide much information to describe the microscopic state of the system. We will now make this correspondence between entropy and information more quantitative.

Many questions require just an answer of yes or no. Such an answer is defined to provide one bit of information. It is then implicitly assumed that the two possible answers will occur with the same probability if the question could be asked several times under the same conditions. One bit of information is needed to tell a person to do one of two possible things. In order to do one of four things {A,B,C,D} a person must be given two bits of information. First he must be told to do one in the group {A,B} or the group {C,D}. When this subgroup is determined, it requires one more bit of information to determine which of the two remaining possibilities to choose. More generally, if there are N possible

choices to make, it requires $I = \log_2 N$ bits of information to determine one of these.

These considerations can easily be generalized to other kinds of information or media. There are approximately thirty letters in the alphabet. If they are produced independently, for example by a monkey at a typewriter, each letter in such a text would have an information content of around 5 bits/character. A page of text, 50 lines with 80 characters contains therefore $5 \times 4000 = 2 \times 10^4$ bits. Such a book with 500 pages contains therefore 10^7 bits of information. We will later see that the real number is somewhat lower since the information content in more intelligent text is actually less than 5 bits per character, perhaps down to almost 1 bit.

In the genetic DNA code there are 4 bases, C,G, T and A. Assuming that they appear at random, each provide for two bits of information. In the double helix the distance between each base is 1.2×10^{-7} cm. The genetic DNA code in a fruit fly is 1.2 cm long and contains 10^7 bits of information which is the same as in the above book. In a virus it is only 10^4 bits and in a human it is almost 10^{10} bits, i.e. one thousand books are needed to write it all down.

A black or white pixel on a TV screen corresponds to one bit. Since a full screen is made of 600 lines with 500 pixels each, one TV image contains 3×10^5 bits. This is more than a thousand words of typically five letters. Since the screen is updated 25 times per second, we see that the TV produces almost a book of information every second. A video tape with a 90 minutes program corresponds therefore to almost 5000 books of information. But this is under the assumption that all the TV pixels appear at random which is generally not the case.

We have here assumed that the N possibilities have equal probability $P = 1/N$. Then we can write instead

$$I = -\log_2 P = -k \log P \tag{3.66}$$

where the constant $k = \log 2 = 1.44\ldots$ can be considered to be equivalent to the Boltzmann constant. This formula will now be generalized to give the information content of a message where each symbol has a different probability P to occur or be produced. A symbol here can be almost anything, a spoken word or sentence, a textbook, a TV picture, a character being produced at a typewriter, a binary digit in a data stream and so on. This more general definition of information content seems to satisfy all the requirements we would intuitively have about it.

As a simple example, consider a oil lamp in a car. It is usually green saying that everything is ok and we hardly notice it. When there is a problem, it lights red and we get really worried. If the probability to show red is $P_R = 1/1024$ then the probability to show green is $P_G = 1023/1024$. The information we receive when it is green, is therefore only $I_G = 0.0014$ bits. On the other hand, when it is red, we receive $I_R = 10$ bits of information which is a factor 7000 more and we jump in the driver's seat.

When the information source produces messages or symbols not at random, we can assume that each symbol s is produced with a certain probability P_s.

When these probabilities are independent of time, i.e. the same yesterday as tomorrow, we say that the source is ergodic. The average information in each symbol produced will then be

$$I = -k \sum_s P_s \log P_s \ . \tag{3.67}$$

This is just Gibb's formula for the entropy of a system in a statistical ensemble. We can therefore say that the entropy is just the information needed to completely describe the microscopic state of the system. It was this realization which made the physicist L. Szilard in 1927 lay the foundation of modern information theory. But it was C. Shannon who twenty years later made it all into a new scientific discipline.

If the four symbols {A,B,C,D} are produced with the probabilities $P_A = 1/2, P_B = 1/4, P_C = 1/8$ and $P_D = 1/8$ we find from the above formula that the information content is $I = 1.75$ bits per symbol. If they all had appeared at random, it would have been $I = 2$ bits. One can show quite easily that the maximum information production always occurs when the symbols are made at random. A monkey at a typewriter produces more information than an educated student. But we know that there is usually not much interesting content in most information produced, so we should not be surprised by this conclusion.

If the N symbols are produced completely at random, then the information content is $I_{max} = k \log N$ per symbol. We will now show that this is actually the maximum possible. It follows that

$$\begin{aligned} I_{max} - I &= k(\log N + \sum_s P_s \log P_s) \\ &= k \sum_s P_s \log N P_s \end{aligned}$$

Now $\log x \geq 1 - 1/x$ so we find the bound

$$I_{max} - I \geq k \sum_s P_s (1 - \frac{1}{N P_s}) = k(1 - 1) = 0$$

which proves the assertion.

The letters do not occur with the same probabilities in a human language. In English the most common letter is 'e' with the probability $P_e = 0.131$, then follows 't' and 'o' with probabilities $P_t = 0.090$ and $P_o = 0.082$. The letter 'e' is also most common in written French, with $P_e = 0.159$ followed by $P_a = 0.094$ and $P_i = 0.084$. These are certainly averages over all possible written texts in these two languages. Using such frequencies for all the letters in the two languages, one finds the average information content per letter to be 4.13 bits in English and 4.01 bits in French. A typical English book should therefore be slightly longer when translated to French if it is to contain the same amount of information.

From the above letter frequencies we see that the information content in each letter is certainly below 5 bits as it would have been if they appeared completely at random. But we also know that some letters occur with much greater probabilities together with certain letters than others. After 'j' in English one expects a vocal while after 'q' one is almost certain to find a 'u'. This means that if one looks at groups of letters, the information content per letter will be smaller and therefore below 4 bits.

Considering words in English, the most common word is "the" followed by "of", "and" and "to". There is an empirical relationship, called Zipf's law, which states that the probability for word number w in this ordering is $P_w = 0.1/w$. So the probability $P_{the} = 0.1$, $P_{of} = 0.05$ and so on in English. Summing up the contributions from $N = 8727$ words, Shannon found that the information content was on the average

$$I = -k \sum_{w=1}^{N} P_w \log P_w = 11.8 \text{ bits}$$

per word. Since each word contains typically five letters, there is then only 2.1 bits of information in every English letter. Looking at even bigger groups of letters than words, Shannon surmised that the information content could be brought down to around one bit per character.

Chapter 4

Real Gases and Liquids

In the ideal gas there are no interactions between the particles. It can only be in one, gaseous phase which is quite close to the state most real systems reach at very high temperatures and low densities. But most systems are usually at temperatures and densities where the interactions are important. They give rise to deviations from ideal gas behavior and can even cause transitions to other states like the liquid or solid phases. An exact result for the thermodynamics of a real gas follows from the virial theorem. It can be used to derive an approximate equation of state for such an interacting system. The crudest version of this dates back to van der Waal.

Equations of state describe the bulk properties of fluids. A different type of interactions in real systems is introduced by the boundary conditions, as in the case of osmosis. This phenomenon is characterized by the presence of a semi-permeable membrane that lets only one substance through, and blocks the other. The result is a pressure difference across the membrane, that is known as osmotic pressure. This chapter starts with a theoretical basis for equations of state for real system and ends with a discussion of osmosis.

4.1   Correlation functions

In most gases and liquids the dominant interaction will be via a two-particle potential $u(\mathbf{r}_i - \mathbf{r}_j)$. We will here only consider such systems. The potential has the typical form shown in Fig.4.1. When the separation between the particles is very small, it becomes very repulsive and one says that the particles have a hard core. At larger separations $|\mathbf{r}_i - \mathbf{r}_j|$ it becomes weakly attractive and then goes slowly to zero at increasing separations.

A physically realistic interaction potential is the Lennard-Jones potential

$$u(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^{6} \right] \tag{4.1}$$

where the functional forms of the repulsive and attractive parts can be explained
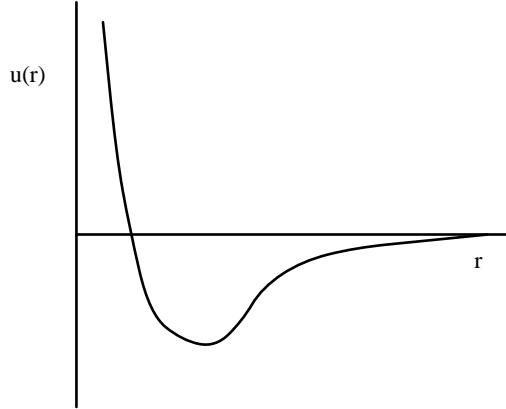
Figure 4.1: Inter-particle potential consists of a repulsive part at short distances and a weaker, attractive part at longer distances.

in terms of the more fundamental interactions between the atoms. It has the form shown in Fig.4.1. The minimum $u_{min} = -\epsilon$ is located at $r_{min} = 2^{1/6}\sigma$. For the noble gas argon one finds the parameters $\epsilon/k = 120\,K$ and $\sigma = 3.4\text{Å}$.

For analytical calculations one often approximates the potential with a hard-sphere potential

$$u(r) = \begin{cases} \infty & \text{if } r < d \\ 0 & \text{otherwise} \end{cases} \quad . \tag{4.2}$$

Adding a square well attractive part to this for a finite distance outside the hard-core diameter d still makes it analytically tractable.

All of the properties of the system will follow from the Hamiltonian

$$H(\mathbf{p},\mathbf{r}) = \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m} + U(\mathbf{r}_1, \mathbf{r}_2, \ldots \mathbf{r}_N) \tag{4.3}$$

when it contains N particles and where the potential energy $U = \sum_{i<j} u(\mathbf{r}_i - \mathbf{r}_j)$. The canonical partition function is then

$$Z_N(T,V) = \frac{1}{N!} \int d\omega \, e^{-\beta H(\mathbf{p},\mathbf{r})} = \frac{1}{N!} \frac{Q_N}{\Lambda^{3N}} \tag{4.4}$$

where Λ is the thermal wavelength (3.36) and

$$Q_N(T,V) = \int d^{3N}r \, e^{-\beta U(\mathbf{r}_1, \mathbf{r}_2, \ldots \mathbf{r}_N)} \tag{4.5}$$

is called the configuration integral. The equation of state then follows from

$$\frac{P}{kT} = \frac{\partial}{\partial V} \log Q_N \; . \tag{4.6}$$

For a macroscopically large number of particles, the general integral can only be done numerically by, for example, Monte Carlo integration. However, it is possible to show that the small integrals Q_2, Q_3 and so on will determine the physics in the virial expansion of the equation of state.

From the above we see that the probability to find the particles in the gas in a certain configuration $(\mathbf{r}_1, \mathbf{r}_2, \ldots \mathbf{r}_N)$ is

$$P_N(\mathbf{r}_1, \mathbf{r}_2, \ldots \mathbf{r}_N) = \frac{1}{Q_N} e^{-\beta U(\mathbf{r}_1, \mathbf{r}_2, \ldots \mathbf{r}_N)} \ . \tag{4.7}$$

It can be used to obtain different correlation functions in the gas from the microscopic density at position $\mathbf{r}$,

$$n(\mathbf{r}) = \sum_{i=1}^{N} \delta(\mathbf{r} - \mathbf{r}_i) \ . \tag{4.8}$$

The two most important ones are the average density

$$\rho = \langle n(\mathbf{r}) \rangle \tag{4.9}$$

and the two-particle correlation function

$$G(\mathbf{r} - \mathbf{r}') = \langle n(\mathbf{r}) \, n(\mathbf{r}') \rangle \ . \tag{4.10}$$

It contains information about the distribution of particles relative to each other. Since the interactions are supposed to only depend on the relative distances between the particles, all results must be translational invariant. This means that the correlation functions can only depend on coordinate differences like $\mathbf{r} - \mathbf{r}'$ in (4.10).

The same argument implies that the average $\langle n(\mathbf{r}) \rangle$ must be be independent of the position $\mathbf{r}$. This can be verified by an explicit calculation from the definition

$$\langle n(\mathbf{r}) \rangle = \frac{1}{Q_N} \sum_{i=1}^{N} \int d^3r_1 \, d^3r_2 \ldots d^3r_N \, \delta(\mathbf{r} - \mathbf{r}_i) \, e^{-\beta U(\mathbf{r}_1, \mathbf{r}_2, \ldots \mathbf{r}_N)} \ .$$

It gives N equal terms of which we only have to consider the first one. Integrating over $\mathbf{r}_1$ we then have

$$\langle n(\mathbf{r}) \rangle = N \frac{\int d^3r_2 \ldots d^3r_N \, e^{-\beta U(\mathbf{r}, \mathbf{r}_2, \ldots \mathbf{r}_N)}}{\int d^3r_1 \, d^3r_2 \ldots d^3r_N \, e^{-\beta U(\mathbf{r}_1, \mathbf{r}_2, \ldots \mathbf{r}_N)}} \ .$$

Since the potential energy U depends on coordinate differences, these two integrals differ only by a factor $\int d^3r_1 = V$ in the denominator. The net result is therefore $\langle n(\mathbf{r}) \rangle = N/V = \rho$ as claimed.

The two-particle distribution (4.10) is most important. Inserting the densities in the average and splitting the double sum into two terms, it can be written as

$$G(\mathbf{r} - \mathbf{r}') = \sum_{i \neq j}^{N} \langle \delta(\mathbf{r} - \mathbf{r}_i) \, \delta(\mathbf{r}' - \mathbf{r}_j) \rangle + \delta(\mathbf{r} - \mathbf{r}') \sum_{i=1}^{N} \langle \delta(\mathbf{r} - \mathbf{r}_i) \rangle \ .$$

The first part contains $N(N-1)$ equal terms corresponding to each particle interacting with $N-1$ others. When the separation $|\mathbf{r} - \mathbf{r}'|$ becomes large, the corresponding interaction energy goes to zero and it goes to the ideal gas limit $N(N-1)/V^2 = \rho^2$. This term is called the pair correlation function $g(\mathbf{r} - \mathbf{r}')$ and is defined by

$$\rho^2 g(\mathbf{r}_1 - \mathbf{r}_2) = N(N-1)\frac{1}{Q_N}\int d^3r_3 \ldots d^3r_N e^{-\beta U(\mathbf{r}_1,\mathbf{r}_2,\ldots\mathbf{r}_N)} \qquad (4.11)$$

so that it approaches one for large separations. We can now write the two-particle distribution function as

$$G(\mathbf{r} - \mathbf{r}') = \rho^2 g(\mathbf{r} - \mathbf{r}') + \rho\, \delta(\mathbf{r} - \mathbf{r}') \ . \qquad (4.12)$$

The last term describes the correlation of the particle with itself. For isotropic gases and liquids $g(\mathbf{r}-\mathbf{r}') = g(r)$ where $r = |\mathbf{r}-\mathbf{r}'|$ is the separation between the two points. It is therefore also called the radial distribution function. From the way $G(\mathbf{r} - \mathbf{r}')$ was defined, we see that it gives the probability to find a particle at the position $\mathbf{r}'$ given that there is one at $\mathbf{r}$ irrespectively of where all the others are. When $\mathbf{r}'$ approaches $\mathbf{r}$, there is certainly going to be a particle. This is taken care of by the δ-function in (4.12) so $g(r)$ describes only correlations with other particles.

Another way of saying this is to take the origin to be at the position of a certain particle. Then $\rho g(r)$ is the average density of particles at distance r away. The average number of other particles within a distance R from the origin is therefore

$$n(R) = 4\pi\rho \int_0^R dr\, r^2 g(r) \ . \qquad (4.13)$$

When R becomes very large, the integral gives the homogeneous result $n(R) = (4\pi/3)\rho R^3$.

If the particles have a short-range repulsive core of radius r_{min}, the correlation function $g(r)$ has the typical form shown in Fig. 4.2. It goes to zero for separations $r < r_{min}$, reaches a peak at $r \geq r_{min}$ and goes to the ideal gas limit $g(r) \to 1$ for large separations.

These correlation functions are intimately connected with the fluctuations in the number of particles in a finite volume of the gas. As in the grand canonical ensemble, this is measured by the quantity

$$\langle N^2 \rangle - \langle N \rangle^2 = \int d^3r \int d^3r' \left[\langle n(\mathbf{r})\, n(\mathbf{r}') \rangle - \langle n(\mathbf{r}) \rangle \langle n(\mathbf{r}') \rangle \right] \ .$$

Using (4.10) and (4.12) we can write this as

$$\begin{aligned}
\langle N^2 \rangle - \langle N \rangle^2 &= \int d^3r \int d^3r' \left[\rho^2 g(\mathbf{r},\mathbf{r}') + \rho\, \delta(\mathbf{r} - \mathbf{r}') - \rho^2 \right] \\
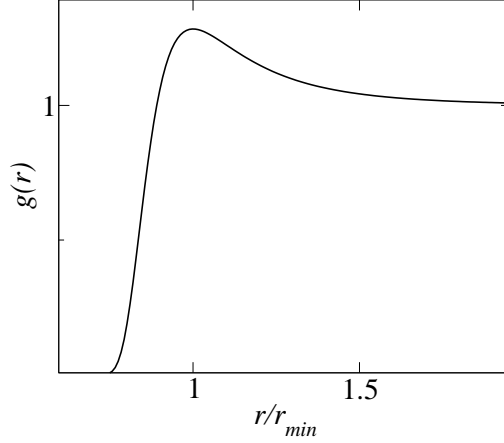&= N + N\rho \int d^3r\, (g(r) - 1)
\end{aligned}$$

Figure 4.2: The pair correlation function has a peak for small separations. At longer separations it approaches the ideal gas value of one.

The special combination

$$h(r) = g(r) - 1 \tag{4.14}$$

is called the reduced pair correlation function. From (4.11) follows that $\int d^3r\, g(r) = V$ in the canonical ensemble which would result in $\int d^3r\, h(r) = 0$. But for the sub-volume of the gas we consider here, the number of particles is not fixed and we must work in the grand canonical ensemble.

From (3.62) we can then relate the above integral over the reduced pair correlation function to the isothermal compressibility,

$$1 + \rho \int d^3r\, h(r) = kT\rho K_T \;. \tag{4.15}$$

When the system is close to the critical point, the right hand side is very large. This implies that the correlation function must become more and more long-ranged as the system approaches criticality where the compressibility diverges. We can see this behavior in many other systems near second order phase transitions.

We can use the pair correlation function $g(r)$ to calculate the average potential energy of the particles. Since there are $N(N-1)/2$ pair interactions, we have

$$\begin{aligned}
\langle U \rangle &= \frac{1}{2}N(N-1)\,\langle u(r_{12}) \rangle \\
&= \frac{1}{2}N(N-1)\frac{1}{Q_N}\int d^{3N}r\, u(r_{12})\, e^{-\beta U}
\end{aligned}$$

$$= \frac{1}{2}N(N-1)\frac{1}{Q_N}\int d^3 r_1 \int d^3 r_2\, u(r_{12}) \int d^3 r_3 \ldots d^3 r_N\, e^{-\beta U}$$

$$= \frac{1}{2}\int d^3 r_1 \int d^3 r_2\, u(r_{12})\, \rho^2 g(r_{12})$$

where $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$. Using translational invariance we can do one integration and get

$$\langle U \rangle = N\rho \frac{1}{2}\int d^3 r\, u(r)\, g(r) \;. \tag{4.16}$$

Since the average kinetic energy is $3kT/2$ per particle from the virial theorem, we then obtain for the average energy per particle

$$\langle E \rangle / N = \frac{3}{2}kT + \frac{1}{2}\rho \int d^3 r\, u(r)\, g(r) \;. \tag{4.17}$$

Knowing the interparticle energy and the pair correlation function, this exact formula gives the internal energy of the system and therefore also the specific heat. The main problem is to find the correlation function from a given potential.

At low densities it is possible to find an approximate expression for the pair correlation function. From (4.11) we see that it is in general given by the multiple integrals

$$\rho^2 g(\mathbf{r}_1 - \mathbf{r}_2) = N(N-1)\, e^{-\beta u(r_{12})}\frac{1}{Q_N}\int d^3 r_3 \ldots \int d^3 r_N e^{-\beta \sum'_{i<j} u(r_{ij})} \tag{4.18}$$

where the primed sum in the exponent means that the pair (12) should not be included. When the density is not too large, the dominant contribution to the dependence on the separation r_{12} comes from the first exponent. In the other exponents the particles are on the average far removed from each other and we can set $u(r_{ij})$ there. We then find in this limit

$$g(r) = e^{-\beta u(r)} \;. \tag{4.19}$$

The repulsive part of the inter-particle potential $u(r)$ at short distances makes $g(r)$ go to zero when $r \to 0$. At large separations, the potential goes to zero and the pair correlation function approaches one. This behavior at low densities explains the main features in Fig.4.2. When the density becomes higher, the function is not so smooth anymore. It gets a more wiggly behavior due to the closer packings of the particles in the system.

In thermodynamics one concentrates on the macroscopic properties of a system like equation of states, specific heats and compressibilities. For most of these quantities there is a very indirect connection between what one can measure and the detailed, microscopic properties of the system. On the other hand, the pair correlation function $g(r)$ reflects more directly the interactions and molecular structure of the gas-liquid system. And even more importantly, it can be directly measured in scattering experiments so to give a direct look into the inner, microscopic workings of the thermodynamic system.

4.2 The virial theorem

In connection with the microcanonical ensemble in the previous chapter we derived the virial theorem (3.26). It can also be proven quite easily in the canonical ensemble. From the definition

$$\theta = -\sum_{i=1}^{N} \mathbf{r}_i \cdot \dot{\mathbf{p}}_i \tag{4.20}$$

of the virial, where the sum goes over the N particles in the system, we can write

$$\theta = \sum_{i=1}^{N} [\dot{\mathbf{r}}_i \cdot \mathbf{p}_i - \frac{d}{dt}(\mathbf{r}_i \cdot \mathbf{p}_i)] \ .$$

Using the fact that the time average of a total derivative is zero in an ergodic system, we find that the average of the virial is

$$\langle \theta \rangle = \sum_{i=1}^{N} \langle \dot{\mathbf{r}}_i \cdot \mathbf{p}_i \rangle = 2 \langle K \rangle \tag{4.21}$$

where K is the kinetic energy of the particles. Using Hamilton's equation $\dot{\mathbf{r}}_i = \partial H/\partial \mathbf{p}_i$, the average of the virial is now given by the phase space integral

$$
\begin{aligned}
\langle \theta \rangle &= \frac{1}{Z_N} \sum_{i=1}^{N} \int d\omega \, \mathbf{p}_i \cdot \frac{\partial H}{\partial \mathbf{p}_i} e^{-\beta H} \\
&= -\frac{kT}{Z_N} \sum_{i=1}^{N} \int d\omega \, \mathbf{p}_i \cdot \frac{\partial}{\partial \mathbf{p}_i} e^{-\beta H}
\end{aligned}
$$

By a partial integration where the boundary term vanishes, we are the left with

$$
\begin{aligned}
\langle \theta \rangle &= 3kT \frac{1}{Z_N} \sum_{i=1}^{N} \int d\omega \, e^{-\beta H} \\
&= 3NkT \tag{4.22}
\end{aligned}
$$

For the kinetic energy we therefore have the result $\langle K \rangle = \frac{3}{2} NkT$ which we already have used.

In the virial (4.20) $\dot{\mathbf{p}}_i = \mathbf{F}_i$ is the force acting on particle i. It is made up of two terms, $\mathbf{F}_i = \mathbf{F}_i^{ext} + \mathbf{F}_i^{int}$ where $\mathbf{F}_i^{ext}$ is due to the forces from the walls of the volume containing the particles, and $\mathbf{F}_i^{int}$ is due to the interactions with the other particles. Since the average force from a small area element $\Delta \mathbf{S}_i$ in the wall on particle i at position $\mathbf{r}_i$ is $\mathbf{F}_i^{ext} = -P\Delta \mathbf{S}_i$, the total contribution from the external forces to the average of the virial is

$$\langle \theta_{ext} \rangle = P \oint d\mathbf{S} \cdot \mathbf{r} = 3PV \tag{4.23}$$

from Gauss's integration theorem where V is the volume of the gas.

The force on particle i from the other particles is

$$\mathbf{F}_i^{int} = -\frac{\partial U}{\partial \mathbf{r}_i} = -\sum_{i \neq j} \frac{\partial u(r_{ij})}{\partial \mathbf{r}_i}$$

We can now calculate the contribution of these forces to the average virial exactly as we derived the average of the potential energy in (4.16). It gives

$$\langle \theta_{int} \rangle = \frac{N}{2} \rho \int d^3r \, r u'(r) \, g(r) \ . \tag{4.24}$$

Adding these two contributions together and using (4.22) we find the virial equation of state

$$P = \rho \left[kT - \frac{1}{6} \rho \int d^3r \, r u'(r) \, g(r) \right] \ . \tag{4.25}$$

Just like the average potential energy we found in (4.16), this is an exact result for the thermodynamics of a classical gas. Again, it can only yield useful results when we know the pair correlation function $g(r)$ resulting from the interaction potential $u(r)$.

The above result can be derived much more directly from (4.6) for the pressure by using the dimensionless variables $\mathbf{x}_i = V^{-\frac{1}{3}} \mathbf{r}_i$ in the configuration integral Q_N. Taking the volume derivative, we then immediately obtain

$$P = kT \left[\frac{N}{V} - \frac{\beta}{2} N(N-1) \langle \frac{1}{3} \frac{r}{V} u'(r) \rangle \right]$$

which is just the above virial equation of state.

When the density of the gas is low, we can use the approximate result (4.19) for the pair correlation function in (4.25). It then becomes

$$\begin{aligned} \frac{P}{kT} &= \rho - \frac{1}{6} \rho^2 \int d^3r \, r \frac{d}{dr} \left(1 - e^{-\beta u(r)} \right) \\ &= \rho + \frac{1}{2} \rho^2 \int d^3r \, [1 - e^{-\beta u(r)}] \end{aligned} \tag{4.26}$$

after a partial integration. It ay be shown that these are just the first two terms in the virial expansion of the equation of state. It then takes the general form

$$\frac{P}{kT} = \sum_{n=1}^{\infty} B_n(T) \, \rho^n \tag{4.27}$$

where $B_n(T)$ are the virial coefficients with $B_1 = 1$. In the above derivation we found the second virial coefficient

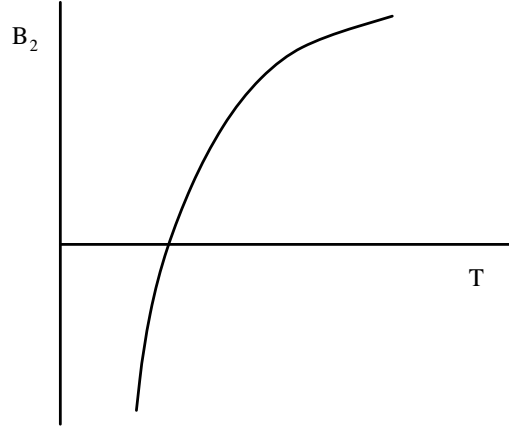$$B_2(T) = \frac{1}{2} \int d^3r \, [1 - e^{-\beta u(r)}] \tag{4.28}$$

Figure 4.3: The second virial coefficient increases with temperature for gases with attraction between the particles.

which turns out to be correct for arbitrary densities.

A typical behavior of the inter-particle potential $u(r)$ was shown in Fig.4.1. For separations below the hard-core diameter d it is very repulsive. It is then followed by a weakly attractive part. We can therefore approximate the second virial coefficient (4.28) when the temperature is high by splitting it up in two terms,

$$
\begin{aligned}
B_2(T) &\simeq 2\pi \int_0^d dr\, r^2 + \frac{2\pi}{kT} \int_d^\infty dr\, r^2 u(r) \\
&\equiv b - a/kT
\end{aligned}
\tag{4.29}
$$

where the constant $b = 2\pi d^3/3$ is one-half of the hard-core particle volume and $a = -2\pi \int_d^\infty dr\, r^2 u(r)$ is a positive quantity due to the long-range attraction between the particles. The equation of state is then in this approximation

$$
\frac{P}{kT} = \rho + \rho^2 \left(b - a/kT\right) .
\tag{4.30}
$$

We see that the second virial coefficient is negative at low temperatures where the pressure will be below the ideal-gass pressure. This is caused by the attractive part of the potential between the particles. B_2 becomes positive at higher temperatures where the repulsive part of the potential dominates. For any potential of the general form in Fig.4.1, we will find that this virial coefficient varies with temperature as shown in Fig.4.3. It goes through zero at a certain temperature called the Boyle temperature T_B.

4.3   Mean field theory for the van der Waals equation

The equation of state (4.30) contains the first two terms of the virial expansion of the equation of state. It is a perturbative expansion which should be most accurate when the gas density ρ is low. For this reason it will not give any phase transition to a liquid state with a high density. That will only follow from a non-perturbative calculation. The simplest and most famous example of this is the van der Waals equation of state written down in 1873.

It can be derived in many different ways. The method which can most easily be generalized to other problems in phase transitions, is the mean field approximation. We then go back to (4.6) from which everything would follow if we only could do the configuration integral Q_N. Since this is generally impossible, we try to do it instead approximately by assuming that the mutual particle interactions can be replaced by the interaction through a common or mean potential $\bar{u}$ when they are outside each others hard cores. Then we have reduced the problem to a system of independent particles. For the configuration integral we then simply have $Q_N = Q_1^N$ where

$$Q_1 = \int d^3r \, e^{-\beta\bar{u}} \tag{4.31}$$

gives the value for each particle. Since the mean potential $\bar{u}$ is independent of $\mathbf{r}$, it simply gives $Q_1 = (V - Nb) \, e^{-\beta\bar{u}}$ where $V - Nb$ is the volume available for each particle. The pressure will then be

$$
\begin{aligned}
P &= NkT\frac{\partial}{\partial V} \log\left[(V - Nb) \, e^{-\beta\bar{u}}\right] \\
&= \frac{NkT}{V - Nb} - N\frac{\partial \bar{u}}{\partial V} \, .
\end{aligned}
\tag{4.32}
$$

The last term can be non-zero since the mean potential $\bar{u}$ depends on the density of particle and hence on the volume.

We can find this term from the average potential energy is (4.16). In this approximation we can set the pair correlation function $g(r) = 0$ when $r < d$ and $g(r) = 1$ outside the hard core. Then it follows directly that $\langle U \rangle = -N\rho a$ where a is the same quantity as in (4.29). In the mean field approximation we must also have $\langle U \rangle = N\bar{u}$ so that $\bar{u} = -\rho a$. From (4.32) we then obtain

$$P = \frac{NkT}{V - Nb} - a\,\frac{N^2}{V^2} \tag{4.33}$$

which is the van der Waal's equation of state. Expanding the first denominator, we get the corresponding virial expansion with B_2 as in (4.29) and $B_n = b^{n-1}$ when $n > 2$. Only the second virial coefficient is affected by the attractive part of the potential, all the others are due to the hard-core repulsion.

The pressure at high temperatures is dominated by the first term in (4.33) and is essentially that of an ideal gas. At lower temperatures we will begin to see

the effect of the last, attractive part and the isotherms will deviate from the ideal gas hyperbolas. At sufficiently low T the derivative $\partial P/\partial V$ will change sign as V is changed, as is illustrated in Fig. 4.4 along BCD. The compressibility is therefore negative and the system is not thermodynamically stable here. This signals a phase transition to a liquid phase.
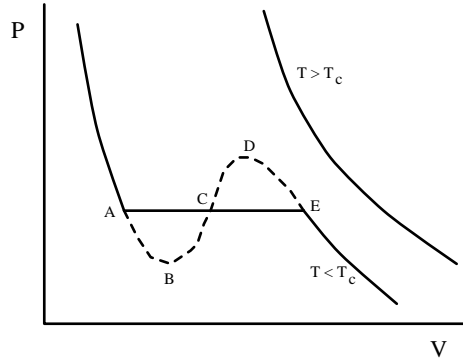

Figure 4.4: Isotherms resulting from the Van der Waals equation above and below T_c.

We can interpret this in the following way: Plotting P as a function of V instead of the other way around we get a multivalued function, as in Fig. 4.5. In order to trace the pressure through these multiple values we may introduce a parametrization of $C_{unstable}$, $P = P(s)$ with $0 \leq s \leq 1$ where $s = 0$ corresponds to the point a and $s = 1$ corresponds to b, see Fig. 4.5. Using the thermodynamic relation

$$dG = VdP - SdT = VdP \tag{4.34}$$

along isotherms where $dT = 0$, we may integrate the Gibbs free energy along $C_{unstable}$

$$\Delta G = \int dPV(P) = \int ds \frac{\partial P}{\partial s} V(P(s)) \tag{4.35}$$

to obtain the graph $C'_{unstable}$ shown in the figure. However, if the system is allowed to equilibrate, it will minimize G and, therefore, never venture out on the unstablel path. Rather, as P is increased, it will pass directly from a to b, and the corresponding volume change

$$\Delta V = \Delta \frac{\partial G}{\partial P} \tag{4.36}$$

corresponds to the gas-liquid phase transition, i.e. $\Delta V = V_l - V_g$, where V_g and V_l are the volumes of the gas and the liquid, respectively. At the critical point $\Delta \partial G/\partial P = 0$ and the volume changes continuously.

As we pass from a to b there is no change in the free energy

$$\Delta G = 0 = \int dP \frac{\partial G}{\partial P} = \int dPV = A_1 - A_2 \tag{4.37}$$
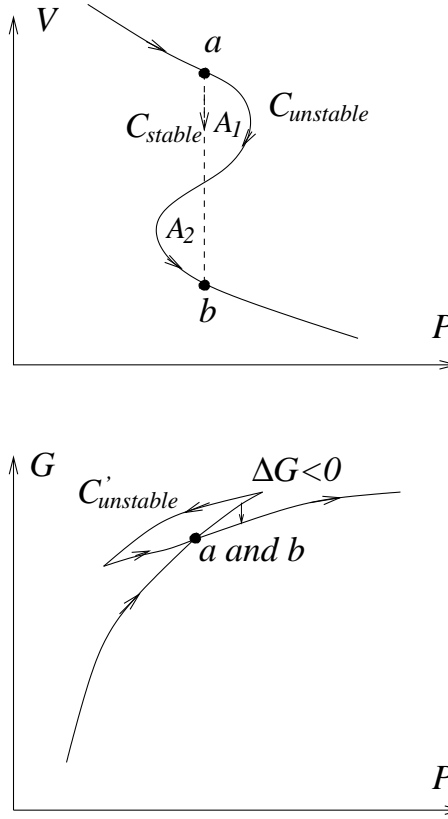
Figure 4.5: The volume as a function of pressure, and the corresponding Gibbs free energy as the fluid passes throught the phase transition.

where the parameterization is implied in order to give meaning to the P-integration. The fact that $A_1 = A_2$ allows us to construct the horizontal path in Fig. 4.4, a geometric construction known as the Maxwell construction.

Very small, or very pure systems, where nucleation sites lack, may actually move onto the unstable paths in Fig. 4.5. They are then in the metastable states characteristic of undercooled or superheated systems. A superheated liquid will burst into boiling with an excess energy to spend, and supercooled vapor may exist in clouds.

When the temperature increases, the transition region decreases. At the critical temperature T_c the compressibility diverges. Thus the derivative

$$\left(\frac{\partial P}{\partial V}\right)_T = -\frac{NkT}{(V - Nb)^2} + \frac{2aN^2}{V^3} \tag{4.38}$$

must vanish. In addition, we must also have that the second derivative

$$\left(\frac{\partial^2 P}{\partial V^2}\right)_T = \frac{2NkT}{(V-Nb)^3} - \frac{6aN^2}{V^4} = 0 \tag{4.39}$$

is zero since the critical point is here an inflection point. These two equations together with the equation of state can easily be solved for the critical values of the thermodynamic variables. One obtains

$$V_c = 3Nb, \qquad P_c = \frac{a}{27b^2}, \qquad kT_c = \frac{8a}{27b} . \tag{4.40}$$

The van der Waals equation of state is seen to imply that one should always have

$$P_c V_c = \frac{3}{8} NkT_c \tag{4.41}$$

at the critical point. For most real gases the numerical factor on the right turns out to be near 0.3 which is not too far off from 3/8.

In terms of these values we can construct a universal equation of state which should be valid for all gases. Defining the dimensional variables

$$v = \frac{V}{V_c}, \qquad p = \frac{P}{P_c}, \qquad t = \frac{T}{T_c} \tag{4.42}$$

we can write van der Waals equation (4.33) as

$$p = \frac{8t}{3v-1} - \frac{3}{v^2} . \tag{4.43}$$

Substances with the same values of these scaled variables are said to be in corresponding states. This universal equation of state is obviously not more accurate than the original equation. But it turns out that many real gases show similar behavior near the critical point when described in terms of scaled variables. It is first during the last two decades after the renormalization group was introduced in statistical physics that we have begun to understand such scaling behavior.

The critical region is best characterized by the critical exponents of the different thermodynamic variables. They can be calculated by writing

$$p = 1 + \Delta p, \qquad v = 1 + \Delta v, \qquad t = 1 + \Delta t . \tag{4.44}$$

All the Δ-terms will go to zero at the critical point. Substituting this expansion into (4.43) and keeping only the leading terms, we find

$$\Delta p = (4 - 6\Delta v)\Delta t - \frac{3}{2}\Delta v^3 . \tag{4.45}$$

On the critical isotherm, we have $\Delta t = 0$ and hence $\Delta p = -(3/2)\Delta v^3$. Measurements on real gases give

$$\frac{P - P_c}{P_c} \propto \left(\frac{V - V_c}{V_c}\right)^\delta \tag{4.46}$$

where the critical exponent $\delta = 4.5 \pm 0.5$. The van der Waals result $\delta = 3$ is smaller, but comes out in all mean field theories.

One can similarly obtain the critical exponent for the compressibility K_T. Taking the derivative of both sides of (4.45) with respect to the volume, we get $(\partial p/\partial v)_t = -6\Delta t$. We therefore find near the critical point $K_T = (T_c/6P_c)(T - T_c)^{-1} \sim (T - T_c)^{-\gamma}$ where $\gamma = 1$. The experimental value is $\gamma = 1.25 \pm 0.05$ is in reasonable agreement with theory.

Other critical exponents can be calculated for the gas-liquid system. In a later chapter on magnetic phase transitions we will meet the same exponents again and they will then be discussed in more detail.
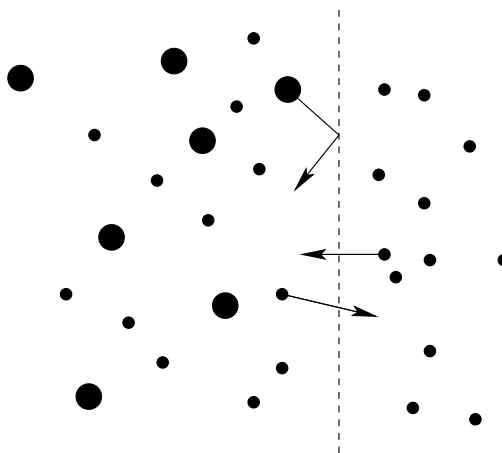
4.4   Osmosis

Figure 4.6: A semi-permeable membrane where the small molecules may pass through but where the large molecules may not.

Osmosis is the spontaneous net movement of a solvent, through a semi-permeable membrane from a solution of low solute concentration to a solution with high solute concentration The action of a semi-permeable membrane is illustrated in Fig 4.6. Solvent molecules are typically water while the solute molecules are those that are dissolved in the water. Osmosis is important in biological systems as many biological membranes are semi-permeable. In general, these membranes are impermeable to organic solutes with large molecules, such as polysaccharides, while permeable to water and small, uncharged solutes. Permeability may depend on solubility properties, charge, or chemistry as well as solute size. Osmosis provides the primary means by which water is transported into and out of cells.

The osmotic pressure is defined to be the pressure required to maintain an equilibrium, with no net movement of solvent. In the following we derive

the osmotic pressure difference as a function of solute concentration from the assumption of a dilute solution.

We will need to know the chemical potential of the water molecules with and without the solute molecules present, as it is this chemical potential that will be constant across the membrane in equilibrium. We will use the relations $\mu = \partial G/\partial N$ and $G = -kT \log Z_P$ to obtain μ. For this purpose, assume first that a single solute molecule is added to the water, so that the free energy is

$$G(P,T,N) = G_0(P,T,N) + \alpha(P,T,N) \tag{4.47}$$

where $\alpha(P,T,N)$ is the small addition to the Gibbs free energy due to the addition of the molecule. Since the solution is dilute, the solute molecules are far apart, and we may ignore their interactions. For this reason we could write $G(P,T,N,n) = G_0(P,T,N) + n\alpha(P,T,N)$ where n is the number of solute molecules. But the expression $G(P,T,N,n) = G_0(P,T,N) + n\alpha(P,T,N)$ fails to take into account that the solute molecules are identical. This is the expression that would result if, in the partition function of equation (3.37), all the solute molecules where taken to be different. In order to compensate for the over-counting associated with identical particles we must in fact divide the partition function by $n!$. Since this $n!$ factor survives when the constant pressure partition function of equation (**??**) is computed, we get

$$G(P,T,N,n) = G_0(P,T,N) + n\alpha(P,T,N) + kT \ln n! \; . \tag{4.48}$$

Using Stirlings approximation $\ln n! \approx n \ln(n/e)$ we may rewrite the above expression as

$$G(P,T,N,n) = G_0(P,T,N) + nkT \ln((n/e)e^{\alpha(P,T,N)/kT}) \; . \tag{4.49}$$

Now, we use that G is an extensive function, so that

$$G(P,T,\lambda N,\lambda n) = \lambda G(P,T,N,n) \; . \tag{4.50}$$

This implies that the $(n/e)e^{\alpha(P,T,N)/kT}$ must be an intensive quantity, and this can only happen if the N-dependence in α is such that we may rewrite it as

$$\frac{n}{e}e^{\alpha(P,T,N)/kT} = \frac{n}{N}f(P,T) \; , \tag{4.51}$$

and the free energy takes the form

$$G(P,T,N,n) = G_0(P,T,N) + nkT \ln\left(\frac{n}{N}f(P,T)\right) \; . \tag{4.52}$$

The chemical potential of the water then becomes

$$\mu = \frac{\partial G(P,T,N,n)}{\partial N} = \mu_0(P,T) - \frac{kTn}{N} \; , \tag{4.53}$$

where $\mu_0(P,T) = \partial G_0(P,T,N)/\partial N$ is the water chemical potential without the solute molecules. Note that $\mu = \mu(P,T,c)$ where $c = n/N$ is the solute fraction.

Now, on the other side of the membrane, where there are no solute molecules, the pressure P_0 will be different, and the water will have the chemical potential $\mu_0(P_0, T)$. The equilibrium condition may then be written as

$$\mu_0(P, T) - \frac{kTn}{N} = \mu_0(P_0, T) \ . \tag{4.54}$$

Expanding the difference $\mu_0(P, T) - \mu_0(P_0, T) \approx (\partial\mu_0/\partial P)\Delta P$ to first order in $\Delta P = P - P_0$, and using the Maxwell relation $\partial\mu/\partial P = \partial V/\partial N = 1/\rho$, equation (4.54) reduces to

$$\mu_0(P, T) - \mu_0(P_0, T) \approx \frac{\Delta P}{\rho} = \frac{kTn}{N} \ , \tag{4.55}$$

or

$$\Delta P V = nkT \ . \tag{4.56}$$

This expression, which has exactly the same form as the ideal gas formula, is known as van't Hoff's formula and describes the osmotic pressure difference across a semi-permeable membrane. It is interesting to note that while the ideal gas by definition involves non-interacting particles, the solute molecules may very well interact with the solvent molecules. The only assumption is that they do not interact with each other. Osmosis releases energy, and can be made to do work, as when a growing tree-root splits a stone.

Chapter 5

Quantum Gases and Liquids

Statistical mechanics of free particles are governed by quantum mechanics in two widely different ways. First it gives a correct description of the energetics of each particle in a system, being electrons, atoms or more complex molecules. But even more importantly, it prescribes very definite permutation properties of the wave function of all the particles in the system. As a consequence, the classically free particles are not completely free anymore since they are no longer allowed to occupy the different available energy levels independently of the other particles. Their motion is correlated and there seems to be statistical forces acting between them. These quantum effects can have dramatic, physical manifestations in both bosonic and fermionic systems of macroscopic sizes. Some of the most important of these will be discussed in this chapter.

5.1 Statistics of identical particles

We have a system of N indistinguishable particles moving in a common potential $V = V(\mathbf{r})$. The Hamiltonian operator for one of the particles with position vector $\mathbf{r}_i$ is

$$\widehat{H}(i) = \frac{1}{2m}\widehat{\mathbf{p}}_i^2 + V(\widehat{\mathbf{r}}_i) \tag{5.1}$$

where $\widehat{\mathbf{p}}_i = -i\hbar\boldsymbol{\nabla}_i$ is the momentum operator. Its energy is one of the eigenvalues ε_k of the Schrödinger equation

$$\widehat{H}(i)\psi_k(\mathbf{r}_i) = \varepsilon_k\psi_k(\mathbf{r}_i) \tag{5.2}$$

where $\psi_k(\mathbf{r}_i)$ is the corresponding eigenfunction. If the particles have non-zero spin $\widehat{\mathbf{S}}$, the quantum number k would also also include it. The Hamiltonian (5.1) is independent of spin and the eigenvalues ε_k will then be the same for different spin projections $\widehat{S}_z$. Hence, they will all be degenerate.

