Study notes for Statistical Physics

A concise, unified overview of the subject

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Acknowledgement

Some of the more elementary pedagogical material in this book has previously appeared as part of `Renormalization Methods: A Guide for Beginners' (Oxford University Press: 2004), and is reprinted here by kind permission of the publishers of that work.

I would also like to thank Jorgen Frederiksen who very kindly read the manuscript and pointed out several minor errors.

Preface

This book began life some years ago as a set of hand-written lecture notes which were photocopied and given out to students. The course at that time was called *Statistical Physics 2* and was a final-year undergraduate option, following on from the earlier, introductory course. An attractive feature of the advanced course was its unified treatment of equilibrium ensembles, in which a combinatorial argument was used once only, to derive an equilibrium probability distribution, which could then be directly applied to many different physical situations. This was in marked contrast to the more elementary course which carried out a different combinatorial argument for each of the various different applications. In my view the more advanced approach was very much simpler, with less potential for confusion.

At that time the remainder of the course was heavily biased towards a specialized treatment of critical phenomena, reflecting the research interests of my predecessors, and had become unpopular. When I took over, I reduced the amount of critical phenomena, and in its place added material on time-dependence, on return to equilibrium, and on transport equations. In particular, I introduced the reversibility paradox and the concept of *the arrow of time*. This material proved to be a popular source of class discussions and had the pedagogic virtue of challenging superficial assumptions about the subject.

The lecture notes developed over the years into the present book form. As it had been generally found helpful by students, I thought that it would be a good idea to make it more widely available. I envisage it as proving helpful to someone who is already taking a course on statistical physics and who would like a different perspective on the subject.

In this book we concentrate on the use of the probability distribution to specify a macroscopic physical system in terms of its microscopic configuration. Then, from the normalisation of the distribution, we may obtain the partition function $\mathcal{Z}$; and, by using bridge equations such as $F = -kT \ln \mathcal{Z}$, we may obtain the macroscopic thermodynamics of the system, in terms of the free energy F, the Boltzmann constant k, and the absolute temperature T.

The book is in three parts, as follows:

Part 1: Statistical ensembles We use the principle of maximum entropy to obtain a general form for the probability distribution (and hence partition function) for an ensemble which is subject to two non-trivial constraints. This result is readily specialised to the canonical and grand canonical ensembles, and is then applied to problems involving non-interacting particles, such as cavity radiation and spins on a lattice.

Part 2: The many-body problem The procedures of Part 1 are then extended to the case where particle interactions, due to Coulomb or molecular binding forces, lead to a coupled Hamiltonian. We see that such coupling no longer allows us to factorise the partition function into products of single-particle forms. We consider the general methods of tackling this problem by means of mean-field theories and perturbation expansion, and conclude with the ultimate form of many-body problem when the system is close to a phase transition.

Part 3: The arrow of time We now consider systems out of equilibrium and show how an exact theory leads to the paradoxical result that the system energy does not change with time. We find that if we coarse-grain our system description (i.e. reduce the amount of detailed information contained in it) then the entropy increases with time and our description becomes consistent with the second law. We treat both classical (Liouville's equation) and quantum (Fermi's master equation) theories.

We see how the return to equilibrium is accompanied by macroscopic fluxes and how the relevant transport equations may be derived. We also consider the dynamics of fluctuations and associated diffusion processes.

An underlying theme of the book is the development of irreversible behaviour. At the macroscopic (or everyday) level, we are all familiar with the idea of irreversibility with time. In broad terms, everything (and everyone, for that matter) is born, grows old and dies. The reverse phenomenon never occurs! Yet if we specify any macroscopic system at a microscopic level, the basic interactions are reversible in time. So, in some way, the symmetry with respect to time is broken in going from a microscopic to a macroscopic description of the system.

This situation has long been regarded as paradoxical, and indeed as posing the fundamental question of statistical mechanics. If the collisions between the constituent molecules of a gas, for instance, obey Newton's laws of motion (or, equivalently, the equations of quantum mechanics) then each such collision can be reversed in time without violating the governing equations. Thus, the microscopic governing equations imply no preferred direction in time for the assembly as a whole. In other words, at the microscopic level there seems to be no particular reason why an isolated assembly should go to equilibrium and then stay there.