The full Hamiltonian for the whole system of particles is then

$$\widehat{H} = \sum_{i=1}^{N} \widehat{H}(i) \ . \tag{5.3}$$

Even if the particles interact with an external potential, it is customary to say that the particles are free since they do not have mutual interactions. That would be the case if, for instance, the potential contained a term $V_{int} = V_{int}(\mathbf{r}_1, \mathbf{r}_2, \cdots, \mathbf{r}_N)$ which could not be split up into N separable terms as here.

If we denote one of their energy eigenfunctions by $\Psi_s = \Psi_s(1, 2, \cdots, N)$, their combined energy E_s in this state follows from the many-particle Schrödinger equation

$$\widehat{H}\Psi_s = E_s \Psi_s \ . \tag{5.4}$$

Since $\widehat{H}$ is a sum of independent terms, we know immediately that Ψ_s is given by products of one-particle wave-functions,

$$\Psi_s = \prod_{i=1}^{N} \psi_{k_i}(\mathbf{r}_i) \tag{5.5}$$

so that the corresponding eigenvalue is $E_s = \sum_{i=1}^{N} \varepsilon_{k_i}$. At this stage where we have not yet made use of the indistinguishability of the particles, we can still say in which one-particle state each of them are.

The Hamiltonian (5.3) is invariant under all permutations of the identical particles. These different transformations generate the symmetric group. It can be built up from more elementary operations which are interchanges of one particle by another. Let us consider one of these which we denote by $\widehat{P}$. It interchanges particle i with particle j, i.e. it performs the operation $\mathbf{r}_i \leftrightarrow \mathbf{r}_j$. The mathematical expression for the invariance of the Hamiltonian is thus

$$\widehat{P}\widehat{H}\widehat{P}^{-1} = \widehat{H} \ . \tag{5.6}$$

This is equivalent to $[\widehat{H}, \widehat{P}] = 0$. According to quantum theory, we can then find eigenstates of the Hamiltonian which are also eigenstates of the permutation operator $\widehat{P}$. Since this conclusion holds for all the different permutation operators, it is a very strong condition. The product state in (5.5) does obviously not have this property. Mathematically, one says that the eigenstates Ψ_s must be singlets of the permutation group, i.e.

$$\widehat{P}\Psi_s = p\Psi_s \ . \tag{5.7}$$

Performing the same interchange again, we then get

$$\widehat{P}^2\Psi_s = p\,\widehat{P}\Psi_s = p^2\Psi_s \ .$$

But the operator $\widehat{P}^2$ is just the identity operator. Thus, the eigenvalues satisfy $p^2 = 1$ and can only be $p = \pm 1$. They correspond to the two singlet representations of the permutation group, the completely symmetric and the completely

antisymmetric representation. Only these two are allowed eigenstates of the Hamiltonian. Identical particles having symmetric statistics are called bosons while those having antisymmetric statistics are fermions.

Until a few years go it was generally believed that these arguments applied to systems in all dimensions. But it was pointed out by J.M. Leinaas and J. Myrheim in 1976 that it is only for systems in dimensions $d > 2$ that we have $\widehat{P}^2 = 1$. This surprising and important discovery is illustrated in Fig. 5.1. The two particles on the left are interchanged by a rotation of $180°$ normal to the plane. It is here the operation $\widehat{P}$. Similarly, the two particles on the right are interchanged by the same rotation in the opposite direction, i.e. $\widehat{P}^{-1}$. If the particles are in three or more dimensions, we can rotate the configuration on the left an angle of $180°$ around an axis through the two particles and we find them in the configuration on the right. Thus we have $\widehat{P} = \widehat{P}^{-1}$. But for particles in two dimensions, we can not perform this latter rotation out of the plane and we have in general no relation between $\widehat{P}$ and $\widehat{P}^{-1}$. We then have the possibility for new statistics in two dimensions. Since the symmetry of the wave-functions can then in principle be anything between what we have for bosons and fermions, the corresponding particles are called anyons. The physics of many-particle systems of anyons is not yet understood.
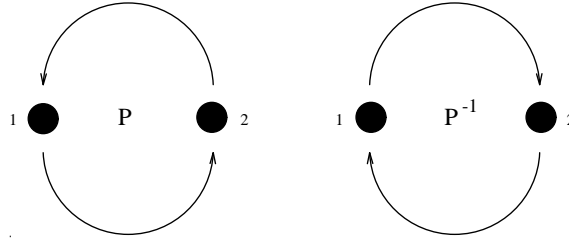

Figure 5.1: Interchange of two identical particles can be made in one direction or the opposite.

It is simplest to demonstrate this permutation symmetry in the case of two particles with labels i and j. If they can be in two one-particle states ψ_a and ψ_b, the simple product state (5.5) is $\psi_a(\mathbf{r}_i)\psi_b(\mathbf{r}_j)$. Under an interchange of the particles, this state goes into $\psi_a(\mathbf{r}_j)\psi_b(\mathbf{r}_i)$ and is therefore not a permutation eigenstate. But adding these two products, we see that the symmetric combination

$$\Psi_S(\mathbf{r}_i, \mathbf{r}_j) = \sqrt{\frac{1}{2}} \left[\psi_a(\mathbf{r}_i)\psi_b(\mathbf{r}_j) + \psi_a(\mathbf{r}_j)\psi_b(\mathbf{r}_i) \right] \tag{5.8}$$

is. It is invariant under all permutations and is the correct wave-function for two

bosons. Similarly, the difference between the products give the antisymmetric combination

$$\Psi_A(\mathbf{r}_i, \mathbf{r}_j) = \sqrt{\frac{1}{2}} \left[\psi_a(\mathbf{r}_i)\psi_b(\mathbf{r}_j) - \psi_a(\mathbf{r}_j)\psi_b(\mathbf{r}_i) \right] \tag{5.9}$$

which just changes sign under an interchange. It is the wave-function for two fermions.

The antisymmetric wave-function is seen to identically vanish when they are in the same state, i.e. $\psi_a = \psi_b$. This is the Pauli principle which says there can never be more than one fermion in a one-particle state. Moreover we see that it becomes small and eventually vanish when the two fermions approach each other. This mean that the probability to find two identical fermions near each other is smaller than if they had been distinguishable. There seems to be an abstract force due to the statistics trying to keep them away from each other. For bosons we see just the opposite effect. They have a larger probability to be found at the same place than two distinguishable particles would have had. There seems to be an effective attraction between bosons because of their symmetric statistics.

Combined wave-functions for more than two fermions or bosons are easily constructed in the same way. For example, we notice that the antisymmetric wave-function (5.9) can be written as the determinant

$$\Psi_A(\mathbf{r}_i, \mathbf{r}_j) = \left| \begin{array}{cc} \psi_a(\mathbf{r}_i) & \psi_b(\mathbf{r}_i) \\ \psi_a(\mathbf{r}_j) & \psi_b(\mathbf{r}_j) \end{array} \right| . \tag{5.10}$$

The wave-function for N fermions is then given by the larger determinant

$$\Psi_A(\mathbf{r}_1, \mathbf{r}_2, \cdots, \mathbf{r}_N) = \left| \begin{array}{cccc} \psi_a(\mathbf{r}_1) & \psi_b(\mathbf{r}_1) & \cdots & \psi_k(\mathbf{r}_1) \\ \psi_a(\mathbf{r}_2) & \psi_b(\mathbf{r}_2) & \cdots & \psi_k(\mathbf{r}_2) \\ \vdots & & & \vdots \\ \psi_a(\mathbf{r}_N) & \psi_b(\mathbf{r}_N) & \cdots & \psi_k(\mathbf{r}_N) \end{array} \right| . \tag{5.11}$$

It vanishes when two of the one-particle states are the same or if two or more particles have the same position coordinates. For bosons we can also write the symmetric wave-function in the same way except for changing all the minus signs to plus signs when it is evaluated as a sum of different products. This symmetric combination is sometimes called a permanent.

With these symmetric or antisymmetric wave-functions the particles have completely lost their classical identities. Even if the wave-functions still involve a finite set of one-particles states, it is now impossible to relate any of these to any particular particle. Each particle has now the same probability to be found in any of these states. We can only describe the full many-particle state $\Psi_{S,A}$ by saying how many, and not which, particles are in each one-particle state ψ_k with energy ε_k. Denoting this occupation number by n_k, we can write the energy of the system of particles as

$$E_s = \sum_k n_k \varepsilon_k . \tag{5.12}$$

If $n_k = 0$, there are no particles in the system with the quantum number k. The many-particle states $\Psi_{S,A}$ is uniquely characterized by this set $\{n_k\}$ of occupation numbers.

The difference between classical and quantum statistics can be illustrated by considering two identical particles in a harmonic oscillator potential. If we ignore the zero-point energy, the one-particle state ψ_n has energy $\varepsilon_n = n\hbar\omega$ with $n = 0, 1, 2, \cdots$. Thus, we have the one-particle partition function

$$Z_1 = \sum_{n=0}^{\infty} e^{-n\beta\hbar\omega} = \frac{1}{1-x} \tag{5.13}$$

with $x = e^{-\beta\hbar\omega}$. If the particles are supposed to obey Maxwell-Boltzmann statistics, we can then immediately write down the two-particle partition function as

$$Z_2^{MB} = \frac{1}{2!} Z_1^2 = \frac{1}{2} \frac{1}{(1-x)^2} \; . \tag{5.14}$$

This is the classical result we have used before and which is trivially extended to the case of N particles.

In the product Z_1^2 there are two identical terms where one particle is in a state ψ_a and the other in some other state ψ_b. Dividing by 2! we then allow for the fact that the particles after all are indistinguishable and we can not say which one is in ψ_a and which one is in ψ_b. These configurations then get the same weight 1 in the sum. But we have then really made a small mistake. Since Z_1^2 involves only one term where the two particles are in the same state, these configurations will then get the weight $1/2$ after we divide the product by 2!. Bosons are allowed to occupy the same one-particle state. So, in order to correct this classical counting, we add these diagonal terms with the same factor $1/2$ in front. Thus we have

$$Z_2^{BE} = Z_2^{MB} + \frac{1}{2} D \tag{5.15}$$

where the compensating term D obviously is

$$D = \sum_{n=0}^{\infty} e^{-2n\beta\hbar\omega} = \frac{1}{1-x^2} \; . \tag{5.16}$$

The two-particle partition function for bosons is therefore

$$Z_2^{BE} = \frac{1}{(1-x)(1-x^2)} \; . \tag{5.17}$$

Fermions are not allowed to occupy the same state, so these diagonal terms in the classical result (5.14) must be removed. In this way we find the partition function for two fermions

$$Z_2^{CD} = Z_2^{MB} - \frac{1}{2} D = \frac{x}{(1-x)(1-x^2)} \; . \tag{5.18}$$

It is easy to show that in the classical region where $\beta\hbar\omega \ll 1$, the quantum correction D will be negligible. The particles can then occupy highly excited states and it becomes very improbable that two of them will occupy the same state. Fermions and bosons have then the same, classical partition functions and hence also the same thermodynamics.

With more than two particles in the oscillator, one needs a more efficient method to calculate these partition functions. We only have to make sure that we count each distinct configuration of particles once. For N bosons we then get the partition function as the multiple sum

$$Z_N^{BE} = \sum_{n_1 \geq n_2}^{\infty} \sum_{n_2 \geq n_3}^{\infty} \cdots \sum_{n_N \geq 0}^{\infty} x^{n_1+n_2+\cdots+n_N} = \frac{1}{1-x}\frac{1}{1-x^2}\cdots\frac{1}{1-x^N} \, . \tag{5.19}$$

The internal energy of this many-particle system is then found to be

$$U = -\frac{\partial}{\partial\beta} Z_N^{BE} = \frac{\hbar\omega}{e^{\hbar\omega/kT}-1} + \frac{2\hbar\omega}{e^{2\hbar\omega/kT}-1} + \cdots + \frac{N\hbar\omega}{e^{N\hbar\omega/kT}-1} \, . \tag{5.20}$$

When $T \to 0$ we see that it goes to zero since all the particles will then be in the groundstate.

In the case of fermions, we must exclude the cases with more than one article in the same same. Thus we get

$$Z_N^{FD} = \sum_{n_1 > n_2}^{\infty} \sum_{n_2 > n_3}^{\infty} \cdots \sum_{n_N \geq 0}^{\infty} x^{n_1+n_2+\cdots+n_N} = \frac{1}{1-x}\frac{x}{1-x^2}\cdots\frac{x^{N-!}}{1-x^N} \, . \tag{5.21}$$

The factors in the numerator will now give a non-zero value

$$E_0 = \hbar\omega \sum_{n=0}^{N-1} n = \frac{1}{2}\hbar\omega N(N-1) \tag{5.22}$$

for the internal energy at zero temperature. We then have one fermion in each of the N lowest one-particle states.

5.2   Blackbody radiation and the photon gas

When a body is heated to the temperature T, it will radiate energy. It is electromagnetic radiation at this temperature and is usually called thermal radiation. One defines its intensity $I(\theta, T)$ as the energy radiated per unit time per unit area per unit solid angle in the direction θ away from the normal to the surface. It usually follows the cosine law $I(\theta, T) = I(T)\cos\theta$. The emitted energy in all directions

$$E(T) = 2\pi I(T) \int_0^{\pi/2} d\theta \sin\theta \cos\theta = \pi I(T) \tag{5.23}$$

is called the total emissive power or the emittance. Since the radiation contains all wavelengths λ, we can write

$$E(T) = \int_0^{\infty} d\lambda \, E(\lambda, T) \tag{5.24}$$

where $E(\lambda, T)$ is the spectral emittance. When the body is exposed to the radiation from another body with non-zero temperature, a fraction $a(\lambda, T)$ of the radiation is absorbed and the rest $r(\lambda, T) = 1 - a(\lambda, T)$ is reflected if we ignore transmission. A black body is defined to absorb all radiation, i.e. $a(\lambda, T) = 1$ for all wavelengths.

Thermal radiation was first systematically investigated by Gustav R. Kirchhoff around 1859. He proved that $E(\lambda, T)/a(\lambda, T)$ is the same for all bodies and is therefore a universal function which equals the spectral radiation intensity of a black body. Consider different bodies in an enclosure of thermal radiation. At thermodynamic equilibrium just as much energy is absorbed as emitted by each body at every wavelength. Since the absorbed energy is $a(\lambda, T) I$ when it is exposed to a radiation intensity $I = I(\lambda, T)$ and the emitted energy is $E(\lambda, T)$, the theorem follows. Equivalently, the radiation I hitting the body must equal the energy leaving it. This latter equals the reflected radiation $r(\lambda, T) I$ plus the emitted energy $E(\lambda, T)$. Then again we get the Kirchoff theorem. It implies that a good absorber is also a good emitter. A perfectly white body is defined to have $a(\lambda, T) = 0$ and has therefore no thermal emission.
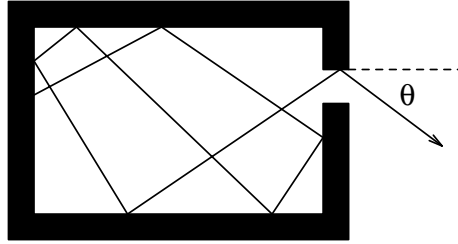

Figure 5.2: The radiation coming through the opening is black with the same temperature as the enclosing walls.

We can make blackbody radiation by making a small opening in an enclosure which is kept at a temperature T a shown in Fig.5.2. All radiation incident on the hole are effectively absorbed. Radiation from inside the cavity can escape through the hole which will act as the surface of a black body. If the radiation with spectral energy density $\mathcal{E}(\lambda, T) = U(\lambda, T)/V$ moved only normal to the opening with the light velocity c, the emittance would be just $c\mathcal{E}/2$ since only the radiation moving towards the hole would escape. But since the radiation inside the cavity, moves in all possible direction in front of the hole, they will on average have an effective velocity of $c\cos\theta$ towards the hole. The effective velocity is therefore only

$$c \int_0^{\pi/2} d\theta \sin\theta \cos\theta = \frac{c}{2}$$

and we have the important relation

$$E(\lambda, T) = \frac{c}{4}\mathcal{E}(\lambda, T) \tag{5.25}$$

between the spectral emittance of a black body and the energy density of thermal radiation.

Detailed measurements enabled J. Stefan in 1879 to conclude that the total emittance $E(T)$ had to increase as the fourth power of the temperature,

$$E(T) = \sigma\, T^4 \tag{5.26}$$

where $\sigma = 0.567 \times 10^{-7} W m^{-2} K^{-4}$ is Stefan's constant. This famous result was explained in 1884 by L. Boltzmann. From Maxwell's electromagnetic theory he knew that the pressure P in the x-direction was given by the square of the x-components of the field. Since the pressure must be the same in all three directions, it is just one third of the energy density, i.e.

$$P = \frac{1}{3}\mathcal{E} \; . \tag{5.27}$$

This result applies also at finite temperatures where the total energy density is

$$\mathcal{E}(T) = \int_0^\infty d\lambda\, \mathcal{E}(\lambda, T) \; . \tag{5.28}$$

Considering the work performed by this radiation in a Carnot process, Boltzmann concluded that it had the functional form

$$\mathcal{E}(T) = a\, T^4 \; . \tag{5.29}$$

From (5.25) we then see that the Stefan-Boltzmann constant is $a = 4\sigma/c$.

The total radiation energy U is the enclosure with volume V is $U = \mathcal{E}V$. When the thermally isolated radiation expands reversibly by a small amount ΔV, it performs the work $P\Delta V$ against some external agent. The energy density changes to $\mathcal{E} + \Delta\mathcal{E}$ and energy conservation requires

$$\mathcal{E}V = (\mathcal{E} + \Delta\mathcal{E})(V + \Delta V) + \frac{1}{3}\mathcal{E}\,\Delta V \; .$$

In the limit where $\Delta V \to 0$, we then get $d\mathcal{E}/\mathcal{E} = -(4/3)\,dV/V$ which integrated gives $\mathcal{E} \propto V^{-4/3}$.

This simple reasoning is just a rewriting of the First Law $T\,dS = dU + P\,dV$ which gives

$$dS = \frac{V}{T}d\mathcal{E} + \frac{4}{3}\left(\frac{\mathcal{E}}{T}\right)dV \; .$$

For an adiabatic change, $dS = 0$ and the above result follows. Now we can also find how the energy density varies with the temperature. Writing $d\mathcal{E} = (d\mathcal{E}/dT)\,dT$ and requiring dS to be a perfect differential, it follows that

$$\frac{1}{T}\frac{d\mathcal{E}}{dT} = \frac{4}{3}\frac{d}{dT}\left(\frac{\mathcal{E}}{T}\right) \; .$$

Taking the derivatives and collecting terms, we find $d\mathcal{E}/dT = 4\mathcal{E}/T$ which gives the Stefan-Boltzmann law (5.29).

We can now evaluate the differential dS which integrated gives the entropy

$$S = \frac{4}{3}VT^3 \; . \tag{5.30}$$

Hence, in an adiabatic change of the gas the temperature varies as $T \propto V^{-1/3}$. When the volume $V = L^3$ expands, the temperature decreases as $T \propto 1/L$.

A more detailed analysis by W. Wien in 1893 based upon electromagnetism and thermodynamics led to the result that the spectral energy density had to have the form

$$\mathcal{E}(\lambda, T) = \frac{1}{\lambda^5} f(\lambda T) \,. \tag{5.31}$$

Instead of being a function of two independent arguments, $\lambda^5 \mathcal{E}$ is a function of only one variable. The spectral form of the energy density at one temperature is then directly related to the form at any other temperature. This represents one of the first non-trivial scaling results in physics and was later confirmed by accurate measurements repeated at different temperatures.

One important consequence of Wien's result is the relation

$$\lambda_m T = b = \text{const} \tag{5.32}$$

between the wavelength where $\mathcal{E}(\lambda, T)$ has its maximum and the temperature. The higher it is, the shorter is the wavelength where the radiation is most intense. It is called Wien's displacement law and follows directly from taking the derivative of (5.31). At the maximum we have

$$\frac{d\mathcal{E}}{d\lambda} = 0 = -5\lambda^{-6} f(\lambda T) + T\lambda^{-5} f'(\lambda T)|_{\lambda_m}$$

which gives $5f(\lambda_m T) = \lambda_m T f'(\lambda_m T)$. Solving the equation, it results in a certain value b for the product $\lambda_m T$ characterizing the maximum. The experimental value for the constant was found to be $b = 0.29 \, cm \, K$.

A combination of phenomenological analysis and deep, theoretical insight led Max Planck in the fall of 1900 to his famous formula for the energy density of thermal radiation. He wrote it as

$$\mathcal{E}(\lambda, T) = \frac{8\pi hc}{\lambda^5} \frac{1}{e^{hc/\lambda kT} - 1} \tag{5.33}$$

where k is Boltzmann's constant and h was a new constant Planck was forced to introduce. We see that it has the scaling form (5.31) previously predicted by Wien. When plotted as function of the wavelength λ, it has the general shape shown in Fig.5.3. Experimental data were now reproduced by using the values $h = 6.55 \times 10^{-34} \, Js$ and $k = 1.35 \times 10^{-23} \, J/K$ for these constants. They should be compared with the modern values $h = 6.625 \times 10^{-34} \, Js$ and $k = 1.380 \times 10^{-23} \, J/K$. Since k is given in terms of the gas constant R as $k = R/N_A$, Planck obtained in this way one of the first accurate values for Avogadro's number N_A and therefore indirectly the scale of the atomic world.

Planck derived his radiation formula from assuming that the electromagnetic field could be treated classically. It interacted with the matter in the walls which

he furthermore assumed could be described as harmonic oscillators. The formula then followed if these oscillators could absorb and emit radiation with frequency $\nu = c/\lambda$ only in discrete quanta of energy

$$\varepsilon = h\nu \ . \tag{5.34}$$

Later it turned out that it was this last assumption which went fundamentally against classical physics and which he resisted very much himself, which held the key to the correct derivation of this result.

It was first after Einstein's explanation of the photoelectric effect in 1905 that a correct understanding of Planck's formula emerged. Instead of quantizing the atomic matter in the walls containing the radiation, it was the electromagnetic field itself that had to be quantized. The quanta are photons which can be treated as the particles in this new quantum gas.

Let us consider a cubic cavity of volume $V = L^3$ within a body of temperature T. Since it does not contain any matter, the electric field within the cavity satisfies the electromagnetic wave equation

$$\left(\nabla^2 - \frac{1}{c^2} \frac{\partial^2}{\partial t^2} \right) \mathbf{E}(\mathbf{x}, t) = 0 \ . \tag{5.35}$$

The solution can always be written as the Fourier series

$$\mathbf{E}(\mathbf{x}, t) = \sqrt{\frac{1}{V}} \sum_{\mathbf{k}} \mathbf{E}_{\mathbf{k}}(t) \, e^{i\mathbf{k} \cdot \mathbf{x}} \tag{5.36}$$

where the sum goes over all possible modes with wavenumbers $\mathbf{k}$ where $|\mathbf{k}| = 2\pi/\lambda$. Inserting this in the wave equation, we see that the amplitudes must satisfy the differential equation

$$\ddot{\mathbf{E}}_{\mathbf{k}} + c^2 k^2 \, \mathbf{E}_{\mathbf{k}} = 0 \ . \tag{5.37}$$

But this is just the equation of motion for a harmonic oscillator with angular frequency $\omega = kc$. Thus the quantum theory of the electromagnetic field is given by the quantum mechanics of the harmonic oscillator. If the energy of the oscillator is $\epsilon_n = n\hbar\omega$, disregarding the zero-point energy, we say that the corresponding mode of the field contains or is occupied by n photons. This is the point in the derivation where we make use of the fact that photons are bosons so that we can have any number of them in the single photon quantum state labeled by the wavenumber $\mathbf{k}$. Since the average energy at temperature T of the photons in this oscillator mode is

$$\langle \, \epsilon_{\mathbf{k}} \, \rangle = \frac{\sum_{n=0}^{\infty} n\hbar\omega \, e^{-n\hbar\omega/kT}}{\sum_{n=0}^{\infty} e^{-n\hbar\omega/kT}} = \frac{\hbar\omega}{e^{\hbar\omega/kT} - 1}, \tag{5.38}$$

we obtain the total thermal radiation energy from all the modes of the field as the sum

$$U(T) = 2 \sum_{\mathbf{k}} \langle \, \epsilon_{\mathbf{k}} \, \rangle \ .$$

We have here multiplied by a factor 2 since the electric field has two independent transverse polarization states. This follows from the Maxwell equation $\boldsymbol{\nabla}\cdot\mathbf{E} = 0$ which gives $\mathbf{k}\cdot\mathbf{E_k} = 0$. The vector $\mathbf{E_k}$ is therefore orthogonal to the propagation vector $\mathbf{k}$.

When the volume V is large, the modes are so dense in the wavenumber $\mathbf{k}$ that the sum can be obtained the same way as in the sum (2.48) over modes for a non-relativistic quantum particle in a box. We then get the integral

$$U(T) = 2V \int \frac{d^3k}{(2\pi)^3} \frac{\hbar\omega}{e^{\hbar\omega/kT} - 1} \; .$$

Now using $\omega = kc$, we find that the energy density $\mathcal{E}(T) = U(T)/V$ can be written as

$$\mathcal{E}(T) = \int_0^\infty d\omega \, \mathcal{E}(\omega, T) \tag{5.39}$$

where the spectral density is

$$\mathcal{E}(\omega, T) = \frac{\omega^2}{\pi^2 c^3} \frac{\hbar\omega}{e^{\hbar\omega/kT} - 1} \; . \tag{5.40}$$

This is just Planck's result (5.33) expressed in terms of the angular frequency ω instead of the wavelength λ. It follows from $\omega = 2\pi c/\lambda$ and the requirement $\mathcal{E}(\lambda, T) \, d\lambda = \mathcal{E}(\omega, T) \, d\omega$ which must be satisfied in order to give the same integrated energy density.

In the long-wavelength limit where $\lambda kT \gg hc$, we can approximate the denominator in the Planck formula (5.33) by

$$e^{hc/\lambda kT} - 1 \simeq \frac{hc}{\lambda kT}$$

and it simplifies to

$$\mathcal{E}(\lambda, T) \simeq \frac{8\pi}{\lambda^4} kT \; . \tag{5.41}$$

Since Planck's constant has canceled out, there are no quantum effects in this reduced formula. It had previously been derived by Rayleigh and Jeans using the classical result $\langle \epsilon_\mathbf{k} \rangle = kT$ for the average energy of the oscillator mode at finite temperature. Similarly, in the short-wavelength limit $\lambda kT \ll hc$ we see that Planck's formula takes the form

$$\mathcal{E}(\lambda, T) = \frac{C_1}{\lambda^5} e^{-C_2/\lambda T} \tag{5.42}$$

where the constants $C_1 = 8\pi hc$ and $C_2 = hc/k$. It was also written down earlier by Wien who combined his scaling formula (5.31) with the the Maxwell distribution $u \propto e^{-\epsilon/kT}$ to arrive at this form with unknown constants C_1 and C_2.

In order to verify Wien's displacement law (5.32), we take the derivative of the energy density (5.33) with respect to λ. It gives the equation $y = 5(1 - e^{-y})$ where $y = hc/\lambda_m kT$. We see that the solution is $y \simeq 5$. Writing $y = 5 - \delta$ and keeping only the leading terms, we obtain $\delta \simeq 5e^{-5} = 0.03$. The maximum in the intensity is therefore given by $\lambda_m T \simeq hc/4.97k$ which agrees with the measured value $b = 0.29\ cm\ K$.

We can now calculate the total energy in the radiation field by integrating the spectral density (5.40). Replacing the integration variable ω with $x = \hbar\omega/kT$, we find

$$\mathcal{E}(T) = \left(\frac{kT}{\hbar}\right)^4 \frac{\hbar}{\pi^2 c^3} \int_0^\infty dx \frac{x^3}{e^x - 1} \ . \tag{5.43}$$

The finite integral has the value $I_3 = \pi^4/15$ and we recover the radiation law (5.29) with the Stefan-Boltzmann constant $a = \pi^2 k^4/15\hbar^3 c^3$. Needless to say, it agrees with the measured value.

Integrals of the form

$$I_p = \int_0^\infty dx \frac{x^p}{e^x - 1} \tag{5.44}$$

can be expressed by the Riemann zeta-function $\zeta(s)$. When $s > 1$, it is given by the infinite sum

$$\zeta(s) = \sum_{n=1}^\infty \frac{1}{n^s} \ . \tag{5.45}$$

One can show that $\zeta(2) = \pi^2/6$ and $\zeta(4) = \pi^4/90$.

Multiplying the numerator and denominator in the integral by e^{-x} and expanding the resulting denominator in a geometric series, we find

$$I_p = \sum_{n=1}^\infty \int_0^\infty dx\, x^p e^{-nx} \ .$$

This integral is just the definition of the Γ-function which gives

$$\int_0^\infty dx\, x^p e^{-nx} = \frac{p!}{n^{p+1}} \ . \tag{5.46}$$

In this way we obtain for the desired integral

$$I_p = p! \sum_{n=1}^\infty \frac{1}{n^{p+1}} = p!\,\zeta(p+1) \ . \tag{5.47}$$

Thus $I_3 = 6\pi^4/90 = \pi^4/15$ as used above. It will appear many other places in the discussion of quantum gases

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The average number of photons in the mode with wavenumber $\mathbf{k}$ is from (5.38) just

$$\langle n_\mathbf{k} \rangle = \frac{1}{e^{\hbar\omega/kT} - 1} \tag{5.48}$$

since each photon in this mode has the energy $\epsilon_{\mathbf{k}} = \hbar\omega$. Integrating over all modes, we find the photon number density

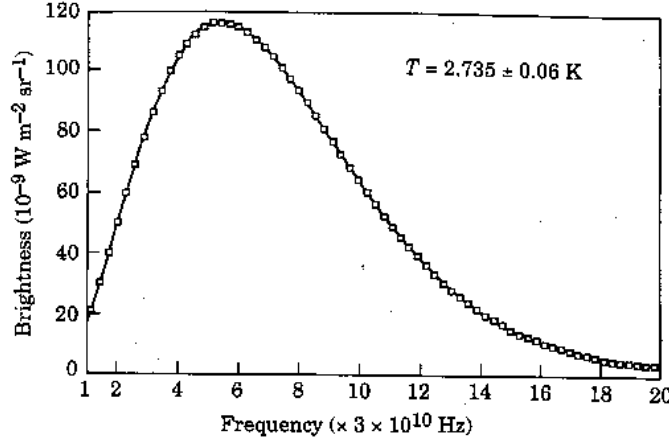$$n(T) = 2 \int \frac{d^3k}{(2\pi)^3} \frac{1}{e^{\hbar\omega/kT} - 1}$$

Figure 5.3: Spectral energy density of the cosmic blackbody radiation measured by the COBE satellite. The fit corresponds to a temperature $T = 2.735 \pm 0.06$K.

This integral can be done in the same way as for the energy density. We then obtain

$$n(T) = 2.404 \left(\frac{kT}{\hbar}\right)^3 \frac{1}{\pi^2 c^3} = 20.3\, T^3\, cm^{-3}\, K^{-3} \tag{5.49}$$

where we used $I_2 = 2\zeta(3) = 2.404$.

In 1965 Penzias and Wilson discovered that the universe is filled with black-body radiation of temperature $T \simeq 3K$. It was immediately explained as the cooled-down remnant of the very hot radiation present in the universe just after the Big Bang. It provides detailed information about the conditions in the universe at that early time and meant an enormous leap in the understanding of this era and has many cosmological implications.

Since then one has studied this background radiation much more accurately. The most recent results for the energy spectrum from the COBE satellite is shown in Fig.5.3. It fits beautifully to the Planck formula with a temperature of $T = 2.73 \pm 0.01\, K$. From (5.49) we see that it corresponds to $n = 413$ photons per cm^3 left over from the initial bang 15 billion years ago. In all directions of space one finds the same temperature to an accuracy of $\Delta T/T \simeq 10^{-5}$ when local motion is corrected for. On these scales one sees a very isotropic universe which present-day research in astrophysics is trying to explain.

5.3   Phonons and the Debye theory of specific heats

The simplest picture one has of a solid state material is a regular lattice with atoms occupying all the sites as indicated in Fig.5.3. In a metal the atoms are replaced by ions and there are conduction electrons floating more or less freely around between the ions.
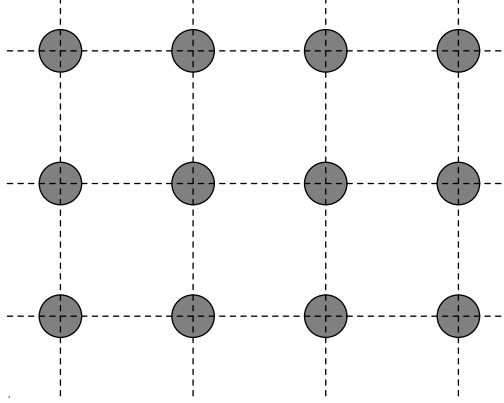

Figure 5.4: The atoms in a solid are held in equilibrium positions by elastic forces and form a regular lattice.

At temperatures much below the melting temperature, the atoms will vibrate around their equilibrium positions. Assuming that each of the N atoms is only coupled to its nearest neighbors with a common coupling constant K, we can write the Hamiltonian for the lattice as

$$H = \frac{1}{2m}\sum_{i=1}^{3N}(p_i^2 + \omega^2 q_i^2) + \frac{1}{2}\sum_{i<j} K(q_i - q_j)^2 \qquad (5.50)$$

which describes a set of coupled harmonic oscillators. The common frequency ω would arise if the atoms were uncoupled. There are $3N$ independent coordinates and momenta since each atom can vibrate in 3 different directions. By introducing normal coordinates

$$Q_i = \sum_{j=1}^{3N} a_{ij} q_j \qquad (5.51)$$

and corresponding momenta, one can determine the coefficients a_{ij} in such a way that the Hamiltonian takes the diagonal form

$$H = \frac{1}{2}\sum_{i=1}^{3N}(P_i^2 + \omega_i^2 Q_i^2) \qquad (5.52)$$

which is a sum of harmonic oscillators. Using classical, statistical mechanics we then see that the internal energy of these lattice vibrations is just $U = 3NkT$. This follows directly from the virial theorem for a Hamiltonian which is quadratic both in momenta and coordinates. The specific heat is therefore just $C_V = 3Nk$ which is Dulong-Petit's law. It was found to be in agreement with measurements on insulators at relatively high temperatures. For metals there should be an additional contribution coming from the electron gas. Again, using classical statistics, it should be of the order of $3k/2$ per electron. This addition to the Dulong-Petit value was not seen and represented a real problem for the understanding of metals.

The first quantum theory for these solid state specific heats was made in 1907 by Einstein. He treated each oscillator in (5.52) by quantum mechanics. In analogy with the quantization of the electromagnetic field, we now say that if the oscillator with frequency ω_i has the energy $n_i \hbar \omega$, there are n_i phonons in this mode. The phonons are the quanta of lattice vibrations as the photons are the quanta of electromagnetic oscillations. The average energy of the phonons with frequency ω_i is therefore

$$\langle \epsilon_i \rangle = \frac{\hbar \omega_i}{e^{\hbar \omega_i / kT} - 1} \ . \tag{5.53}$$

In addition, Einstein assumed that the oscillators were not coupled as in (5.50). Hence, they had all the common frequency ω. Their internal energy is then simply

$$U = \frac{3N\hbar \omega}{e^{\hbar \omega / kT} - 1} \ . \tag{5.54}$$

Taking the derivative with respect to the temperature, we then find the specific heat

$$C_V = 3Nk \left(\frac{\hbar \omega}{kT} \right)^2 \frac{e^{\hbar \omega / kT}}{\left(e^{\hbar \omega / kT} - 1 \right)^2} \ . \tag{5.55}$$

In the limits of very low and high temperature, it takes the simpler forms

$$C_V = \begin{cases} 3Nk \left(\frac{\hbar \omega}{kT} \right)^2 e^{-\hbar \omega / kT}, & T \ll \hbar \omega / k \\ 3Nk, & T \gg \hbar \omega / k \end{cases} \ . \tag{5.56}$$

Above the characteristic Einstein temperature $T_E = \hbar \omega / k$ we recover the Dulong-Petit law. Comparing with measurements as in Fig.5.5, we see that at lower temperatures it reproduces quite well the trend of the data and gives a specific heat which goes to zero at very low temperatures in agreement with the third law.

But more detailed measurements revealed that the specific heat did not approach zero exponentially with the temperature as it should according to (5.56). In 1912 a better theory was constructed by P. Debye. He abandoned the unrealistic assumption of Einstein that all the vibrations have the same
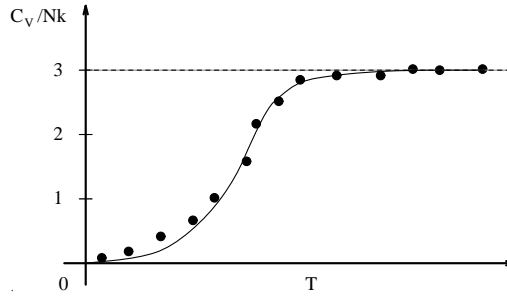
Figure 5.5: Einstein's theory gave specific heats which were too small at low temperatures.

frequency. He accepted the fact that there should be $3N$ normal modes, each with its own frequency ω_i as in the Hamiltonian (5.52). Instead of (5.54) one should therefore have the internal energy

$$U = \sum_{i=1}^{3N} \frac{\hbar\omega_i}{e^{\hbar\omega_i/kT} - 1} \ .$$
(5.57)

Introducing the density of modes

$$D(\omega) = \sum_{i=1}^{3N} \delta(\omega - \omega_i),$$
(5.58)

we can write the internal energy as the integral

$$U = \int_0^\infty d\omega \, \frac{\hbar\omega}{e^{\hbar\omega/kT} - 1} D(\omega) \ .$$
(5.59)

When the number of particles N is very large, the different frequencies can be considered to form a continuum with density $D(\omega)$, i.e. there are $D(\omega)\Delta\omega$ frequencies between ω and $\omega + \Delta\omega$. We obviously have the normalization

$$\int_0^\infty d\omega \, D(\omega) = 3N$$
(5.60)

which follows directly from the definition (5.58).

Taking the derivative of the internal energy (5.59) with respect to the temperature, we find the specific heat

$$C_V = k \int_0^\infty d\omega \left(\frac{\hbar\omega}{kT}\right)^2 \frac{e^{\hbar\omega/kT}}{\left(e^{\hbar\omega/kT} - 1\right)^2} D(\omega) \ .$$
(5.61)

Because of the constraint (5.60) on the density of modes, it is reasonable to expect that there is an upper frequency ω_D above which there are no modes. For temperatures $T \gg \hbar\omega_D/k$ we can therefore make the approximation

$$e^{\hbar\omega/kT} \simeq 1 + \frac{\hbar\omega}{kT}$$

in the integral (5.61) for the specific heat. Thus, at these high temperatures it becomes

$$C_V = k \int_0^\infty d\omega \, D(\omega) = 3Nk$$

in agreement with the Dulong-Petit law.

At very low temperatures it is the low-frequency part of the phonon spectrum which is important. This corresponds to long wavelengths where the lattice can be treated as an elastic continuum. The lattice vibrations are then just sound waves where the discrete amplitudes $q_i(t)$ are replaced by the continuum sound field $q(\mathbf{x}, t)$. It is now described by the wave equation

$$\left(\nabla^2 - \frac{1}{v^2} \frac{\partial^2}{\partial t^2} \right) q(\mathbf{x}, t) = 0 \tag{5.62}$$

where v is the sound velocity. As for the electromagnetic field we introduce the Fourier expansion

$$q(\mathbf{x}, t) = \sqrt{\frac{1}{V}} \sum_\mathbf{k} q_\mathbf{k}(t) \, e^{i\mathbf{k} \cdot \mathbf{x}} \tag{5.63}$$

in modes of definite wavenumber $\mathbf{k}$ where V is the volume of the system. Each modes is then seen to satisfy the equation of motion

$$\ddot{q}_\mathbf{k} + v^2 k^2 \, q_\mathbf{k} = 0 \tag{5.64}$$

which again is a harmonic oscillator with frequency $\omega = vk$. The thermal energy of the phonons in the mode with wavenumber $\mathbf{k}$ is then

$$\langle \, \epsilon_\mathbf{k} \, \rangle = \frac{\hbar \omega}{e^{\hbar \omega / kT} - 1}, \tag{5.65}$$

and the total internal energy is

$$U(T) = 3 \sum_\mathbf{k} \langle \, \epsilon_\mathbf{k} \, \rangle \,. \tag{5.66}$$

We have here multiplied by a factor three since the sound field can have a longitudinal polarization along $\mathbf{k}$ in addition to the two transverse polarizations.

Even if this description of the lattice vibrations is only valid in the long-wavelength limit, Debye assumed that it was valid for all the modes. Replacing the sum in (5.66) by an integral,

$$U(T) = 3V \int \frac{d^3 k}{(2\pi)^3} \frac{\hbar \omega}{e^{\hbar \omega / kT} - 1}$$

and using the continuum result $\omega = vk$, we find for the internal energy

$$U(T) = \frac{3V}{2\pi^2 v^3} \int_0^{\omega_D} d\omega \, \omega^2 \frac{\hbar \omega}{e^{\hbar \omega / kT} - 1} \,. \tag{5.67}$$

Comparing with (5.59), we see that in this approximation the density of modes is

$$D(\omega) = \frac{3V\omega^2}{2\pi^2 v^3} \tag{5.68}$$

for all frequencies less than the Debye frequency ω_D and zero otherwise. In order to satisfy the normalization (5.60), ω_D is determined by the integral

$$\frac{3V}{2\pi^2 v^3} \int_0^{\omega_D} d\omega\, \omega^2 = 3N$$

which gives

$$\omega_D = v(6\pi^2 \rho)^{1/3} \tag{5.69}$$

in terms of the density $\rho = N/V$ of atoms in the solid.

If the lattice distance in the solid is a, we will find the density to be $\rho = 1/a^3$ and thus a Debye frequency of $\omega_D \simeq 4v/a$. For copper we have $a = 2.3 \times 10^{-8}\, cm$ and a sound velocity of $v = 2.6 \times 10^5\, cm/s$. This gives $\omega_D = 4.5 \times 10^{13}\, s^{-1}$. The numerical value for the characteristic Debye temperature $T_D = \hbar\omega_D/k$ is then $T_D = 350\, K$. Even at room temperatures we will then have quantum corrections to the specific heat.

In Fig.5.6 we we give an example of how the physical density of modes $D(\omega)$ compares with the Debye approximation. While they will by construction agree at low frequencies, the large discrepancies at higher frequencies will have little effect at low temperatures where it is important that the theory works.
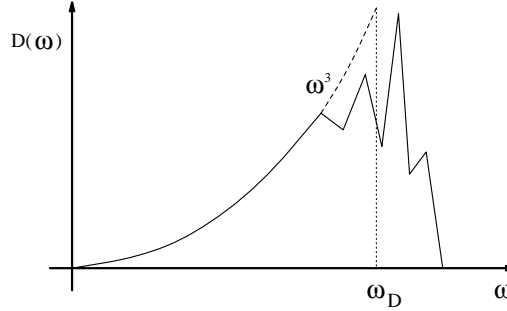

Figure 5.6: The Debye approximation to the phonon density of states is best at low frequencies.

We can now find the specific heat from (5.61) using the density of modes (5.68). Changing integration variable to $x = \hbar\omega/kT$, we can write the result as

$$C_V = 3NkF(T_D/T) \tag{5.70}$$

where we have introduced the Debye function

$$F(y) = \frac{3}{y^3} \int_0^y dx \, \frac{x^4 e^x}{(e^x - 1)^2} \tag{5.71}$$

and $T_D = \hbar \omega_D / k$. At temperatures much above the Debye temperature T_D we can replace $e^x - 1$ with x in the integral and find $F(y \to 0) = 1$. This gives just the Dulong-Petit result. In the opposite, low-temperature limit where $T_D \ll T$, we can take the upper limit in the integral to be infinite. By a partial integration we then

$$\int_0^\infty dx \, \frac{x^4 e^x}{(e^x - 1)^2} = -\left. \frac{x^4}{e^x - 1} \right|_0^\infty + 4 \int_0^\infty dx \, \frac{x^3}{e^x - 1} \; .$$

The first term vanishes in both limits while the last integral is just $I_3 = \pi^4 / 15$ in (5.43) which gives the energy density of the black body radiation. Hence, we have for the Debye function in this limit

$$F(y \to \infty) = \frac{3}{y^3} \frac{4}{15} \pi^4 = \frac{4\pi^4}{5y^3}$$

and the specific heat at very low temperatures is

$$C_V = \frac{12}{5} N k \pi^4 \left(\frac{T}{T_D} \right)^3 \; . \tag{5.72}$$

It varies with temperature as $C_V \propto T^3$ which agrees very well with measurements. This behavior at very low temperatures is often called the Debye T^3 law.

From the general result (5.70) for the specific heat, we see that it can be said to have an universal form in this approximation since it varies the same way with temperature for all solids when plotted in terms of T/T_D. Since this is experimentally found to be true also for metals, it must mean that the contribution from the conduction electrons is negligible at these temperatures. We will see that this is a consequence of the Fermi-Dirac statistics which govern their thermal behavior.

5.4 Bosons at non-zero chemical potential

Comparing our results for the mean energies of photons or phonons in a mode with wavenumber **k** with the expressions we derived in Chapter 2 for particles obeying Bose-Einstein statistics, we see that photons and phonons both have zero chemical potential μ. This is due to our inability to exactly fix their numbers in the presence of an confining enclosure at finite temperature T. For massive particles like mesons or bosonic atoms the situation is different. As long as the temperature and their interaction energies are much lower than

their masses, we can always determine their exact number. In an open system it is regulated by the chemical potential.

We will again consider free particles without any interactions. Each can then take an energy ε_s which is a non-degenerate eigenvalue of the one-particle Schrödinger equation. A quantum state of a system of many such particles is then completely determined by just stating how many particles n_s have the energy ε_s. They enter the description in a completely symmetric way done since they are indistinguishable. We cannot say which particles take the different energies, only how many there are in the different energy levels. The total number of particles in the system is therefore

$$N = \sum_s n_s \tag{5.73}$$

and their energy is

$$E = \sum_s n_s \varepsilon_s \ . \tag{5.74}$$

In the canonical ensemble we must then calculate the partition function

$$Z = e^{-\beta F} = \sum_{\{n_s\}} e^{-\beta \sum_s n_s \varepsilon_s} \tag{5.75}$$

which give the Helmholtz free energy $F(T, V)$. It is obtained by summing over all the quantum states specified by the set of occupation numbers $\{n_s\}$ keeping the total number of particles (5.73) fixed. However, this turns out to be mathematically difficult and will not be pursued further here.

It is much simpler to use the grand canonical ensemble derived in Chapter 3. The partition function

$$\Xi = e^{-\beta \Omega} = \sum_{\{n_s\}} e^{-\beta(E - \mu N)} \tag{5.76}$$

then gives the Landau free energy $\Omega(T, V, \mu) = -PV$ and is the unrestricted sum over all sets of occupation numbers $\{n_s\}$ taken to be independent of their total sum. Inserting the expressions (5.73) and (5.74) for N and E, we get

$$\Xi = \prod_s \sum_{n_s} e^{-\beta(\varepsilon_s - \mu)n_s} \ . \tag{5.77}$$

For bosons the occupation number n_s can take any value between zero and infinite. The sum is then a simple geometric series giving

$$e^{-\beta \Omega} = \prod_s \sum_{n_s=0}^{\infty} e^{-\beta(\varepsilon_s - \mu)n_s} = \prod_s \left[1 - e^{-\beta(\varepsilon_s - \mu)} \right]^{-1} \tag{5.78}$$

as long as $\mu \leq \varepsilon_s$. Thus the chemical potential for free bosons must be less or at most equal to the lowest one-particle energy. We then have for the free energy

$$\Omega = kT \sum_s \log \left[1 - e^{-\beta(\varepsilon_s - \mu)} \right] \ . \tag{5.79}$$

The mean number of particles follow from $N = -\partial\Omega/\partial\mu$ which gives

$$N = \sum_s \frac{1}{e^{\beta(\varepsilon_s - \mu)} - 1} \; . \tag{5.80}$$

This implies that the average number of particles with energy ε_s is

$$\langle n_s \rangle = \frac{1}{e^{\beta(\varepsilon_s - \mu)} - 1} \tag{5.81}$$

which is just the Bose-Einstein distribution (2.68). It gives the total internal energy of the system

$$U = \sum_s \frac{\varepsilon_s}{e^{\beta(\varepsilon_s - \mu)} - 1} \tag{5.82}$$

which agrees with what we previously used for photons and phonons when $\mu = 0$.

In the classical limit the temperature is high and/or the density low so that the occupation numbers $\langle n_s \rangle \ll 1$. This corresponds to having a large and negative chemical potential so the fugacity $\lambda = e^{\beta\mu} \ll 1$. Now making use of the expansion

$$\log\left(1 - x\right) = -\sum_{n=1}^{\infty} \frac{x^n}{n} \tag{5.83}$$

we find from (5.79) the leading terms

$$\Omega = -kT\left[\lambda \sum_s e^{-\beta\varepsilon_s} + \frac{1}{2}\lambda^2 \sum_s e^{-2\beta\varepsilon_s} + \cdots\right] \tag{5.84}$$

in this limit. The individual sums can here be expressed by the one-particle partition function

$$Z_1 = \sum_s e^{-\beta\varepsilon_s} \; . \tag{5.85}$$

Keeping only the first term, we then have $\beta\Omega = -\lambda Z_1$ so that the grand canonical partition function for free bosons in the classical limit is

$$\Xi = e^{\lambda Z_1} = \sum_{N=0}^{\infty} \lambda^N \frac{Z_1^N}{N!} \; . \tag{5.86}$$

From (3.64) we know that it can also be written in terms of the N-particle canonical partition function Z_N as

$$\Xi = \sum_{N=0}^{\infty} \lambda^N Z_N \; .$$

Comparing with our quantum mechanical result above, we see that we must have $Z_N = Z_1^N/N!$. This is the famous $N!$ we had to introduce rather *ad hoc* in classical statistical mechanics of identical particles in Chapter 2. Here it comes out naturally in the classical limit from the symmetric treatment of indistinguishable bosons.

From (5.84) we see that we can evaluate corrections to the ideal gas equation of state due to quantum effects. Expanding the particle number (5.80) in powers of λ, we get

$$\rho = \lambda \left(\frac{Z_{1\beta}}{V} \right) + \lambda^2 \left(\frac{Z_{2\beta}}{V} \right) + \cdots$$

when we introduce the particle number density $\rho = N/V$ and denote the partition function (5.85) by $Z_{1\beta}$. To lowest order, this gives the fugacity $\lambda = (V/Z_{1\beta})\rho$. Including the second term we obtain the more accurate result

$$\lambda = \left(\frac{V}{Z_{1\beta}} \right) \rho - \left(\frac{Z_{2\beta}}{V} \right) \left(\frac{V}{Z_{1\beta}} \right)^3 \rho^2 + \cdots . \tag{5.87}$$

The pressure now follows from (5.84) which gives

$$\begin{aligned} P &= kT \left[\lambda \left(\frac{Z_{1\beta}}{V} \right) + \frac{1}{2}\lambda^2 \left(\frac{Z_{2\beta}}{V} \right) + \cdots \right] \\ &= kT \left[\rho - \frac{1}{2} \left(\frac{V}{Z_{1\beta}} \right) \left(\frac{Z_{2\beta}}{Z_{1\beta}} \right) \rho^2 + \cdots \right] \end{aligned} \tag{5.88}$$

when inserting the fugacity and expanding again. These are just the first two terms in the virial expansion of the quantum equation of state. We see that the second virial coefficient for bosons is

$$B_2(T) = -\frac{1}{2} \left(\frac{V}{Z_{1\beta}} \right) \left(\frac{Z_{2\beta}}{Z_{1\beta}} \right) . \tag{5.89}$$

Since the partition functions are always positive, the pressure in the ideal gas of bosons is reduced because of quantum effects. There is a statistical "attraction" between the particles because of their willingness to occupy the same quantum states.

For free and non-relativistic particles in a box of volume V the one-particle states can be labeled by the momentum $\mathbf{p}$ and have the energy $\varepsilon_{\mathbf{p}} = \mathbf{p}^2/2m$. The lowest energy is then $\varepsilon_0 = 0$ so that the chemical potential must be negative or at most zero. In the partition function (5.85) we can replace the sum over states by the now standard phase space integration

$$\sum_{\mathbf{p}} = V \int \frac{d^3p}{(2\pi\hbar)^3} = \frac{V}{4\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \int_0^\infty d\varepsilon \, \varepsilon^{\frac{1}{2}} \tag{5.90}$$

when the box volume V is macroscopically large and the particle moves in three dimensions. We then recover the known result $Z_1 = V/\Lambda^3$ where the thermal

wavelength is

$$\Lambda = \left(\frac{2\pi\beta\hbar^2}{m}\right)^{1/2} = \frac{h}{\sqrt{2\pi mkT}} \ . \tag{5.91}$$

The virial coefficient (5.88) is then $B_2 = -\Lambda^3/2^{5/2}$. We see that the quantum correction to the pressure (5.88) is given by the quantity $\rho\Lambda^3$ which is small in the classical limit.

From (5.79) we can now obtain a general result for the Landau free energy. Isolating the contribution from the ground state, we have

$$
\begin{aligned}
\frac{\Omega}{kT} &= \log\left(1-\lambda\right) + \sum_{\mathbf{P}} \log\left[1 - e^{-\beta(\varepsilon_{\mathbf{P}}-\mu)}\right] \tag{5.92}\\
&= \log\left(1-\lambda\right) + \frac{V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\int_0^\infty d\varepsilon\,\varepsilon^{\frac{1}{2}}\log\left[1 - e^{-\beta(\varepsilon-\mu)}\right] . \tag{5.93}
\end{aligned}
$$

As long as $\lambda < 1$ we can safely drop the first term, which comes from the particles in the ground state, since we are interested in the thermodynamic limit where $N, V \to \infty$ for fixed ρ. A partial integration of the second term then gives

$$\Omega = -\frac{V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\frac{2}{3}\int_0^\infty d\varepsilon\,\varepsilon^{\frac{3}{2}}\frac{e^{-\beta(\varepsilon-\mu)}}{1 - e^{-\beta(\varepsilon-\mu)}}$$

since the boundary term is seen to vanish. But this resulting integral is essentially just the total internal energy

$$U = \frac{V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{1/2}\int_0^\infty d\varepsilon\,\varepsilon^{\frac{1}{2}}\frac{\varepsilon}{e^{\beta(\varepsilon-\mu)}-1} \tag{5.94}$$

of the gas. Introducing the energy density $\mathcal{E} = U/V$, we have the important relation

$$P = \frac{2}{3}\mathcal{E} \tag{5.95}$$

for non-relativistic particles. This should be contrasted with the corresponding result $P = (1/3)\mathcal{E}$ for the thermal pressure of the photon gas which is relativistic.

Expanding the logarithm in (5.93) and interchanging integration and summation, we get

$$\frac{\Omega}{kT} = \log\left(1-\lambda\right) - \frac{V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\sum_{n=0}^\infty\frac{\lambda^n}{n}\int_0^\infty d\varepsilon\,\varepsilon^{\frac{1}{2}}e^{-n\beta\varepsilon} \ .$$

The first term is the contribution from the particles in the ground state while the infinite sum gives the contribution from the particles in the excited states. The integrals are straightforward and give

$$\int_0^\infty d\varepsilon\,\varepsilon^{\frac{1}{2}}e^{-n\beta\varepsilon} = \frac{\frac{1}{2}!}{(n\beta)^{3/2}} = \frac{\sqrt{\pi}}{2n^{3/2}}(kT)^{3/2} \ .$$

Inserting these expressions and simplifying the sum, we can write the resulting pressure as

$$\frac{P}{kT} = -\frac{1}{V} \log(1 - \lambda) + \frac{1}{\Lambda^3} g_{\frac{5}{2}}(\lambda) \tag{5.96}$$

when we make use of the poly-logarithmic function

$$g_p(\lambda) = \sum_{n=1}^{\infty} \frac{\lambda^n}{n^p} . \tag{5.97}$$

It is convergent for $\lambda \leq 1$. When $\lambda = 1$ we see that it is given by the Riemann zeta-function as $g_p(1) = \zeta(p)$.

We can similarly expand (5.80) for the mean number of particles in the system. However, it is simpler to use $\rho = \partial P / \partial \mu$ and make use of the above expansion to obtain for the density

$$\rho = \frac{1}{V} \frac{\lambda}{1 - \lambda} + \frac{1}{\Lambda^3} g_{\frac{3}{2}}(\lambda) . \tag{5.98}$$

The first term gives the number of particles in the ground state. As long as $\lambda < 1$ it is negligible because it is divided by the macroscopic volume V. We can now in principle keep any finite number of terms in the polylogarithmic function and solve for the fugacity λ as a power series in the density ρ. To second order in the fugacity we have from (5.87)

$$\lambda = \rho \Lambda^3 - \frac{1}{2}(\rho \Lambda^3)^2 + \cdots . \tag{5.99}$$

Including higher order terms and inserting the result in the pressure (5.96), we can then systematically obtain the higher virial coefficients in the equation of state.

In the normal region where $\lambda < 1$ we can drop the first term in (5.98) so that the fugacity is determined by

$$\rho \Lambda^3 = g_{\frac{3}{2}}(\lambda) . \tag{5.100}$$

The internal energy is given in terms of the pressure (5.96) as $U = 3PV/2$ and becomes

$$U = \frac{3}{2} V \frac{kT}{\Lambda^3} g_{5/2}(\lambda) = \frac{3}{2} NkT \frac{g_{\frac{5}{2}}(\lambda)}{g_{\frac{3}{2}}(\lambda)} . \tag{5.101}$$

We can now obtain the specific heat in this region. From (5.97) we find that

$$\lambda \frac{d}{d\lambda} g_p(\lambda) = g_{p-1}(\lambda) \tag{5.102}$$

which gives

$$\frac{\partial}{\partial \lambda} g_{\frac{3}{2}}(\lambda) = \frac{1}{\lambda} g_{\frac{1}{2}}(\lambda) .$$

Taking now the derivative of (5.100) with respect to the temperature at fixed density we similarly find

$$\frac{\partial}{\partial T} g_{\frac{3}{2}}(\lambda)|_\rho = -\frac{3}{2T} g_{\frac{3}{2}}(\lambda) .$$

Combining these two results, it follows that

$$\left(\frac{\partial \lambda}{\partial T}\right)_\rho = -\frac{3\lambda}{2T} \frac{g_{\frac{3}{2}}(\lambda)}{g_{\frac{1}{2}}(\lambda)} . \tag{5.103}$$

We can now find the specific heat from (5.101) by direct differentiation and obtain

$$C_V = \frac{3}{2} Nk \left[\frac{5}{2} \frac{g_{\frac{5}{2}}(\lambda)}{g_{\frac{3}{2}}(\lambda)} - \frac{3}{2} \frac{g_{\frac{3}{2}}(\lambda)}{g_{\frac{1}{2}}(\lambda)} \right] . \tag{5.104}$$

To lowest order in λ the parenthesis reduces to $1 + \lambda/2^{7/2} + \cdots$ and thus

$$C_V = \frac{3}{2} Nk \left[1 + \frac{1}{2^{7/2}} \rho \Lambda^3 + \cdots \right] . \tag{5.105}$$

The specific heat is seen to increase above the ideal gas value at lower temperatures.

5.5   Bose-Einstein condensation and superfluid ^4He

The quantum effects in the gas depend on the quantity $\rho \Lambda^3$ which is small in the classical limit. Working at fixed density ρ, we see from (5.99) that the fugacity will first increase by lowering the temperature at fixed density. At even lower temperatures λ approaches the value one and it must be obtained numerically as a root of (5.98). Since the function $g_{\frac{3}{2}}(\lambda)$ is steadily increasing with λ as shown in Fig.5.7, this is quite straightforward. At a temperature T_c determined by

$$\rho \Lambda_c^3 = g_{\frac{3}{2}}(1) = \zeta(3/2) = 2.612 \tag{5.106}$$

it is so close to one that we must reckon with the number of particles in the ground state,

$$N_0 = \langle\, n_0 \,\rangle = \frac{1}{e^{-\beta\mu} - 1} = \frac{\lambda}{1 - \lambda} \tag{5.107}$$

which now seems to diverges. This signals that a macroscopically large number of particles will start to occupy the lowest-energy state. It is called a Bose-Einstein condensation. The fugacity is $\lambda = 1 - 1/N_0$ and the chemical potential
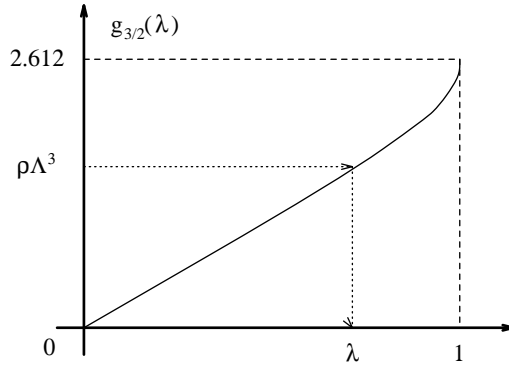
Figure 5.7: Graphical determination of fugacity as function of density and temperature.
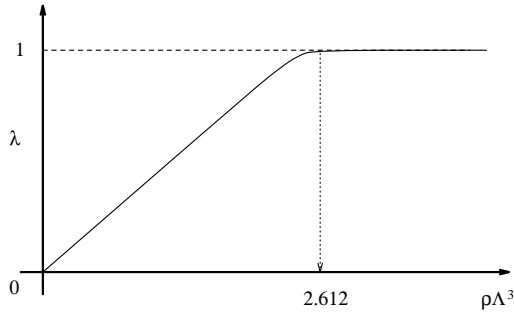

Figure 5.8: Fugacity as function of temperature and density in the ideal Bose-Einstein gas.

is $\mu/kT = -1/N_0$. When N_0 becomes macroscopic this can safely be taken to be zero. Below the critical temperature

$$T_c = \frac{2\pi\hbar^2}{km}\left(\frac{\rho}{2.612}\right)^{2/3} \tag{5.108}$$

we therefore have $\lambda = 1$ as shown in Fig.5.8.

Below the critical temperature we will have $\rho\Lambda^3 > 2.612$. Equation (5.98) can then be written as $N = N_0 + N_e$ where

$$N_e = 2.612\,V\Lambda^3 = N\left(\frac{T}{T_c}\right)^{3/2} \tag{5.109}$$

is the number of particles in the excited states. It goes to zero with decreasing temperature. At the same time the number in the ground state

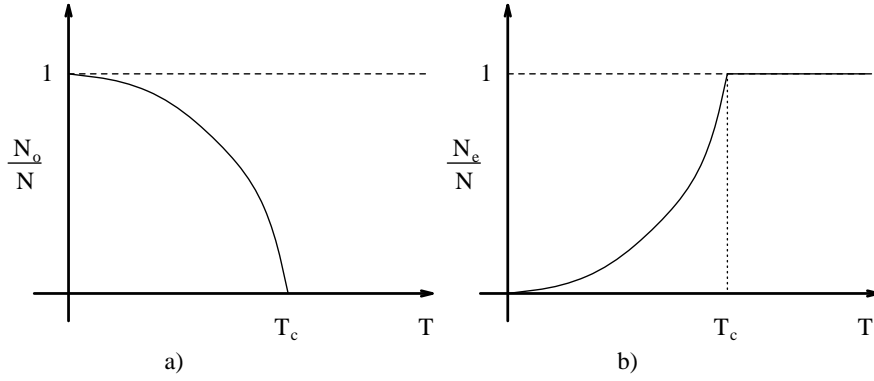$$N_0 = \left[1 - \left(\frac{T}{T_c}\right)^{3/2}\right]N \tag{5.110}$$

Figure 5.9: Fractions of particles in the condensate a) and in excited states b).

increases as shown in Fig.5.9. Below the critical temperature we have a separation of the gas in two phases. The particles in the excited states constitute the normal phase while the condensed phase consists of the particles in the ground state. In contrast to the normal gas-liquid condensation there is here no spatial separation into phases with different properties. Since the particles in the condensate all are in the state with $\mathbf{p} = 0$ one can instead consider the somewhat special Bose-Einstein condensation an ordinary condensation in momentum space. At $T = 0$ we find all the particles in the ground state.

In two dimensions there is no Bose-Einstein condensation at finite temperature. The chemical potential is then determined by

$$N = V \int \frac{d^2p}{(2\pi\hbar)^2} \frac{1}{e^{\beta(\varepsilon_p - \mu)} - 1}$$

where now $d^2p = 2\pi p dp = \pi dp^2 = 2m\pi d\varepsilon$. The integral then becomes

$$\rho = \frac{m}{2\pi\hbar^2} \int_0^\infty \frac{1}{e^{\beta(\varepsilon - \mu)} - 1}$$

which is easily done and gives

$$\lambda = 1 - e^{-\rho\Lambda^2} \ . \tag{5.111}$$

It increases smoothly with decreasing temperature and takes the value $\lambda = 1$ at exactly $T = 0$. Thus there is no Bose-Einstein condensation in this system except for $T = 0$ when all the particles are in the ground state. One can prove that even with interactions between the particles there will be no condensation in two dimensions at non-zero temperatures.

This exact solution now allows us to also find the full virial expansion of the equation of state as shown by Susanne Viefers. Writing

$$\frac{dP}{d\rho} = \frac{\partial P}{\partial \mu} \frac{\partial \mu}{\partial \rho}$$

we see that first derivative is just the density and the second is obtained from (5.111) as

$$\frac{\partial \mu}{\partial \rho} = \frac{kT\Lambda^2}{e^{\rho\Lambda^2} - 1} \ .$$

Hence, we obtain the differential equation

$$\frac{dP}{d\rho} = kT \frac{\rho\Lambda^2}{e^{\rho\Lambda^2} - 1} \tag{5.112}$$

It can be directly integrated by using the famous expansion

$$\frac{x}{e^x - 1} = \sum_{n=0}^{\infty} B_n \frac{x^n}{n!}$$

(5.113)

where B_n are the Bernoulli numbers, $B_0 = 1$, $B_1 = -1/2$, $B_2 = 1/6$, $B_4 = -1/30$, $B_6 = 1/42$ etc. We then find

$$P = kT\rho \left[1 - \frac{1}{4}\rho\Lambda^2 + \frac{1}{36}(\rho\Lambda^2)^2 - \frac{1}{3600}(\rho\Lambda^2)^4 + \frac{1}{211680}(\rho\Lambda^2)^6 + \cdots \right] .$$

(5.114)

One obtains exactly the same result for fermions except for the second virial coefficient which then has the opposite sign.

Only the particles in the excited states will contribute to the thermodynamic properties of the system. Everything follows from the pressure (5.96) which equals minus the Landau free energy density. Since $x \log x$ goes to zero when $x \to 0$, the first term will give nothing in the thermodynamic limit. The pressure becomes

$$P = \frac{kT}{\Lambda^3}\, \zeta(5/2) \;=\; 1.341 \left(\frac{m}{2\pi\hbar^2} \right)^{3/2} (kT)^{5/2}$$

(5.115)

and is shown in Fig.5.10. It is independent of the density which is typical for a gas in equilibrium with its liquid. Thus we call the change in the gas when the temperature is lowered through the critical temperature for a first-order phase transition.

From (5.95) we find the internal energy in the condensed phase to be

$$U = \frac{3}{2}\, V\, \frac{kT}{\Lambda^3}\, \zeta(5/2) \;=\; \frac{3}{2}\, NkT\, \frac{\zeta(5/2)}{\zeta(3/2)} \left(\frac{T}{T_c} \right)^{3/2}$$

(5.116)

At the critical point where $T = T_c$ we see that this agrees with (5.95) which
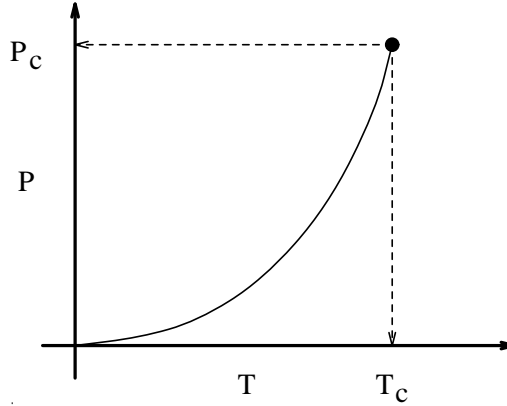

Figure 5.10: The pressure is function of the temperature only in the condensed region.

was derived from the high-temperature expansion. Finally, the entropy follows from $S = -(\partial\Omega/\partial T)_\mu$ which gives

$$S = \frac{5}{2} Vk \frac{1}{\Lambda^3} \zeta(5/2) = \frac{5}{2} Nk \frac{\zeta(5/2)}{\zeta(3/2)} \left(\frac{T}{T_c}\right)^{3/2} . \tag{5.117}$$

It goes to zero when $T \to 0$ in agreement with the third law of thermodynamics. The condensate is seen to make no contributions to the energy and entropy.

From the internal energy (5.116) we can now obtain the specific heat below the critical temperature and write the results as

$$C_V = \frac{15}{4} Nk \frac{\zeta(5/2)}{\zeta(3/2)} \left(\frac{T}{T_c}\right)^{3/2} . \tag{5.118}$$

It increases like $T^{3/2}$ to the critical point. At higher temperatures we can use (5.104) which is seen to give the same result at $T = T_c$ since the last term will vanish there, $g_{\frac{1}{2}}(1)$ being infinite. The combined results are shown in Fig.5.11 where the singular behavior of the specific heat is clearly seen at the critical point. It has here a value

$$C_V(T_c) = \frac{15}{4} Nk \frac{1.341}{2.612} = 1.925 \, Nk \tag{5.119}$$

which is significantly larger than the classical value of $1.5 \, Nk$. This peak in the specific heat signals a transition into the mixed phase of the gas where the particles start to accumulate in the ground state.

Bose-Einstein condensation was first predicted by Satyendra Nath Bose in 1925. Bose submitted a paper to the Zeitschrift fur Physik but was turned down by the peer review. Bose then took his work to Einstein who recognized its merit and had it published under the names Bose and Einstein, hence the acronymn. Seventy years later, the first gaseous condensate was produced by Eric Cornell and Carl Wieman in 1995 at the University of Colorado at Boulder NIST-JILA lab, using a gas of rubidium atoms cooled to 170 nanokelvin. Eric Cornell, Carl Wieman and Wolfgang Ketterle at MIT were awarded the 2001 Nobel Prize in Physics.

We can now get a picture of the full equation of state for the ideal quantum gas of bosons. Below the critical temperature we know from (5.115) that the pressure varies as $T^{5/2}$ as shown in Fig.5.10. Since it is independent of the density, the condensed phase will fall on this line while we have the normal gas phase below and to the right.

Until now we have worked at a fixed density. Varying instead the density of the gas at a fixed temperature, we will find a behavior as illustrated in Fig.5.12. Increasing the density from zero we fill find that the pressure with ρ, but will be below the classical result when the quantum effects become non-negligible.
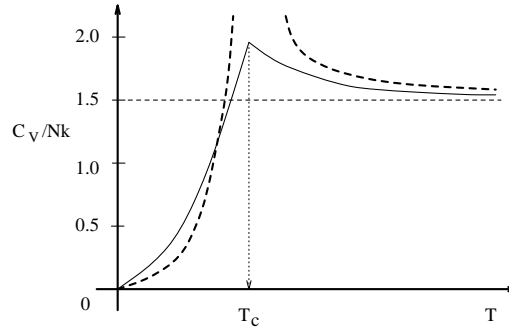
Figure 5.11: Specific heat of the ideal Bose-Einstein gas (full line) and measured values in ^4He (dashed curve).

At a certain critical density ρ_c again given by $\rho_c \Lambda^3 = \zeta(3/2)$, we will start to have condensation into the ground state. Even higher densities will not change the pressure which remains at its critical value P_c. Solving for kT in terms of ρ_c we find it to be

$$P_c = \frac{kT}{\Lambda^3} \zeta(5/2) = 1.341 \frac{2\pi\hbar^2}{m} \left(\frac{\rho_c}{2.612} \right)^{5/3} . \qquad (5.120)$$

The equation of state can now be illustrated by the PVT diagram in Fig.5.13. There is a rising, flat plateau corresponding to the density-independent pressure in the mixed phase. It is separated by a critical ridge from a steadily falling hill which is the pressure in the normal phase.

Bose-Einstein condensation is due to the quantum effects in the gas following from symmetric statistics. The smaller the mass of the particles, the higher is the critical temperature and the more easily should this quantum phenomenon be seen. Thus it should first show up in hydrogen gas H_2. But among these molecules there are relatively strong, attractive forces which makes this gas solidify instead at very low temperatures.

Helium in nature is almost pure ^4He and hence a boson gas. It was first liquefied by Kammerlingh Onnes in 1908 at a temperature of $4.2\,K$ at normal pressure. As is typical of boiling, gas bubbles then rise to the surface and the liquid is very agitated. When the temperature is reduced further down to $T_\lambda = 2.2\,K$, the boiling suddenly stops. The liquid becomes very smooth and one can see through it. It has made a transition into a new

phase now called *He II* while the liquid phase above T_λ is called *He I*. The phase diagram is shown in Fig.5.14. It has a critical point at $T = 5.2\,K$ and pressure $P = 2.26\,atm$. We see that T_λ really marks a triple point where the gas and the two liquid phases are in equilibrium. The λ-line marks the transition between *He II* and *He II*. While the transition between the gas and the liquid phases are of first order, the λ-transition is continuous and is usually called a second-order transition.
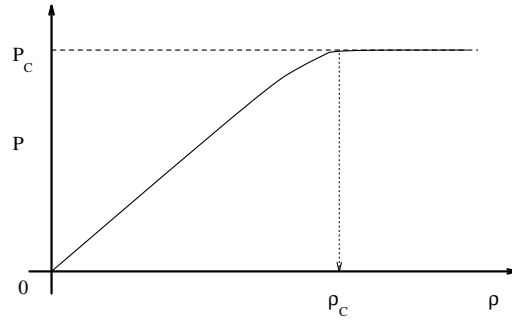
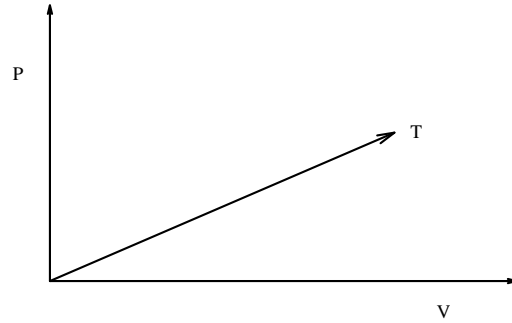Figure 5.12: Pressure of the ideal Bose-Einstein gas at a given temperature as function of the density.

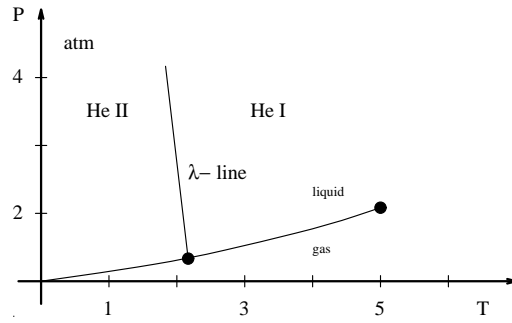Figure 5.13: Equation of state for the ideal Bose-Einstein gas.

Figure 5.14: Phase diagram for ^4He. There is also a solid phase at much higher pressures.

In 1938 P. Kapitza discovered that the viscosity in *He II* became exceedingly small when the temperature was reduced below T_λ. It can flow through small pores without any resistance and we say that it is a superfluid. If an empty beaker is dipped down into *He II*, the liquid will flow up along the outside walls

and into the beaker. When it is lifted up again, the liquid crawls out of the beaker again.

The name λ-transition comes from the form of the specific heat. As is shown in Fig.5.11, it diverges at the transition temperature T_λ. At very low temperatures it increases from zero like T^3 and approaches the classical value at high temperatures. It has the shape of the Greek letter λ.

One of the first to suggest that this transition could be explained as a Bose-Einstein condensation was F. London in 1938. The zero-energy condensate should then be the superfluid component while the particles in the excited states compose the normal component. If we use the atomic mass $m = 6.65 \times 10^{-24}\,g$ for helium and the liquid density $\rho = 2.2 \times 10^{-22}\,cm^{-3}$, we find from (5.108) the critical temperature $T_c = 3.1\,K$ which is surprisingly close to the observed transition temperature $T_\lambda = 2.2\,K$.

But there are also many features in the observed helium system which do not agree with the results for an ideal boson gas. First of all, since we have neglected the weak, but non-zero interactions between the atoms, we do not find the normal, first-order transition into the liquid phase *He I* and the associated normal, critical point at $T = 5.2\,K$. Second, the transition across the λ-line is of second order, while theory predicts a first-order transition. Also the transition pressure should increase with temperature as shown in Fig.5.10, but the physical phase diagram in Fig.5.14 shows that it actually decreases along the λ-line. Helium expands when it is cooled down into the superfluid phase as water does when it freezes into ice. As already pointed out, the specific heat increases from zero like T^3 instead of $T^{3/2}$ and the specific heat diverges at the critical value in physical helium. At zero temperature only around 10% of the particles are found in the condensate while the Bose-Einstein theory predicts 100%.

Using modern quantum theory one can today better understand the superfluid properties of interacting bosons at low temperatures. The interaction potential will have the same form as the Lennard-Jones potential in Fig.4.1 for real, classical gases. As in real gases one will again find an ordinary condensation of helium into the liquid phase *He I* due to attractive part of the potential. It has the hard-core repulsion which primarily gives rise to superfluidity. At very low temperatures it will then have many properties similar to what we found in solids. Instead of one-particle excitations with energy $\varepsilon = p^2/2m$ as in the ideal case, we can now have collective sound excitations of the system where many particles act together in a coherent way. The corresponding phonon excitations with energies $\varepsilon = vp$ will then explain the T^3 behavior of the low-temperature specific heat as in the Debye theory. In addition, we find that the pressure in the condensed phase is no longer independent of the density. In Fig.5.10 the condensed phase will then be above the plotted curve and thus in better agreement with the physical phase diagram Fig.5.14. Even at zero temperature there will be a non-vanishing pressure in the gas due to the repulsion. There are no longer any restrictions on the chemical potential and it becomes positive at very low temperatures when it starts to condense.

With interactions between the particles, we can now longer talk about one-particle energies and condensation into the $\psi_{\mathbf{p}=0}$ quantum state. However, it

turns out that we can instead introduce a macroscopic wave function $\phi(\mathbf{x})$ which describes all the particles in the superfluid condensate. The absolute square of the wave function, $\phi^*(\mathbf{x})\phi(\mathbf{x})$, is then no longer the probability to find one particle in position $\mathbf{x}$, but the density of particles in the condensate at this position.

We can now construct an approximate expression for the Landau free energy Ω describing in a qualitative way the phase transition. The particles in the condensate has a momentum $\mathbf{p} = (\hbar/i)\boldsymbol{\nabla}$. At low temperatures where we can neglect entropy effects, we then have $\Omega = \langle \widehat{H} - \mu\widehat{N} \rangle$ and thus

$$\Omega = \int d^3x \left[\frac{\hbar^2}{2m}(\boldsymbol{\nabla}\phi^*) \cdot (\boldsymbol{\nabla}\phi) + \kappa\,(\phi^*\phi)^2 - \mu\,\phi^*\phi \right] \, . \tag{5.121}$$

The first term is the density of kinetic energy $\mathbf{p}^2/2m$ of the particles in the condensate and the middle term represents the repulsion between the particles with a strength given by the constant κ. In the last term μ is the chemical potential and the integral over $\phi^*\phi$ gives the total number of particles. In thermodynamic equilibrium, this free energy should be minimal. Since the kinetic piece always is positive, we reduce the energy by taking $|\phi| = const$. The free energy is then given by the last two terms which often is called the effective potential of the condensate,

$$V_{eff} = \kappa\,(\phi^*\phi)^2 - \mu\,\phi^*\phi \, . \tag{5.122}$$

In the normal phase μ is negative and it has the form shown in Fig.5.15 with a minimum for $|\phi| = 0$. The density of particles in the condensate is therefore zero as expected. On the other hand, when $\mu > 0$, the effective potential has a non-zero minimum at

$$\phi_0 = \sqrt{\frac{\mu}{2\kappa}} \tag{5.123}$$

which gives the energy density $V_{eff}(\phi_0) = -\mu^2/4\kappa$. Since this is lower than the energy of the normal phase with $\phi = 0$, the condensed phase is now the thermodynamically stable one. If we assume that the chemical potential varies like $\mu \propto (T_\lambda - T)$ near the phase transition, the modulus of ϕ varies as

$$|\phi| \propto (T_\lambda - T)^{1/2} \tag{5.124}$$

below the critical point as shown in Fig.5.16. The number of particles $\phi^*\phi$ in the condensate varies then with temperature similarly to what we found for the ideal Bose-Einstein gas in Fig.5.9.

The interaction term $\kappa\,(\phi^*\phi)^2$ in 5.121) can be understood in the following way. Consider a gas of electrons and protons. If the electrons have the wave function $\psi_e(\mathbf{x})$, the density of electrons at position $\mathbf{x}$ is $\rho_e = \psi_e^*(\mathbf{x})\psi_e(\mathbf{x})$. Similarly, the density of protons is $\rho_p = \psi_p^*(\mathbf{x})\psi_p(\mathbf{x})$ if they have the wave function $\psi_p(\mathbf{x})$. The Coulomb attraction between electrons and protons will thus be $V_{ep} \propto -e^2\rho_e\rho_p = -e^2\psi_e^*\psi_e\psi_p^*\psi_p$ where e is the electric charge. The
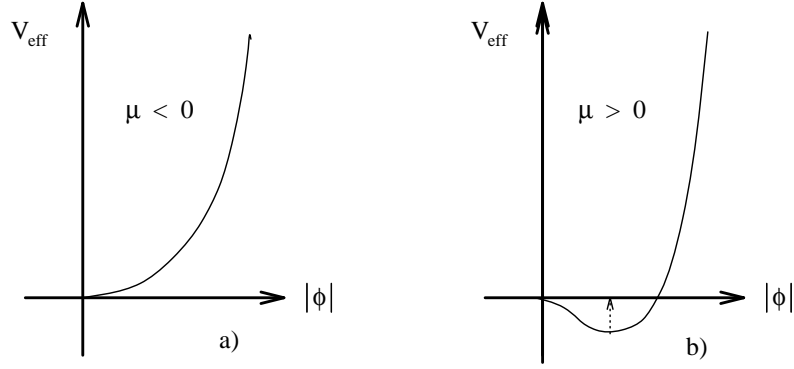
Figure 5.15: Effective potentials for ^4He. The normal phase is stable in a) while the superfluid phase is stable in b).
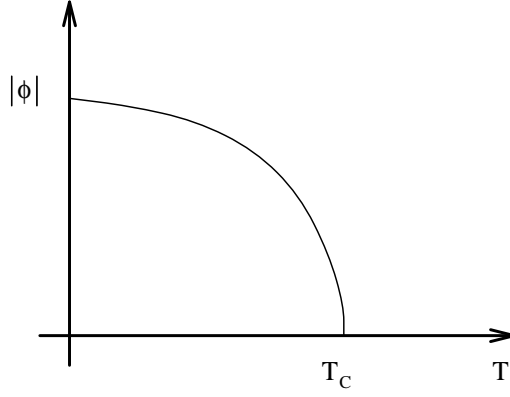

Figure 5.16: Order parameter for ^4He as function of temperature. Above the critical temperature there is no superfluid condensate.

same reasoning then gives a Coulomb repulsion energy $V_{ee} \propto e^2 \rho_e \rho_e = e^2 (\psi_e^* \psi_e)^2$ which has the form we used for the repulsion between the helium atoms.

The macroscopic wave function ϕ is usually called the order parameter for the quantum liquid. We see that both the free energy (5.121) and the effective potential remain unchanged if it is replaced by

$$\phi \to \phi\, e^{i\chi} \tag{5.125}$$

where the phase χ is independent of the position. This is called a global $U(1)$ phase transformation after the name for the corresponding mathematical Lie group. Since ϕ is complex, we see that V_{eff} looks like a Mexican hat when plotted in terms of the real and imaginary components. The condensate minimum

can be any place at the bottom of the rim of the hat at position

$$\phi = \phi_0 \, e^{i\alpha} \, .$$

For any choice of the constant angle α there is a minimum of the energy. We say that we have an infinitely degenerate ground state. The system chooses a particular value of α and the $U(1)$ symmetry is said to be spontaneously broken.

This rather abstract phenomenon, which was first seen in the superfluid transition of ^4He, plays an even more important role in unified theories of the fundamental interactions between elementary particles. It provides a mechanism for them to be massive by the condensation of Higgs bosons. At very high temperatures in the early universe, the condensate goes away and all of the particles become massless. The corresponding phase transition results in an enormous inflation of the universe which has many welcome consequences in cosmology.

Helium gas contains a very small amount of the isotop ^3He which are fermions. When it is isolated from the main component, we have a weakly interacting gas which condenses to a normal liquid around $3\,K$. But there is now no λ-transition into a superfluid phase. This clearly demonstrates that it is the symmetric Bose-Einstein statistics which causes the condensation in ^4He.

However, it was discovered in 1972 that at much lower temperatures around $2\,mK$, there is also a condensation in ^3He. But here it takes place because the fermions get paired into composites which effectively act as bosons which can condense. This phenomenon is very similar to what happens when electrons become superconducting in metals and can only be understood by considering interacting particles obeying Ferm-Dirac statistics.

5.6   Fermion gases at finite temperature

We will now develop the thermodynamics of particles obeying Fermi-Dirac statistics using the grand canonical ensemble. The Pauli principle allows only one fermion in each quantum state and the partition function (5.77) becomes

$$\Xi = \prod_s \sum_{n_s=0}^{1} e^{-\beta(\varepsilon_s - \mu)n_s} = \prod_s \left[1 + e^{-\beta(\varepsilon_s - \mu)} \right] \, . \tag{5.126}$$

Instead of the Landau free energy expression (5.79) for bosons, it is now for fermions

$$\Omega = -kT \sum_s \log \left[1 + e^{-\beta(\varepsilon_s - \mu)} \right] \, . \tag{5.127}$$

The mean number of particles in the system at a given temperature and chemical potential is then

$$N = -\left(\frac{\partial \Omega}{\partial \mu} \right)_T = \sum_s \frac{1}{e^{\beta(\varepsilon_s - \mu)} + 1} \tag{5.128}$$

with an average number in the quantum state labeled by s given by the Fermi-Dirac distribution

$$\langle n_s \rangle = \frac{1}{e^{\beta(\varepsilon_s - \mu)} + 1} \ .$$
(5.129)

The internal energy

$$U = \sum_s \varepsilon_s \langle n_s \rangle = \sum_s \frac{\varepsilon_s}{e^{\beta(\varepsilon_s - \mu)} + 1}$$
(5.130)

will be a function of the chemical potential. This can be eliminated by solving (5.128) for the fugacity $\lambda = e^{\beta\mu}$. We can then obtain the energy of the system as a function of the number of particles it contains.

The fugacity $\lambda = e^{\beta\mu}$ will always become much less than one at high enough temperatures. We can then expand the the partition function (5.127) in powers of λ. As in the case of bosons we then get the virial expansion for the pressure. The leading term is given by the second virial coefficient and it turns out to be given by the same expression as for bosons (5.89) when written in terms of one-particle partition functions, but with opposite sign. Thus the pressure is larger in the fermion gas than in the ideal gas because of the effective "Pauli repulsion" between the particles because of their antisymmetric statistics. This should be contrasted with the pressure in the boson gas where the pressure is lower as shown in Fig.5.17.
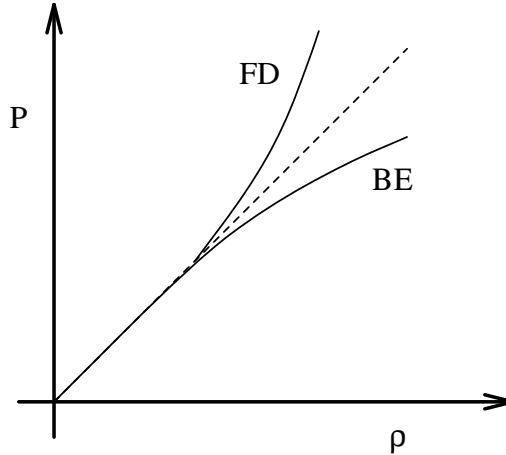

Figure 5.17: The pressure in the quantum fermion gas is larger than in the classical, ideal gas while it is smaller in the quantum boson gas.

At low temperatures the thermodynamics is governed by the chemical potential. For free bosons it must be less than the lowest one-particle energy in the system and is thus usually taken to be negative or at most zero. This gives rise to Bose-Einstein condensation. For fermions instead, there are no such restriction and the chemical potential can be positive. This will now give rise to different macroscopic quantum effects.

At exactly zero temperature we see from the Fermi-Dirac distribution (5.129) that the ground state of the system consists of having all states occupied with energies up to a maximal energy called the Fermi energy ε_F as shown in Fig.5.18. This will then also be the value of the chemical potential. One says that the gas is degenerate. From (5.130) we then obtain the ground state energy of the system as

$$E_0 = \sum_{s=0}^{F} \varepsilon_s \ .$$ (5.131)

Fermions usually have spin $S = 1/2$ and this expression must be multiplied by a spin degeneracy factor $g = 2$ since there can then be two particles in each energy level.