It is, of course true that the paradox can be resolved, if only in a rather superficial way, by insisting upon taking a probabilistic view at even the macroscopic level (as well as at the microscopic level: we shall enlarge on this point presently). That is, our normal deterministic view is that if an isolated assembly is not in equilibrium at some initial time, then as time goes on, it will move to equilibrium. However, we could replace this statement by adopting the view that the equilibrium state is merely the most probable state. Then we do not rule out reversibility in time: we merely say that it is highly improbable.

Nevertheless, from our point of view, there is merit in studying the question at a much more technical level, for two quite pragmatic reasons. First, we are led to consider the concept of *coarse graining*, in which we systematically reduce the fineness of resolution of our microscopic description. Second, (and this also arises from the first point) we are also led to consider the all-important transport equations, which describe the macroscopic flows of momentum, heat and mass, which accompany the movement of an assembly towards equilibrium.

Lastly, we complete these introductory remarks by making a general observation about whether we should use a quantum representation or a classical representation for the microscopic constituents of an assembly. For a purely microscopic description of the assembly, we know of course, that the quantum description is (in our present state of knowledge) the correct one. But we are also aware that for certain limiting cases (high temperatures or low densities, for instance) the classical description can be used without significant error. It is also true that the statistical uncertainties associated with large numbers and finite-sized systems can overwhelm some of the characteristic features of the quantum mechanical description and to some extent blur the distinction between the two representations. In practical terms, this distinction can boil down to the following:

- In a quantum representation, particles are inherently indistinguishable and occupy discrete states. This means that any microstate of the assembly is one of a denumerable set of such states. As time goes on, the assembly fluctuates randomly from one discrete microstate to another.

- In a classical representation, particles are distinguishable, because their motion is deterministic and predictable, and any initial labelling is preserved. The microstate of the assembly is a continuous function of time.

From a pragmatic point of view, it is clear that the quantum description facilitates the evaluation of probabilities and particularly of statistical weights. On the other hand, it may be less immediately obvious, but we shall see later that the evolution in time of an assembly is more easily studied in the classical representation. Thus, when we are concerned with general procedures (as we mostly shall be), we shall allow practical considerations to decide the question of 'classical *versus* quantum'. However, we shall have to consider formally the transition from one system of description to another, so that we can be sure that results established by quantum means are equally valid in a classical description of the microstate. This will be done from time to time, where it occurs naturally.

Part I

Statistical ensembles

Chapter 1

Introduction

In this first chapter we revise the basic concept of elementary statistical physics, which is that a macroscopic physical system can be represented by an assembly of microscopic particles. We also state a number of basic definitions, and then extend the idea of the isolated assembly to the *statistical ensemble* or 'assembly of assemblies'; and show that the Boltzmann entropy, as given by equation (1.3) for an isolated assembly, can be used to derive an expression for an assembly in an ensemble, as given by equation (1.10). This form of entropy is then used in subsequent chapters to determine the most probable distribution for the assembly which corresponds to maximum entropy..

Formally we consider a macroscopic system to be an assembly of N identical particles in a box. In general, the number N is very large. For instance, for air at STP, N is of the order 3×10^{19} for one cubic centimetre of gas.

If we specify the state of our assembly at the macroscopic (i.e. thermodynamic) level, then we usually require only a few numbers, such as N particles in a box of volume V, at temperature T, and with total energy E or pressure P. Such a specification is known as a *macrostate*, and we write it as:

$$\text{macrostate} \equiv (E, V, N, T, P \ldots).$$

Note that for a simple gas in equilibrium only three of these variables are independent. That is, if we specify the three E, V and N, we can obtain all the others $T, P, S \ldots$ from those three.

On the other hand, we may specify the state of our assembly at the microscopic level; for instance, in the classical assembly, by giving the positions and velocities of all the individual molecules. Evidently this requires of the order of $6N$ numbers and is known as the *microstate* of the assembly. On both classical and quantum pictures, the microstates are rapidly changing functions of time, even in isolated assemblies. This is a point which we shall develop in some detail later on.

It is, of course, evident that there will be many ways in which the microscopic variables of an assembly can be arranged. This means that for any one macrostate, there will be many possible microstates. We define the

$$\text{statistical weight} \equiv \Omega(E, V, N \ldots)$$

of a particular macrostate $(E, V, N \ldots)$ as the number of microstates corresponding to that particular macrostate.