For the system of spinless fermions in a harmonic oscillator potential considered in the first section of this chapter, the energy levels are just $\varepsilon_n = n\hbar\omega$ and the chemical potential is determined by the equation

$$N = \sum_{n=0}^{\infty} \frac{1}{e^{\beta(n\hbar\omega-\mu)} + 1} \ .$$ (5.132)

At low temperatures where $kT < N\hbar\omega$ we then find approximately $\mu \simeq N\hbar\omega + \mathcal{O}(kT/N\hbar\omega)^2$ and the energy (5.130) becomes to leading order

$$E_0 \simeq \hbar\omega \sum_{n=0}^{N-1} n = \frac{1}{2}\hbar\omega N(N-1) \ .$$

It is just the ground state energy we found in the canonical ensemble.

In the high-temperature limit $kT > N\hbar\omega$ we see that terms in the sum (5.132) are so dense that we can replace it by the integral

$$N = \frac{kT}{\hbar\omega} \int_0^{\infty} dx \frac{\lambda}{e^x + \lambda}$$

which gives the fugacity $\lambda = e^{\hbar\omega N/kT} - 1 \simeq \hbar\omega N/kT$. We are now in the regime where Maxwell-Boltzmann statistics rule and the internal energy is to leading order

$$U = \lambda \sum_{n=0}^{\infty} n\hbar\omega\, e^{-\beta hbar\omega} \simeq \left(\frac{\hbar\omega}{kT}\right) N\hbar\omega \left(\frac{kT}{\hbar\omega}\right)^2 = NkT$$

as expected. A more accurate result valid down to lower temperatures can be obtained by using the Euler-Maclaurin summation formula for the evaluation of the fugacity.

For spin-1/2 fermions at zero energy in a 3-dimensional box of volume V the sum over momenta $\mathbf{p}$ can be done as for bosons by the phase space integral

$$2 \sum_{\mathbf{p}} = 2V \int \frac{d^3p}{(2\pi\hbar)^3} = \frac{V}{2\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} \int_0^{\infty} d\varepsilon\, \varepsilon^{\frac{1}{2}} \ .$$ (5.133)

The Landau free energy (5.127) is then given by

$$\Omega = -kT \frac{V}{2\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} \int_0^{\infty} d\varepsilon\, \varepsilon^{\frac{1}{2}} \log\left[1 + e^{-\beta(\varepsilon-\mu)}\right]$$ (5.134)
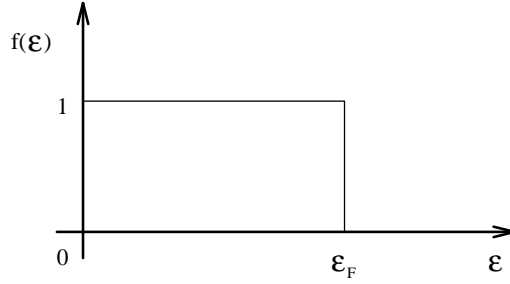
Figure 5.18: The Fermi-Dirac distribution at zero temperature. There are no occupied states above the Fermi energy.

and similarly for the internal energy (5.130) which becomes

$$U = \frac{V}{2\pi^2} \left(\frac{2m}{\hbar^2}\right)^{1/2} \int_0^\infty d\varepsilon \, \varepsilon^{\frac{1}{2}} \frac{\varepsilon}{e^{\beta(\varepsilon-\mu)} + 1} \; . \tag{5.135}$$

As for bosons, we perform in $\Omega = -PV$ a partial integration to show that the pressure also in the fermion gas is given in terms of the energy density as $P = (2/3)\mathcal{E}$.

Now at zero temperature we get from (5.128) for the total number of fermions in the gas

$$N = \frac{V}{2\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} \int_0^{\varepsilon_F} d\varepsilon \, \varepsilon^{\frac{1}{2}} = \frac{V}{3\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} \varepsilon_F^{3/2} \; .$$

Solving for the fermion energy in terms of the number density $\rho = N/V$, we find

$$\varepsilon_F = \frac{\hbar^2}{2m}(3\pi^2\rho)^{2/3} \; . \tag{5.136}$$

Writing it as $\varepsilon_F = p_F^2/2m$, we see that the particles of highest energy have the Fermi momentum $p_F = (3\pi^2\rho)^{2/3}$. For the zero-point internal energy we similarly obtain

$$E_0 = \frac{V}{2\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} \int_0^{\varepsilon_F} d\varepsilon \, \varepsilon^{\frac{3}{2}} = \frac{V}{5\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} \varepsilon_F^{5/2} \; .$$

The average energy per fermion $\bar{\varepsilon} = E_0/N$ is therefore $\bar{\varepsilon} = (3/5)\,\varepsilon_F$ at zero temperature. Correspondingly, for the energy density $\mathcal{E}_0 = E_0/V$ we see that our results are equivalent to

$$\mathcal{E}_0 = \frac{\hbar^2}{10\pi^2 m}(3\pi^2\rho)^{5/3} \; . \tag{5.137}$$

Even at zero temperature there will thus be a non-zero pressure

$$P_0 = \frac{\hbar^2}{15\pi^2 m}(3\pi^2\rho)^{5/3} \tag{5.138}$$

in the gas due to the Pauli repulsion. It is this macroscopic quantum effect which keeps degenerate stars from collapsing.

For massless fermions with spin degeneracy $g = 2$ and energy $\varepsilon = pc$ the sum over momentum eigenstates is now instead

$$2\sum_{\mathbf{p}} = 2V\int \frac{d^3p}{(2\pi\hbar)^3} = \frac{V}{\pi^2(\hbar c)^3}\int_0^\infty d\varepsilon\,\varepsilon^2 \ . \tag{5.139}$$

Partial integration of the expression for the corresponding Landau free energy gives then the pressure $P = (1/3)\mathcal{E}$ as for photons which also are massless.

At zero temperature we then obtain the Fermi energy from

$$N = \frac{V}{\pi^2(\hbar c)^3}\frac{1}{3}\varepsilon_F^3$$

which gives

$$\varepsilon_F = \hbar c(3\pi^2\rho)^{1/3} \tag{5.140}$$

when expressed in terms of the number density. The ground state energy is similarly

$$E_0 = \frac{V}{\pi^2(\hbar c)^3}\frac{1}{4}\varepsilon_F^4$$

which corresponds to an average energy $\bar{\varepsilon} = (3/4)\varepsilon_F$ per particle. The pressure then follows from the energy density

$$\mathcal{E}_0 = \frac{\hbar c}{4\pi^2}(3\pi^2\rho)^{4/3} \ . \tag{5.141}$$

We notice that it goes like $\rho^{4/3}$ for relativistic particles while it goes like $\rho^{5/3}$ for non-relativistic particles. This apparently small difference in the equations of state for these two kinds of matter have important consequences in astrophysics for the stability of stars.
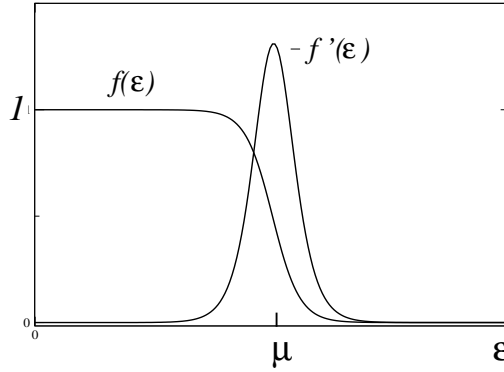

Figure 5.19: The Fermi-Dirac distribution changes rapidly in an energy interval of size $\Delta\varepsilon \simeq kT$ around the chemical potential.

When the temperature gets raised from zero, some of the particles at the Fermi level will be excited to higher states and the Fermi-Dirac distribution will get its sharp corners a little rounded as shown in Fig.5.19. In order to find the chemical potential, it must now be obtained from

$$N = \frac{V}{2\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} \int_0^\infty d\varepsilon\, \varepsilon^{\frac{1}{2}} \frac{1}{e^{\beta(\varepsilon-\mu)}+1} \qquad (5.142)$$

and then used in (5.135) to obtain the internal energy. Both of these integrals are of the general form

$$F_p = \int_0^\infty d\varepsilon\, f(\varepsilon)\phi_p(\varepsilon) \qquad (5.143)$$

where $f(\varepsilon)$ is the Fermi-Dirac distribution and

$$\phi_p(\varepsilon) = \frac{V}{2\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} \varepsilon^p \qquad (5.144)$$

where we need it for the powers $p = 1/2$ or $3/2$. A partial integral now gives

$$F_p = \Phi_p(\varepsilon)f(\varepsilon)\big|_0^\infty - \int_0^\infty d\varepsilon\, f'(\varepsilon)\Phi_p(\varepsilon)$$

where we have introduced the integrated ϕ_p-function

$$\Phi_p(\varepsilon) = \int_0^\varepsilon d\varepsilon\, \phi_p(\varepsilon) \,. \qquad (5.145)$$

The first term vanishes in both limits and we are left with

$$F_p = -\int_0^\infty d\varepsilon\, f'(\varepsilon)\Phi_p(\varepsilon) \,. \qquad (5.146)$$

Writing the Fermi-Dirac distribution as

$$f(\varepsilon) = \frac{1}{2} - \frac{1}{2}\tanh\frac{\varepsilon-\mu}{2kT} \qquad (5.147)$$

we see that the derivative

$$f'(\varepsilon) = -\frac{1}{4kT}\frac{1}{\cosh^2\frac{\varepsilon-\mu}{2kT}} \qquad (5.148)$$

at low temperatures is sharply peaked around the Fermi energy ε_F. We can therefore approximate the integral by expanding $\Phi_p(\varepsilon)$ in a Taylor series around this value,

$$\Phi_p(\varepsilon) = \Phi_p(\mu) + (\varepsilon-\mu)\Phi_p'(\mu) + \frac{1}{2}(\varepsilon-\mu)^2\Phi_p''(\mu) + \cdots .$$

We then get

$$F_p = K_0 \Phi_p(\mu) + K_1 \Phi_p'(\mu) + \frac{1}{2} K_2 \Phi_p''(\mu) + \cdots \qquad (5.149)$$

where we have introduced the simpler integrals

$$K_n = - \int_0^\infty d\varepsilon \, (\varepsilon - \mu)^n f'(\varepsilon) \,. \qquad (5.150)$$

The simplest is $K_0 = f(0) - f(\infty) = 1$. In the others we change the integration variable to $x = \beta(\varepsilon - \mu)$. Since $f'(\varepsilon)$ is essentially zero for $\varepsilon < 0$, we also extend the lower limit of integration down to $-\infty$. Then

$$K_n = (kT)^2 \int_{-\infty}^\infty dx \frac{x^n e^x}{(e^x + 1)^2} \,. \qquad (5.151)$$

Since the integrand is odd when n is odd, we get $K_n = 0$ for n odd. The lowest finite-temperature correction is given by K_2 which becomes after a partial integration

$$K_2 = (kT^2 \int_{-\infty}^\infty dx \frac{2x}{e^x + 1} = (kT)^2 \frac{\pi^2}{3} \,.$$

Including for completeness the next term, we then have

$$F_p = \Phi_p(\mu) + \frac{\pi^2}{6} (kT)^2 \Phi_p''(\mu) + \frac{7\pi^4}{360} (kT)^4 \Phi_p^{(4)}(\mu) + \cdots \qquad (5.152)$$

which is called the Sommerfeld expansion.

From the definitions (5.144) and (5.145) now follows

$$\Phi_p(\mu) = \frac{V}{2\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \frac{\mu^{p+1}}{p+1} \qquad (5.153)$$

from which $\Phi_p''(\mu)$ can be obtained directly. In the calculation of the number N of particles the exponent $p = 1/2$ which then gives

$$N = \frac{V}{3\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \mu^{\frac{3}{2}} \left[1 + \frac{\pi^2}{8} \left(\frac{kT}{\mu} \right)^2 + \cdots \right] \qquad (5.154)$$

where we only include the leading term. Similarly, the energy becomes with $p = 3/2$ as

$$U = \frac{V}{5\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \mu^{\frac{5}{2}} \left[1 + \frac{5\pi^2}{8} \left(\frac{kT}{\mu} \right)^2 + \cdots \right] \,. \qquad (5.155)$$

In the result for N we can express the density N/V in terms of the Fermi energy ε_F. Solving for the chemical potential, we then obtain

$$\mu = \varepsilon_F \left[1 + \frac{\pi^2}{8} \left(\frac{kT}{\mu} \right)^2 + \cdots \right]^{-2/3} = \varepsilon_F \left[1 - \frac{\pi^2}{12} \left(\frac{kT}{\mu} \right)^2 + \cdots \right] \qquad (5.156)$$

which is correct to this order. We see that it starts to decrease with increasing temperature. Eventually it will go negative and approach the classical value.

We can now also find the internal energy from combining the results (5.155) and (5.156). It is

$$
\begin{aligned}
U &= \frac{3}{5}N\varepsilon_F \left[1 - \frac{\pi^2}{12}\left(\frac{kT}{\mu}\right)^2 + \cdots \right]^{5/2} \left[1 + \frac{5\pi^2}{8}\left(\frac{kT}{\varepsilon_F}\right)^2 + \cdots \right] \\
&= \frac{3}{5}N\varepsilon_F \left[1 + \frac{5\pi^2}{12}\left(\frac{kT}{\varepsilon_F}\right)^2 + \cdots \right]
\end{aligned}
\tag{5.157}
$$

from which we also can find the corrections to the zero-temperature pressure. It is seen to increase with increasing temperature which happens when particles gets excited to states above the Fermi level. Since the fraction of particles which are involved in this, is kT/ε_F and each gets an increase in energy of typically kT. we should actually expect an approximate energy increase $\Delta U \approx N(kT/\varepsilon_F)kT$. It is seen to agree with the exact result we have.

We met above one of the standard fermionic integrals of the form

$$
J_p = \int_0^\infty dx \frac{x^p}{e^x + 1}
\tag{5.158}
$$

corresponding to the bosonic integral I_p in (5.44). They can be obtained from the bosonic integral

$$
\int_0^\infty dx \frac{x^p}{e^{2x} - 1} = \frac{1}{2}\int_0^\infty dx \left[\frac{1}{e^x - 1} - \frac{1}{e^x + 1} \right]
$$

which equals $I_p/2^{p+1}$. Thus we immediately have the result

$$
J_p = (1 - \frac{1}{2^p})\, I_p = (1 - \frac{1}{2^p})\, p!\,\zeta(p+1) \;.
\tag{5.159}
$$

The integral we met above was $2 \cdot 2\, J_2 = 4\,(1/2)\,(\pi^2/6) = \pi^2/3$. Similarly we get for the integral $K_4 = 2 \cdot 4\, J_3 = 8\,(1 - 1/8)\,6\,(\pi^4/90) = 7\pi^4/15$. This gives the coefficient of the third term in the Sommerfeld expansion (5.152).

From the above results we see that the size of finite-temperature corrections are determined by the quantity kT/ε_F. This makes it natural to define the Fermi temperature $T_F = \varepsilon_F/k$. It can be obtained from the density of the system. For temperatures $T \ll T_F$ we then know that the corrections to the zero-temperature results are negligible.

Taking the derivative of the internal energy with respect to the temperature, we obtain the specific heat for the gas of fermions. We can write the result as

$$
C_V = Nk\frac{\pi^2}{2}\frac{T}{T_F} \;.
\tag{5.160}
$$

It should be compared with the corresponding bosonic result which goes like T^3 at very low temperatures. The linear increase with temperature of the specific heat for ^3He has been confirmed by experiments.

5.7 Degenerate electrons in metals

We will now consider a typical metal like copper. It has atomic weight $63.5\ g/mole$ and a mass density of $9\ g/cm^3$, i.e. a number density of $\rho = 9/63.5\ mole/cm^3$. Avogadro's number is $N_A = 6.022 \times 10^{23}/mole$ so that $\rho = 8.6 \times 10^{22}/cm^3$. There is one conduction electron per copper atom so this will also be the density of electrons in the metal. From (5.136) we then obtain the Fermi energy $\varepsilon_F = 7.3\ eV$. It is of the same order of magnitude as the energies of electrons bound in atoms. Most metals have Fermi energies of this size.
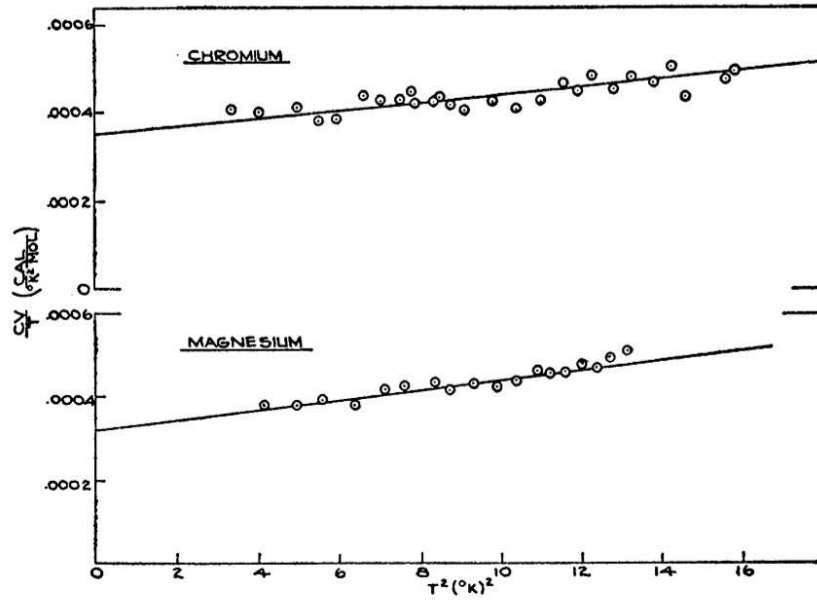

Figure 5.20: The specific heat C_V/T of a solid as function of T^2 has an intercept determined by the electrons and a slope determined by the phonons. This specific heat is measured for Chromium and Magnesium by *S. A. Friedberg, I. Estermann, and J. E. Goldman* 1951.

It is now convenient to convert the Boltzmann constant $k = 1.381 \times 10^{-23}\ J/K$ to more appropriate units where $k = 8.617 \times 10^{-5}\ eV/K$. Then we see that $1\ eV$ is equivalent to $11605\ K$ degrees. The Fermi temperature for copper is thus $T_F = 85000\ K$. At room temperature $T = 300\ K$ and below we will the have $T/T_F \ll 1$ and the electrons are very degenerate. Copper will melt long before it reaches its Fermi temperature.

The small finite-temperature corrections can be seen in the specific heat for copper. From (5.160) we see that the electrons will give a contribution of the order of 1dominated by the contribution from the lattice vibrations which we have calculated in the Debye approximation. The small, electronic contribution can however be seen at very low temperatures. Writing the specific for the metal

as $C_V = aT + bT^3$ where the first terms comes from the electrons and the latter from phonons, we see that when C_V/T is plotted against T^2, one should obtain a straight line as shown in Fig.5.20. It is slope given by the constant b which is obtained from Bose-Einstein statistics and an intercept which follows from Fermi-Dirac statistics. By extrapolating the line to $T = 0$ one can measure the intercept and thus determine the Fermi temperature for the metal.

5.8   White dwarfs and neutron stars

When a star has exhausted its nuclear fuel which keeps it at a temperature T, the radiation pressure going like T^4 is no longer sufficient to stand against the gravitational force trying to pull it together. If its mass is not much larger than the solar mass $M_\odot = 1.99 \times 10^{33} \, g$, it will then collapse to a white dwarf star with a radius much smaller than the solar radius $R_\odot = 696\,000 \, km$ and with an internal pressure now due to degenerate electrons.

The best known white dwarf is Sirius B which is a companion to the nearby star Sirius. It has a radius of $R = 5300 \, km$ and a mass of $M = 1.05 M_\odot$. Its density is thus very large. If $m_N = 1.67 \times 10^{-24} \, g$ is the mass of a proton, it contains $N_B = M/m_N = 1.25 \times 10^{57}$ nucleons. There will be approximately two nucleons per electron and assuming a constant density, we then have an electron density $n_e = (N_B/2)/(4\pi R^3/3) = 1.0 \times 10^{30} \, cm^{-3}$. We will in this section denote the mass density by ρ. It corresponds to a Fermi energy of

$$\varepsilon_F = \frac{\hbar^2}{2m_e}(3\pi^2 n_e)^{2/3} = 5.9 \times 10^{-14} \, J = 0.37 \; MeV$$

and hence a Fermi temperature of $T_F = 4.3 \times 10^9 \; K$. The temperatures in white dwarfs are typically of the order of $10^7 \; K$ or less so that we can safely neglect all finite-temperature corrections for degenerate electron gas.

We will try to estimate the mass and radius of such a degenerate star, again assuming that the density and hence also the pressure is constant. When the star is in equilibrium, we must have that the pressure from the electrons balance the inward force per unit area due to gravity. The electronic pressure in the non-relativistic case is $2/3$ of the energy density (5.137), i.e.

$$P_{NR} = \frac{\hbar^2}{15\pi^2 m_e}(3\pi^2 n_e)^{5/3} \; . \tag{5.161}$$

Since the mass density is $\rho = 3M/4\pi R^3$, we will now take $n_e = \rho/m_N$ since the calculation will just be approximate anyhow. Thus we find

$$P_{NR} = \frac{3\hbar^2}{20\pi m_e}\left(\frac{9\pi}{4}\right)^{2/3}\left(\frac{M}{m_N}\right)^{5/3} R^{-5} \; . \tag{5.162}$$

We can obtain the pressure from the gravitational energy U_G. If we define

$$m(r) = \int_0^r d^3 r \rho = \frac{4}{3}\pi\rho r^3 \tag{5.163}$$

as the mass inside a radius r, then we have the potential energy

$$\Delta U_G = -\frac{Gm(r)}{r}\, 4\pi\rho r^2 \Delta r$$

of a radial shell of thickness Δr. Integrating this up from $r = 0$ to $r = R$ gives

$$U_G = -\frac{16}{15}G\rho^2\pi^2 R^5 = -\frac{3}{5}\frac{GM}{R}\ . \tag{5.164}$$

The inward, gravitational pressure is then

$$\begin{aligned}
P_G &= -\frac{\partial U_G}{\partial V} = -\frac{1}{4\pi R^2}\frac{dU_G}{dR}\\
&= \frac{4\pi}{3}G\rho^2 R^2 = \frac{3G}{4\pi}\frac{M^2}{R^4}\ .
\end{aligned} \tag{5.165}$$

Setting this equal to the electronic pressure, we get the relation

$$R = \frac{1}{5}\left(\frac{9\pi}{4}\right)^{2/3}\frac{\hbar^2}{Gm_e m_N^2}\left(\frac{m_N}{M}\right)^{1/3}\ . \tag{5.166}$$

It shows the surprising result that the larger the mass is, the smaller the radius of the star will be. This means increasing densities and the electrons will eventually be relativistic when the mass of the star is sufficiently large. In the extreme relativistic limit we can ignore the mass of the electrons. Their pressure is then follows as $1/3$ of the energy density (5.141),

$$P_{ER} = \frac{\hbar c}{12\pi^2}(3\pi^2 n_e)^{4/3}\ . \tag{5.167}$$

Expressing the electronic density is terms of the mass density and equating this pressure to the gravitational pressure (5.165), we see that the radius now cancels out. The mass of the degenerate star in this extreme limit becomes

$$M = \frac{3\sqrt{\pi}}{16}m_N\left(\frac{\hbar c}{Gm_N^2}\right)^{3/2}\ . \tag{5.168}$$

Its size is given by the nucleon mass and the dimensionless number

$$\frac{\hbar c}{Gm_N^2} = 1.71 \times 10^{38}\ . \tag{5.169}$$

Inserting the above value for m_N, we find that the limiting mass is $M = 1.8\,M_\odot$ when we neglect the numerical constant in front. It is roughly of the same size as the mass of Sirius B. No white dwarfs have been found with larger masses. So in this sense we can say that our model calculation is surprisingly good.

From (5.166) we can now also estimate the size of such a degenerate star as long as the electrons are non-relativistic electrons. Dropping again the numerical constant in front, we then find with our result for M/m_N a value $R = 5100\,km$

which also is very good. We would expect the radius to be smaller for a relativistic star.

We can relate the number (5.169) to the ratio of the electric $F_E = -e^2/4\pi\epsilon_0 r^2$ and the gravitational force $F_G = -Gm_N^2/r^3$ between a proton and an anti-proton. Then

$$\frac{\hbar c}{Gm_N^2} = \left(\frac{4\pi\epsilon_0\hbar c}{e^2}\right)\frac{F_E}{F_G} \ .$$

The dimensionless number in front is the inverse fine-structure constant $\alpha = e^2/4\pi\epsilon_0\hbar c = 1/137$ used in atomic physics and quantum electrodynamics. Thus we have $F_E/F_G = 137 \times 1.71 \times 10^{38} = 2.34 \times 10^{40}$.

One can make the calculation much more realistic by giving up the main assumption about the density being constant in the star. It will actually vary from a very high value in the center of the star to almost zero at the surface. This implies that the Fermi energy will also vary with the distance from the center and thus also the pressure. One can then formulate the stability problem as two coupled differential equations which in general can be solved numerically. Different stars are then parameterized my the value of the density in the center. When this goes to infinity, the mass of the star does not diverge, but approaches a limiting value $M = 1.4\,M_\odot$. It was first discovered by S. Chandrasekhar in 1931.

An initial star with a mass somewhat higher than the Chandrasekhar mass can get rid of the excess through nova explosions and end up as a white dwarf. If the initial mass is much higher, the star will become a supernova with a remnant which is a neutron star. It consists purely of neutrons since electrons have combined with the protons. They stabilize the star by the same mechanism as in a white dwarf. By the same arguments we can then conclude that there also is an upper limit of the order of $M_\odot$ for the mass of a neutron star. The radius, however, will be much smaller because it is now set by the neutron mass and not by the electron mass as is seen from (5.166). Since $m_N/m_e = 1838$, we expect the typical radii of neutron stars to be a few kilometers. Neutron stars are primarily observed as pulsars and have these characteristic sizes.

If the the mass of the initial star is even higher, the neutron pressure is not strong enough to prevent the collapse and it will end up as a black hole with a size given by the Scwarzschild radius $R = 2GM/c^2$ where M is the mass of the hole. S. Hawking discovered in 1973 that quantum effects make the black hole into a black body with temperature $T = \hbar c^3/8\pi GM$. According to the Stefan-Boltzmann law, it will thus radiate energy by an amount $4\pi R^2\sigma T^4 \propto M^{-2}$. There are yet no observations to confirm the existence of this Hawking radiation.

Chapter 6

Magnetic Systems and Spin Models

Statistical mechanics was historically developed to gain a microscopic understanding of the physical properties of gases and liquids. With the introduction of quantum mechanics this goal was to a large extent achieved. But there was one area which for a long time defeated all attempts by conventional statistical mechanics to reveal its inner secrets. This was second order phase transitions and the critical exponents. In many ways these were easier to study in magnetic materials than in the gas/liquid systems. With Onsager's exact solution of the 2-dimensional Ising model one also had for the first time a detailed theoretical prediction for the behaviour of a ferromagnetic system near the critical point. But it was first in the last twenty years with the introduction of the renormalization group that one obtained a complete understanding of critical systems in general. The concepts and insight gained from the study of magnetic systems permeates today many other branches of modern physics.

6.1 Thermodynamics of magnets

The First Law of a thermodynamical system was established in Chapter 1 and can be formulated as in (1.5). It involves the work ΔW the system can perform. For a magnetic system it can be found from considering a piece of material in an external, magnetic field created by many windings of a current-carrying wire as shown in Fig.6.1. When we turn on the battery, a current I will go through the wire. It creates a magnetic field which will be constant in the material when the solenoid is long and thin. If the total number of windings is N, the magnitude of the field is

$$H = \frac{NI}{L} \tag{6.1}$$

where L is the length of the solenoid.

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When the magnetic flux Φ through the solenoid is changing, it will generate an electromotive force $\mathcal{E} = -\partial\Phi/\partial t$. The work done by the battery in a short
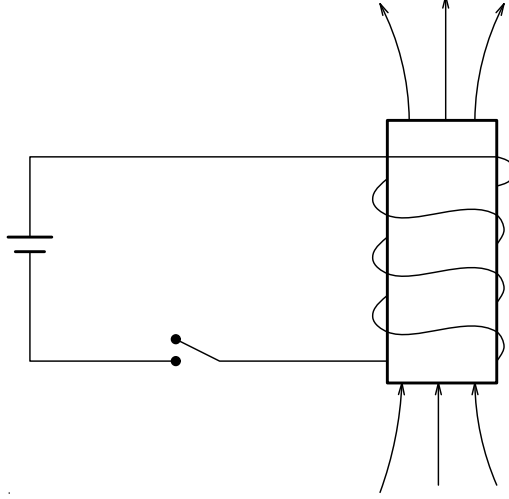

Figure 6.1: Magnetization of material by external current.

time interval Δt is therefore

$$\Delta W_b = \mathcal{E}I\Delta t = I\Delta\Phi \ . \tag{6.2}$$

Since the total flux is $\Phi = NBA$ where A is the cross-sectional area of the solenoid and B the magnetic induction, we can write the work as

$$\Delta W_b = VH\Delta B \tag{6.3}$$

when if express the current I in terms of the magnetic field (6.1) and introduce the volume $V = AL$ of the material in the solenoid. Using now the general relation

$$\mathbf{B} = \mu_0(\mathbf{H} + \mathbf{M}) \tag{6.4}$$

expressing the magnetic induction $\mathbf{B}$ in terms of the external field $\mathbf{H}$ and the magnetization $\mathbf{M}$, we finally have for the work done by the battery

$$\begin{aligned} \Delta W_b &= V\mu_0 H(\Delta H + \Delta|\mathbf{M}|) \\ &= V\Delta(\frac{1}{2}\mu_0 H^2) + V\mu_0\, H\Delta|\mathbf{M}| \end{aligned} \tag{6.5}$$

The first part is the increase of the energy in the magnetic field and would also be the same in the absence of the material. The last term represents the magnetic work done by the field on the material. We know that it contains

many microscopic or atomic magnets and work has to be performed in aligning them with the external field. This work is equal and opposite to the magnetic work done by the material which is therefore

$$\Delta W_m = -V \mu_0 \, H \Delta |\mathbf{M}| \ . \tag{6.6}$$

It is this term we will need in the First Law for a magnetic system.

At this stage it is convenient to change the notation a bit. In (6.4) the magnetization $\mathbf{M}$ is really the magnetic moment density, i.e. an intensive quantity. When it is multiplied with the volume V in (6.6), it gives the total magnetization of the material. We will in the following denote this extensive quantity by the symbol M. In addition, we will denote the magnetic induction $\mu_0 H$ of the external field by B. This relabeling of variables will in the following not cause any difficulties.

In this new notation (6.6) can be written as

$$\Delta W = -B \, \Delta M \ . \tag{6.7}$$

The differential form of the First Law (1.9) takes then the form

$$dU = TdS + BdM \tag{6.8}$$

when we replace the gas work $dW = PdV$ with the magnetic work $dW = -BdM$. Both P and B are intensive while the variables V and M are extensive. It follows that

$$T = \left(\frac{\partial U}{\partial S}\right)_M \qquad B = \left(\frac{\partial U}{\partial M}\right)_S \tag{6.9}$$

and we can establish new Maxwell relations exactly as in Chapter 1 for the gas-liquid system.

We can now by analogy also write down all the thermodynamic potentials. While the internal energy is $U = U(S, M)$, the enthalpy

$$H(S, B) = U - BM \tag{6.10}$$

is a function of the external field. The last term represents the interaction energy of the total magnetization of the system with the field. By a corresponding Legendre transformation one obtains the Helmholtz free energy as

$$F(T, M) = U - TS \ . \tag{6.11}$$

Using (6.8) we have the differential version

$$dF = -SdT + BdM \tag{6.12}$$

with

$$S = -\left(\frac{\partial F}{\partial T}\right)_M \qquad B = \left(\frac{\partial F}{\partial M}\right)_T \ . \tag{6.13}$$

Performing the similar Legendre tramsformation on the enthalpy (6.10), one finds the Gibbs free energy

$$G(T, B) = H - TS \tag{6.14}$$

with

$$dG = -SdT - MdB \tag{6.15}$$

which gives

$$S = -\left(\frac{\partial G}{\partial T}\right)_B \qquad M = -\left(\frac{\partial G}{\partial B}\right)_T \tag{6.16}$$

by inspection.

In all these relations the magnetization M is the component along the external field $\mathbf{B}$. But the work term (6.7) is really $dW = -\mathbf{B} \cdot d\mathbf{M}$ and we should have kept the thermodynamic variables as vector quantities throughout. Some of the thermodynamic derivatives would then be vector derivatives. The equation for the total magnetization in (6.16) would for example be replaced by

$$M_i = -\left(\frac{\partial G}{\partial B_i}\right)_T \tag{6.17}$$

for the component in the i-th direction where now $G = G(T, \mathbf{B})$.

The change in magnetization with respect to a change in the magnetic field is measured by the the susceptibility. When the magnetization is along the field it is

$$\chi = \left(\frac{\partial M}{\partial B}\right)_T \tag{6.18}$$

as first used in (6.14). But in the more general case it measures the response of the magnetization in the i-th direction with respect to a change in the magnetic field in the j-th direction, i.e.

$$\chi_{ij} = \left(\frac{\partial M_i}{\partial B_j}\right)_T = \left(\frac{\partial^2 G}{\partial B_i \partial B_j}\right)_T . \tag{6.19}$$

It is then a symmetric tensor. However, in most cases the magnetization will be completely along the external field and there will be no need for this generalization.

A complete undewrstanding of the magnetic properties of a system can only come from quantum mechanics. For the simplest case of one electron with electric charge e in a magnetic field $\mathbf{B} = \boldsymbol{\nabla} \times \mathbf{A}$, the Hamiltonian is

$$\widehat{H} = \frac{1}{2m}(\widehat{\mathbf{p}} - e\mathbf{A})^2 - \mu_B \, \widehat{\boldsymbol{\sigma}} \cdot \mathbf{B} \tag{6.20}$$

where $\mu_B = e\hbar/2m$ is a Bohr magneton and $\widehat{\boldsymbol{\sigma}} = (\widehat{\sigma}_x, \widehat{\sigma}_y, \widehat{\sigma}_z)$ is the Pauli spin vector. The eigenvalues of this operator gives the allowed energies for the particle. They will depend on the value of the external field B.

In the general case the magnetic system will have energy eigenvalues $E_s = E_s(B)$ where the quantum number s denotes the corresponding quantum state. The partition function will then give the Gibbs free energy,

$$Z(T, B) = \sum_s e^{-\beta E_s(B)} = e^{-\beta G(T,B)} \tag{6.21}$$

since the energy eigenvalues depends on the magnetic field. This is to be expected since the one-particle Hamiltonian (6.20) describes both the internal effects of the field plus the external coupling via the magnetic moment. The average energy is therefore not the internal energy of the system, but its enthalpy

$$\begin{aligned} H &= \langle E(B) \rangle \\ &= \frac{1}{Z} \sum_s E_s(B)\, e^{-\beta E_s(B)} = -\frac{\partial}{\partial \beta} \log Z \end{aligned} \tag{6.22}$$

We have already seen an example of this in (6.17) where the average energy of one particle is just the average magnetic moment times the field. This is in agreement with (6.10) for the case when the internal energy is zero.

The response of the enthalpy with respect to changes in the temperatures,

$$C_B = \left(\frac{\partial H}{\partial T} \right)_B \tag{6.23}$$

is the specific heat at constant external field in analogy with the constant-pressure specific heat C_P in (1.22) for the gas-liquid system. It will be calculated for several different systems in the following.

6.2 Magnetism

Magnetic materials were historically divided into three classes according to their behaviour in a magnetic field. A piece of material which was attracted to a magnetic field, was called paramagnetic. On the other hand, if it was repelled, it was said to be diamagnetic. Some paramagnetic materials even turned into permanent magnets themselves in external magnetic fields. When they were heated up, the induced magnetic moment went away. This very special and important class is called ferromagnetic.

For weak, external field, the induced magnetic moment in the material is $\mathbf{M} = \chi \mathbf{B}$. The interaction energy $U_B = -\mathbf{M} \cdot \mathbf{B}$ will therefore be lowered when a material with positive susceptibility moves into stronger fields. A paramagnetic material has therefore $\chi > 0$. Ferromagnets also have positive susceptibilities which become very large near the phase transition to the non-magnetic state. Similarly, diamagnetic materials have $\chi < 0$.

Both paramagnetic and diamagnetic behaviour follow from the simple Hamiltonian (6.20). In a constant magnetic field, the vector potential is $\mathbf{A} = \frac{1}{2}\mathbf{B} \times \mathbf{r}$ which satisfies $\boldsymbol{\nabla} \cdot \mathbf{A} = 0$. Inserting this, we can rewrite the Hamiltonian as

$$\widehat{H} = \frac{1}{2m}\widehat{\mathbf{p}}^2 + \frac{e^2}{8m}(\widehat{x}^2 + \widehat{y}^2)\,B^2 - \mu_B\,(2\widehat{\mathbf{S}} + \widehat{\mathbf{L}}) \cdot \mathbf{B} \tag{6.24}$$

when we measure spins in units of $\hbar$ and take the magnetic field along the z-axis. The angular momentum operator is therefore $\widehat{\mathbf{L}} = \widehat{\mathbf{r}} \times \widehat{\mathbf{p}}/\hbar$ and the spin $\widehat{\mathbf{S}} = \frac{1}{2}\widehat{\boldsymbol{\sigma}}$. The first term is the kinetic energy of the electron in the absence of external fields. When the field is turned on, the particle will change its motion in the orbit to counteract the field according to Lenz's law. This change in the energy is described by the second term in the Hamiltonian. Since it is positive and increases with the square of the field, it will give a negative susceptibility typical of diamagnetic behaviour.

Paramagnetism is due to the third term in the Hamiltonian (6.24). For weak fields it gives a contribution to the energy which can be obtained from the effective Hamiltonian

$$\widehat{H} = -\widehat{\mathbf{m}} \cdot \mathbf{B} \tag{6.25}$$

where the magnetic moment operator is

$$\widehat{\mathbf{m}} = g\mu_B\,\widehat{\mathbf{J}}\,. \tag{6.26}$$

It depends on the total spin angular momentum operator

$$\widehat{\mathbf{J}} = \widehat{\mathbf{S}} + \widehat{\mathbf{L}} \tag{6.27}$$

and Lande's g-factor which is a function of the quantum numbers L, S and J. An electron with $L = 0$ has $g = 2$.

In many paramagnetic crystals the interaction between the magnetic moments on different atoms or ions is very weak. When such a material is placed in a magnetic field, each atom gives a contribution to the energy which follows from (6.25) and (6.26). With the B-field along the z-axis, the energy eigenvalues are

$$\varepsilon_m = -g\mu_B\,Bm \tag{6.28}$$

where $m = -J, -J+1, \cdots, J-1, J$ are the possible values of the spin projection operator $\widehat{J}_z$. The free energy follows from the partition function

$$Z = \sum_{m=-J}^{J} e^{\beta g\mu_B Bm} = e^{-\beta G}\,. \tag{6.29}$$

This is a geometric series

$$Z = a^{-J} + a^{-J+1} + \cdots + a^J$$

with $a = e^{x/J}$ and $x = \beta g\mu_B BJ$. Since $aZ = Z - a^{-J} + a^{J+1}$, we have

$$Z = \frac{a^{J+1} - a^{-J}}{a - 1} = \frac{\sinh \frac{2J+1}{2J} x}{\sinh \frac{x}{2J}} \ .$$ (6.30)

From the Gibbs free energy $G = -kT \log Z$ now follows the magnetization with the use of (6.16). In this way we obtain the magnetization from one atom or ion. The result can be written as

$$m = \langle \widehat{m}_z \rangle = -\frac{\partial G}{\partial B} = g\mu_B J B_J(x)$$ (6.31)

where

$$B_J(x) = \frac{2J+1}{2J} \coth \frac{2J+1}{2J} x - \frac{1}{2J} \coth \frac{x}{2J}$$ (6.32)

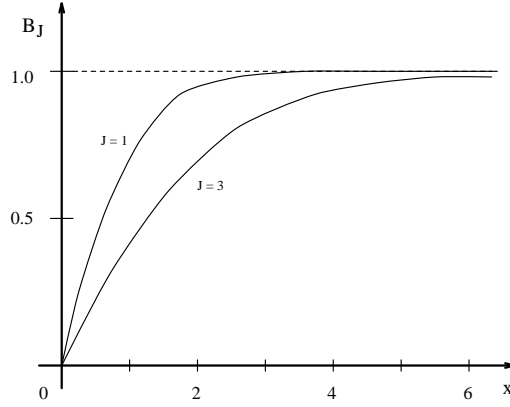is known as the Brillouin function. It is plotted in Fig.6.2 for several values of

Figure 6.2: Scetch of the Brillouin function for two different values of the spin J.

the spin quantum number J. For small values of x it increases linearly,

$$B_J(x) = \frac{J+1}{3J} x + \mathcal{O}(x^3)$$ (6.33)

as follows from the expansion $\coth x = 1/x + x/3 + \mathcal{O}(x^3)$. When the argument is large, it approaches one for all values of J. In very strong fields the magnetic moment gets completely aligned with the field and attains it maximum value $\mu = g\mu_B J$.

When the spin J is very large the Brillouin function becomes

$$B_J(x)|_{J \gg 1} = L(x) = \coth x - \frac{1}{x}$$ (6.34)

when x is kept finite. This limiting expression is called the Langevin function and is the result for the magnetization in the classical limit.

The classical energy of a magnetic moment $\boldsymbol{\mu}$ in a magnetic field is $E = -\boldsymbol{\mu} \cdot \mathbf{B}$. It gives rise to the classical partition

$$Z = \int_0^{2\pi} d\phi \int_0^{\pi} d\theta \sin\theta \, e^{\beta\mu B \cos\theta} = 4\pi \frac{\sinh\beta\mu B}{\beta\mu B} \tag{6.35}$$

when we measure the polar angle θ from the direction of $\mathbf{B}$. The same result is obtained if we for large J replace the summation in (6.29) with an integration. Calculating now the magnetization from the corresponding free energy, we find

$$m = \mu L(\beta\mu B) \tag{6.36}$$

where $L(x)$ is the Langevin function (6.34). It has the same general shape as the Brillouin function in Fig.6.2.
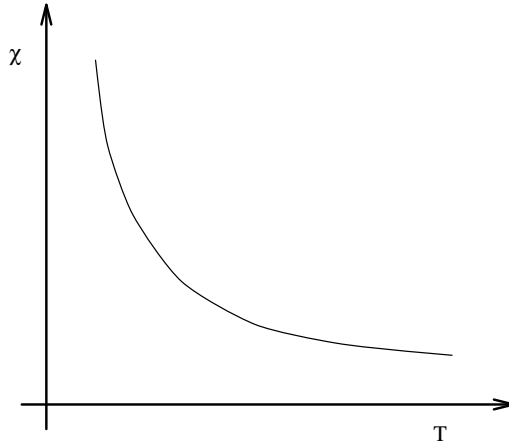

Figure 6.3: Variation of the susceptibility with the temperature T for a paramagnetic material.

In the other limit when the spin $J = 1/2$ the Brillouin function simplifies to

$$\begin{aligned} B_{\frac{1}{2}}(x) &= 2\coth 2x - \coth x \tag{6.37} \\ &= \frac{1 + \coth^2 x}{\coth x} - \coth x = \tanh x \tag{6.38} \end{aligned}$$

and the magnetization becomes $m = \mu_B \tanh\beta\mu_B B$ since $g = 2$. This agrees with what we already in (6.21) obtained for spin-1/2 particles in a magnetic field.

The Brillouin function in Fig.6.2 changes from the linear regime to the asymptotic regime for $x \approx J$, i.e. when $g\mu_B B \approx kT$. Since the Bohr magneton is $\mu_B = 9.274 \times 10^{-24}\, JT^{-1}$. Taking $g = 1$ this corresponds to a field of the order $B = 450\, T$ at room temperature $T = 300\, K$ and $B = 1.5\, T$ when
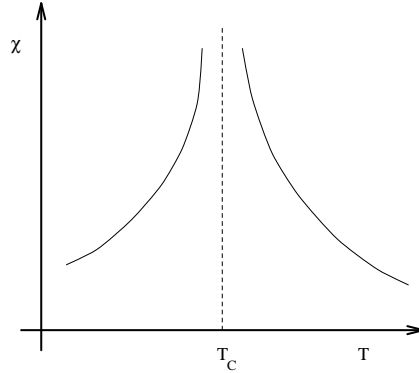
Figure 6.4: The susceptibility diverges at the critical temperature T_c for a ferromagnetic material.

$T = 1\,K$. Remember that all magnetic fields above a few Teslas are very strong. So except for very low temperatures, we will be in the linear regime where we can approximate the Brillouin function with (6.33). The magnetization (6.31) varies then linearly with the magnetic field giving the susceptibilty

$$\chi = \frac{g^2\mu_B^2 J(J+1)}{3kT} \; . \tag{6.39}$$

It decreases at higher temperatures as shown in Fig.6.3 in agreement with the experimentally established Curie's law $\chi = C/T$. This also follows from the classical result (6.36) giving $\chi = \mu^2/3kT$. Comparing with (6.39) we find for the classical magnetic moment $\mu = g\mu_B\sqrt{J(J+1)}$.

A similar behaviour of the susceptibilty is also seen in ferromagnets at very high temperatures when they no longer have any permanent magnetization. It is then approximately given by the Curie-Weiss law

$$\chi = \frac{C}{T - T_C} \tag{6.40}$$

where T_C is the Curie temperature. When $T < T_C$ the induced magnetization becomes permanent. More accurate measurements reveal that the susceptibility varies like

$$\chi \propto |T - T_c|^{-\gamma} \tag{6.41}$$

where the critical temperature T_c is slightly below the Curie temperature T_C as shown in Fig.6.4. It diverges when the temperature approaches T_c. The value of this critical exponent is found to be around $\gamma = 1.4$. Both this qualitative behaviour of the susceptibilty and the value of γ is very similar to what we found in Chapter 2 for the gas-liquid critical transition.

At the critical temperature and in zero magnetic field it is also found that the specific heat C_B diverges like

$$C_B \propto |T - T_c|^{-\alpha} \; . \tag{6.42}$$

When the critical exponent $\alpha > 0$, it has a variation with temperature of the same form as the susceptibility in Fig.6.4. For most magnets α has a value near zero.
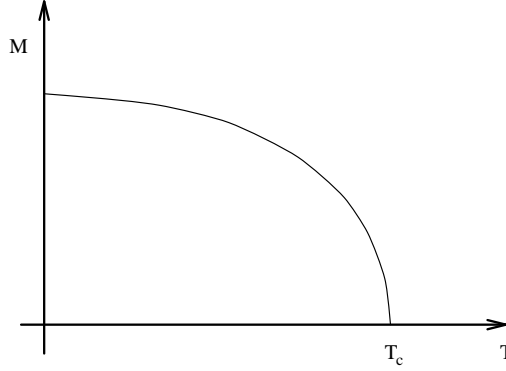

Figure 6.5: Magnetization is zero above the temperature T_c for a ferromagnetic material.

In zero external field the magnetization varies with the temperature as shown in Fig.6.5. When the ferromagnetic material is cooled down from temperatures $T > T_c$, where the magnetization is zero, it suddenly develops a spontaneous magnetization when T goes through the critical temperature. The resulting magnetization can be positive or negative, depending on local conditions in the experiment. For temperatures near T_c it is found to vary as

$$M \propto \begin{cases} (T_c - T)^\beta, & T < T_c \\ 0, & T > T_c \end{cases} \tag{6.43}$$

where the new critical exponent is found to be near $\beta = 0.35$ which is very close to the corresponding exponent in the gas-liquid transition.

Neutron scattering experiments reveal that the atomic spins are strongly ordered over long distances when a ferromagnet is below the critical temperature. They point roughly in the same directions and thereby create a macroscopically observable magnetization. On the other hand, in antiferromagnets the spins are also ordered but in opposite directions so to give no net observable magnetization. Antiferromagnets are much more theoretically interesting than practically useful.

6.3 Models of magnetic systems

The atomic magnets or spins in a paramagnet are so weakly coupled to each other that when the external magnetic field is turned off, they cease to be aligned by thermal fluctuations and there is no longer any macroscopic magnetization. On the other hand, in a ferromagnet there must be strong forces between the spins which keep the spins ordered as long as the temperature is below T_c.

The force aligning the spins can not be an ordinary dipole interaction between the atomic magnets. Two such magnets separated by the distance r have an interaction energy of

$$U = \frac{\mu_0}{4\pi r^3} \left[\mathbf{m}_1 \cdot \mathbf{m}_2 - (\mathbf{m}_1 \cdot \mathbf{n})(\mathbf{m}_2 \cdot \mathbf{n}) \right] \tag{6.44}$$

where $\mathbf{n} = \mathbf{r}/r$. Taking for the atomic magnetic moment $m = \mu_B$, we find for a typical separation of $r = 2\,\mathring{A}$ that $U \approx \mu_0 \mu_B^2 4\pi/r^3 \approx 10^{-24}\,J$ which is $5 \times 10^{-6}\,eV$. When kT exceeds this energy, i.e. $T > 0.1\,K$, the thermal fluctuations will dominate over the ordering force and there will be no alignment of the magnets. But ferromagnets exhibit permanent magnetization up to typical critical temperatures between $100\,K$ and $1000\,K$. THus the spin interaction must be more than a thousand times stronger and cannot be of magnetic origin.

The explanation was found from quantum mechanics by Heisenberg and is due to the indistinguishability of the electrons. To illustrate the effect, consider two electrons moving in the potential of two nearby ions and having no explicit spin interactions. Their wave function can then be taken to be the symmetric combination

$$\psi_s(\mathbf{r}_1, \mathbf{r}_2) = \phi_1(\mathbf{r}_1)\,\phi_2(\mathbf{r}_2) + \phi_1(\mathbf{r}_2)\,\phi_2(\mathbf{r}_1) \tag{6.45}$$

where $\phi_i(\mathbf{r})$ is the wave function of one electron in the potential from ion i. The combined wave function ψ_s is non-zero in the middle between the two ions. Both electrons have then a finite probability to be found there and their negative charges will bind the two positively charged ions. Since the total wave function of the two electrons must be antisymmetic, it means that their spin wave function must be antisymmetric since the orbital part (6.45) is symmetric. They will therefore form a spin singlet

$$\chi_0 = \sqrt{\frac{1}{2}}\, \left[\uparrow\downarrow - \downarrow\uparrow \right]. \tag{6.46}$$

But even if this singlet state binds the ions together, it gets a higher energy from the Coulomb repulsion between the electrons when they are near each other in the region between the ions. In order to reduce this energy, one must also consider the antisymmetric wave function

$$\psi_s(\mathbf{r}_1, \mathbf{r}_2) = \phi_1(\mathbf{r}_1)\,\phi_2(\mathbf{r}_2) - \phi_1(\mathbf{r}_2)\,\phi_2(\mathbf{r}_1) \tag{6.47}$$

which has zero probability for the electrons to be found simultaneously in the middle between the ions. This orbital wave function must now be combined with one of the symmetric triplet spin wave functions

$$\chi_1 = \begin{cases} \uparrow\uparrow & S_z = +1 \\ \sqrt{\frac{1}{2}}\,[\uparrow\downarrow + \downarrow\uparrow] & S_z = 0 \\ \downarrow\downarrow & S_z = -1 \end{cases} \tag{6.48}$$

in order to give again a totally antisymmetric wave function for both electrons. Which of the two states, the singlet with total spin $S = 0$ or the triplet with

$S = 1$, gives the lowest energy for the combined system can now only be decided by a detailed quantum mechanical calculation based on the explicit form of the two orbital wave functions (6.45) and (6.47).

The total spin of the two electrons is given by the operator $\widehat{\mathbf{S}} = \widehat{\mathbf{S}}_1 + \widehat{\mathbf{S}}_2$. Since both of the operators $\widehat{\mathbf{S}}_1^2$ and $\widehat{\mathbf{S}}_2^2$ have the eigenvalues 3/4, we find that the singlet and triplet states are characterized by the the operator

$$\widehat{\mathbf{S}}_1 \cdot \widehat{\mathbf{S}}_2 = \begin{cases} -\frac{3}{4}, & S = 0 \\ +\frac{1}{4}, & S = 1 \end{cases} . \tag{6.49}$$

It can be used to describe the energy difference between these two states by the effective Heisenberg Hamiltonian

$$\widehat{H} = -J\,\widehat{\mathbf{S}}_1 \cdot \widehat{\mathbf{S}}_2 . \tag{6.50}$$

When the so-called exchange constant J, which can be calculated from the knowledge of the atomic wave functions, is positive, the spins prefer to align in a triplet state. If it is negative, the spins form a singlet and are paired in opposite directioons as in an antiferromagnet. Its magnitude is set by the Coulomb interaction between two electrons in a solid which is of the order $1\,eV$. This coupling is therefore strong enough to explain the high transition temperatures in ferromagnets.

The Heisenberg Hamiltonian (6.50) can be generalized to describe the interaction between all the spins in a crystal lattice coupled together by electron exhange. If the spin operator at lattice site $\mathbf{x}$ is $\widehat{\mathbf{S}}_{\mathbf{x}}$ as in Fig.**??**, the Hamiltonian can be written as

$$\widehat{H} = -J\sum_{<\mathbf{x},\mathbf{x}'>} \widehat{\mathbf{S}}_{\mathbf{x}} \cdot \widehat{\mathbf{S}}_{\mathbf{x}'} - \mu \sum_{\mathbf{x}} \mathbf{B}_{\mathbf{x}} \cdot \widehat{\mathbf{S}}_{\mathbf{x}} \tag{6.51}$$

where we have assumed that only nearest neighbour spins are interacting as indicated by the bracket in the first sum. We have here also included the coupling to an external magnetic field $\mathbf{B}_{\mathbf{x}}$ through the magnetic moment operator as in (6.25). In general there could be also couplings to spins with larger separations. The spin operator $\widehat{\mathbf{S}}_{\mathbf{x}}$ is now supposed to be the total spin angular momentum operator for all the electrons in the atom or ion at site $\mathbf{x}$. It was denoted by $\widehat{\mathbf{J}}$ in (6.27). When the exchange constant J is positive, the Hamiltonian will describe spins which will tend to align and we have a model for a ferromagnet. On the other hand, when $J < 0$ the Hamiltonian gives a model for an antiferromagnet.

The variables in the quantum Heisenberg model are the operators $\widehat{\mathbf{S}}_{\mathbf{x}} = (\widehat{S}_{\mathbf{x}x}, \widehat{S}_{\mathbf{x}y}, \widehat{S}_{\mathbf{x}z})$ with the standard spin commutator

$$[\widehat{S}_{\mathbf{x}x}, \widehat{S}_{\mathbf{x}'y}] = i\delta_{\mathbf{x}\mathbf{x}'}\widehat{S}_{\mathbf{x}z} . \tag{6.52}$$

In order to investigate the detailed, magnetic properties of the model, we need to find the energy eigenvalues of the Hamiltonian. Because of these non-commuting spin operators, this is in general extremely difficult or impossible for macroscopic systems. Only the ground state and the first excitations in the 1-dimensional Heisenberg model with spin $S = 1/2$ have been obtained exactly. In this model the spins are all situated along a chain.

6.4 The Ising model and spin correlation functions

In the Ising the spins can only be in two directions which are usually said to be up or down respectively. The Hamiltonian (6.51) can then be written as

$$H = -J \sum_{<\mathbf{x},\mathbf{x}'>} \sigma_{\mathbf{x}} \sigma_{\mathbf{x}'} - \sum_{\mathbf{x}} B_{\mathbf{x}} \sigma_{\mathbf{x}} \tag{6.53}$$

where $\sigma = \pm$ are called Ising spins. Here is also the coupling to an external field $B_{\mathbf{x}}$ which in general can vary over the different lattice sites. We could have included an explicit magnetic moment, but it is now convenient to take it to be $\mu = 1$ since its magnitude is irrelevant.

The model was invented by Lenz before the Heisenberg model was established. Ising was Lenz's student and was asked to investigate the model. He was able to calculate the partition function exactly in the special case when the spins where on a chain, i.e. in $d = 1$ dimensions. Lars Onsager solved the much more difficult case in $d = 2$ dimensions for zero external field. Since it involves commuting spin variables, one says that it is a classical model even if the spins can only point in two quantized directions. It can also be derived from the spin $S = 1/2$ quantum Hamiltonian (6.51) by keeping only the interactions between the z-components of the spins.

In addition to the thermodynamic properties, one also wants to study how the spins are ordered on the lattice for different temperatures and fields. This information can be obtained from the spin correlation functions. As for the gas-liquid system, the simplest of these is the one-spin correlation function in the Ising model

$$m_{\mathbf{x}} = \langle \sigma_{\mathbf{x}} \rangle = \frac{1}{Z} \sum_{\{\sigma\}} \sigma_{\mathbf{x}} \, e^{-\beta H[\sigma]} \tag{6.54}$$

which is just the magnetization on lattice site $\mathbf{x}$. When the external field is constant, the system is invariant under translations and $m_{\mathbf{x}}$ will be the same on all the sites. We say that the magnetization is permanent if it is non-zero when we first take the termodynamic limit where the number of lattice sites goes to infinity, and then let the external field become zero. When that is the case, the Z_2 symmetry of the Hamiltonian is said to be spontaneously broken since $m = \langle \sigma_{\mathbf{x}} \rangle$ is not invariant under the group. This phenomenon is very important in modern condensed matter physics.

While the magnetization tells if the spins are ordered or not, it is the two-spin correlation function

$$\langle \sigma_{\mathbf{x}} \sigma_{\mathbf{x}'} \rangle = \frac{1}{Z} \sum_{\{\sigma\}} \sigma_{\mathbf{x}} \sigma_{\mathbf{x}'} \, e^{-\beta H[\sigma]} \tag{6.55}$$

which contains information about how the spins are ordered with respect to each other. If it is large, there is a high probability to find the spins on the

two sites in the same direction. The spins are said to be strongly correlated. Correspondingly, when it is small, the probability to point in the same direction is also small and we say that the spins are uncorrelated. It can be measured by neutron scattering experiments in the same way as the pair correlation function was measured in gas-liquid systems.

When the field at lattice site $B_{\mathbf{x}'}$ is varied, one will in general see that the magnetization at some other site $\mathbf{x}$ will also vary. This response is measured by the position-dependent susceptibility

$$\chi(\mathbf{x}, \mathbf{x}') = \frac{\partial m_{\mathbf{x}}}{\partial B_{\mathbf{x}'}} \ . \tag{6.56}$$

Taking the derivative of (6.54) we get

$$\frac{\partial m_{\mathbf{x}}}{\partial B_{\mathbf{x}'}} = -\frac{1}{Z^2} \frac{\partial Z}{\partial B_{\mathbf{x}'}} \sum_{\{\sigma\}} \sigma_{\mathbf{x}} \, e^{-\beta H[\sigma]} + \frac{1}{Z} \, \beta \sum_{\{\sigma\}} \sigma_{\mathbf{x}} \, \sigma_{\mathbf{x}'} \, e^{-\beta H[\sigma]} \ .$$

If we then use

$$\frac{\partial Z}{\partial B_{\mathbf{x}'}} = \beta \sum_{\{\sigma\}} \sigma_{\mathbf{x}'} \, e^{-\beta H[\sigma]} = \beta \langle \sigma_{\mathbf{x}'} \rangle$$

we see that the generalized susceptibility is then given by the much more transparent expression

$$\chi(\mathbf{x}, \mathbf{x}') = \beta C(\mathbf{x}, \mathbf{x}') \ . \tag{6.57}$$

Here we have introduced the so-called irreducible spin correlation function

$$C(\mathbf{x}, \mathbf{x}') = \langle \sigma_{\mathbf{x}} \, \sigma_{\mathbf{x}'} \rangle - \langle \sigma_{\mathbf{x}} \rangle \langle \sigma_{\mathbf{x}'} \rangle \tag{6.58}$$

which always will go to zero for large separations of the spins, even in the magnetized phase. When the external field is constant or zero, we again have translational invariance so that $\chi(\mathbf{x}, \mathbf{x}') \to \chi(\mathbf{x} - \mathbf{x}')$ and $C(\mathbf{x}, \mathbf{x}') \to C(\mathbf{x} - \mathbf{x}')$ only depend on their mutual separation. The thermodynamic susceptibilty

$$\chi = \left(\frac{\partial m}{\partial B} \right)_T \tag{6.59}$$

is then obtained as the sum of the generalized susceptibilty over all the lattice sites, i.e

$$\chi = \beta \sum_{\mathbf{x}} C(\mathbf{x} - \mathbf{x}') = \beta \sum_{\mathbf{x}} \langle \, (\sigma_{\mathbf{x}} - m)(\sigma_{\mathbf{x}'} - m) \, \rangle \ . \tag{6.60}$$

It provides a new example of a fluctuation-dissipation theorem connecting the macroscopic susceptibility to the microscopic fluctuations of the lattice spins.

The thermodynamic susceptibility χ is always positive. It is here defined per spin in the system. Previously we defined it as the response of the system magnetization $M = \sum_{\mathbf{x}} \langle \sigma_{\mathbf{x}} \rangle$ to variations in the external field, i.e. $\chi = (\partial M / \partial B)_T$. By tracing through the same steps as in the above derivation we find

$$\chi = kT \left[\frac{1}{Z} \frac{\partial^2 Z}{\partial B^2} - \left(\frac{1}{Z} \frac{\partial Z}{\partial B} \right)^2 \right] \ .$$

Defining $\sigma = \beta \sum_{\mathbf{x}} \sigma_{\mathbf{x}}$, we can then rewrite this as

$$\chi = kT \left[\langle \sigma^2 \rangle - \langle \sigma \rangle^2 \right] = \beta \sum_{\mathbf{x}, \mathbf{x}'} C(\mathbf{x} - \mathbf{x}') \ .$$

Since it is given by the square of the spin fluctuation, it is positive. Comparing with (6.60), we see that these two expressions just differ by the number of spins in the system.

Correlation functions for other spin models are defined similarly to (6.58). Experimentally or by numerical methods, they all found to fall off with the spin separation $|\mathbf{x} - \mathbf{x}'|$. In the critical region one can parametrize these functions by the general form

$$C(\mathbf{x} - \mathbf{x}') = \frac{const}{|\mathbf{x} - \mathbf{x}'|^{d-2+\eta}} \, e^{-|\mathbf{x} - \mathbf{x}'|/\xi} \tag{6.61}$$

for separations much larger than the lattice spacing. Here d is the dimension of lattice and η is a new, critical exponent which is usually quite small. The spins are correlated within distances set by the correlation length ξ. It becomes very large near the critical point where it is found to vary with the temperature as

$$\xi \propto |T - T_c|^{-\nu} \ . \tag{6.62}$$

At the critical point it diverges similarly to the susceptibility in Fig.6.3 and the correlation function falls off as a power of the spin separation instead. Spins at all length scales are then influenced by each other in a cooperative phenomenon.

6.5 Exact solutions of Ising models

We will first investigate the 1-dimensional Ising model with N spins. In zero field the Hamiltonian (6.53) becomes

$$H = -J \sum_{i=1}^{N-1} \sigma_i \sigma_{i+1} \ . \tag{6.63}$$

It can be considered as the sum over $N - 1$ bonds between pairs of nearest neighbour spins. Each bond contributes an energy $-J$ if the spins are parallel and $+J$ if they are antiparallel. Assuming that $J > 0$ we find the lowest energy state when all the spins point in the same direction. The model has therefore two ground states, $\uparrow\uparrow\uparrow\uparrow \ \cdots \ \uparrow\uparrow$ and $\downarrow\downarrow\downarrow\downarrow \ \cdots \ \downarrow\downarrow$, each with the energy

$E_0 = (N-1)J$. At exactly zero temperature all the spins are ferromagnetically ordered with a magnetization per spin of $m = \langle \sigma_i \rangle = 1$ in the up state.

When the temperature is slightly increased, the next higher states are excited. For an open chain with free ends, these are of the form $\uparrow\uparrow\downarrow\downarrow \cdots \downarrow\downarrow$ with energy $E_1 = (N-3)J$. The excitation energy $\Delta E = 2J$ for all these degenerate states and comes from the bond in the chain where the spins change direction. This kind of elementary excitation is sometimes called a kink.

In a cyclic chain where spin σ_N is coupled back to σ_1, the first possible excitation is the turn of one spin, i.e. $\uparrow\uparrow\downarrow\uparrow \cdots \uparrow\uparrow$ with excitation energy $\Delta E = 4J$ since it involves two excited bonds. The lowest excitation will here always involve two kinks with some arbitrary separation, $\uparrow\uparrow\downarrow\downarrow \cdots \downarrow\uparrow$, because of the circle topology.

Since these excitations can occur anywhere along the chain, we expect them to wash out any tendency to spontaneous magnetization at finite temperature. More formally, we see this from the free energy cost $\Delta F = \Delta E - T\Delta S$ of creating one kink excitation. Since it can occur at N different places in the chain, it has the entropy $\Delta S = k \log N$. The corresponding cost in free energy is therefore $\Delta F = 2J - kT \log N < 0$ when $N \to \infty$ and the temperature is not zero. Thus, the kinks will be created spontaneously and destroy the magnetization as soon as $T > 0$.

The probability for a fluctuation that costs an energy ΔE is

$$P = W e^{-\beta \Delta E}$$

if it can take place in W different ways. This can be written as

$$P = e^{-\beta \Delta F} \tag{6.64}$$

where $\Delta F = \Delta E - kT \log W$. When $\Delta F \leq 0$ the probability $P \geq 1$ and the process will take place spontaneously.

In the 2-dimensional Ising model the first excitations are islands of turned spins in the background of ferromagnetically ordered spins as shown in Fig.is. The energy of such an island with L excited bonds along the periphery has an energy $\Delta E = 2LJ$. For a given length of the periphery, the island can have very many different shapes. When we go around the periphery, we can at any bond move in three different directions which will not take us back again. The number of different shapes of such an island is therefore $W = 3^L$. Its free energy is $\Delta F = L(2J - kT \log 3)$ and becomes negative when $T > T_c = 2J/k \log 3$. The magnetization should therefore be washed away above this temperature which shold be a reasonable estimate of the critical temperature. Using different arguments, Kramers and Wannier found in 1941 the exact value

$$\frac{kT_c}{J} = \frac{2}{\log(\sqrt{2}+1)} = 2.269\ldots \tag{6.65}$$

which is quite close to the above estimate.

One can use similar arguments to show that for the Heisenberg models which have the continuous symmetry group $O(N)$, there can be spontaneous magnetization at non-zero temperatures only when the dimensions of the spin systems $d > 2$. The 2-dimensional Heisenberg
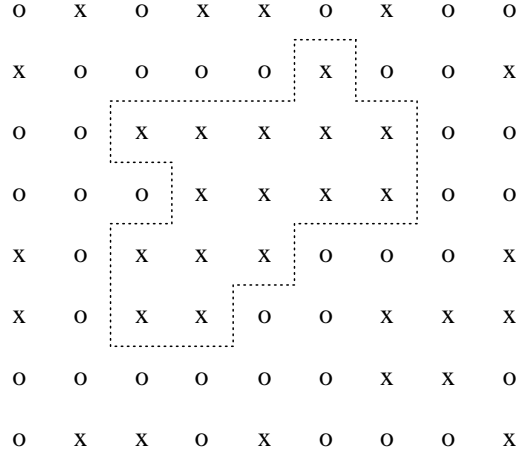
```
o    x    o    x    x    o    x    o    o

x    o    o    o    o    x    o    o    x

o    o    x    x    x    x    x    o    o

o    o    o    x    x    x    x    o    o

x    o    x    x    x    o    o    o    x

x    o    x    x    o    o    x    x    x

o    o    o    o    o    o    x    x    o

o    x    x    o    x    o    o    o    x
```

Figure 6.6: Magnetized island in the 2-dimensional Ising model. Spin up $= x$ and spin down $= o$.

model has only a magnetization at $T = 0$.

We will now calculate the exact partition function for the 1-dimensional Ising model (6.63). The sum over the 2^N spin configurations simplifies to

$$Z_N = \sum_{\sigma_1 = \pm 1} \sum_{\sigma_2 = \pm 1} \cdots \sum_{\sigma_N = \pm 1} e^{\beta J (\sigma_1 \sigma_2 + \sigma_2 \sigma_3 \cdots + \sigma_{N-1} \sigma_N)} . \tag{6.66}$$

Summing first over the last spin σ_N, we find the recursion relation

$$Z_N = (2 \cosh K) \, Z_{N-1} \tag{6.67}$$

where $K = \beta J$. Iterating, one gets

$$Z_N = (2 \cosh K)^{N-2} Z_2 .$$

The 2-spin partition function Z_2 involves the four spin configurations $\uparrow\uparrow$, $\uparrow\downarrow$, $\downarrow\uparrow$ and $\downarrow\downarrow$ which gives $Z_2 = 4 \cosh K$. In this way we find

$$Z_N = 2^N \cosh^{N-1} K . \tag{6.68}$$

When the number of spins $N \gg 1$, the free energy per spin G/N becomes

$$g = -kT \log \left(2 \cosh \beta J \right) . \tag{6.69}$$

It is a smooth function of the temperature and there is as expected no phase transition in this model. For all temperatures $T > 0$ the magnetization is zero. The internal energy per spin is

$$\frac{U}{N} = -\frac{1}{N} \frac{\partial}{\partial \beta} \log Z_N = -J \tanh \beta J \tag{6.70}$$
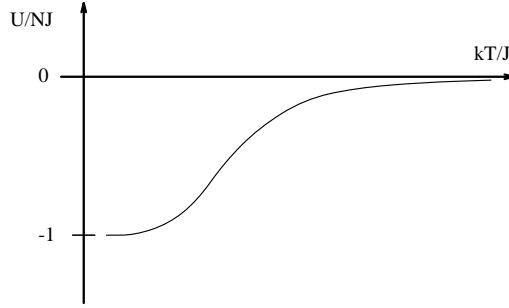
Figure 6.7: Internal energy per spin in the 1-dimensional Ising model as function of temperature.

and varies smoothly with the temperature as shown in Fig.6.7. Taking the derivative with respect to the temperature, gives the spesific heat

$$C_B = Nk \left(\frac{\beta J}{\cosh \beta J} \right)^2 . \tag{6.71}$$

In Fig.6.8 it is seen to go to zero when the temperature decreases. The Ising model is in agreement with the third law of thermodynamics because its classical spins are quantized.
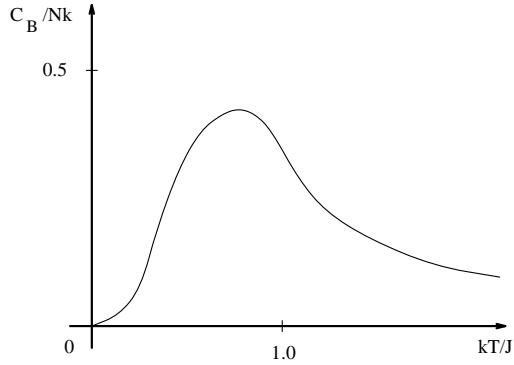
Figure 6.8: Specific heat in the 1-dimensional Ising model as function of temperature.

It should be obvious that the method which allowed the simple solution (6.65) for the Hamiltonian (6.63) can also be used to solve the somewhat more general model

$$H = - \sum_{i=1}^{N-1} J_i \, \sigma_i \, \sigma_{i+1} \tag{6.72}$$

where the couplings between neighbouring spins are different. The partition function is now

$$Z_N = 2^N \prod_{i=1}^{N-1} \cosh K_i \qquad (6.73)$$

with $K_i = \beta J_i$. This solution can be used to obtain the spin correlation function (6.58). We first calculate the correlator between neighbouring spins,

$$
\begin{aligned}
\langle \sigma_1 \sigma_2 \rangle &= \frac{1}{Z_N} \sum_{\{\sigma\}} \sigma_1 \sigma_2 \, e^{-\beta H[\sigma]} \\
&= \frac{\partial}{\partial K_1} \log Z_N = \tanh K_1 \qquad (6.74)
\end{aligned}
$$

Now since $\sigma_i^2 = 1$ we have $\langle \sigma_1 \sigma_3 \rangle = \langle \sigma_1 \sigma_2 \sigma_2 \sigma_3 \rangle$ which in the same way gives

$$\langle \sigma_1 \sigma_3 \rangle = \frac{\partial}{\partial K_1} \frac{\partial}{\partial K_2} \log Z_N = \tanh K_1 \tanh K_2 \; .$$

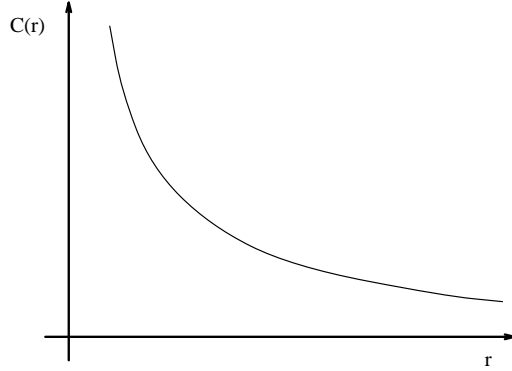In this way we find for the correlation function

Figure 6.9: Correlation function in the 1-dimensional Ising model at a given temperature.

$$\langle \sigma_i \sigma_j \rangle = \tanh^{|i-j|} K \qquad (6.75)$$

when the couplings become equal. Since $\tanh K < 1$, it decreases rapidly for increasing spin separation $r = |i - j|$ as shown in Fig.6.9. The result can be written as

$$C(r) = e^{-r/\xi} \; . \qquad (6.76)$$

It decays to a value $1/e$ at a separation equal to the correlation length

$$\xi = \frac{1}{\log \coth \beta J} = \begin{cases} \frac{1}{2} e^{2J/kT}, & T \to 0 \\ \log (kT/J), & T \to \infty \end{cases} \; . \qquad (6.77)$$

At small temperatures the correlation length is seen to grow exponentially. This is consistent with $T = 0$ being a special kind of critical point.

When we next try to calculate the partition function by the same method for the 1-dimensional Ising model in an external field,

$$H = -J\sum_{i=1}^{N-1} \sigma_i \sigma_{i+1} - B\sum_{i=1}^{N} \sigma_i \tag{6.78}$$

we find that it doesn't work. But looking back at the form (6.66) of the partition sum, we see that it can be written as

$$Z_N = \sum_{\sigma_1 = \pm 1} \sum_{\sigma_2 = \pm 1} \cdots \sum_{\sigma_N = \pm 1} V_{\sigma_1 \sigma_2} V_{\sigma_2 \sigma_3} \cdots V_{\sigma_{N-1} \sigma_N} V_{\sigma_N \sigma_1} \tag{6.79}$$

when we assume that the spins are on a cyclic chain. V is a 2×2 matrix

$$V_{\sigma\sigma'} = e^{\beta J \sigma \sigma'} = \begin{pmatrix} e^{\beta J} & e^{-\beta J} \\ e^{-\beta J} & e^{\beta J} \end{pmatrix} \tag{6.80}$$

called the transfer matrix. The partition sum (6.79) is then just

$$Z_N = \sum_{\sigma_1 = \pm 1} V_{\sigma_1 \sigma_1}^N = \operatorname{Tr} V^N \ . \tag{6.81}$$

We can now diagonalize V by a matrix A. Since $\operatorname{Tr} V^N = \operatorname{Tr} A V^N A^{-1}$, the trace is given by the eigenvalues $\lambda_+ = 2\cosh\beta J$ and $\lambda_- = 2\sinh\beta J$, i.e.

$$Z_N = \lambda_+^N + \lambda_-^N = (2\cosh\beta J)^N (1 + \tanh^N \beta J) \ . \tag{6.82}$$

In the thermodynamic limit $N \to \infty$ it agrees with the previous result (6.68).

With this method we can now find the partition function in an external field. From the Hamiltonian (6.78) we construct the transfer matrix

$$V_{\sigma\sigma'} = e^{\beta J \sigma \sigma' + \frac{1}{2}(\sigma + \sigma')} = \begin{pmatrix} e^{\beta J + \beta B} & e^{-\beta J} \\ e^{-\beta J} & e^{\beta J - \beta B} \end{pmatrix} \tag{6.83}$$

with eigenvalues

$$\lambda_\pm = e^{\beta J} \cosh\beta B \pm \sqrt{e^{-2\beta J} + e^{2\beta J}\sinh^2\beta B} \ . \tag{6.84}$$

In the thermodynamic limit, the partition function is again dominated by the largest eigenvalue so that the Gibbs free energy per spin becomes

$$\begin{aligned} g &= -kT\log\lambda_+ \\ &= -J - kT\log\left(\cosh\beta B + \sqrt{e^{-4\beta J} + \sinh^2\beta B}\right) \end{aligned} \tag{6.85}$$

The external magnetic field will now induce a magnetization in the spin chain

$$m = \left(\frac{\partial g}{\partial B}\right)_T = \frac{\sinh\beta B}{\sqrt{e^{-4\beta J} + \sinh^2\beta B}} \ . \tag{6.86}$$

Calculating the zero-field susceptibility, one finds that it diverges like the correlation length (6.77) in the limit $T \to 0$.

6.6 Weiss mean field theory

All the different spin models can be solved approximately by different methods. One of the oldest, simplest and still quite accurate method is mean field theory. The name stems from the replacement of the interactions between different spins by the interaction of free spins in the mean magnetic field created by the other spins in a self-consistent way.

It is easiest to demonstrate the method for the Ising model with the Hamiltonian (6.53) and a constant magnetic field. The first term can be rewritten as

$$H = -J \sum_{\mathbf{x}} \sigma_{\mathbf{x}} \sum_{\mathbf{x}' \in \mathbf{x}} \sigma_{\mathbf{x}'} - B \sum_{\mathbf{x}} \sigma_{\mathbf{x}} \tag{6.87}$$

where the sum over $\mathbf{x}'$ goes over the nearest neighbour positions to the lattice site $\mathbf{x}$. On a d-dimensional lattice this is the coordination number which for a cubic lattice is $z = 2d$. The mean field approximation now consists in replacing these neighbouring spins by their average value $m = \langle \sigma_{\mathbf{x}} \rangle$ which is just the constant magnetization,

$$\sum_{\mathbf{x}' \in \mathbf{x}} \sigma_{\mathbf{x}'} \Rightarrow zm \ .$$

The Ising Hamiltonian (6.87) is then changed into the approximate Hamiltonian

$$H_{MF} = -B_{eff} \sum_{\mathbf{x}} \sigma_{\mathbf{x}} \tag{6.88}$$

where the Weiss mean magnetic field is

$$B_{eff} = B + Jzm \ . \tag{6.89}$$

It consists of the external field plus the field due to the magnetization of its nearest neighbours.

The magnetization of the mean field Hamiltonian (6.88) is $m = \tanh \beta B_{eff}$ or

$$m = \tanh \left((zJm + B)/kT \right) \ . \tag{6.90}$$

We solve this equation first when the external field B is zero,

$$m = \tanh \frac{zJm}{kT} \ . \tag{6.91}$$

Plotting both sides of the equation as in Fig.6.10, we see that there will be two non-zero solutions in addition to $m = 0$ when the derivative of tanh at the origin is larger than one, i.e. when

$$T < T_c = zJ/k \ . \tag{6.92}$$

When the temperature increases, the magnetization $m = \pm m_0$ becomes smaller and eventually becomes zero when $T = T_c$. For higher temperatures we only
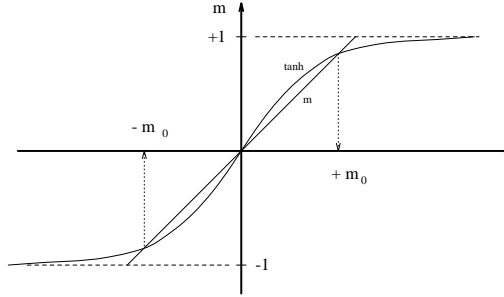
Figure 6.10: Self-consistent solutions for the magnetization in the mean field approximation.

have the paramagnetic solution $m = 0$. The spontaneous magnetization has a dependence on the temperature which is very similar to that observed experimentally in Fig.6.5.

A more detailed description of the magnetization near the critical point follows from using the expansion $\tanh x = x - x^3/3 + \ldots$ in (6.91). Keeping only the leading terms, it gives

$$\frac{T_c - T}{T} m = \frac{1}{3} \left(\frac{T_c}{T} \right)^3 m^3 . \tag{6.93}$$

The left hand side is negative when $T > T_c$ and we have only the $m = 0$ solution. Below this temperature we find the permanent magnetization

$$m = \pm\sqrt{3} \left(\frac{T}{T_c} \right)^{3/2} \left(1 - \frac{T}{T_c} \right)^{\frac{1}{2}} . \tag{6.94}$$

Comparing with the general form of the magnetization in (6.43), we the critical exponent $\beta = 1/2$ in the mean field approximation.

From (??) we can now also obtain the internal energy $U = \langle H \rangle$ in the mean field approximation. It is simply

$$U/N = -\frac{1}{2} Jzm^2 \tag{6.95}$$

and thus zero above the critical temperature. When the temperature is just below T_c, it becomes $U/N = -(3/2)k(T_c - T)$. It is plotted in Fig.6.11 together with the exact Onsager result in $d = 2$ dimensions. The agreement is rather poor around the critical point. In $d = 3$ dimensions it is somewhat better. But in all dimensions $d \geq 2$ the mean field approximation predicts a specific heat with a finite jump at the critical point instead of a divergence as experimentally observed.

When the magnetic field is non-zero, we must solve (6.90). Near the critical point, both B and m are small. Expanding again the right hand side, we then
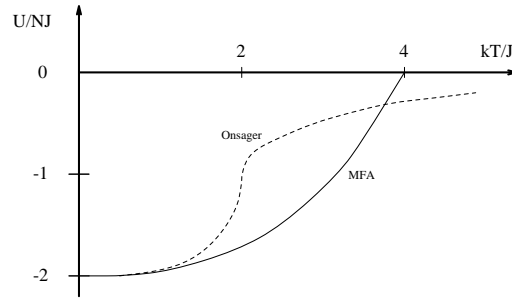
Figure 6.11: Internal energy per spin in the 2-dimensional Ising model. Full line is the result from the Mean Field Approximation and the dashed line is the exact Onsager result.

obtain

$$\frac{B}{kT} = \frac{T - T_c}{T_c}\, m + \frac{1}{3}m^3 \tag{6.96}$$

to leading order in $T - T_c$. If we now solve for the magnetization, we will find a variation with temparture as shown in Fig.6.12. It is non-zero for all finite temperatures, but becomes small when T becomes very large as in typical paramagnets. When $T = T_c$ it is seen from (6.96) to depend on the field according to the simple relation

$$B \propto |m|^\delta \ . \tag{6.97}$$

where the critical exponent $\delta = 3$. In the 2-dimensional Ising model it has the value $\delta = 15$, while in $d = 3$ dimensions it is around $\delta = 4.8$. Again we see that
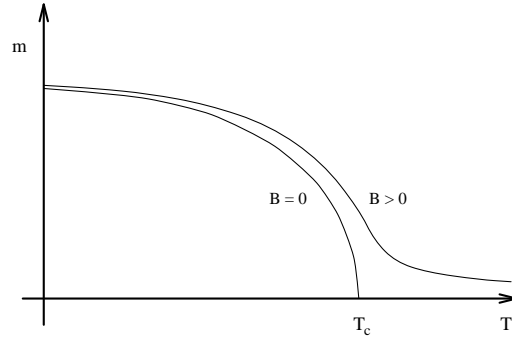

Figure 6.12: Variation of the magnetization with temperature. There is no phase transition when the external field is non-zero.

the MFA result is better in higher dimensions.

Plotting the magnetization as function of the field as in Fig.6.13, one finds that the susceptibility should diverge at the critical point since the curve is

tangential to the m-axis when $T = T_c$. This follows directly from (6.96) by taking the derivative with respect to m on both sides and then letting $m \to 0$,

$$\chi^{-1} = \left(\frac{\partial B}{\partial m} \right)_T = k(T - T_c) \ . \tag{6.98}$$

According to (6.41) this implies that the susceptibility exponent $\gamma = 1$ in the mean field approximation. Below the critical temperature, the magnetization is non-zero with the magnitude (6.94), but the exponent is easily found to be the same. This mean field exponent compares quite well with the $d = 3$ value which is $\gamma = 1.24$.

The mean field theory naturally explains the existence of a phase transition in the Ising model. It predicts a second order phase transition between a paramagnetic high-temperature phase and a ferromagnetic phase at low temperatures and most of the critical exponents are typically within 50 This is really quite impressive when one takes into account the crudeness and simplicity of the approximation. Also comparing the critical temperature with the exact result (6.65) for the 2-dimensional Ising model for which the coordination number $z = 4$, the agreement is rather poor. It even predicts a phase transition at finite temperature for the 1-dimensional model which is disasterous. In $d = 3$ dimensions, however, the agreement is better. This can be explained by the smaller fluctuations we expect to find in higher dimensions where each spin is surrounded by more neighbours. Away from the critical point, the fluctuations are generally smaller as is demonstrated by the behaviour (6.61) of the spin correlation function (6.58). We would then expect this method to give more accurate results.
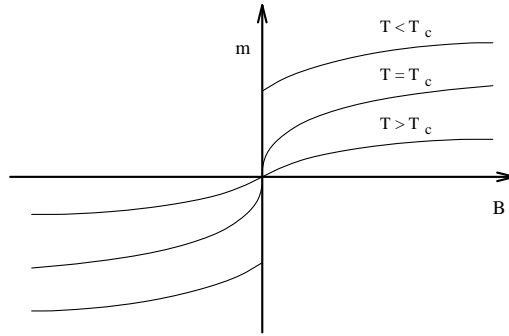
Figure 6.13: Magnetization as function of the external field for different temperatures.

The strong fluctuations which ruins the accuracy of the mean field approximation in low dimensions are due to the short-range interactions we have here assumed between the spins. With long-range interactions more spins are coupled and the fluctuations would be strongly damped. In that case we would find that the mean field approximation becomes both qualitatively and quantitavely

very useful for the understanding of phase transitions even in 1-dimensional systems.

6.7 Landau mean field theory

Other spin models of magnetic systems besides the Ising model can be investigated using the Weiss mean field theory. Again we will find critical exponents which are independent of the dimension of the system. But, perhaps even more surprising, they are exactly the same for all the different models. This must mean that the critical behaviour in the mean field approximation must follow from more general principles in a framework which is common for all such magnetic systems. It was found by Landau and can easily be generalized to give a detailed description of phase transitions in many other systems as well. It is a phenomenological theory which is basically constructed to contain the essential physics of the system near the critical point. In most cases it can be derived from the more fundamental spin Hamiltonian.

The main idea behind this mean field approximation is the assumption that the Helmholtz free energy density $f(m, T)$ is a regular function near the critical point. Since the magnetization m is very small here, we can make the Taylor expansion

$$f(m) = f_0(T) + \frac{1}{2}r(T)\,m^2 + \frac{1}{4}u(T)\,m^4 \tag{6.99}$$

when we drop higher terms. The first term is the non-critical part of the free energy and the coefficients $r(T)$ and $u(T)$ are assumed to be smooth and analytic functions of temperature. Only even powers of the magnetization have been kept for the Ising model. It has the symmetry group Z_2 which requires invariance of the free energy under the spin inversion, i.e. when $m \to -m$. For the Heisenberg model with the symmetry group $O(3)$ the expansion would be slightly different since then would the magnetization be a vector $\mathbf{m}$.
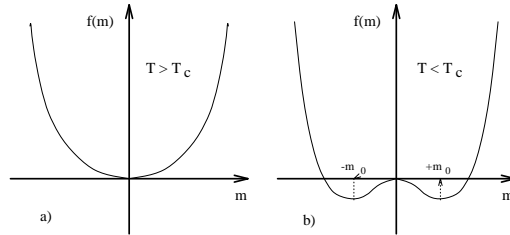

Figure 6.14: Landau free energy as function of the magnetization above and below the critical temperature.

Thermodynamic equilibrium in an external magnetic field B is given by the condition $(\partial f/\partial m)_T = B$, i.e.

$$rm + um^3 = B \ . \tag{6.100}$$

When the field is zero, this corresponds to the minimum of the free energy (6.99). When $T > T_c$ we want this to be at $m = 0$. This we can achieve by having both $r(T) > 0$ and $u(T) > 0$ at these temperatures. On the other hand, when $T < T_c$ we want the minimum to be at a non-zero value for the magnetization. This can be obtained if $r(T)$ has the form $r(T) = \alpha (T - T_c)$ and $u(T)$ is positive. Without loss of of the essential physics, we can then take $u(T)$ to be constant.

The thermodynamic potential (6.99) will then vary with the magnetization as shown in Fig.6.14 for temperatures above and below the critical temperature. From (6.100) with $B = 0$ follows the values of the magnetization at the minima of the potential,

$$
m = \begin{cases} \pm\sqrt{\frac{\alpha}{u}}\,(T_c - T)^{\frac{1}{2}}, & T < T_c \\ 0, & T > T_c \end{cases} .
\tag{6.101}
$$

The non-zero magnetization below the critical is not invariant under the symmetry group Z_2. In the thermodynamically stable state of the system it is hidden or spontaneously broken. As in the previous section, we find the critical exponent $\beta = 1/2$. When $B > 0$ and $T = T_c$ it gives $B = um^3$ so that the exponent $\delta = 3$. Taking the derivative of (6.100) with respect to m gives

$$
\left(\frac{\partial B}{\partial m}\right)_T = r + 3um^2 .
\tag{6.102}
$$

Above the critical temperature where $m = 0$ this implies that the zero-field susceptibility exponent is $\gamma = 1$. It is also obtained below T_c when we use the result (6.101) for the magnetization.