1.1 The isolated assembly

The term 'isolated' essentially means energy or thermal isolation. That is, the total energy E of the assembly is constant. In order to have a definite example, we consider an ideal gas of N particles in a box of volume V. (Note: E, V and N are *constraints* on the values of energy, volume and particle number for the assembly.)

We invoke a very simple quantum mechanical description of the assembly, in which each particle has access to states with energy levels

$$\epsilon_0, \epsilon_1, \epsilon_2 \ldots$$

Then a microstate of the assembly is the particular way in which the N particles are divided up among the energy levels.

- n_0 particles on level ϵ_0

- n_1 particles on level ϵ_1

$\vdots$

-
- n_s particles on level ϵ_s

Also, the total energy of the assembly is given by

$$E = \sum_s n_s \epsilon_s, \tag{1.1}$$

such that

$$\sum_s n_s = N. \tag{1.2}$$

This way of expressing the energy of an assembly in terms of the number of single particles on a level is known as the *occupation number representation*. If we know the energy levels of the assembly, then we may simply express the microstate as

$$\text{microstate} \equiv \{n_0, n_1, n_2 \ldots n_s\} \equiv \{n_s\}.$$

We now make two basic postulates about the microscopic description of the assembly. First, we assume that all microstates are equally likely. This leads us to the immediate conclusion that the probability of any given microstate occurring is given by

$$p(\{n_s\}) = 1/\Omega,$$

where Ω is the total number of such equally likely microstates.

Second, we assume that the Boltzmann definition of the entropy, in the form

$$S = k \ln \Omega, \tag{1.3}$$

where k is the Boltzmann constant, may be taken as being equivalent to the usual thermodynamic entropy. In particular, we shall assume that the entropy S, as defined by (1.3), takes a maximum value for an isolated assembly in equilibrium.

These assumptions lead to a consistent and successful relationship between microscopic and macroscopic descriptions of matter. They may therefore be regarded as justifying themselves in practice. However, although they are the key to statistical physics, they are in the end just assumptions. We now consider the way in which we can put them to use.

1.2 Method of the most probable distribution

Introductory courses in statistical physics, are mainly concerned with equilibrium states of isolated assemblies. We will find it helpful to begin by considering what is meant by a nonequilibrium state. In this way we can understand how restrictive the elementary approach actually is.

We continue to discuss our isolated assembly, but for the moment it is not yet fully isolated. We prepare it in the following way. We heat up some part of the box of gas molecules, in order to create a nonuniformity. That is, we create a temperature gradient in the box from the hotter part to the colder parts. Of course there are many ways in which we can create such nonuniformities, but let us for the present just consider a particular one. If we now isolate the assembly again, then we know that as time goes on the assembly will move to equilibrium. And, it doesn't matter how we set up this nonuniform initial state, the assembly will always move to the same equilibrium state. Therefore, (given the values of few parameters such as temperature, volume and pressure) it is a unique state.

Obviously there is an infinite number of possible initial states, but the essential point is that they all move to the same universal equilibrium state. If one liked, one could think of the macrostate of the assembly as being stable with respect to perturbations about equilibrium.

Let us now say a little more about what we mean by all this. If we continue with the example of a temperature gradient, what this implies is that the temperature obtained from an average over many molecules in some small part of the box is higher than the temperature obtained from a similar average over some other part of the box. That is, we do our averages over boxes which are small compared to the box which contains the assembly, but are large compared to the size of a molecule; and, indeed, large enough to contain many molecules. This means that individual molecules really have no knowledge as to whether they are in equilibrium or not. And this is a very important concept. Nonequilibrium conditions are only to be discovered by some kind of macroscopic examination of the assembly.

As time goes on, molecular collisions will redistribute the extra kinetic energy associated with the regions of higher temperature. The extra kinetic energy will be shared out so that we end up with a uniform mean level over the box. At the macroscopic level, we would observe this as the flow of heat from one point in space to another, at a rate governed by the macroscopic temperature gradient and the thermal conductivity of the gas. So, by equilibrium we mean that the average (or macroscopic) properties of the assembly are constant in space and time.