From (6.13) we find the entropy $s = -(\partial f/\partial T)_m = -\alpha m^2/2 + f_0'(T)$. The specific heat $c = T(\partial s/\partial T)$ will therefore show a finite jump of magnitude $\Delta c = \alpha^2 T_c/2u$ at the critical temperature above a continuous background. In terms of the corresponding critical exponent (6.42) one says that $\alpha = 0$ in the mean field approximation.

In this approach the correlation exponents can also be found by extententing the theory to include a magnetization $m_{\mathbf{x}} = \langle \sigma_{\mathbf{x}} \rangle$ which varies slowly from site to site. In the same spirit as above, we can then write the free energy density as as

$$
f(m_{\mathbf{x}}) = f_0(T) + \sum_{\mathbf{x}} \frac{r}{2}\, m_{\mathbf{x}}^2 + \frac{u}{4}\, m_{\mathbf{x}}^4 + \frac{1}{2} \sum_{\mathbf{x}' \in \mathbf{x}} (m_{\mathbf{x}} - m_{\mathbf{x}'})^2
\tag{6.103}
$$

where the last term includes the deviation from the magnetization on the neighbouring sites. The complete free energy is then

$$
F[m] = \sum_{\mathbf{x}} f(m_{\mathbf{x}}) .
\tag{6.104}
$$

A small variation in the magnetization $m_{\mathbf{x}} \to m_{\mathbf{x}} + \delta m_{\mathbf{x}}$, gives a corresponding small change

$$
\delta F = \sum_{\mathbf{x}} B_{\mathbf{x}}\, \delta m_{\mathbf{x}}
\tag{6.105}
$$

in the free energy when $B_{\mathbf{x}}$ is the magnetic field on this site.

When we now restict ourselves to a description of the system only on large scales where the microscopic details are not observed, we can replace the lattice magnetization $m_{\mathbf{x}}$ by the continuum magnetization $m(\mathbf{x})$. The last term in (6.103) becomes then the square of the gradient of the magnetization and the sum (6.104) becomes an integral over the whole system

$$F[m] = F_0(T) + \int d^d x \left[\frac{1}{2} (\boldsymbol{\nabla} m)^2 + \frac{r}{2} m^2 + \frac{u}{4} m^4 \right] \ . \qquad (6.106)$$

It is now a functional, i.e. a function of the function $m(\mathbf{x})$. The gradient term in the integral is the lowest order contribution coming from the non-constant magnetization. Higher derivatives will not be important when we are only interested in the behaviour of the magnetic systems at large scales.

For a given magnetic field $B(\mathbf{x})$ we can now derive the corresponding equilibrium magnetization $m(\mathbf{x})$ by finding the minimum of the Landau free energy (6.106). It is obtained by subjecting the magnetization to an infinitesemal variation $m(\mathbf{x}) \to m(\mathbf{x}) + \delta m(\mathbf{x})$. The resulting change in the free energy is then

$$\delta F[m] = \int d^d x \left[(\boldsymbol{\nabla} m) \cdot \delta(\boldsymbol{\nabla} m) + rm\delta m + um^3 \delta m \right] \ .$$

Now $\delta(\boldsymbol{\nabla} m) = (\boldsymbol{\nabla} \delta m)$ and after a partial integration where we can throw away the surface terms, we get

$$\delta F[m] = \int d^d x \left[-\nabla^2 m + rm + um^3 \right] \delta m(\mathbf{x}) \ . \qquad (6.107)$$

From the continuum version of (6.105) we then see that the magnetization must be a solution to the differential equation

$$-\nabla^2 m(\mathbf{x}) + rm(\mathbf{x}) + um^3(\mathbf{x}) = B(\mathbf{x}) \ . \qquad (6.108)$$

Similar equations always appear in the Landau mean field approximation for non-constant order parameter as one often calls the magnetization in this example. In the special case when it is constant, the equation simplifies to (6.100)

One can derive the differential equation for $m(\mathbf{x})$ in a more systematic way using the functional derivative. For a system in one dimension, consider the functional

$$F[m] = \sum_i a m_i^n$$

where m_i is the magnetization at lattice site i and a is the lattice spacing. Then we have the ordinary partial derivative $\partial F/\partial m_i = anm_i^{n-1}$. In the continuum limit it is replaced by $F[m] = \int dx\, m^n(x)$. The corresponding functional derivative $\delta F/\delta m(x)$ is defined by analogy so that $\delta F/\delta m(x) = nm^{n-1}(x)$. It is seen to be obtained from the partial derivative in the limit

$$\frac{\delta F[m]}{\delta m(x_i)} = \lim_{a \to 0} \frac{1}{a} \frac{\partial F}{\partial m_i} \ . \qquad (6.109)$$

As a first consequence we have the useful result

$$\frac{\delta m(x_i)}{\delta m(x_j)} = \delta(x_i - x_j) \tag{6.110}$$

since $\partial m_i/\partial m_j = \delta_{ij}$. It also follows directly from the definition $\delta m(x') = \int dx\, \delta(x - x')\, \delta m(x)$ of the δ-function. If the functional has the more general form $F[m] = \int dx\, f(m)$, we now obtain

$$\frac{\delta F[m]}{\delta m(x_i)} = \int dx\, f'(m(x)) \frac{\delta m(x)}{\delta m(x_i)} = f'(m(x_i))$$

from the resulting integral of the δ-function.

If the functional involves a gradient term like

$$F[m] = \frac{1}{2} \int dx\, (\nabla m)^2 = \sum_i a(m_i - m_{i+1})^2/2a^2,$$

we first find the partial derivative

$$\frac{\partial F}{\partial m_i} = \frac{1}{a}(2m_i - m_{i+1} - m_{i-1}) = -\frac{1}{a}[(m_{i+1} - m_i) - (m_i - m_{i-1})]$$

in the discrete case. Going to the continuum limit, we see that it becomes the derivative of the derivative, i.e. the double derivative

$$\frac{\delta F[m]}{\delta m(x)} = -\nabla^2 m(x)\ .$$

Taking now the functional derivative of the free energy (6.107) and using the local equilibrium condition

$$\frac{\delta F[m]}{\delta m(\mathbf{x})} = \mathbf{B}(\mathbf{x}), \tag{6.111}$$

we immediately get the result (6.108).

We can now also derive the correlation function in the Landau approximation. Using (6.57) we can obtain it from the generalized susceptibility $\chi(\mathbf{x}, \mathbf{x}') = \partial m(\mathbf{x})/\partial B(\mathbf{x}')$ which measures the response of the magnetization at point $\mathbf{x}$ to a change in the magnetic field at point $\mathbf{x}'$. It follows from (6.111) by taking the functional derivative on both sides of the equation with respect to $B(\mathbf{x}')$ using (6.110). One then obtains the differential equation

$$[-\nabla^2 + r + 3um^2]\, \chi(\mathbf{x}, \mathbf{x}') = \delta(\mathbf{x} - \mathbf{x}')\ . \tag{6.112}$$

When the magnetization m is constant we recover translational invariance and $\chi(\mathbf{x}, \mathbf{x}')$ will only depend on the separation $\mathbf{x} - \mathbf{x}'$). Introducing the Fourier transform

$$\chi(\mathbf{x} - \mathbf{x}') = \int \frac{d^d q}{(2\pi)^d}\, \chi(\mathbf{q})\, e^{i\mathbf{q}\cdot(\mathbf{x} - \mathbf{x}')}$$

the differential equation becomes

$$[q^2 + r + 3um^2]\, \chi(\mathbf{q}) = 1\ .$$

The corresponding Fourier component of the correlation function is therefore

$$C(\mathbf{q}) = \frac{kT}{q^2 + r + 3u\,m^2} \ . \tag{6.113}$$

Just the the Fourier transform of the density-density correlation function for a gas-liquid system gave directly the angular distribution of scattered light or X-rays, this spin-spin correlation function can be measured in neutron scattering on the magnetic system.

Assuming first that $T > T_c$ so that $m = 0$, we now obtain the correlation function in the most important case of $d = 3$ dimensions from the integral

$$C(\mathbf{x}) = \int \frac{d^3q}{(2\pi)^3} \frac{kT}{q^2 + r} \, e^{i\mathbf{q}\cdot\mathbf{x}} \ . \tag{6.114}$$

It can easily be done using complex contour integration. The result has the same form as the Yukawa potential,

$$C(\mathbf{x}) = \frac{kT}{4\pi|\mathbf{x}|} e^{-|\mathbf{x}|/\xi} \tag{6.115}$$

where the correlation length

$$\xi = \sqrt{\frac{1}{r}} \propto (T - T_c)^{-\frac{1}{2}} \ . \tag{6.116}$$

Below the critical temperature one must use the result (6.101) for the magnetization but the correlation length is still found to have the same critical behaviour. Comparing with the standard form (6.61), we see that the two correlation exponents are $\eta = 0$ and $\nu = 1/2$. For the Ising model in $d = 3$ dimensions solved by numerical methods one obtains $\eta = 0.04$ and $\nu = 0.63$.

The definition of the critical exponents and their values in the mean field approximation can now be summed up in the following table:

Specific heat:	$C_B \propto |T - T_c|^{-\alpha}$	$\alpha = 0$
Order parameter:	$M \propto (T_c - T)^{\beta}$	$\beta = 1/2$
Susceptibility:	$\chi \propto |T - T_c|^{-\gamma}$	$\gamma = 1$
Critical isotherm:	$B \propto |M|^{\delta}$	$\delta = 3$
Critical correlation function:	$C(\mathbf{q}) \propto \mathbf{q}^{-2+\eta}$	$\eta = 0$
Correlation length:	$\xi \propto |T - T_c|^{-\nu}$	$\nu = 1/2$

All of these exponents are not independent of each other. From (6.113) we see that the correlation function for $\mathbf{q} = 0$ and above the critical temperature is $C(\mathbf{q} = 0) = kT/r$. Writing (6.56) in the continuum limit as

$$\chi = \beta \int d^d x \, C(\mathbf{x}) = \beta \, C(\mathbf{q} = 0) \tag{6.117}$$

we have $\chi = r^{-1} = \xi^2$. For the corresponding critical exponents this implies

$$\gamma = 2\nu \ . \tag{6.118}$$

It is called a scaling relation for reasons which will be clear later. It is obviously satisfied by the mean field exponents. But more surprisingly, it is also approximately satisfied by the exponents in other models. In Chapter 4 it was derived within the Ornstein-Zernike theory which is a mean field approximation for the gas-liquid system. One should therefore be able to derive it from more general principles. In the next chapter we will see that such scaling relations between the critical exponents follow from the renormalization group.

The magnetization m in the free energy (6.99) is the order parameter for the magnetic system described by the Ising model. Its value tells us in which thermodynamic phase the system is. It is here the smoothed out average $m = \langle \sigma \rangle$ where the Ising spin σ is really the component S_z of the spin $\mathbf{S}$. We therefore say that this order parameter has $N = 1$ components. On the other hand, in the full Heisenberg model we will have an order parameter $\mathbf{m} = \langle \mathbf{S} \rangle$ which has $N = 3$ components. Since this system is invariant under the 3-dimensional rotation group $O(3)$, the Landau free energy must be rotational invariant. It must therefore have the form

$$F[\mathbf{m}, T] = F_0(T) + \int d^d x \left[\frac{1}{2} \left(\boldsymbol{\nabla} \mathbf{m} \right)^2 + \frac{r}{2} \mathbf{m}^2 + \frac{u}{4} \mathbf{m}^4 \right] \qquad (6.119)$$

with $\mathbf{m}^2 = \mathbf{m} \cdot \mathbf{m}$. Although it has a more complicated structure, the critical exponents are found to be exactly the same as for the Ising model as long as we are in the mean field approximation.

Monte Carlo simulations of the Ising model give results that are different from the mean field values. They can also be approximately calculated by other numerical methods. The corresponding Landau free energy will be given by (6.119) where now the order parameter $\mathbf{m}$ has $N = 2$ components. In $d = 3$ it will have a phase transition with critical exponents which are different from the Heisenberg values.

Exponent	Ising $d = 2, N = 1$	Ising $d = 3, N = 3$	MFA
α	0 (log)	0.11	0 (step)
β	1/8	0.32	1/2
γ	7/4	1.24	1
δ	15	4.90	3
η	1/4	0.04	0
ν	1	0.63	1/2

Table 6.1: Critical exponents in different spin models for magnetic phase transitions.

In the above table the known values for critical exponents in the different spin models are given. We see that the exponents take different values depending on the dimension d of the spin model and the the number of components N of the order parameter. Since the introduction of the renormalization group for critical phenomena, one can now actually calculate their values from the Landau

free energy by properly taking care of the fluctuations which are ignored in the mean field approximation.

Chapter 7

Stochastic Processes

The methods of statistical mechanics we have developed so far are applicable to systems of many particles in equilibrium. Thermodynamic variables measured at different times have the same values. There is similarly no time dependence in the average values of microscopic variables. But this stationary state is almost always the result of an evolution of the system through a continuous set of states from an initial, non-equilibrium state in which the system is prepared. This evolution is a very complex process governed by the dynamics of all the particles involved. At appears to be quite random and is called a stochastic process. It is first when one compares the non-equilibrium evolution of many identical systems from the same initial state that one discovers that they also obey simple laws which accurately describe their behavior. The most important of these new statistical methods will be developed in this chapter and applied to a few illustrative and important physical examples.

7.1 Random Walks

Probably the simplest and most important stochastic process is the random walk. It plays the same rôle in non-equilibrium statistical mechanics as the hydrogen atom does in atomic physics. Most of its basic properties are obtained by considering the walk in one dimension. We then have a system which can be a particle or a person who at given, separated times takes a step to the right with probability p or to the left with probability q. We then obviously have $p + q = 1$. After N steps there will be R to the right and $L = N - R$ to the left. The net displacement to the right is $S = R - L$. If these walks are repeated a large number of times, the net displacement will vary from $S = +N$ to $S = -N$.

There is only one walk which gives the maximal displacement $S = N$. It corresponds to having all the steps taken to the right. Since the probability for each such step is p, the probability for having this walk is $P_N(N) = p^N$. When there is one step to the left among these N steps, the net displacement is $S = N - 2$. It can occur at any of the N different times with the probability

q. Thus the overall probability of finding such a walk with $R = N - 1$ steps to the right, is $P_N(N - 1) = Np^{N-1}q$.

In this way we see that the probability to find a walk with R steps to the right among which all the N steps is given by the Bernoulli probability distribution

$$P_N(R) = \binom{N}{R} p^R q^{N-R} \tag{7.1}$$

where $\binom{N}{R} = N!/R!\,(N-R)!$ is the number of such walks. The total probability for N steps irrespective of the number taken to the right, is then

$$\sum_{R=0}^{N} P_N(R) = (p+q)^N = 1 \tag{7.2}$$

as it should be.

We can now use this normalized probability distribution to calculate different, average properties of a walk with N steps. For instance, the average number of steps to the right is

$$\langle R \rangle = \sum_{R=0}^{N} R\, P_N(R) = \sum_{R=0}^{N} \binom{N}{R} R\, p^R q^{N-R} \;. \tag{7.3}$$

The sum is easily done by writing $Rp^R = p\,(d/dp)p^R$. We then have

$$
\begin{aligned}
\langle R \rangle &= \sum_{R=0}^{N} p\, \frac{d}{dp} p^R q^{N-R} \binom{N}{R} = p\, \frac{d}{dp} \sum_{R=0}^{N} \binom{N}{R} p^R q^{N-R} \\
&= p\, \frac{d}{dp} (p+q)^N = Np\,(p+q)^{N-1} = Np \;.
\end{aligned}
\tag{7.4}
$$

This result is to be expected since of N steps, a fraction p is taken to the right. Since the displacement in one walk is $S = 2R - N$, we find for the average over a great many walks

$$\langle S \rangle = 2\langle R \rangle - N = 2Np - N(p+q) = N(p-q) \;. \tag{7.5}$$

The symmetric walk has the same probability going to the left as to the right. Then $p = q = 1/2$ and the average displacement is zero as expected.

It is easy to generate these random walks oneself. For symmetric walks one can just toss a coin. Head means a step to the right and tail mains a step to the left. One full walk is then generated by N tosses. In order to calculate statistical averages, one needs a large number M of such walks. They form together a statistical ensemble which can be used in the same way as ensembles were previously used for systems equilibrium. If the final displacement of walk number m is S_m, we can then numerically obtain the average displacement from

$$\langle S \rangle = \frac{1}{M} \sum_{m=1}^{M} S_m \tag{7.6}$$

in the limit $M \to \infty$. Other averages are similarly defined.

When the walk is not symmetric, it can not so easily be generated by a tossing a coin. Sometimes one can make use of a die. If, for example, the probability for a right step is $p = 2/3$, it is taken every time one of the numbers $\{1, 2, 3, 4\}$ comes up. In the two other cases one jumps to the left. When p has some arbitrary value, one must use a random number generator. They furnish random numbers r evenly distributed between zero and one. If $r < p$, one jumps to the right, if not, one jumps to the left. Repeating the operation, one generates the full walk. It is easy to program a calculator or small computer to rapidly produce these walks.

These methods of generating random walks are the simplest examples of what is called Monte Carlo simulations. A real walk is simulated on a piece of paper or on a computer screen. The Monte Carlo name comes from the use of the random processes generated by a coin, die, computer or roulette wheel. We will discuss such simulations of stochastic processes in greater detail later in this chapter.

In many cases we are interested in just the magnitude of the displacement irrespective of which direction it is. It can be obtained from the average $\langle R^2 \rangle$. Using the same trick as above for $\langle R \rangle$, we find

$$
\begin{aligned}
\langle R^2 \rangle &= \sum_{R=0}^{N} R^2 \, P_N(R) = \left(p \frac{d}{dp} \right)^2 \sum_{R=0}^{N} \binom{N}{R} p^R \, q^{N-R} \\
&= \left(p \frac{d}{dp} \right)^2 (p+q)^N = pN(p+q)^{N-1} + p^2 N(N-1)(p+q)^{N-2} \\
&= pN + p^2 N(N-1) = (Np)^2 + Npq .
\end{aligned}
\tag{7.7}
$$

Since the absolute displacement is given by $S^2 = (2R - N)^2$, we obtain for the average

$$
\begin{aligned}
\langle S^2 \rangle &= 4\langle R^2 \rangle - 4N\langle R \rangle + N^2 \\
&= N^2(4p^2 - 4p + 1) + 4Npq = N^2(p-q)^2 + 4Npq .
\end{aligned}
\tag{7.8}
$$

The first term is just the square of the average displacement (7.6). Hence we can write the result as

$$
\Delta S^2 \equiv \langle S^2 \rangle - \langle S \rangle^2 = 4Npq
\tag{7.9}
$$

which gives the fluctuation around the average, final position of the walk. For the symmetric walk, we have $\langle S \rangle = 0$ and thus

$$
\langle S^2 \rangle = N .
\tag{7.10}
$$

We see that displacement increases with time as $|S| = N^{1/2}$ where the exponent is characteristic for random walks. For an ordinary, directed walk we know that it is one. The random walk is for obvious reasons much more inefficient in covering a given distance.

It is easy to derive the central result (7.10) more directly. If the position of the walker after N steps is S_N, it will be at $S_{N+1} = S_N + 1$ with probability p at the next moment of time or at $S_{N+1} = S_N - 1$ with probability q. Squaring these two equations and taking the average, we obtain the recursion relation

$$\langle S^2 \rangle_{N+1} = \langle S^2 \rangle_N + 1 \tag{7.11}$$

in the symmetric case $p = q = 1/2$. Starting at the origin with $\langle S^2 \rangle_0 = 0$, we then obtain $\langle S^2 \rangle_1 = 1$, $\langle S^2 \rangle_2 = 2$ and so on.

When the number N of steps is very large, we can approximate the Bernoulli distribution (7.1) by a Gaussian distribution. This is most easily shown in the symmetric case when $p = q = 1/2$. The probability for a net displacement of S steps to the right is then

$$P(S, N) = \left(\frac{1}{2}\right)^N \frac{N!}{R! \, L!} \; . \tag{7.12}$$

Using Stirling's formula $n! = \sqrt{2\pi n} \, n^n e^{-n}$, we then get

$$\begin{aligned} P(S, N) &= \sqrt{\frac{N}{2\pi RL}} \, e^{N \log N - R \log R - L \log L - N \log 2} \\ &= \sqrt{\frac{N}{2\pi RL}} \, e^{-R \log (2R/N) - L \log (2L/N)} \end{aligned}$$

where $2R/N = 1 + S/N$, $2L/N = 1 - S/N$ and $RL = (1/4)(N^2 - S^2)$. Now expanding the logarithms to lowest order in S/N, we find

$$P(S, N) = \sqrt{\frac{2}{\pi N}} \, e^{-S^2/2N} \; . \tag{7.13}$$

In the prefactor we have made the approximation $1 - S^2/N^2 \simeq 1$. This is due to the exponent which forces S^2 to be of the order N. Thus $N^2/S^2 \propto 1/N$ and can be neglected when N is very large. The result is seen to be an ordinary Gaussian distribution with average value $\langle S \rangle = 0$ and width $\langle S^2 \rangle = N$ as we already have found.

The approximate Gaussian formula is in practice quite accurate also when S is of the same order as N and N is rather small. This is illustrated in Table 7.1 where we have compared the approximate probability (7.13) with the exact Bernoulli distribution (7.1) for a walk with $N = 10$ steps.

When the number N of steps in the walk gets very large, we can assume that each step is very small of length a. If the walk takes place along the x-axis, the final position of the walker will then be $x = Sa$ which we now can assume is a continuous variable. Similarly, it the time interval τ between each consecutive step is also very small, the walk takes a time $t = N\tau$ which also will be a continuous variable. The probability for the walker to be at position x at time t is then from (7.13)

$$P(x, t) = \frac{1}{2a} \sqrt{\frac{2\tau}{\pi t}} \, e^{-x^2 \tau / 2a^2 t} \; .$$

S	0	2	4	6	8	10
$P_{10}(S)$	0.246	0.205	0.117	0.044	0.010	0.001
Gauss	0.252	0.207	0.113	0.042	0.010	0.002

Table 7.1: Probabilities for a random walk with ten steps.

The factor $1/2a$ in front is needed to normalize this continuous probability distribution since the separation between each possible final position in walks with the same number of steps is $\Delta x = 2a$. Introducing the diffusion constant

$$D = \frac{a^2}{2\tau} \tag{7.14}$$

we can write the result as

$$P(x, t) = \sqrt{\frac{1}{4\pi Dt}} \, e^{-x^2/4Dt} \ . \tag{7.15}$$

At any given time it is a Gaussian distribution which is very peaked around $x = 0$ at early times and gets flatter at later times. Physically, this just reflects the fact that the probability to find the particle away from the origin increases with time. The area under the curve, however, remains constant. This is due to the normalization of the probability distribution which in the discrete case was given by (7.2). Now it becomes

$$\int_{-\infty}^{\infty} dx \, P(x, t) = 1 \tag{7.16}$$

as is easy to check by direct integration.

Equipped with this normalized probability distribution, we can now calculate different properties of the continuous random walk. The mean position of the walker at time t is

$$\langle \, x(t) \, \rangle = \int_{-\infty}^{\infty} dx x P(x, t) = 0 \tag{7.17}$$

as we already know. Again it must be stressed that this average of the final position x is taken over a large number of symmetric walks, all starting at position $x = 0$ at time $t = 0$ and lasting a time t. The absolute displacement is similarly given by the average

$$\langle \, x^2(t) \, \rangle = \int_{-\infty}^{\infty} dx x^2 P(x, t) = 2Dt \tag{7.18}$$

which is just the continuous version of the discrete result (7.10).

Random walks can easily be generalized to higher dimensions. For example, in two dimensions the walker can move in four direction at ever step in time,

up or down, right or left. In the symmetric case the probabilities for these four possibilities are equal to 1/4. If we let a random walk go on indefinitely, we will discover that it eventually comes back to the initial point one or more times and that the curve completely covers the two-dimensional plane. Random walks in three dimensions have neither of these properties.

The continuous probability distribution in three dimensions can be obtained from the product of three probabilities (7.13), one for each direction. On the average every time step will involve a step in each direction. The probability density for finding the walker at the position $\mathbf{x} = (x, y, z)$ is thus

$$
\begin{aligned}
P(\mathbf{x}, t) &= \left(\frac{1}{2a}\right)^3 \left(\frac{2}{\pi N/3}\right)^{3/2} e^{-\mathbf{x}^2/2Na^2} \\
&= \left(\frac{1}{4\pi Dt}\right)^{3/2} e^{-\mathbf{x}^2/4Dt}
\end{aligned} \tag{7.19}
$$

where $D = a^2/2\tau$ is the diffusion constant in three dimensions. With the unit normalization

$$
\int d^3x \, P(\mathbf{x}, t) = 1 \tag{7.20}
$$

we now find the mean position of the walker at time t as

$$
\langle \, x_i(t) \, \rangle = \int d^3x \, x_i \, P(\mathbf{x}, t) = 0 \tag{7.21}
$$

while the squared displacement follows from the average

$$
\langle \, x_i(t)x_j(t) \, \rangle = \int d^3x \, x_i x_j \, P(\mathbf{x}, t) = 2\delta_{ij}Dt \, . \tag{7.22}
$$

It gives as expected

$$
\langle \, \mathbf{x}^2(t) \, \rangle = \langle \, x^2(t) \, \rangle + \langle \, y^2(t) \, \rangle + \langle \, z^2(t) \, \rangle = 6Dt \tag{7.23}
$$

which also follows directly from the one-dimensional result (7.18).

In a Monte Carlo simulation one can again obtain these averages by starting a random walker in the initial position $\mathbf{x} = 0$, measuring his final position at time t, repeating this for a large number of identical walkers and then calculating the different averages over the accumulated data. Obviously, this is equivalent to starting off a large number of identical walkers at time $t = 0$ at the origin $\mathbf{x} = 0$ and then measure the different averages at a later time t. We then have a process where a large number of particles are slowly spreading out from the origin so that the mean distance to the particles increases like $t^{1/2}$. In this way we see that the random walk of one particle gives a microscopic description of diffusion which is basically a process involving a very large number of particles.

Diffusive processes are abundant, giving rise to heat conduction in solids, the spreading of momentum in a viscous fluid or the statistical behavior of

stock prises. However, in order to have a simple, mental picture of a diffusive process, consider a very small drop of colored dye in stationary water. After some time we will see it spreading out over a larger area and thinning out in concentration. The central limit theorem is a natural basis for a more general discussion of diffusion.

7.2 The central limit theorem

In the previous chapter a random walk was shown to have a Gaussian distribution. The central limit theorem generalizes this result to a sum of steps of random length as well as direction. We will use this result to describe diffusion in terms of the diffusion equation.

Gaussian distributions are highly common and may be found everywhere in nature, politics and economy. For that reason we should look for an explanation that does not rely on physical law.

Very often a variable X of interest is the sum of a large number of increments, so that

$$X = \sum_{i=1}^{N} x_i \qquad (7.24)$$

where the x_i are random variables with a distribution $p(x)$ and zero mean $\langle x \rangle = 0$. This distribution may have any form, but the variance of x must be finite, so that we may define

$$\sigma^2 = \int dx x^2 p(x) . \qquad (7.25)$$

The question now is what the distribution for X is. The probability of finding a given X is the sum of the probabilities of all the sets $\{x_i\}$ that sum up to X. This sum may be written

$$P(X) = \int dx_1 dx_2 .... dx_N p(x_1) p(x_2) .... p(x_N) \delta(X - \sum_{i=1}^{N} x_i) . \qquad (7.26)$$

To progress we take the Fourier transform of $P(x)$

$$
\begin{aligned}
\hat{P}(k) &= \frac{1}{2\pi} \int dX e^{-ikX} P(X) \\
&= \frac{1}{2\pi} \int dX e^{-ikX} \int dx_1 dx_2 .... dx_N \delta(X - \sum_{i=1}^{N} x_i) p(x_1) p(x_2) .... p(x_N) \\
&= \frac{1}{2\pi} \int dx_1 dx_2 .... dx_N e^{-ik \sum_{i=1}^{N} x_i} p(x_1) p(x_2) .... p(x_N) \\
&= \frac{1}{2\pi} \prod_{i=1}^{N} \int dx_i e^{-ikx_i} p(x_i) \\
&= (2\pi)^{N-1} \prod_{i=1}^{N} \hat{p}(k) = \frac{1}{2\pi} (2\pi \hat{p}(k))^N ,
\end{aligned}
\qquad (7.27)
$$

where $\hat{p}(k)$ is the Fourier transform of $p(x)$ The above result is a generalized convolution theorem. We then invert the transform to get back to $P(X)$:

$$P(X) = \int dk e^{ikX} \hat{P}(k) = \frac{1}{2\pi} \int dk e^{ik'X/N} (2\pi \hat{p}(k'/N))^N \tag{7.28}$$

where we have made the substitution $k' = Nk$. We may write $\hat{p}(k)$ in terms of $p(x)$ as

$$\hat{p}(k) = \frac{1}{2\pi} \int dx e^{-ikx} p(x) = \frac{1}{2\pi} \sum_{n=0}^{\infty} \frac{(-ik)^n \langle x^n \rangle}{n!} \ , \tag{7.29}$$

where we have used the Taylor series for the exponential. Since $\langle x \rangle = 0$, the linear term in $\hat{p}(k)$ vanishes. The 0'th order term is $1/(2\pi)$ and the second order term is $-(k\sigma)^2/(4\pi)$. For that reason we may make the following approximations

$$(2\pi \hat{p}(k/N))^N \approx \left(1 - \frac{(k\sigma)^2}{2N^2} \right)^N \to e^{-k^2 \sigma^2/(2N)} \tag{7.30}$$

when $N \to \infty$. In the above we have used the formula $(1 + x/N)^N \to e^x$ with $x = -(k\sigma)^2/2N$. Using the above approximation in equation (7.28) we get

$$
\begin{aligned}
P(X) &= \int dk e^{ikX} \hat{P}(k) \\
&= \frac{1}{2\pi} \int dk e^{ikX - k^2 N \sigma^2/2} \\
&= \frac{1}{\sqrt{2\pi N \sigma^2}} e^{-\frac{X^2}{2N\sigma^2}} \tag{7.31}
\end{aligned}
$$

where, in the end, we have performed the Gaussian integral. This result is the central limit theorem. It shows that X has a Gaussian distribution with variance $\langle X^2 \rangle = N\sigma^2$.

The central limit theorem will be used in the context of diffusion and the Langevin equation. However, it is also a usefull tool to understand many of the random processes we are surrounded by. Fluctuations are everywhere, and the theorem will sometimes let you distinguish between a fluctuation and a trend. If, for instance, a newspapers reports that the total tax income in the city of Oslo is dramatically decreasing, it may be a simple calculation to find that the decrease is within the expected year-to-year variation.

7.3   Diffusion and the diffusion equation

We start in one dimension and consider the particle, or molecule, as it performs a random walk due to molecular collisions. If the molecule starts out at $x = 0$ at $t = 0$ we may write for its position

$$x(t) = \sum_{i=1}^{N_0} \Delta y(t_i) \tag{7.32}$$

where the step-length $\Delta y(t_i)$ has a finite variance $\sigma^2 = \langle \Delta y^2 \rangle$. For this reason we may apply the central limit theorem and immediately write down the probability of finding the particle at some other position at a later time:

$$P(x,t) \propto e^{\frac{-x^2}{2N_0\sigma^2}} . \tag{7.33}$$

We will not need the microscopic information of σ^2, and we observe that $N_0 \propto t$, so we can make the replacement $2N_0\sigma^2 \rightarrow 4Dt$, where D is the diffusion constant. Writing things like this equation (7.33) may immediately be used to show that $\langle x^2 \rangle = 2Dt$. By normalization we then get

$$P(x,t) = \frac{e^{\frac{-x^2}{4Dt}}}{\sqrt{4\pi Dt}} , \tag{7.34}$$

which is just equation (7.15) again. Note that

$$P(x,t) = \frac{e^{\frac{-x^2}{4Dt}}}{\sqrt{4\pi Dt}} \rightarrow \delta(x) \tag{7.35}$$

when $t \rightarrow 0$. This is just the mathematical statement that we initially know where the particle is located. If we have $N \gg 1$ particles, initially all at the position x_0, their concentration

$$C(x,t) = \frac{\Delta N}{\Delta x} = NP(x,t), \tag{7.36}$$

and we note that their number is conserved as

$$\int dx C(x,t) = N . \tag{7.37}$$

It is always possible to consider an arbitrary concentration profile at some time $t = 0$ as a sum of delta-functions through the identity

$$C(x,0) = \int dx_0 C(x_0,0)\delta(x - x_0). \tag{7.38}$$

If the particles do not interact with each other, their evolution is independent, so that each delta-function evolves independently according to equation (7.34). This means that the concentration at some later time t is

$$C(x,t) = \int dx_0 C(x_0,0)\frac{e^{\frac{-(x-x_0)^2}{4Dt}}}{\sqrt{4\pi Dt}}, \tag{7.39}$$

where the probability function $e^{\frac{-(x-x_0)^2}{4Dt}}/\sqrt{4\pi Dt}$ is usually reffered to as the Green's function for diffusion.

Figure 7.1 illustrates a one-dimensional system populated with particles and the net current J_x (number of particles per unit time) passing a given point
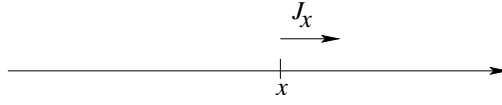
Figure 7.1: Diffusive current J_x along the x-axis.

$x > 0$. Since particle are neither created, nor destroyed, this current equals the rate of change of the particle number to the right of x. Taking all particles to start out at $x = 0$ this statement of particle conservation may be written

$$
\begin{aligned}
J_x &= \frac{d}{dt} \int_x^\infty dx\, NP(x,t) \\
&= \frac{d}{dt} \int_{\frac{x}{\sqrt{Dt}}}^\infty \frac{du}{4\pi} Ne^{-u^2/4} \\
&= \frac{x}{\sqrt{Dt}} \frac{1}{2t} \frac{Ne^{\frac{-x^2}{4Dt}}}{4\pi} \\
&= \frac{x}{2t} NP(x,t) = -D\frac{\partial}{\partial x} NP(x,t),
\end{aligned}
\tag{7.40}
$$

where we have made the substitution $u = x/\sqrt{Dt}$. The relation

$$
J_x = -D\frac{\partial C(x,t)}{\partial x}
\tag{7.41}
$$

is known as Ficks law, and since it is linear in C, it must hold for any sum of initial delta-function shaped initial concentrations, and therefore, for any initial concentration profile.

In 3D we can locally align the x-axis with ∇C. Then there are locally no variations in the transverse directions, and by symmetry, the diffusive flow must be in the direction of the gradient. This implies that the equation (7.40) generalizes to

$$
\mathbf{J} = -D\nabla C \ .
\tag{7.42}
$$

In 3D $C(\mathbf{x},t)$ is a particle number per volume, rather than length, and $\mathbf{J}$ is the number of particles per unit time and area that flows through space. The diffusion constant has, as always, dimensions of length^2/time.

Ficks law holds, as we have seen, for particles that do not interact with each other. For small gradients it may be generalized to the case of interacting particle by the introduction of a C-dependent diffusion coefficient $D(C)$. We shall not, however, make use of such generalizations.

The fact that particles are not created or annihilated may be stated by saying that inside a given volume V in space, the particle number change is entirely due to flow across the surface of that volume, or in mathematical terms:

$$
\frac{d}{dt} \int_V dV\, C(\mathbf{x},t) = -\int d\mathbf{S} \cdot \mathbf{J} = D \int d\mathbf{S} \cdot \nabla C = -\int dV D\nabla^2 C
\tag{7.43}
$$

where Ficks law and Gauss' theorem have been used to re-write the surface integral. By simply moving the right hand side to the left, and taking the time-derivative inside the integral, this equation becomes

$$\int_V dV \left(\frac{\partial C}{\partial t} - D\nabla^2 C \right) = 0, \tag{7.44}$$

which holds for any integration volume V. Therefore the integrand must be zero and

$$\frac{\partial C}{\partial t} = D\nabla^2 C . \tag{7.45}$$

This equation is known as the diffusion equation and results from the combination of Ficks law and local mass conservation.
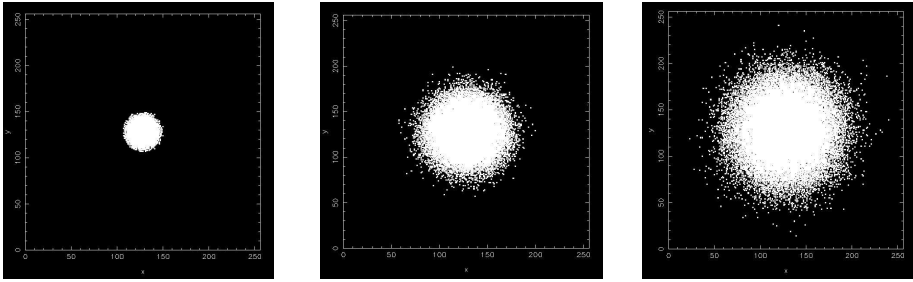

Figure 7.2: The evolution of 60 000 random walkers. Time increases from left to right.

Figure 7.2 shows the evolution of a finite set of random walkers that spread diffusively. Note that, even though each random walker has no preference to move either way, their density spreads out irreversibly. Figure 7.3, which displays the result of a density variation only in the x-direction, shows how their collective behavior confirms to equation (7.36).

For a spatial delta-pulse of concentration in 3D equation (7.45) has the solution

$$P(\mathbf{x}, t) = P(x, t)P(y, t)P(z, t), \tag{7.46}$$

which is easily checked by writing the equation in the form

$$\left(\frac{\partial}{\partial t} - \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) P(\mathbf{x}, t) = 0 . \tag{7.47}$$

By the same arguments of linearity as above the concentration in 3-dimensional space may be written

$$C(\mathbf{x}, t) = \int d^3 x_0 C(\mathbf{x}_0, 0) \frac{e^{-(\mathbf{x}-\mathbf{x}_0)^2/4Dt}}{(4\pi Dt)^{3/2}} . \tag{7.48}$$

This is formally the general solution to the initial value problem given by the diffusion equation and a given initial condition $C(\mathbf{x}, 0)$.
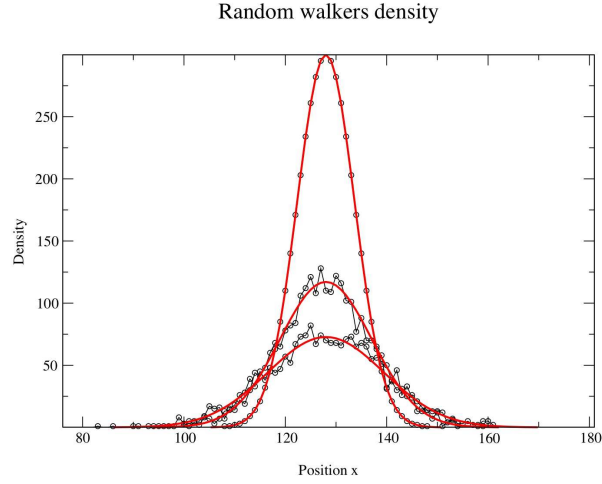
Random walkers density

Figure 7.3: Density profiles corresponding to the same random walker algorithm as in Figures 7.2. However, the random walkers are initialized as a strip with translational symmetry in the y-direction, and a Gaussian density profile in the x-direction. The density profiles are averaged in the y-direction which extends 200 sites. The full lines show the solution of the 1d diffusion equation. Note the noise in the measured graphs.

7.4 Markov chains

Random walks and diffusion are two of the simplest examples of a much larger class of stochastic processes called Markov chains. They are all characterized by the fundamental property that whatever happens at any instance is independent of what happened at earlier times. It only depends on the *state* of the particle or system. For the random walker, the state at any time was just its position. From any given state the system can then jump to another state with a certain probability. When these transition probabilities are independent of time, we say that the process is *stationary*. We will here consider only such Markov processes.

A.A. Markov (1856-1922) was a Russian mathematician who worked at the University in St. Petersburg. He did important work in number theory, limits of integrals and convergence of infinite series. Later he moved to probability theory where he proved the central limit theorem, i.e. that the sum of many random variables will approach a Gaussian distribution in the limit where the number of independent variables goes to infinity. The idea about chained, stochastic events came from his study of how vowels and consonants appeared in the poem "Yevgeny Onegin" by Pushkin. He received an honorary degree from the University of Oslo in 1902 at the Abel centennial that year.

In order to introduce the concepts and formalism needed in this chapter, let us first consider a simple problem from elementary probability theory. We are going to draw numbers from two boxes. Box A contains the numbers $\{1, 2, \ldots, 9\}$ and box B contains the numbers $\{1, 2, \ldots, 5\}$. We now ask for the probability to draw an even (E) or an odd (O) number from one of the boxes selected at random. The probability to draw an even number from box A is obviously $P(E|A) \equiv W_{EA} = 4/9$, while an odd number has the probability $P(O|A) \equiv W_{OA} = 5/9$. Similarly, $W_{EB} = 2/5$ and $W_{OB} = 3/5$. Since one box is chosen at random, the probability to choose box A is $P_A = 1/2$ and thus also $P_B = 1/2$. The probability P_E for drawing an even number is now given by the probability to draw an even number from box A times the probability that this box is chosen plus the same for box B. We thus have the probabilities

$$
\begin{aligned}
P_E &= W_{EA}\, P_A + W_{EB}\, P_B \\
P_O &= W_{OA}\, P_A + W_{OB}\, P_B
\end{aligned}
$$

which gives $P_E = 19/45$ and $P_O = 26/45$. As a check, we notice that $P_E + P_O = 1$.

These equations obviously invites to be written in matrix form as

$$
\begin{pmatrix} P_E \\ P_O \end{pmatrix} = \begin{pmatrix} W_{EA} & W_{EB} \\ W_{EB} & W_{OB} \end{pmatrix} \begin{pmatrix} P_A \\ P_B \end{pmatrix} . \tag{7.49}
$$

In a more compact notation we can write this as $P_i' = \sum_j W_{ij} P_j$ or simply $P' = WP$. The column vectors on both sides have the property that all their components are positive, i.e. $P_i \geq 0$. In addition, the sum of their elements are one,

$$
\sum_i P_i = 1 . \tag{7.50}
$$

They are said to be *probability vectors*. Similarly, all the elements of the matrix W are positive, i.e. $W_{ij} \geq 0$. Also, the sum of the elements in any column is one,

$$
\sum_i W_{ij} = 1 . \tag{7.51}
$$

Such matrices will in the following be called probability or *stochastic matrices*.

We can now define a stationary Markov processes. We consider a system which at some time has a probability P_j to be in a state j of a set $\{\ldots, i, j, k, \ldots\}$. These probabilities form a probability vector $P = (P_i)$. In the next moment of time it can make a jump to any other state in this set via a stochastic transition matrix $W = (W_{ij})$. The resulting state probability vector is then given by $P' = WP$. If we denote the initial vector by $P = P(n)$ and the final one by $P' = P(n + 1)$ where the argument n measures the step in time, we have in general

$$
P(n + 1) = WP(n) . \tag{7.52}
$$

The subsequent time development can then be read off from the probability vectors $P(n+2) = WP(n+1) = W^2 P(n)$, $P(n+3) = WP(n+2) = W^3 P(n)$ and so on. It is obviously of interest to find out what we can say about the state of the system after a large number of such stochastic transitions.

Before we consider this problem in general, let us first consider a simple example of a Markov process. It involves a student who can be in only two states. He is reading or he is sleeping. If he reads one day, he sleeps for certain the next day. If a sleeps one day, he will sleep or read the next day with equal probability. His transition matrix is thus

$$W = \begin{pmatrix} 0 & 1/2 \\ 1 & 1/2 \end{pmatrix} \tag{7.53}$$

Let us now calculate the probability for finding this student reading after a few days if he sleeps on the 0th day. His probability vector the first day is then

$$P(1) = \begin{pmatrix} 0 & 1/2 \\ 1 & 1/2 \end{pmatrix} \begin{pmatrix} 0 \\ 1 \end{pmatrix} = \begin{pmatrix} 1/2 \\ 1/2 \end{pmatrix} . \tag{7.54}$$

This is just what follows from the definition of the transition matrix. He has a 50% chance of reading the first day. The following day his state is given by

$$P(2) = \begin{pmatrix} 0 & 1/2 \\ 1 & 1/2 \end{pmatrix} \begin{pmatrix} 1/2 \\ 1/2 \end{pmatrix} = \begin{pmatrix} 1/4 \\ 3/4 \end{pmatrix} \tag{7.55}$$

so he has only a 25% chance of reading. However, on the third day the probability for reading jumps up to $P_R(3) = 3/8$ while on the fourth day it is down to $P_R(4) = 5/16$. It seems to settle down to value around $P_R \approx 0.33$ in the long run.

These probabilities must be understood in the ordinary sense of probability calculus. A single student is always certainly reading or sleeping. But if consider a large ensemble of students, let's say 480, with the same work habits, then on the first day 240 of these will be sleeping and 240 will be reading. The next day 120 will be reading, while on the fourth day 180 are reading. A few days later approximately 160 are reading and 320 are sleeping. At subsequent times the numbers of reading and sleeping students don't change anymore. The distribution of students over the two possible states has become stationary and the system is in equilibrium. But if we follow one particular student, we will still see that he reads and sleeps from day to day as he always has done.

If the Markov chain ends up in a stationary distribution, i.e. is given by the probability vector $P^* = P(n \to \infty)$, it follows from the definition (7.52) that it must satisfy the eigenvalue equation

$$P^* = WP^* . \tag{7.56}$$

This fixed-point vector is obviously attained independently of the initial state $P(0)$ of the system.

In the case of the student two-state problem, we can write $P^* = (x, 1 - x)$. With the transition matrix (7.53) the eigenvalue problem becomes $x = (1/2)(1 - x)$ which gives immediately $x = P_R^* = 1/3$ as obtained approximately above.

The long-time development is given by $W^n = WW^{n-1}$. In the limit $n \to \infty$ we therefore have $W^\infty = (P^* P^* \cdots P^*)$ or in more detail

$$
W^\infty = \begin{pmatrix}
P_1^* & P_1^* & \cdots & P_1^* \\
P_2^* & P_2^* & \cdots & P_2^* \\
P_3^* & P_3^* & \cdots & P_3^* \\
\vdots & \vdots & \vdots & \vdots
\end{pmatrix} . \tag{7.57}
$$

Whatever initial state we start from, the system will attain the same equilibrium state at late times. An obvious question is if such a fixed-point vector P^* exists for any Markov chain. It can be shown that it does provided the transition matrix W doesn't have any zero elements. W is then said to be a *regular* stochastic matrix.

We stated in the beginning that random walks can be described as Markov chains. In the simplest example of one dimension the state space is infinite and given by the lattice sites on the open line, i.e. $\{\ldots, -2, -1, 0, 1, 2, \ldots\}$. The transition matrix is thus also infinite and thus not so easy to write down in general. But when we only have transitions between nearest neighbor sites with p for the probability for a right jump and q for a left jump, it t takes the simple form with zeros along the main diagonal, q's along the upper bi-diagonal and p's along the lower bi-diagonal, all other matrix elements being zero. The state evolution equation (7.52) for one-dimensional random walk is thus

$$
P_i(n + 1) = p\, P_{i-1}(n) + q\, P_{i+1}(n) . \tag{7.58}
$$

It's content is obvious. In order to arrive at site i at time, the particle as to make a right jump from a previous position $i - 1$ or a left jump from a previous position $i + 1$. If it starts at site $i = 0$ at time $n = 0$ so that we have the initial probability distribution $P_i(0) = \delta_{i0}$, the above recursion relation can be solved for $P_i(n)$ to give the standard result obtained in the beginning of this chapter.

Instead of writing down all the elements of the transition matrix W, which can be rather cumbersome in many cases, it is much more convenient to draw the corresponding *transition diagram* containing the same information. All the states of systems are denoted by small circles. If a transition between two states is allow, these two states are connected by a line carrying an arrow giving the direction of the transition and the corresponding matrix element. A state can thus be connected with a transition line to itself. In Fig. 1 we show the transition diagram for the previous student problem and in Fig. 2 it is shown for the infinite random walk.

In a Markov chain there is a finite time difference τ between each transition. When $\tau \to 0$, we have a continuous time development. Defining now $W^n \equiv W(t, 0)$ where the time lapse t is given by $t = n\tau$, we have then for the corresponding probability vector $P(t) = W(t, 0)P(0)$. Since the transition

matrix is assumed to be stationary, we must have $W(s - t, 0) = W(s, t)$ and thus $P(s) = W(s, t)P(t)$ when $s > t$. Now $P(t) = W(t, u)P(u)$ when $t > u$, so that $W(s, u) = W(s, t)W(t, u)$. This is the Chapman-Kolmogorov equation. On component form, it gives

$$W_{ij}(s, u) = \sum_k W_{ik}(s, t)W_{k,j}(t, u) \tag{7.59}$$

which are non-linear constraints the transition matrix elements must satisfy.

As an example we can consider diffusion in d-dimensional space. Then the state space is given by the continuous coordinate $\mathbf{x}$ and the transition matrix W becomes $W_{ij}(t', t) \rightarrow W(\mathbf{x}', t'; \mathbf{x}, t)$. The probability distribution $P(\mathbf{x}, t)$ which is proportional with the particle concentration $C(\mathbf{x}, t)$, will then evolve according to the basic equation

$$P(\mathbf{x}', t') = \int d^d x\, W(\mathbf{x}', t'; \mathbf{x}, t)P(\mathbf{x}, t) \tag{7.60}$$

which is just the same as the previous diffusion evolution equation (7.48). The transition matrix must still satisfy the basic requirement (7.51) which now is

$$\int d^d x'\, W(\mathbf{x}', t'; \mathbf{x}, t) = 1 . \tag{7.61}$$

In addition, it must satisfy the Chapman-Kolmogorov equation (7.59)

$$W(\mathbf{x}'', t''; \mathbf{x}, t) = \int d^d x'\, W(\mathbf{x}'', t''; \mathbf{x}', t')W(\mathbf{x}', t'; \mathbf{x}, t) . \tag{7.62}$$

From the beginning of this chapter, we know that it is just the diffusion kernel In d dimensions is

$$W(\mathbf{x}', t'; \mathbf{x}, t) = \left(\frac{1}{4\pi D(t' - t)} \right)^{d/2} \exp\left(-\frac{(\mathbf{x}' - \mathbf{x})^2}{4D(t' - t)} \right) \tag{7.63}$$

when $t' > t$.

7.5   The master equation

In most cases it is impossible to construct the finite-time transition matrix $W(s, t)$. The situation is similar to quantum theory where the time evolution of state vector or wave function is given by the Schrödinger equation. This differential equation expresses the change in the wave function over an infinitesimal time interval in terms of the Hamiltonian operator. By integration one can then obtain the development of the state vector in a finite time interval.

A similar approach to stochastic process will be to consider the limit of the evolution equation $P(s) = W(s, t)P(t)$ in the limit $s \rightarrow t$. First of all, when $s = t$ we must have that W just becomes the identity matrix, i.e. $W_{i,i}(t, t) = \delta_{ij}$.

For an infinitesimal time evolution $s = t + \tau$ with $\tau \ll t$, we have then to first order in τ,

$$W_{ij}(t + \tau, t) = \delta_{ij} + \tau W'_{ij} . \tag{7.64}$$

Separating out the diagonal elements of W'_{ij} by writing

$$W'_{ij} = c_i \delta_{ij} + w_{ij}, \tag{7.65}$$

it follows that

$$W_{ij}(t + \tau, t) = (1 + c_i \tau)\delta_{ij} + \tau w_{ij} . \tag{7.66}$$

However, the diagonal c_i and non-diagonal w_{ij} elements are not independent since they stem from a stochastic matrix. It implies the condition (7.51) which gives

$$\sum_i W_{ij}(t + \tau, t) = 1 = (1 + c_j \tau) + \tau \sum_i w_{ij} \tag{7.67}$$

After a relabeling of indices we obtain

$$c_i = -\sum_j w_{ji} . \tag{7.68}$$

The infinitesimal evolution of the state vector is thus given by

$$\begin{aligned} P_i(t + \tau) &= (1 + c_i \tau)P_i(t) + \tau \sum_j w_{ij} P_j(t) \\ &= P_i(t) + \tau \sum_j (w_{ij} P_j - w_{ji} P_i) \end{aligned}$$

In the limit $\tau \to 0$ we then have the differential equation

$$\frac{dP_i}{dt} = \sum_j (w_{ij} P_j - w_{ji} P_i) . \tag{7.69}$$

It has the same form for all stochastic processes given the infinitesimal transition elements w_{ij} in the same way as the Schrödinger equation has the same form for all quantum processes given in terms of the corresponding Hamiltonian. Since it applies in principle to all continuous Markov processes, it is called the master equation inspired by the function of a master key which in principle will open all doors.

The physical content of the master equation is easy to describe. If we picture the probabilities P_i as the fraction of systems in an ensemble being in the state i, the first term on the right-hand side of (7.69) is just the number of systems in other states jumping into this particular state. Similarly, the last term is the number of systems jumping out of this state and into other states. It thus decreases the number of systems in state i and comes therefore with a minus sign.

As a simple example of what the equation gives, let us again consider random walk in one dimension. If we assume that there are only microscopic jumps in and out of neighboring sites, it follows directly from (7.69) that the probability to find the system at site i changes with time according to

$$\frac{dP_n}{dt} = w_{n,n+1}P_{n+1} + w_{n,n-1}P_{n-1} - w_{n+1,n}P_n - w_{n-1,n}P_n \ . \qquad (7.70)$$

Assuming first that the microscopic transition probabilities in the right and directions are constant along the chain, i.e. $w_{n,n+1} = w_{n-1,n} = w_L$ and $w_{n,n-1} = w_{n+1,n} = w_R$, the master equation takes the form

$$\frac{dP_n}{dt} = w_L(P_{n+1} - P_n) + w_R(P_{n-1} - P_n) \ . \qquad (7.71)$$

Denoting the separation between the lattice sites by a, we have $P_{n\pm1} = P(x\pm a)$. In the limit where $a \to 0$, we can therefore write

$$P_{n\pm1} - P_n = \pm a\frac{\partial P}{\partial x} + \frac{a^2}{2}\frac{\partial^2 P}{\partial x^2} \qquad (7.72)$$

when we drop higher terms in the Taylor expansion. The difference equation (7.72) then becomes the differential equation

$$\frac{\partial P}{\partial t} = a(w_L - w_R)\frac{\partial P}{\partial x} + \frac{a^2}{2}(w_L + w_R)\frac{\partial^2 P}{\partial x^2} \ . \qquad (7.73)$$

This equation is known as the Fokker-Planck equation for asymmetric random walk. In the symmetric case where microscopic jump probabilities to the right and left are the same, $w_L = w_R = w$, it simplifies to the diffusion equation with the diffusion constant $D = a^2 w$.

One of the most fundamental stochastic processes in Nature is radiative decay of atoms or radioactive decay of atomic nuclei. To be specific, let us consider N unstable nuclei with a decay constant λ. This means that any nucleus, independently of how long it has lived, has a probability of $\lambda\delta t$ to decay in a short time interval δt. If the total number of particles which has survived to the time t is $n = n(t)$, the number decaying in the time interval δt is $\delta n = -\lambda n\delta t$. In the limit $\delta t \to 0$ this gives the differential equation $dn/dt = -\lambda n$. It has the solution $n = N\exp(-\lambda t)$ since $n(0) = N$. However, since each individual decay is not a deterministic, but a stochastic process, we expect this standard decay law only to hold in the mean, i.e. for $\langle n(t)\rangle$. In practice, when continuously monitoring the original number of N nuclei, one will find the their number fluctuates in general around the mean value[1]

$$\langle n(t)\rangle = Ne^{-\lambda t} \ . \qquad (7.74)$$

---

[1]A more mathematically consistent notation for the average of n at time t would be $\langle n\rangle(t)$, but we will here stick with more convenient $\langle n(t)\rangle$ used in previous chapters and most physics texts.

The characteristic time $\tau = 1/\lambda$ is called the radioactive lifetime of the nuclei. Only when observing a large ensemble of systems, each containing N nuclei, will the mean number of surviving nuclei be given exactly by this exponential decay law.

The stochastic nature of radioactive decay can be brought forward by using the master equation (7.69). $P_n(t)$ will then denote the probability for having exactly n survived nuclei at time t. This number can decrease by having a decay of one of the n nuclei or it can increase by having a decay from the state with $n + 1$ nuclei. The master equation thus takes the form

$$\frac{dP_n}{dt} = \lambda(n+1)P_{n+1} - \lambda n P_n \ . \tag{7.75}$$

It will now be solved with the boundary condition $P_n(t = 0) = \delta_{nN}$. At very late times there should be no surviving nuclei and we expect to find $P_n(t = \infty) = \delta_{n0}$.

Before we solve this equation for the N unknown functions $P_n(t)$, we will first show how the average number of particles

$$\langle n(t) \rangle = \sum_{n=0}^{N} n P_n(t) \tag{7.76}$$

changes with time. Taking the time derivative on both sides and using (7.75), we have

$$\frac{d}{dt}\langle n \rangle = \lambda \sum_{n=0}^{N} n[(n+1)P_{n+1} - n P_n] \tag{7.77}$$

In the first sum on the right-hand side we change summation variable from $n+1$ to n. Using that $P_{N+1} = 0$, it follows that

$$\frac{d}{dt}\langle n \rangle = \lambda \sum_{n=0}^{N} [(n-1)n P_n - n^2 P_n] = -\lambda \langle n \rangle \tag{7.78}$$

which just proves the expected result (7.74). But we can now also obtain the fluctuation around this mean value. It is given by $\langle n^2(t) \rangle$ which can be calculated as above. From

$$\frac{d}{dt}\langle n^2 \rangle = \lambda \sum_{n=0}^{N} n^2[(n+1)P_{n+1} - n P_n] \tag{7.79}$$

we again redefine the summation variable in the first term on the right-hand side and thereby get

$$\begin{aligned} \frac{d}{dt}\langle n^2 \rangle &= \lambda \sum_{n=0}^{N} [(n-1)^2 n P_n - n^3 P_n] \\ &= \lambda[\langle n \rangle - 2\langle n^2 \rangle] \ . \end{aligned} \tag{7.80}$$

Multiplying both sides with $e^{2\lambda t}$ and reordering terms, the equation can then be written as

$$\frac{d}{dt}\left[e^{2\lambda t}\langle n^2\rangle\right] = e^{2\lambda t}\lambda\langle n\rangle = \lambda N e^{\lambda t} \tag{7.81}$$

After a direct integration

$$e^{2\lambda t}\langle n^2\rangle - N^2 = N(e^{\lambda t} - 1) \tag{7.82}$$

we then have the final result

$$\langle n^2(t)\rangle = N^2 e^{-2\lambda t} + Ne^{-\lambda t}(1 - e^{-\lambda t}) \, . \tag{7.83}$$

The fluctuation $\langle\Delta n^2\rangle = \langle n^2\rangle - \langle n\rangle^2$ in the number of surviving nuclei is thus

$$\langle\Delta n^2(t)\rangle = Ne^{-\lambda t}(1 - e^{-\lambda t}) \tag{7.84}$$

and is plotted in Fig. 3. It is seen to vanish at times $t = 0$ and $t = \infty$, in both cases because the number of nuclei at those times are fixed. The function has a maximum at $t_{1/2} = \ln 2/\lambda$ which is just the half-life time.

One of the simplest methods of finding the decay probabilities $P_n(t)$ is through their *generating function* defined by

$$G(s,t) = \sum_{n=0}^{N} s^n P_n(t) \tag{7.85}$$

for $s < 1$. Its partial derivative with respect to time follows directly from the master equation (7.75) as

$$\frac{\partial G}{\partial t} = \lambda\sum_{n=0}^{N} s^n[(n+1)P_{n+1} - nP_n] \tag{7.86}$$

The first term on the right-hand side can now be expressed by the partial derivative

$$\frac{\partial G}{\partial s} \;\; = \;\; \sum_{n=0}^{N} ns^{n-1}P_n = \sum_{n=1}^{N} ns^{n-1}P_n \tag{7.87}$$

$$= \;\; \sum_{n=0}^{N}(n+1)s^n P_{n+1} \tag{7.88}$$

while the second term is similarly expressed by $s(\partial G/\partial s)$. Thus we have the differential equation

$$\frac{\partial G}{\partial t} = \lambda(1-s)\frac{\partial G}{\partial s} \tag{7.89}$$

satisfied by the generating function. Introducing the new variable $x = \ln(1-s)$, it takes the form $(\partial G/\partial t) + \lambda(\partial G/\partial x) = 0$ which means that $G(s,t) = g(x-\lambda t)$.

The unknown function $g(x)$ can now be determined from the boundary condition $G(s,0) = s^N$ which follows from $P_n(0) = \delta_{nN}$ in the defining equation (7.85). Since $s = 1 - e^x$, we then have that $g(x) = (1 - e^x)^N$ and thus in general

$$G(s,t) = \left(1 - e^{x-\lambda t}\right)^N = \left[1 - (1 - s)\, e^{-\lambda t}\right]^N .\qquad(7.90)$$

Using the binomial expansion and comparing with (7.85), we obtain the result

$$P_n(t) = \binom{N}{n} e^{-\lambda n t} \left(1 - e^{-\lambda t}\right)^{N-n} \qquad(7.91)$$

for the decay probabilities. When $n = N$ this gives simply $P_N(t) = e^{-\lambda N t}$ which could also obtained directly from integration of the master equation (7.75). All the other probabilities can then be obtained by successive integration of the remaining first-order, inhomogeneous differential equations, thus confirming the result (7.91).

From the result (7.91) it is now easy to calculate different expectation values. From (7.87) we have for instance that $(\partial G/\partial s)|_{s=1} = \langle n \rangle$. The derivative of (7.90) with respect to s with $s = 1$ gives then immediately the result (7.74). Similarly, we get

$$\left(\frac{\partial^2 G}{\partial s^2}\right)_{s=1} = \langle n^2 \rangle - \langle n \rangle \qquad(7.92)$$

$$= N(N-1)e^{-2\lambda t} \qquad(7.93)$$

which reproduces the result (7.83).

The probabilities (7.91) are seen to be given by simply the binomial distribution function. A deeper understanding of this problem should then have allowed us to write down this result without explicitly solving the master equation. This follows from the realization that $p = e^{-\lambda t}$ is the probability for a nucleus to have survived until time t. Then $q = 1 - p$ is the probability for the nucleus to have decayed in this time. In order to have exactly n nuclei left at time t, then n out of the initial number N must have survived and $N - n$ must have decayed. Thus we have

$$P_n = \binom{N}{n} p^n (1 - p)^{N-n} \qquad(7.94)$$

which is just the result (7.91).

7.6   Monte Carlo methods

Casinos have a predictable average income, even though their winnings are based on random processes. Monte Carlo methods have their name for a similar reason: They too are based randomness, yet they have systematic average outputs.

The starting point for Monte Carlo methods is the master equation equation (7.75). Many systems satisfy, what is known as detailed balance, a condition
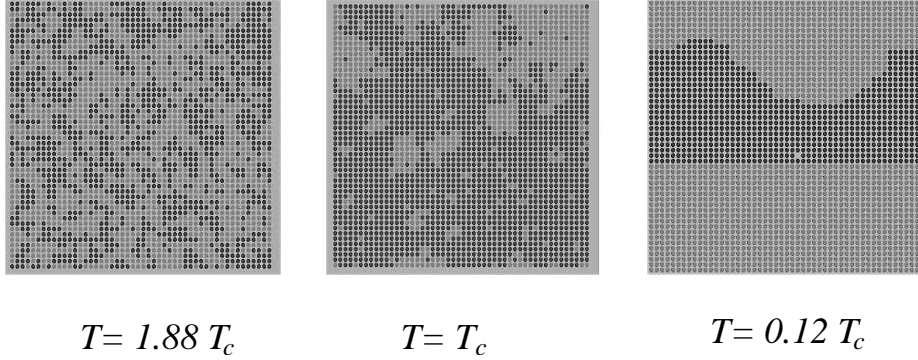
$$T= 1.88\ T_c \qquad\qquad T= T_c \qquad\qquad T= 0.12\ T_c$$

Figure 7.4: Snapshots of Ising model simulations using the Monte Carlo method at various temperatures.

which says that the $s \to s'$ transition rate is directly balanced by the $s' \to s$ transition rate,

$$w_{s's}P_{s'} = w_{ss'}P_s \ . \tag{7.95}$$

In steady state, when $\partial P(s)/\partial t = 0$, equation (7.89) then becomes

$$w_{s's}P_{s'} = w_{ss'}P_s \ . \tag{7.96}$$

The particular method known as the Metropolis: algorithm is derived by setting

$$w_{ss'} = \begin{cases} e^{-\beta \Delta E_{ss'}} & \text{when } \Delta E_{ss'} > 0 \\ 1 & \text{otherwise} \end{cases} \tag{7.97}$$

where $\Delta E_{ss'} = E_{s'} - E_s$ is the energy increase in the $s \to s'$ transition. Note that for any sign of $e^{-\beta \Delta E_{ss'}}$ the relation

$$\frac{w_{ss'}}{w_{s's}} = e^{-\beta \Delta E_{ss'}} \tag{7.98}$$

holds. Detailed balance then implies

$$\frac{w_{ss'}}{w_{s's}} = \frac{P_{s'}}{P_s} \ , \tag{7.99}$$

or equivalently

$$\frac{P_{s'}}{e^{-\beta E_{s'}}} = \frac{P_s}{e^{-\beta E_s}} \ . \tag{7.100}$$

Since the left hand side is s-independent, this must be the case also for the right, hand side, or, in other words

$$P_s \propto e^{-\beta E_s} \ , \tag{7.101}$$

which is just the Boltzmann distribution. The Metropolis algorithm is therefore a way of producing the canonical distribution.

The transition probabilities of equation (7.97) may be realized in the following way: First, a random state s' is chosen, and $\Delta E_{ss'}$ computed. The actual chose of s' may be done in many ways, as long as it doesn't exclude any parts of the state-space that we need to average over. Then the transition is accepted if $\Delta E_{ss'} < 0$. If $\Delta E_{ss'} > 0$ a random number $0 \leq x \leq 1$ is picked from a flat distribution, and the state is accepted if $x < e^{-\beta \Delta E_{ss'}}$. In this way a series of states $\{s_i\}$, $i = 1, ...N$ will be generated that samples the Boltzmann distribution.

Figure 7.4 shows the result of a Monte Carlo simulation of the Ising model at different temperatures on a 50 by 50 lattice. For $T = T_c$ it is instructive to
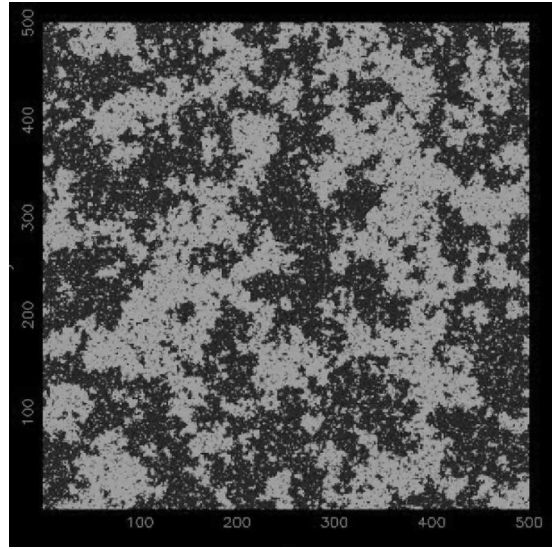

Figure 7.5: Snapshots of a Monte Carlo simulation of an Ising model at critical temperature on a 500x500 lattice.

look at a somwhat bigger lattice: Figure 7.5 shows a Monte Carlo simulation of a 500 by 500 lattice at $T = T_c$. Note that the sizes of magnetic domains range from the scale of a single lattice site to the size of the whole lattice. This means that the average domain size will always reflect the system size. When the lattice size diverges, so will the average domain size and the correlation length, in agreement with the equation (6.62).

Since the Metropolis algorithm samples the Boltzmann distribution, any equilibrium average may be computed. Since fluctuations are also computed through equilibrium averages, these are available too. If G_s is a variable of the system, its average is given as

$$\langle G_s \rangle = \frac{1}{N} \sum_{i=1}^{N} G_{s_i} \ . \tag{7.102}$$

If for instance you want to simulate the equilibrium state of a liquid the energy E_s must correspond to the interaction energies of the liquid molecules. Such a simulation will give the density fluctuations in the liquid, but it will not give the time evolution of the liquid. The time evolution is given by Newtons second law, or the Scrodinger equation, and the Monte Carlo transitions do not capture this. The Monte Carlo method is suited for simulations of equilibrium averages, and not the dynamics of the system. As such it is very efficient as it allows for the discontinuous motion between states. The molecular dynamics technique,on the other hand, which integrates Newtons second law for every molecule in the fluid, is very slow because the molecules can only be moved a small fraction of the mean free path for every time step. The Monte Carlo technique does not have this restriction and is therefore much faster.

The average computed from equation (7.102) is an average over the most likely states of the system. However, the states that are separated from the most likely energy values will have a vanishing probability of being visited for any macroscopic N-values. The number of microstates is so enormous (like 2^N, where N is the number of particles) that only a tiny fraction of them will ever be visited. This is in a sense the same situation as for a real system in the canonical ensemble, where the probability of having an energy substantially away from the average is vanishingly small.

In some cases though we would like to know the full probability distribution, even for unlikely values of the thermodynamic quantities. Such a case is the probability $P(M_0, T, N)$ of seeing a magnetization M_0 in an N-spin Ising magnet at temperature T and zero external field B. This probability may be written

$$P(M_0, T, N) = \sum_{s, M_s = M_0} P_s = \frac{1}{Z} \sum_{s, M_s = M_0} e^{-\beta E_s} . \qquad (7.103)$$

Here we may replace $Z = e^{-\beta F(\overline{M}, T, N)}$, since, when $B = 0$ the Gibbs and Helmholtz free energies are equal, $G = F$. Since the energy may be taken as a function of M, T and N, that is, $E = E(M, T, N)$, the sum

$$\sum_{s, M_s = M_0} e^{-\beta E_s} \approx e^{-\beta E(M, T, N) + S(M, T, N)/k} = e^{-\beta F(M, T, N)} . \qquad (7.104)$$

Combined with the expression for Z this gives

$$P(M_0, T, N) \approx e^{-\beta \Delta F(M_0, T, N)} , \qquad (7.105)$$

where the free energy deviation is $\Delta F(M_0, T, N) = F(M_0, T, N) - F(\overline{M}, T, N)$.

Note that since $\Delta F(M_0, T, N)/(kT) \sim N$, $P(M_0, T, N) \sim e^{-N}$ for any value where $\Delta F(M_0, T, N)$ is of the order of $F(M_0, T, N)$. Since this probability is too small to be reached by the standard Monte Carlo algorithm, a modification is called for.

For this purpose define $G_s = \Theta(M_s - M_0)$ where $\Theta(M_s - M_0) = 1$ when $M_s = M_0$ and 0 otherwise. The average computed from equation (7.102) is then

exactly the desired probability:

$$\frac{1}{N}\sum_{i=N}^{N} G_{s_i} = \langle\Theta(M_{s_i}-M_0)\rangle = \sum_s P_s\Theta(M_s-M_0) = \sum_{s,M_s=M_0} P_s = P(M_0,T,N) \, .$$
(7.106)

However, there is a catch to this computation. If we use the algorithm of equation (7.97) we will again never get into the $M_0 \le M_s \le M_0 + \Delta M$ regime. We may, however force the computation to stay in this regime by the modification

$$w_{ss'} = \begin{cases} e^{-\beta\Delta E_{ss'}} & \text{when } \Delta E_{ss'} > 0 \text{ and } M_0 \le M_{s'} \le M_0 + \Delta M \\ 1 & \text{when } \Delta E_{ss'} \le 0 \text{ and } M_0 \le M_{s'} \le M_0 + \Delta M \end{cases} \, .$$
(7.107)

Whenever $M_{s'}$ is outside the interval, the transition is not made. This means that the number N_{M_0} of transitions that are carried out is much, much smaller than the number N of transitions that would have been necessary in order to arrive spontaneously in the right regime. The algorithm of equation (7.107) then gives the following

$$P_u(M_0,T,N) = \frac{1}{N_{M_0}}\sum_{i=1}^{N_{M_0}}\Theta(M_{s_i}-M_0) = \frac{N}{N_{M_0}}\frac{1}{N}\sum_{i=1}^{N_{M_0}}\Theta(M_{s_i}-M_0) \, . \text{ (7.108)}$$

This kind of restricted sampling as is defined by equation (7.107) is usually referred to as umbrella sampling. From equation (7.105) we see that

$$\Delta F(M_0,T,N) = -kT\ln P_u(M_0,T,N) - kT\ln\left(\frac{N_{M_0}}{N}\right) \qquad (7.109)$$

where the additive constant $\ln(N_{M_0}/N)$ is hard to calculate. But we are able to calculate $\Delta F(M_0,T,N)$ as a continuous function within each interval from M_0 to $M_0+\Delta M$. Having such a piecewise continuous function, it is always possible to patch the pieces together to a fully continuous function.

This is what has been done to create the graph in Figure 7.6. Here the lattice is fairly small, only 30 by 30 sites. Within each window of width ΔM the simulations can only efficiently cover the regime of the spontaneously occurring fluctuations, and therefore the window width ΔM must be limited. In this case $\Delta M = 40$ for each run. Also, since it is known that $\Delta F(M_0,T,N) = \Delta F(-M_0,T,N)$, only the $M_0 > 0$ part is shown. Figure 7.6 should be compared with the Landau mean field ansatz which is shown in Figure 6.14.
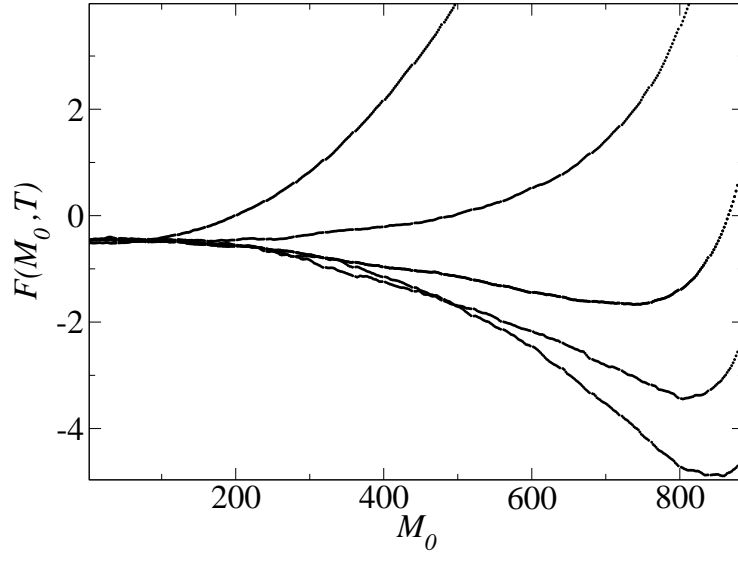
Figure 7.6: The free energy $F(M,T)$ as a function of magnetization M for different temperatures around T_c. The $F = 0$ value is arbitrary. The simulation was done with 900 spins, and the window of allowed M values had a width $\Delta M = 40$ for each run of 8 million iterations of the Monte Carlo algorithm. The coupling had the value $J/kT = 0.64$ for the critical state.

Chapter 8

Non-equilibrium Statistical Mechanics

Non-equilibrium statistical mechanics deals with the evolution of systems toward the equilibrium state, as opposed to equilibrium statistical mechanics, which more properly, is sometimes referred to as statistical statics. Only systems which are close to equilibrium may be captured by non-equilibrium statistical mechanics. In this case the term 'close' requires that equilibrium will be reached through a process that is described by a linear set of equations. If this is not the case, no general formalism exists, and far-from-equilibrium statistical mechanics remains an open, challenging and interesting domain of contemporary research.

The theories we shall develop in this chapter rest on an amazing property of equilibrium systems: They spontaneously generate out-of-equilibrium states, the fluctuations, and the average evolution of the fluctuations coincide with the evolution of much larger perturbations to the system. This is the content of the fluctuation-dissipation theorem, and it is an important part of the basis for the Onsager theory. This property shows up already in the Langevin equation, which describes the rich phenomenon of Brownian motion.

8.1 Brownian motion and the Langevin equation

In 1827, while examining pollen grains and the spores of mosses suspended in water under a microscope, Brown observed minute particles within vacuoles in the pollen grains executing a jittery motion. He then observed the same motion in particles of dust, enabling him to rule out the hypothesis that the motion was due to pollen being alive. Although he did not himself provide a theory to explain the motion, the phenomenon is now known as Brownian motion in his honor.

Before we embark on the analysis of the detailed motion of a Browian particle

Figure 8.1: The robust appearance of Robert Brown (1773–1858) and Paul Langevin (1872-1946).

it is instructive to derive the Einstein relation – a formula that relates the mobility of a Brownian particle to its diffusivity. This relation may be derived using the Boltzmann factor of equilibrium statistical mechanics, or the Langevin equation.

In 1905 A. Einstein was the first to explain diffusion in terms of random walks of individual particles. Einstein's microscopic derivation of the diffusion equation opened up a new chapter in the understanding of diffusion, Brownian motion and other stochastic processes. He showed that the diffusion constant may be related to the mobility μ of the diffusive particles. The mobility is defined as the ratio $\mu = v/F$ where v is the velocity by which the particle moves through its surrounding fluid in response to an external force F. The observation that Einsteins derivation is based on is the following. If a system of diffusing particles is subjected to gravity, the equilibrium state may be considered a balance between a downward flux due to gravity, and an upwards flux due to diffusion:

$$\mu C(\mathbf{x}, t) mg = -D \frac{\partial C}{\partial z}, \tag{8.1}$$

where mg is the gravitational force acting on individual particles, and z is the vertical coordinate. In equilibrium the probability of finding a particle at a given height z is given by the Boltzmann factor $e^{-\beta mgz}$, and therefore the concentration has the same dependence:

$$C(\mathbf{x}, t) \propto e^{-\beta mgz} \tag{8.2}$$

and we find the ratio

$$\frac{1}{C} \frac{\partial C}{\partial z} = -\beta mg . \tag{8.3}$$

When inserted in equation (8.1) this result immediately gives the relation

$$D = \mu kT, \tag{8.4}$$

which is the Einstein relation. It has the remarkable feature that it relates the mobility, a quantity that may be measured, or computed, in the absence of fluctuations, to a quantity D/kT, which is a direct measure of the thermal fluctuations in the system. Since μ determines the amount of (viscous) dissipation when the particle is moved, and D measures the magnitude of the fluctuations, the Einstein relation is also reffered to as a fluctuation-dissipation relation. It is a direct consequence of the so-called fluctuation-dissipation theorem, which will be derived in chapter 8.2.
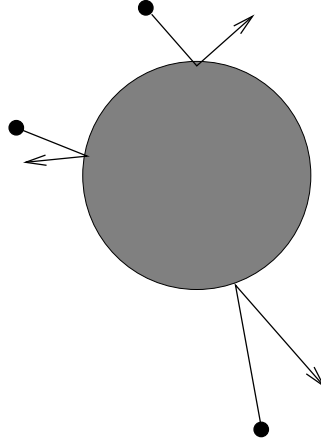

Figure 8.2: Fluid molecules hitting a suspended particle

The Langevin equation is Newtons second law for a Brownian particle, where the forces include both the viscous drag due to the surrounding fluid and the fluctuations caused by the individual collisions with the fluid molecules. In order to describe the statistical nature of the force fluctuations we restate the Central limit theorem, which we have already proved:

When a variable ΔP is a sum of independent increments,δp_i, like a random walk

$$\Delta P = \sum_{i=1}^{N} \delta p_i \qquad (8.5)$$

where $\langle \delta p_i \rangle = 0$ and $\langle \delta p_i^2 \rangle = \sigma^2$, then, when N is large, the random variable ΔP has a Gaussian distribution with $\langle \Delta P^2 \rangle = N\sigma^2$.

Now, take δp_i to be the x-component of the momentum transfer to the Brownian particle from a molecular collision, and let N be the number of collisions during the time Δt. Then ΔP is the x-component of the momentum received by the Brownian particle during the time Δt, and $\langle \Delta P^2 \rangle \propto \Delta t$. The corresponding force $\Delta P/\Delta t$ will have a variance

$$\langle \tilde{F}_x^2 \rangle = \frac{\langle \Delta P^2 \rangle}{\Delta t^2} \propto \frac{1}{\Delta t} \; . \qquad (8.6)$$

In a computer simulation of a Brownian particle one would have to integrate Newtons second law for the particle picking a random force $\tilde{F}(t)$ from a Gaussian distribution at every time-step Δt. Will this force be correlated from time step to time step? No, not as long as Δt is larger than the correlation time of the forces from the molecules, and we shall assume that these correlations may be neglected. In the next chapters we shall obtain the corrections to this approximation.

When this requirement is fulfilled we may hence write the correlation function as

$$\langle \tilde{F}_x(t)\tilde{F}_x(0)\rangle = \left\{ \begin{array}{ccc} \frac{a}{\Delta t} & \text{when} & |t| < \Delta t/2 \\ 0 & \text{when} & |t| > \Delta t/2 \end{array} \right. \tag{8.7}$$

where the constant a could in principle be determined from the variance of Δp_i. In stead we will determine it from the equipartition principle. In the $\Delta t \to 0$ limit the above equation becomes

$$\langle \tilde{F}_x(t)\tilde{F}_x(0)\rangle = a\delta(t) , \tag{8.8}$$

and likewise for the other spatial components of the force which will all be independent of each other.

Since $\langle \tilde{F} \rangle = 0$ the fluctuating force by itself will cause no average decay of the velocity. The macroscopic decay we need is the one caused by viscosity, i.e. $m\dot{v} = -\alpha v$ where m is the particle mass, v is the velocity relative to the surrounding fluid, and α is a constant coefficient, which for a sphere which is small (but larger than a Brownian particle), has the exact form $\alpha = 6\pi\eta r$, where η is the viscosity, r is the spheres radius. This friction law is known as Stokes law, and it is valid when the sphere moves at moderate speeds relative to a viscous fluid.

A version of Newtons 2. law which combines the effects of the fluctuations in the force and the hydrodynamic drag, is the Langevin equation

$$m\frac{d\mathbf{v}}{dt} = -\alpha\mathbf{v} + \tilde{\mathbf{F}} \tag{8.9}$$

where each component of $\tilde{\mathbf{F}}$ has a Gaussian distribution of magnitudes, and a correlation function given by Eq. (8.8). Both forces on the right hand side above come from the molecular fluid. The drag force $-\alpha\mathbf{v}$ represents the velocity dependence, and it is therefore reasonable to postulate that $\tilde{\mathbf{F}}$ is velocity-independent, and therefore

$$\langle \tilde{F}_i v_j \rangle = 0 \tag{8.10}$$

where i and j are Cartesian indices.

The first thing we compute from equation (8.9) is the velocity autocorrelation function. For simplicity we will start out in one dimension, since the generalization to higher dimensions is straightforward. Multiplying equation (8.9) by $e^{\alpha t/m}/m$ we can then write it as

$$\frac{d}{dt}\left(v(t)e^{\frac{\alpha t}{m}}\right) = e^{\frac{\alpha t}{m}}\frac{\tilde{F}(t)}{m} \tag{8.11}$$

which can be integrated from $t = -\infty$ to give

$$v(t) = \int_{-\infty}^{t} dt' e^{\frac{-\alpha(t-t')}{m}} \frac{\tilde{F}(t')}{m} \tag{8.12}$$

where $e^{-\alpha t/m}$ plays the role of a response function. The velocity auto-correlation function now follows directly as

$$
\begin{aligned}
\langle v(t)v(0) \rangle &= \int_{-\infty}^{t} dt' \int_{-\infty}^{0} dt'' e^{-\alpha(t-t'-t'')/m} \langle \tilde{F}(t')\tilde{F}(t'') \rangle / m^2 \tag{8.13} \\
&= \int_{-\infty}^{t} dt' \int_{-\infty}^{0} dt'' e^{-\alpha(t-t'-t'')/m} \frac{a\delta(t'-t'')}{m^2} \tag{8.14} \\
&= \int_{-\infty}^{0} dt'' e^{-\alpha(t-2t'')/m} \frac{a}{m^2} = \frac{a}{2m\alpha} e^{-\alpha t/m} \tag{8.15}
\end{aligned}
$$

where we have used equation (8.8) and the fact that the average $\langle ... \rangle$ commutes with the integration. Note that the first integration above is over t'. Assuming $t > 0$ this guarantees that the $t' = t''$ at some point during the integration and the a non-zero value of the δ-function is sampled.

We may combine equation (8.15) with the equipartition principle to fix a. Since

$$\frac{1}{2}m\langle v^2 \rangle = \frac{kT}{2} \tag{8.16}$$

we get

$$a = 2\alpha kT . \tag{8.17}$$

In other words, the magnitude of the fluctuations increase both with temperature and friction.

We may integrate the velocity over time to get the displacement $x(t)$, and the diffusive behavior linked to the variance $\langle x^2(t) \rangle$. Note that this is a refinement of the random walker, since now the step length is governed by the integration of Newtons 2. law.

Starting from equation (8.12) and using equation (8.8) we get

$$
\begin{aligned}
\langle x^2(t) \rangle &= \int_{0}^{t} dt' \int_{0}^{t} d\bar{t}' \int_{-\infty}^{t'} dt'' \int_{-\infty}^{\bar{t}'} d\bar{t}'' e^{-\alpha(t'-t''+\bar{t}'-\bar{t}'')/m} \frac{2\alpha kT\delta(t''-\bar{t}'')}{m^2} \tag{8.18} \\
&= \frac{2\alpha kT}{m^2} \int_{0}^{t} dt' \int_{0}^{t} d\bar{t}' \int_{-\infty}^{t'} dt'' \Theta(\bar{t}'-t'') e^{-\alpha(t'+\bar{t}'-2t'')/m} \tag{8.19}
\end{aligned}
$$

where the Heaviside function $\Theta(t)$, which is 1 for $t > 0$ and zero otherwise, appeared because the integration over the δ-function is nonzero only if its argument passes 0. The Θ-function will be 0, however, only if $\bar{t}' < t'$, so we get

$$\langle x^2(t) \rangle = \frac{2\alpha kT}{m^2} \int_{0}^{t} dt' \int_{0}^{t} d\bar{t}' \int_{-\infty}^{\min(t',\bar{t}')} dt'' e^{-\alpha(t'+\bar{t}'-2t'')/m} . \tag{8.20}$$

The three remaining integrals are straightforward and gives

$$\langle x^2(t) \rangle = \frac{2\ kT}{\alpha} \left(t - \frac{m}{\alpha} \left(1 - e^{-\alpha t/m} \right) \right) \ . \tag{8.21}$$

When $t \gg m/\alpha$ only the t-term survives and $\langle x^2(t) \rangle = 2Dt$ with

$$D = \frac{kT}{\alpha} \ . \tag{8.22}$$

This relation is again the Einstein relation, now with $\alpha = 1/\mu$. Like the fluctuation-dissipation theorem it relates quantities related to spontaneous fluctuations, D and kT, with a quantity that describe macroscopic decay, α.

When $t \ll m/\alpha$ we Taylor expand the exponential to second order to get

$$\langle x^2(t) \rangle = \frac{kT}{m} t^2 \ , \tag{8.23}$$

that is $\sqrt{\langle x^2(t) \rangle} = v_{th} t$ where $v_{th}^2 = kT/m$ is exactly the thermal velocity that follows from the equipartition principle. Having a finite correlation time m/α for the velocity the Langevin equation thus describes the crossover between the ballistic regime $\sqrt{\langle x^2(t) \rangle} \propto t$ to the diffusive regime $\sqrt{\langle x^2(t) \rangle} \propto \sqrt{t}$.

The Langevin equation is based on the approximation that the friction force has the instantaneous value $-\alpha \mathbf{v}$ and does not depend on the history of the motion. However, the amount of momentum given off by the Brownian particle does depend on the motion-history, and this momentum will change the velocity of the surrounding fluid, which in turn changes the force on the Brownian particle. A correct description then does take the history dependence of the force into account, and this changes the velocity correlation function: In the long time limit the correlation function changes from the $e^{-\alpha t}$ behavior to an $1/t^{d/2}$ behavior, where d is the dimension. This was discovered in the late 1960's, first through computer simulations, then analytically.

Langevin equations show up also outside physics. Stock prices for instance are often described by a Langevin equation.

8.2   The fluctuation dissipation theorem

It is often easier to generalize a particular result than it is to apply a general result to a particular situation. In the following we shall therefore consider the Brownian motion of a particle that is submerged in a thermal fluid and connected to a spring, as illustrated in Fig.8.3. We may subsequently keep in mind that the position variable x could also denote the center of mass position of electric charge or a Fourier component of a fluid interface wave.

In a rough sense the fluctuation dissipation theorem states that a spontaneous equilibrium fluctuation decays like an externally imposed perturbation. To make this statement more precise consider a small perturbation $h \ll kT$ to the system Hamiltonian H. For $t < 0$ the system is governed by $H + h$ while
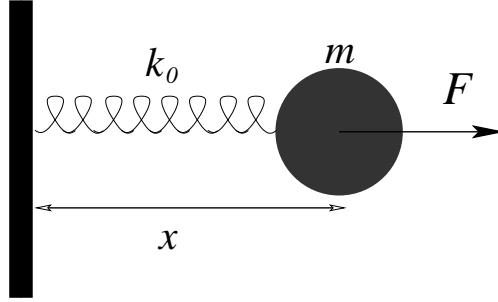
Figure 8.3: Particle submerged in a fluctuating fluid and connected to a spring.

at $t > 0$ it is governed by H. For concreteness, take $h = -Fx$ where F is an external force, i.e. $F = QE$ where Q is an electric charge and E an electric field.