For the particular case of a gas, which is what we are taking as our example, it would nearly always be possible to detect a nonuniformity, and hence nonequilibrium, by considering the number density of molecules as a function of position, and noticing that it was different in different parts of the box. So, for convenience, we will characterise nonequilibrium states by a nonuniform number density. That is, we now generalize our earlier definition of statistical weight to the nonequilibrium case as
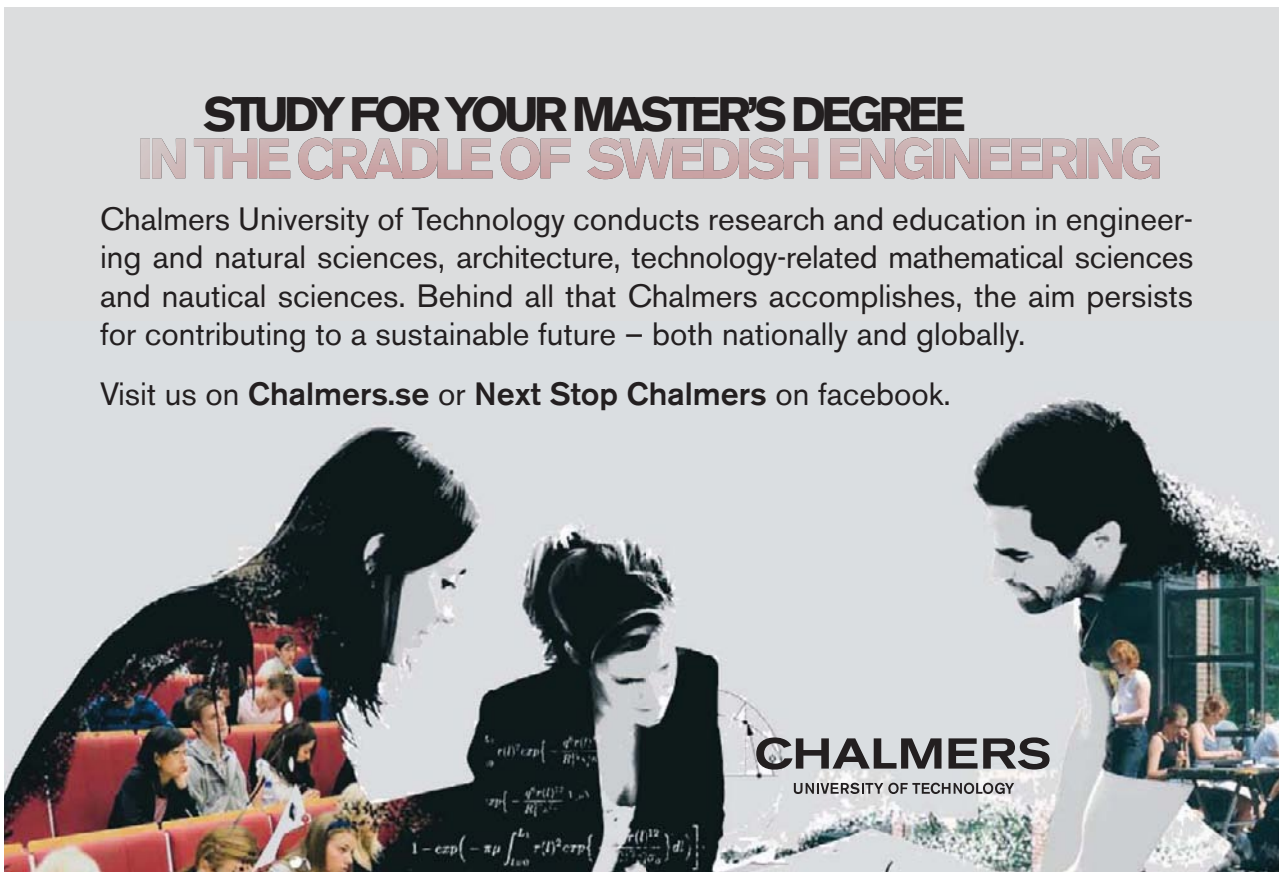
$$\text{statistical weight} \equiv \Omega(E, N, V, n(\mathbf{x}, t)).$$

Hence, when the number density $n(\mathbf{x}, t)$ is constant and equal to N/V, in the limit of large N and V (known as the *thermodynamic limit*), then the assembly has achieved equilibrium.