For brevity we introduce the trace notation, which applies both to classical and quantum systems

$$\text{Tr}X = \int d\omega X = \sum_{\text{quantum states } n} \langle n|X|n\rangle \tag{8.24}$$

where $d\omega$ represents an infinitesimal phase space volume. Then the equilibrium average may be written

$$\langle x \rangle = \text{Tr}\{x(p,q)f(p,q)\} = \frac{\text{Tr}\left\{x(p,q)e^{-\beta H}\right\}}{\text{Tr}e^{-\beta H}} \tag{8.25}$$

where $f(p,q)$ represents the probability distribution in phase space, and x may in fact be one of the q's. The origin of x is defined so that $\langle x \rangle = 0$. Let the correlation function $c(t)$ be defined in the normal way

$$c(t) = \langle x(t)x(0)\rangle = \int d\omega x(t;p,q)x(0;p,q)f(p,q) \tag{8.26}$$

where $x(t;p,q)$ is the value of x at time t given the initial values (p,q). Note that the Hamiltonian of the system fixes the evolution of all the variables from a given initial condition.

The mean value of x after the external force is turned off may be written

$$\overline{x}(t) = \frac{\text{Tr}\{x(t;p,q)e^{-\beta(H-Fx)}\}}{\text{Tr}e^{-\beta(H-Fx)}} \tag{8.27}$$

where the average is taken with the Boltzmann factor $e^{-\beta(H-Fx)}$ since the initial condition is defined with F turned on. Now, since $\beta Fx \ll 1$ we may expand

the numerator to linear order in Fx

$$
\begin{aligned}
\mathrm{Tr} \quad & \{x(t;p,q)e^{-\beta(H-Fx)}\} \\
\approx \quad & \mathrm{Tr}\{x(t;p,q)e^{-\beta H}(1+\beta Fx(0;p,q)\} \\
= \quad & \mathrm{Tr}\{x(t;p,q)e^{-\beta H}\} + \mathrm{Tr}\{x(t;p,q)x(0;p,q)\beta Fe^{-\beta H}\} \\
= \quad & \beta F\langle x(t)x(0)\rangle \mathrm{Tr}e^{-\beta H}
\end{aligned}
\tag{8.28}
$$

where we have used that $\mathrm{Tr}\{x(t;p,q)e^{-\beta H}\}/\mathrm{Tr}e^{-\beta H} = \langle x(t)\rangle = \langle x\rangle = 0$ is independent of t. Likewise, the denominator may be written

$$
\frac{1}{\mathrm{Tr}e^{-\beta(H-Fx)}} \approx \frac{1-F\langle x\rangle}{\mathrm{Tr}e^{-\beta H}} = \frac{1}{\mathrm{Tr}e^{-\beta H}} \; .
\tag{8.29}
$$

Combining the numerator and denominator gives

$$
\overline{x}(t) = \beta F\langle x(t)x(0)\rangle \; ,
\tag{8.30}
$$

for $t>0$. This equation has the form of the fluctuation dissipation theorem. However, the perturbation $h=-Fx$ is not macroscopic as it is smaller than kT, and therefore $\overline{x}$ is not larger than a spontaneous fluctuation. However, if the system is linear so that $\overline{x} \propto F$ even when $h \gg kT$, then $\overline{x}=Fr(t)$ for some response function $r(t)$ and all F within the linear regime. But this relation must also hold for small F, so that $r(t)=\beta\langle x(t)x(0)\rangle$. This means that holds for all F as long as the macroscopic perturbation remains linear, which means that F must be so small that it does not exceed the linear regime of the spring, nor cause any non-linear hydrodynamics when the external force is relaxed. The fluctuation dissipation theorem is then given by equation (8.30).
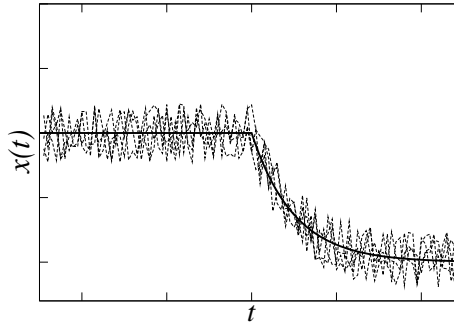

Figure 8.4: Relaxation of $x(t)$ when a constant force is set to zero at $t=0$. The full line represents the ensemble average.

Figures 8.4 and 8.5 give an interpretation of the theorem of equation (8.30). In Fig. 8.5 the subset of spontaneously occurring time series with $x(0)=x_0$
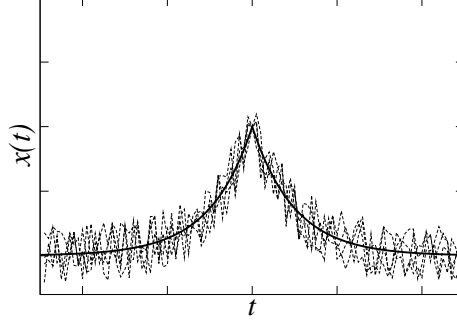
Figure 8.5: Relaxation of $x(t)$ in equilibrium when the average is taken over all time-series with $x(0) = x_0$. The full line represents the ensemble average.

is selected. Since equilibrium averages are invariant under time translation $\langle x(t)x(0)\rangle = \langle x(-t)x(0)\rangle$ and the curves in Fig. 8.5 are (statistically) symmetric around $t = 0$. The fluctuation dissipation theorem states that for $t > 0$ the averaged relaxations of Figs. 8.4 and 8.5 are identical provide the systems are linear in the sense stated above. This is not obvious at all, since the system arrives at its $t = 0$ state with different histories, and the further evolution will in general depend on history.

Dividing equation (8.30) by its $t = 0$ form we may write it as

$$\frac{\overline{x}(|t|)}{\overline{x}(0)} = \frac{\langle x(t)x(0)\rangle}{\langle x^2 \rangle} , \qquad (8.31)$$

where we have extended the time domain by inserting an absolute value of time on the left hand side. If the energy dependence on x is quadratic, as in the present case $E = (1/2)k_0 x^2$, the equipartition theorem holds, $\langle x^2 \rangle = kT/k_0$, and we get

$$\frac{\overline{x}(|t|)}{\overline{x}(0)} = \frac{k_0 \langle x(t)x(0)\rangle}{kT} , \qquad (8.32)$$

which is the form we shall apply in the following.

The fluctuation dissipation theorem may also be derived more directly by splitting the average in the correlation function in the following way:

$$\langle x(t)x(0)\rangle = \langle \overline{x}_{x_0}(t)x(0)\rangle_0 \qquad (8.33)$$

where $\overline{x}_{x(0)}(t)$ is the average over all time-trajectories $x(t)$ that start at x_0 at $t = 0$, and the average $\langle \ \rangle_0$ is over all initial values x_0. By applying as a hypothesis that the average of microscopic fluctuations, such as $\overline{x}_{x_0}(t)$, decay as macroscopic perturbations, we may immediately write equation (8.31). This hypothesis is known as the *regression hypothesis*, and we see that the content of the above proof is to show this hypothesis, and under what conditions it holds.

We shall now specialize to a description that is coarse grained in the sense that it is closed on the level of the variables x and t. We shall only use the linearity in the relation between x and F, and the most general relation we may then write is

$$\overline{x}(t) = \int_{-\infty}^{\infty} dt' \kappa(t - t') F(t') \tag{8.34}$$

where the response function $\kappa(t) = 0$ for $t < 0$, since x can only depend on past, and not future, force-values, i.e. κ is causal.

We shall now switch to Fourier space, and before we proceed , it is useful to write down a few basic relations of Fourier transforms. We define the Fourier transform of a function $f(t)$ the only reasonable way as

$$
\begin{aligned}
\hat{f}(\omega) &= \frac{1}{2\pi} \int_{-\infty}^{\infty} dt f(t) e^{-i\omega t} \\
f(t) &= \int_{-\infty}^{\infty} d\omega \hat{f}(\omega) e^{i\omega t} \ .
\end{aligned}
\tag{8.35}
$$

In the following we list some useful, and easily proven, properties of the Fourier transform, which are shown in the appendix.

First, the convolution theorem: If $\hat{g}(\omega)$ and $\hat{h}(\omega)$ are two transforms and $\hat{f}(\omega) = \hat{g}(\omega)\hat{h}(\omega)$, then

$$f(t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt' g(t') h(t - t') \ . \tag{8.36}$$

The next result is relevant for response functions like $\kappa(t)$: If a function $f_0(t) = 0$ for $t < 0$, then we may extend it to an even function $f(t) = f_0(|t|)$ with the Fourier transform

$$\hat{f}(\omega) = 2\mathrm{Re}(\hat{f}_0(\omega)) \ . \tag{8.37}$$

Finally, we need a theorem that also has a physical content, and is known as the Wiener-Khinchin theorem. It relies on ergodicity, the postulate that time and ensemble averages give the same result. Introducing the finite time transform

$$\hat{f}_T(\omega) = \frac{1}{2\pi} \int_{-T}^{T} dt f(t) e^{-i\omega t} \tag{8.38}$$

we may define the power spectrum

$$S_f(\omega) = \lim_{T \to \infty} \frac{\pi}{T} |\hat{f}_T(\omega)|^2 \ . \tag{8.39}$$

t is shown in the appendix that ergodicity gives

$$\langle f(t) f(0) \rangle = \int_{-\infty}^{\infty} d\omega S_f(\omega) e^{i\omega t} \ , \tag{8.40}$$

which means that finding the auto-correlation function and the power spectrum amounts to the same thing.

Taking the Fourier transform of equation (8.34) and using the convolution theorem gives

$$\hat{\bar{x}}(\omega) = 2\pi\hat{\kappa}(\omega)\hat{F}(\omega) \ . \tag{8.41}$$

The Fourier transform of equation (8.32) has the form

$$\frac{2\text{Re}(\hat{\bar{x}}(\omega))}{\bar{x}(0)} = \frac{kS_x(\omega)}{kT} \ . \tag{8.42}$$

In order to get a well defined expression for $\hat{F}(\omega)$ it useful to assume that it decays slowly to zero as $t \to -\infty$, and write

$$F(t) = F_0\Theta(-t)e^{\lambda t} \ , \tag{8.43}$$

where it is understood that, at the end of the day, the $\lambda \to 0$ limit is taken. This force has the Fourier transform

$$\hat{F}(\omega) = \frac{iF_0}{2\pi(\omega + i\lambda)} \ . \tag{8.44}$$

Combining this expression with the above gives

$$\hat{\bar{x}}(\omega) = \frac{i\hat{\kappa}(\omega)F_0}{\omega + i\lambda}; \ . \tag{8.45}$$

Now, equation (8.42) may be written

$$\begin{aligned}
S_x(\omega) &= \frac{kT}{k\bar{x}(0)}2\text{Re}(\hat{\bar{x}}(\omega)) \\
&= 2kT\text{Re}\left(\frac{i\hat{\kappa}(\omega)}{\omega + i\lambda}\right) \\
&= -2kT\text{Im}\left(\frac{\hat{\kappa}(\omega)}{\omega + i\lambda}\right)
\end{aligned} \tag{8.46}$$

where we have used that $F_0 = k\bar{x}(0)$.

Now, since the Fourier transform of the particle velocity $\hat{u}(\omega) = i\omega\hat{x}$, the velocity power spectrum $S_u(\omega) = \omega^2 S_x(\omega)$ and equation (8.46) gives

$$S_u(\omega) = -2kT\text{Im}(\omega\hat{\kappa}(\omega)) \ , \tag{8.47}$$

in the $\lambda \to 0$ limit.

The velocity autocorrelation function

$$\langle u(t)u(0)\rangle = \int d\omega e^{i\omega t}S_u(\omega) = ikT\int d\omega e^{i\omega t}(\omega\hat{\kappa}(\omega) - \omega\hat{\kappa}^*(\omega)) \ , \tag{8.48}$$

where $\hat{\kappa}^*(\omega) = \hat{\kappa}(-\omega)$, since $\kappa(t)$ is real. This means that we can make the substitution $\omega \to -\omega$ in the second term of the integrand to get

$$\langle u(t)u(0)\rangle = ikT\int d\omega\omega(e^{i\omega t} + e^{-i\omega t})\hat{\kappa}(\omega) \ , \tag{8.49}$$

where it is now explicit that $\langle u(t)u(0)\rangle$ is even in t. Let us therefore assume that $t > 0$, and make the following observation: By definition

$$\kappa(t) = \int d\omega e^{i\omega t}\hat{\kappa}(\omega) . \tag{8.50}$$

Since $\int_0^\infty dt\kappa(t)$ is finite (a finite constant force will produce a finite response), $\hat{\kappa}(\omega) \propto \int dt e^{-i\omega t}\kappa(t) \to 0$ as $\omega \to \infty$. For this reason we may close the ω-integral along the contour C shown in Fig. 8.6. Since
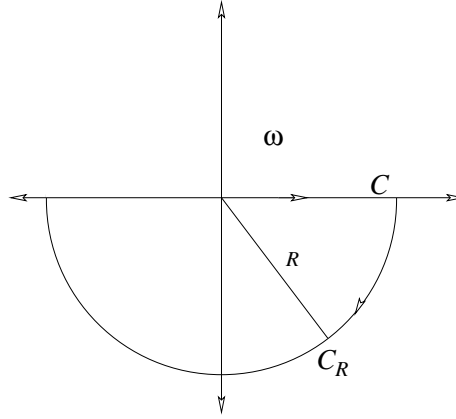

Figure 8.6: Closed integration contour C in the ω-plane. The circular part of the contour is denoted C_R.

$$\kappa(t) = 0 \text{ for } t < 0 . \tag{8.51}$$

we may deduce that $\hat{\kappa}(\omega)$ has no poles in the lower half plane: This also means that the $e^{-i\omega t}$-term in equation (8.49) will give zero contribution when $t > 0$ (we assume that $\omega\hat{\kappa}$ goes to zero as well), and we may simply write

$$\langle u(t)u(0)\rangle = ikT \int d\omega e^{i\omega|t|}\omega\hat{\kappa}(\omega) , \tag{8.52}$$

when $t \neq 0$. Note that the above argument fails when $t = 0$, since, as we will observe, the contribution from the C_R contour vanishes only when $t \neq 0$.

8.3   Generalized Langevin Equation

A description of Brownian motion, that includes the fluctuation (not just the average, as in equation (8.34))is given by the generalized Langevin equation

$$m\ddot{x} = -\int_{-\infty}^{t} dt'\gamma(t-t')\dot{x}(t') + R(t) - kx + F(t) \tag{8.53}$$

where m is the mass, γ is a hydrodynamic response function, $R(t)$ is a fluctuating force of zero mean, and F is the external force as before. Taking first the average, and then the Fourier transform of equation (8.53) we get

$$-m\omega^2\hat{\bar{x}} = -2\pi\hat{\gamma}(\omega)i\omega\hat{\bar{x}} - k\hat{\bar{x}} + \hat{F}(\omega) \ , \tag{8.54}$$

or, equivalently,

$$\hat{\bar{x}}(\omega) = 2\pi\hat{\kappa}(\omega)\hat{F}(\omega) \ , \tag{8.55}$$

with

$$\hat{\kappa}(\omega) = \frac{1/(2\pi)}{-m\omega^2 + 2\pi\hat{\gamma}(\omega)i\omega + k_0} \ , \tag{8.56}$$

which, indeed satisfies $\omega\hat{\kappa} \to 0$. This result for $\hat{\kappa}(\omega)$ may be used to derive the correlation function for $R(t)$.

Writing the Langevin equation in terms of the velocity u, and setting both $F = 0$ and $k = 0$, we get

$$mi\omega\hat{u}(\omega) = -\hat{\gamma}(\omega)2\pi\hat{u}(\omega) + \hat{R}(\omega) \ , \tag{8.57}$$

or

$$\hat{u}(\omega) = \frac{\hat{R}(\omega)}{im\omega + 2\pi\hat{\gamma}(\omega)} \ . \tag{8.58}$$

This equation describes a free Brownian particle with both the spring force and the external force. Taking the modulo square of this equation we obtain

$$S_u(\omega) = \frac{S_R(\omega)}{|im\omega + 2\pi\hat{\gamma}(\omega)|^2} \ . \tag{8.59}$$

Using the expressions equation (8.47) and equation (8.56) to write $S_u(\omega)$ we get

$$\begin{aligned}
S_R(\omega) &= \frac{kT}{\pi}\mathrm{Re}\left(\frac{|im\omega + 2\pi\hat{\gamma}(\omega)|^2}{im\omega + 2\pi\hat{\gamma}(\omega)}\right) \\
&= 2kT\mathrm{Re}(\hat{\gamma}(\omega)) \ ,
\end{aligned} \tag{8.60}$$

where we have written the real part as the sum of the expression and its complex conjugate in order to pass from the first to the second line. It follows from this that the correlation function

$$\langle R(t)R(0)\rangle = kT\gamma(|t|) \ . \tag{8.61}$$

The force correlation function is, in other words, directly given by the hydrodynamic response function. When there is a memory in the response function, i.e. when there is a finite hydrodynamic relaxation time, there is also a memory in the correlations of the thermal force R. The fact that $\gamma(t)$ has a finite decay time is linked to momentum conservation in the fluid: If the Brownian particle increases its momentum, there must be a corresponding momentum decrease in the surrounding fluid. This momentum change in the fluid will spread out hydrodynamically, and this process will take a significant time. The momentum

of the Brownian particle will thus be affected by this process as long as it goes on, as is reflected in the response function γ.

It is instructive to note that the equipartition theorem is reproduced. Setting $t = 0$ in equation (8.49) gives us

$$\langle u^2 \rangle = 2ikT \int d\omega \omega \hat{\kappa}(\omega) \ . \tag{8.62}$$

Substituting from equation (8.56) with $k = 0$ gives

$$\langle u^2 \rangle = \frac{kT}{im\pi} \int d\omega \frac{1}{\omega - 2\pi i \hat{\gamma}(\omega)/m} \ . \tag{8.63}$$

This integral has no poles in the lower half plane. However the integral along C_R will not vanish. Instead we get that

$$
\begin{aligned}
\langle u^2 \rangle &= -\frac{kT}{im\pi} \int_{C_R} d\omega \frac{1}{\omega - 2\pi i \hat{\gamma}(\omega)/m} \\
&= -\frac{kT}{im\pi} \int_{C_R} \frac{d\omega}{\omega} = \frac{kT}{m} \ ,
\end{aligned}
\tag{8.64}
$$

or, in other words $\langle (m/2)u^2 \rangle = kT/2$, which is just the equipartition principle. In the above argument we have used the fact that $\hat{\gamma}(\omega)/\omega \to 0$ when $\omega \to 0$, so that the last term in the above denominator could be neglected.

If we neglect the hydrodynamic memory, we may set

$$\gamma(t) = 2\alpha\delta(t) \tag{8.65}$$

where α is the friction coefficient of equation (8.9). Then equation (8.53) becomes

$$m\ddot{x} = -\alpha\dot{x} + R(t) - kx + F(t) \tag{8.66}$$

with the force correlations

$$\langle R(t)R(0) \rangle = 2kT\alpha\delta(t) \ . \tag{8.67}$$

This is just the good old, Markovian, Langevin equation. Note the factor of 2 in equation (8.65). This factor reflects the fact that the integration domain in equation (8.53) only extends to the point where the argument of the δ-function is 0. Since the δ-function should be considered the limit where some smooth function becomes very peaked, this means that the integration of the δ-function only gives $1/2$, and not 1, as usual.

A more careful hydrodynamic analysis shows that the Markovian Langevin equation is a good description when the mass density of the Brownian particle is much higher than the mass density of the surrounding fluid. It is also clear that the standard Langevin equation is accurate when there is no momentum conservation in the fluid, as is, for instance, the case when the fluid is a thin film on a substrate.

8.4 Green-Kubo relations

Earlier we showed that the Markovian Langevin equation gives rise to diffusion in the long time limit. How does diffusion emerge from the non-Markovian equation? We shall answer this question by going via so-called Green-Kubo relations. These are relations between a transport coefficient, like the diffusivity D, and an equilibrium correlation function.

In order to obtain the diffusivity we may always write the mean square displacement as

$$\langle x^2(t) \rangle = \int_0^t dt' \int_0^t dt'' \langle u(t')u(t'') \rangle \tag{8.68}$$

where may apply the fact that since the average is over a stationary state $\langle u(t')u(t'') \rangle = \langle u(t' - t'')u(0) \rangle$. Writing $f(t) = \langle u(t)u(0) \rangle$ the above expression takes the form

$$\langle x^2(t) \rangle = \int_0^t dt' \int_0^t dt'' f(t' - t'') = \int_0^t dt' \int_{-t'}^{t-t'} d\tau f(\tau) \tag{8.69}$$

if we substitute $\tau = t'' - t'$. Doing the t'-integration by parts gives

$$\langle x^2(t) \rangle = t \int_0^t d\tau f(\tau) + \int_{-t'}^{t-t'} dt' t' (f(t - t') - f(t')) , \tag{8.70}$$

where we have used that $f(t)$ is an even function in t. By adding an subtracting t to t' in the second integral and doing a trivial substitution, we get

$$\langle x^2(t) \rangle = 2t \int_0^t d\tau f(\tau) - 2 \int_0^t d\tau \tau f(\tau) . \tag{8.71}$$

Now, if these integrals converge in the $t \to \infty$ limit, the behavior is diffusive as $\langle x^2(t) \rangle \propto t$, and we may define the diffusivity as usual as

$$
\begin{aligned}
D &= \lim_{t \to \infty} \frac{\langle x^2(t) \rangle}{2t} = \lim_{t \to \infty} \left(\int_0^t d\tau f(\tau) - \frac{1}{t} \int_0^t d\tau \tau f(\tau) \right) \\
&\approx \int_0^\infty d\tau f(\tau) .
\end{aligned} \tag{8.72}
$$

The relation

$$D = \int_0^\infty d\tau \langle u(\tau)u(0) \rangle \tag{8.73}$$

is a Green-Kubo relation. When the integral of the velocity correlation function converges, it defines the diffusivity from measurements on the equilibrium state of the system. Such a formulation is useful in computer simulations, since the simulation may be carried out in equilibrium and no external perturbations are required. It also quantifies how fast the velocity correlations must decay in order for the process to be considered a (diffusive) random walk. The Markovian

Langevin equation gives $\langle u(t)u(0) \rangle = (kT/m)e^{-\alpha t/m}$, so the integral clearly converges and gives $D = kT/\alpha$, which is again the Einstein relation.

But the Markovian Langevin equation does not take into account the fact that the overall momentum of the Brownian particle and the surrounding fluid is conserved. The velocity autocorrelation function $\langle u(t)u(0) \rangle$ will indeed reflect this fact, and it will only decay as fast as a momentum perturbation in the system will propagate away to infinity. To get an idea of how this will happen it is instructive to consider a velocity perturbation $u_x = u_0\delta(z)$ that is one-dimensional in the sense that it is constant along a plane that is perpendicular to the z-direction. For such a perturbation the equation of fluid dynamics, the Navier Stokes equation, reduces to the one-dimensional diffusion equation

$$\frac{\partial u_x}{\partial t} = \nu \frac{\partial^2 u_x}{\partial z^2} \tag{8.74}$$

where ν is the kinematic shear viscosity that describes the shear forces in the fluid. The solution is the well-known diffusive Greens function

$$u_x(z,t) = u_0 \frac{e^{-\frac{z^2}{4\nu t}}}{(4\pi\nu t)^{1/2}} \; . \tag{8.75}$$

In three dimensions, or more generally d dimensions, the flow field becomes more complex, if the momentum perturbation is only introduced at a single point, but it still has the diffusive time-dependence $1/t^{d/2}$ at the point where the perturbation was introduced. Since, by the fluctuation-dissipation theorem, the correlation function decays as a macroscopic perturbation we get that

$$\langle u(t)u(0) \rangle \propto \frac{1}{t^{d/2}} \tag{8.76}$$

for long times. This means that in 3D the Green-Kubo integral $\int dt (1/t^{3/2})$ converges in the long time limit, and all is well with the diffusive behavior of a Brownian particle.

In 2D on the other hand, equation (8.71) would give

$$\langle x^2(t) \rangle \propto t \ln(t) \tag{8.77}$$

and the mean square displacement increases faster than linearly in time. This means that in Flatland, a two-dimensional world, normal diffusive behavior does not exist– thanks to momentum conservation.

Only in 1991 was such anomalous diffusive behavior actually observed. M. van der Hoef and D. Frenkel did this by means of a new simulation technique, known as hydrodynamic lattice gases, that deals effectively with large scale hydrodynamic systems that also has the fluctuations of real fluids. Of course, truly two-dimensional systems do not exist in our three-dimensional world. But two-dimensional descriptions may still apply, and one might imagine that the odd bacteria, living in the fluid of a soap bubble for instance may experience an enhanced availability of nutrition due to the enhanced diffusion there.

Assuming convergence of the Green-Kubo integral, the velocity power spectrum from the Langevin equation may be used to solve the integral. Since the velocity autocorrelation function is even in time

$$D = \int_0^\infty d\tau \langle u(\tau)u(0)\rangle = \frac{1}{2}\int_{-\infty}^\infty d\tau \langle u(\tau)u(0)\rangle = \frac{1}{2}\int_{-\infty}^\infty d\tau \int_{-\infty}^\infty d\omega e^{i\omega t} S_u(\omega) ,$$
(8.78)

and we may interchange the order of integration and use $\int_{-\infty}^\infty d\tau e^{i\omega t} = 2\pi\delta(\omega)$ to write

$$D = \pi S_u(0) = -2\pi kT \lim_{\omega\to 0} \mathrm{Im}(\omega\hat\kappa(\omega)) , $$
(8.79)

where we have inserted our velocity power spectrum equation (8.59). From equation (8.56) with $k_0 = 0$ we have got

$$\omega\hat\kappa(\omega) = \frac{1/(2\pi)}{-m\omega + 2\pi i\hat\gamma(\omega)} \to \frac{1}{(2\pi)^2 i\hat\gamma(0)} ,$$
(8.80)

and

$$D = \frac{kT}{2\pi\hat\gamma(0)} ,$$
(8.81)

which looks very much like the Einstein relation, only that α is replaced by $2\pi\hat\gamma(0)$. What does this mean? By definition, the Fourier transform is

$$2\pi\hat\gamma(0) = \int_{-\infty}^\infty dt\gamma(t) .$$
(8.82)

The force caused by the fluid on a particle moving steadily at the velocity u_0 may be written

$$-\int_{-\infty}^\infty dt'\gamma(t-t')u_0 = u_0\int_{-\infty}^\infty dt'\gamma(t') = \alpha_0 u_0$$
(8.83)

where α_0 is now the steady state drag coefficient. This means that

$$D = \frac{kT}{\alpha_0} ,$$
(8.84)

which is yet again the Einstein relation. However, the interpretation is new. The present version of the Einstein relation tells us that D is only sensitive to the asymptotic, long time, or small frequency, behavior of the response function $\hat\gamma(\omega)$. All the dynamic memory effects contained in the finite frequency dependence of $\hat\gamma(\omega)$ is somehow averaged out in D, unless of course, it causes the Green-Kubo integral to diverge so that the behavior becomes super-diffusive.

8.5   Onsager relations

Consider two containers connected by a small hole through which gas may flow. If the width and length of the hole is of the order of the mean free path of

Figure 8.7:

Lars Onsager (1903-1976)

the gas, non-hydrodynamic effects set in. In particular, it may be observed that temperature differences may drive mass flow and, vice versa, pressure differences will drive heat flow. This is known as the thermomechanic effect and represents an example of a cross phenomena where the driving force of one current drives the other, and the other way around. Onsager reciprocity relations state that these cross-couplings are equal– or, reciprocal– in a certain quantitative sense. Another example involves the cross-coupling between liquids like oil and water, that flow through a porous medium and are forced by individual pressure differences.

Lars Onsager first studied the cross-coupling between a heat flow in one direction and a temperature gradient in another direction in an anisotropic crystal. In 1931 he published a much more general result that relates the flows and forces in thermodynamic systems out of equilibrium, but where a notion of local equilibrium exists. This result deals, which proves reciprocity in macroscopic, irreversible phenomena, is, surprisingly, based on the observation that the underlying micro-dynamics is time reversible. For this he was awarded the Nobel Prize in chemistry (!) in 1968.

Let us denote the quantities that are coupled in our system as x_i. For simplicity we would like these quantities to appear linearly in the Hamiltonian, so that the Fluctuation dissipation theorem applies. This may often be achieved by imagining external springs or other external forces, for instance, in the case of two phases flow, the fluid flow velocity may be identified with the position of a piston subjected to a constant, external force.

A key concept in this context is the entropy production, which we may write as

$$\dot{S} = f_i \dot{x}_i \tag{8.85}$$

where Einsteins summation convention is understood and

$$f_i = \frac{\partial S}{\partial x_i}(x) \tag{8.86}$$

in general is taken at some non-equilibrium value of x. The quantity f_i is known as a thermodynamic force and $\dot{x}_i$ as the conjugate thermodynamic flux.

We shall take the system to be isolated, so that the probability of finding the system at some particular x-values is proportional to the number of microstates compatible with those values:

$$P(x) = \frac{e^{S(x)/k}}{\int dx e^{S(x)/k}} \tag{8.87}$$

where the integration goes over all the x_i's. A particularly practical relation holds between x_i and f_i: Computing the equilibrium average, using the above distribution, gives

$$
\begin{aligned}
\langle x_i f_j \rangle &= \frac{\int dx x_i f_j e^{S(x)/k}}{\int dx e^{S(x)/k}} \\
&= \frac{\int dx x_i \frac{\partial S}{\partial x_j} e^{S(x)/k}}{\int dx e^{S(x)/k}} \\
&= \frac{|_{-\infty}^{\infty} x_i e^{S(x)/k} - k\delta_{ij} \int dx e^{S(x)/k}}{\int dx e^{S(x)/k}} \\
&= -k\delta_{ij}
\end{aligned}
\tag{8.88}
$$

where we have partially integrated and discarded the boundary term, since the extreme values of x_i may be considered of vanishing probability.

We will assume that there is a linear relationship between the fluxes and the forces. For a spring, for instance, a linear force–displacement relationship follows if the spring is within the Hooks law regime, i.e. when $x \ll x^{NL}$, where x^{NL} is the displacement where the spring starts to behave non-linearly. In general, when fluctuation$\ll x \ll x^{NL}$ linearity implies a relation like

$$\dot{x}_i = L_{ik} f_k \tag{8.89}$$

which are macroscopic, linear laws.

In the following we want to say something about the coefficients L_{ik} from the nature of the correlation functions $\langle x_i(t) x_j(0) \rangle$. The key observation is that in a microscopic description the time evolution of $x_i(t)$ and all the microscopic degrees of freedom are governed by a Hamiltonian that guarantees time-reversibility. Hence, if a measurement of $x_i(t)$ were run backwards in time, it would represent a solution of the equations of motion just as well as the forward moving signal. For that reason

$$\langle x_i(t) x_j(0) \rangle = \langle x_i(-t) x_j(0) \rangle . \tag{8.90}$$

Using time-translational invariance of an equilibrium average, we get

$$\langle x_i(t) x_j(0) \rangle = \langle x_i(-t) x_j(0) \rangle = \langle x_i(t-t) x_j(t) \rangle = \langle x_i(0) x_j(t) \rangle . \tag{8.91}$$

Splitting the above averages, as in equation (8.33), we can write

$$\langle \overline{x}_i(t) x_j(0) \rangle_0 = \langle x_i(0) \overline{x}_j(t) \rangle_0 \;, \tag{8.92}$$

where $\overline{x}_i(t)$ is the average over all time evolutions that start out with $x_i = x_i(0)$. Subtracting $\langle x_i(0) x_j(0) \rangle$ on both sides of these equations, replacing $t \to \tau$, and dividing by τ we get

$$\left\langle \frac{\overline{x}_i(\tau) - x_i(0)}{\tau} x_j(0) \right\rangle_0 = \left\langle \frac{\overline{x}_j(\tau) - x_j(0)}{\tau} x_i(0) \right\rangle_0 \;, \tag{8.93}$$

where we shall take τ to be a time that is much larger than the molecular mean free time, and smaller than the macroscopic decay times. Then we may identify $(\overline{x}_i(\tau) - x_i(0))/\tau = \dot{\overline{x}}_i$, and substitute the linear laws of equation (8.89) to get

$$L_{ik} \langle f_k x_j \rangle = L_{jk} \langle f_k x_i \rangle \;. \tag{8.94}$$

Applying the relation of equation (8.88) then gives

$$L_{ij} = L_{ji} \tag{8.95}$$

which are the celebrated Onsager reciprocity relations. The perhaps most striking feature of these relations is that they link a symmetry of macroscopic, irreversible responses to the reversibility of the underlying microdynamics.

In order to apply the Onsager relations the fluxes and forces must be identified, and this is most conveniently done by determining the entropy production in the form of equation (8.85). Since this equation involves only the products $f_i x_i$ a certain amount of freedom exists when defining the fluxes and forces.

Chapter 9

Appendix

9.1 Fourier transforms

Say that you were listening to someone playing the piano, and you were able to hear exactly the combination of keys that were hit. If you could also hear how hard they were hit your ear and brain would, roughly speaking, be doing a Fourier transform. Fourier transforms quantify how much there is of every single frequency in a signal. This is true if the signal is something that varies with time. If the variation is over space, like a set of waves on the sea, the Fourier transform gives you an amplitude for every wavenumber.

To make all this mathematical we start out with a function of time $f(t)$, that we have sampled at a given rate over a certain time interval $2T$ so that we know $f(t_n)$ at the times $t_n = Tn/N$, where $n = -N, -N + 1, ...N - 1$. This is a practical situation, and we will subsequently make the mathematical idealizations of (1) a continuous time ($N \to \infty$) and (2) an infinite measurement interval, $T \to \infty$. We define the Fourier transform as

$$\hat{f}(\omega_k) = \frac{T}{2\pi N} \sum_n f(t_n)e^{-i\omega_k t_n} \tag{9.1}$$

where the discrete frequency $\omega_k = \pi k/T$, and $k = -N, -N + 1, ..., N - 1$ takes just as many values as t_n. Note that the Fourier transform is linear, in fact, it is just a matrix multiplication by a matrix that has the elements $E_{kn} = e^{-i\omega_k t_n} = e^{-i\pi kn/N}$. This matrix is non-singular, and we can invert the transform as

$$f(t_n) = \frac{\pi}{T} \sum_k \hat{f}(\omega_k)e^{i\omega_k t_n} \ . \tag{9.2}$$

To prove this we need to compute the sum

$$\sum_{k=-N}^{N-1} e^{i\omega_k t_n} \quad = \quad \sum_{k=-N}^{N-1} e^{i\pi kn/N}$$

$$= \sum_{k=0}^{2N-1} e^{-i\pi n/N} \left(e^{i\pi n/N} \right)^k$$

$$= \begin{cases} e^{-i\pi n/N} \frac{1-e^{2\pi in}}{1-e^{i\pi n/N}} & \text{when } n \neq 0 \\ 2N & \text{when } n = 0 \end{cases} \quad , \qquad (9.3)$$

where we have made the replacement $k \to k + N$, and used the formula for a geometric sum. Using the fact that $e^{2\pi in} = 1$ we may therefore write

$$\sum_{k=-N}^{N-1} e^{i\omega_k t_n} = 2N\delta_{n0} \ . \qquad (9.4)$$

If we insert equation (9.2) in equation (9.1), or the other way around, and use the above formula, we may indeed verify that equation (9.2) holds. Note also that, by the $n \leftrightarrow k$ symmetry, we get

$$\sum_{n=-N}^{N-1} e^{-i\omega_k t_n} = 2N\delta_{k0} \ . \qquad (9.5)$$

Now, assume that we take t to be continuous, so that $N \to \infty$, while T is kept fixed. Then the time-increment $\Delta t = T/N \to 0$ and we may replace the sum in equation (9.1) by an integral:

$$\hat{f}(\omega_k) = \frac{1}{2\pi} \sum_n \Delta t f(t_n) e^{-i\omega_k t_n} = \frac{1}{2\pi} \int_{-T}^{T} dt f(t) e^{-i\omega_k t} \qquad (9.6)$$

with the inverse

$$f(t) = \frac{\pi}{T} \sum_{k=-\infty}^{\infty} \hat{f}(\omega_k) e^{i\omega_k t} \ . \qquad (9.7)$$

Equation (9.4) takes the form

$$\sum_k e^{i\omega_k t} = \lim_{N\to\infty} 2N\delta_{n0} = \lim_{\Delta t\to 0} 2T\frac{\delta_{n0}}{\Delta t} = 2T\delta(t) \ , \qquad (9.8)$$

where $\delta(t)$ is the Dirac delta function, and equation (9.5)

$$\int dt e^{-i\omega_k t} = 2T\delta_{k0} \ . \qquad (9.9)$$

Finally, we take the $T \to \infty$ limit, and this makes the results even simpler, as now, the frequency as well becomes continuous. Since the increment $\Delta\omega = \pi/T$ we get from equation (9.7) that

$$f(t) = \int_{-\infty}^{\infty} d\omega \hat{f}(\omega) e^{i\omega t} \ , \qquad (9.10)$$

and the inverse

$$\hat{f}(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt f(t) e^{-i\omega t} \; . \tag{9.11}$$

Equation (9.4) and (9.5) take the common form

$$\int_{-\infty}^{\infty} d\omega e^{i\omega t} = 2\pi\delta(t) \text{ and } \int_{-\infty}^{\infty} dt e^{-i\omega t} = 2\pi\delta(\omega) \; . \tag{9.12}$$

In the following we derive some standard relations given in the main text.

9.2 Convolution theorem

If $\hat{g}(\omega)$ and $\hat{h}(\omega)$ are two transforms and $\hat{f}(\omega) = \hat{g}(\omega)\hat{h}(\omega)$, then how may we write $f(t)$ in terms of $g(t)$ and $h(t)$?. The convolution theorem answers this question, and is easily proven by insertion:

$$\begin{aligned}
f(t) &= \int_{-\infty}^{\infty} d\omega \hat{g}(\omega)\hat{h}(\omega) e^{i\omega t} \\
&= \frac{1}{(2\pi)^2} \int_{-\infty}^{\infty} d\omega dt' dt'' g(t') h(t'') e^{i\omega(t-t'-t'')} \\
&= \frac{1}{2\pi} \int_{-\infty}^{\infty} dt' dt'' g(t') h(t'') \delta(t-t'-t'') \\
&= \frac{1}{2\pi} \int_{-\infty}^{\infty} dt' g(t') h(t-t') \; , \tag{9.13}
\end{aligned}$$

which proves the relation.

9.3 Even extension transform

The next result is relevant for response functions, that is, functions that vanish for negative arguments: If a real function $f_0(t) = 0$ for $t < 0$, then we may extend it to an even function $f(t) = f_0(|t|)$ with a Fourier transform given by $\hat{f}_0$. The transform of the even extension of $f_0(t)$ is simply

$$\begin{aligned}
\hat{f}(\omega) &= \frac{1}{2\pi} \int_{-\infty}^{\infty} dt f(t) e^{-i\omega t} \\
&= \frac{1}{2\pi} \int_{-\infty}^{0} dt f_0(-t) e^{-i\omega t} + \frac{1}{2\pi} \int_{0}^{\infty} dt f_0(t) e^{-i\omega t} \\
&= \frac{1}{2\pi} \int_{0}^{\infty} dt f_0(t)(e^{-i\omega t} + e^{i\omega t}) \\
&= 2\mathrm{Re}(\hat{f}_0(\omega)) \; , \tag{9.14}
\end{aligned}$$

where we have used the substitution $t \rightarrow -t$ for the integration over the negative domain.

9.4   Wiener-Khiniche theorem

The Fourier transform contains information both on the amplitude and the phase of a given frequency, so that the analogy with the ear and piano is not strictly correct. If we only want the information on the amplitude, we take the modulo square of the transform. This gives the power spectrum, which we define as

$$S_f(\omega) = \lim_{T \to \infty} \frac{\pi}{T} |\hat{f}_T(\omega)|^2 \; , \tag{9.15}$$

where $\hat{f}_T(\omega)$ is given by equation (9.6) but where we have now equipped the transform with a $_T$ subscript to highlight the T-dependence. Below we will show that the above limit is in fact finite for a signal that respects the physical property know as ergodicity. Ergodicity is the physical postulate that in equilibrium a time-average amounts to the same thing as an ensemble average, i.e.

$$\langle g(0) \rangle = \lim_{T \to \infty} \frac{1}{2T} \int_{-T}^{T} dt g(t) \tag{9.16}$$

for any function g of the dynamical variables in the system. Now, insert the definition of $\hat{f}_T(\omega)$ as given by equation (9.6).

$$
\begin{aligned}
S_f(\omega) &= \lim_{T \to \infty} \frac{1}{4\pi T} \int_{-T}^{T} dt' \int_{-T}^{T} dt'' e^{i\omega(t'-t'')} f(t') f(t'') \\
&= \lim_{T \to \infty} \frac{1}{2T} \int_{-T}^{T} dt' \int_{-T+t'}^{T+t'} \frac{d\tau}{2\pi} e^{-i\omega\tau} f(t') f(t'-\tau) \; . \tag{9.17}
\end{aligned}
$$

Identify the g-function as

$$g(t') = \int_{-T+t'}^{T+t'} \frac{d\tau}{2\pi} e^{-i\omega\tau} f(t') f(t'-\tau) \; . \tag{9.18}$$

This gives

$$S_f(\omega) = \int_{-\infty}^{\infty} \frac{d\tau}{2\pi} e^{-i\omega\tau} \langle f(0) f(\tau) \rangle \; , \tag{9.19}$$

where we have also used that the correlation function is even in τ, since equilibrium averages are invariant under time-translation: $\langle f(-\tau)f(0) \rangle = \langle f(-\tau + \tau)f(\tau) \rangle = \langle f(\tau)f(0) \rangle$. From this equation it also follows directly that

$$\langle f(0) f(\tau) \rangle = \int_{-\infty}^{\infty} d\omega S_f(\omega) e^{i\omega\tau} \; , \tag{9.20}$$

a result which is known as the Wiener-Khiniche theorem. Note that since $\langle f(0)f(\tau) \rangle$ is in general a finite, integrable function equation (9.19) shows that $S_f(\omega)$ is finite and well defined too.

9.5 Solution of 2d Ising models

In 1944 Onsager solved the 2-dimensional Ising in zero magnetic field using the transfer matrix method. It is still one of the most impressive mathematical achievements in omodern theoretical physics. He found that the free energy per spin is

$$\frac{g}{kT} = -\log\left(2\cosh 2K\right) - \frac{1}{2\pi}\int_0^\pi d\theta \log\frac{1}{2}\left(1 + \sqrt{1 - \kappa^2\sin^2\theta}\right) \qquad (9.21)$$

where the coupling constant only appears in the parameter

$$\kappa = \frac{2\sinh 2K}{\cosh^2 2K} \qquad (9.22)$$

with $K = \beta J$. The result can be simplified by expressing it in terms of elliptic integrals. When the argument of the log in the integral is zero, a singularity arises which is the critical point. It happens when $\kappa = \kappa_c = 1$, i.e for $\sinh 2K_c = 1$. The critical coupling is therefore given by $\tanh K_c = \sqrt{2} - 1$ or

$$K_c = \frac{1}{2}\log\left(\sqrt{2} + 1\right) = \frac{1}{2}\cot\frac{\pi}{8} = 0.4407\ldots \qquad (9.23)$$

confirming the earlier Kramers-Wannier result (6.65).

The internal energy follows now from the free energy (9.21). It gives rise to a specific heat which diverges near the critical point like

$$C_B \simeq -Nk\frac{8}{\pi}K_c^2\log|K - K_c| \qquad (9.24)$$

corresponding to a critical exponent $\alpha = 0$.

In 1948 Onsager announced that he had calculated the spontaneous magnetization in the model. It is given the by apparently simple formula

$$m = \begin{cases} [1 - \sinh^{-4} 2K]^{\frac{1}{8}}, & T < T_c \\ 0, & T > T_c \end{cases} . \qquad (9.25)$$

Near the critical point it varies like (6.43) with the exponent $\beta = 1/8$. The actual calculations behind this result were published four years later by C.N. Yang who also later got the Nobel prize. From this result for the magnetization now also followed the zero-field susceptibility which was found to have the critical behavior (6.41) with exponent $\gamma = 7/4$. Finally, the correlation function at the critical point decayed like

$$\langle\sigma_{\mathbf{x}}\,\sigma_{\mathbf{x}'}\rangle \propto |\mathbf{x} - \mathbf{x}'|^{-\frac{1}{4}} \qquad (9.26)$$

for large spin separations. Comparing with the standard form (6.61), we find the correlation spin index $\eta = 1/4$.

In the last few years there have been several attempts to find exact solutions of the 2-dimensional Ising model in an external field with no success yet. The 3-dimensional Ising model has not allowed any exact solutions and is today being investigated by numerical methods, Monte Carlo simulations and the renormalization group.