We can also say that, in the statistical sense, thermal equilibrium is a stationary state of the assembly. By this we mean that, although the actual molecular motion is not stationary, and the assembly fluctuates rapidly through its microstates, all mean properties (as established by some form of macroscopic averaging) are independent of time.

Now the basic idea of statistical mechanics is that the assembly will move from any one of a variety of initial nonequilibrium states, each characterised by some macroscopic regularity such as a temperature gradient or a density gradient, to a less constrained equilibrium state. That is to say, by imposing (say) a temperature gradient on the assembly, we restrict the possibilities open at a microscopic level to that assembly. Thus, as the assembly moves to equilibrium, the corresponding increase in the entropy may be interpreted as an increase in the disorder of the assembly (or equally as a decrease in the amount of information which we have about the microscopic arrangements of the assembly). On this basis, therefore, it is usual to argue that the equilibrium macrostate is the most probable macrostate, as it is associated with the largest number of microstates.

On the face of it, we should now choose the most probable distribution of single particle energy states, in order to maximise the number of microstates. Then we can argue that this 'most probable distribution' is the equilibrium distribution. However, in practice it is the logarithm of the number of microstates which is maximised, and this has the twin merits of both giving the right answer and also corresponding to a definite physical principle. That is, from the Boltzmann form of the entropy (1.3), maximisation of $\ln \Omega$ corresponds to the thermodynamic principle that the entropy of an isolated system will take a maximum value at equilibrium.

If we carry out this procedure, we end up with the well known Boltzmann distribution, which takes the form

$$p_s = \frac{\exp[\epsilon_s/kT]}{\mathcal{Z}}, \tag{1.4}$$

where p_s is the probability of finding any single particle on energy level ϵ_s and the partition function $\mathcal{Z}$ is given by

$$\mathcal{Z} = \sum_s \exp[\epsilon_s/kT]. \tag{1.5}$$

We shall not give details of the derivation as we shall be deriving it by more general methods in the following sections.

It should be understood that this result is the single-particle distribution function. And, in effect, it has been obtained by regarding any one particle as being representative, in the sense that we can obtain its statistics by considering the behaviour of all the other particles. This is a first look at what is called the *ergodic principle.*

That is, let us suppose that we took any one particle and followed it around over a sufficiently long period of time (assuming that we could do such a thing). Then we could build up a picture of its statistical behaviour in terms of how long it spent on energy level 1, how long it spent on energy level 2, and so on. In this way we could (in principle) determine its probability distribution among the available energy levels. Now suppose that instead we took a snapshot of all the particles at one instant of time and constructed a sort of histogram: so many on energy level 1, so many on energy level 2, and so on. In this way we can also construct (in principle) a probability distribution for a representative single particle. If these two distributions are the same, then the assembly is said to be *ergodic.*

This principle is not easily proved, but for most physical assemblies of interest, it is physically plausible that it should hold. In succeeding sections we shall develop these ideas further.

1.3   Ensemble of assemblies: relationship between Gibbs and Boltzmann entropies

At this stage, we abandon the concept of the rigorously isolated assembly, in which the total energy E is constant. Now we should think of an assembly in a heat reservoir, which is held at a constant temperature, and with which it can exchange energy. Then the energy of the assembly will fluctuate randomly with time about a time-averaged value $\overline{E}$, which will correspond to the macroscopic energy of the assembly when at the temperature of the heat reservoir.

Or, alternatively, we may imagine a *gedankenexperiment* in which we have a large number m of N-particle assemblies, each free to exchange energy with a heat reservoir. Then, at an instant of time, each assembly will be in a particular state and we can evaluate the mean value of the energy by taking the value for each of the assemblies, adding them all up, and dividing the sum by m to obtain a value $\langle E \rangle$.

It is usual to refer to the assembly of assemblies as an *ensemble* and hence to call the quantity $\langle E \rangle$ the ensemble average of the energy E. Then the assumption of ergodicity, as discussed in the previous section, is equivalent to the assertion:

$$\overline{E} = \langle E \rangle.$$

It should be noted that the number of assemblies in the ensemble m is quite arbitrary (although, it is a requirement in principle that it should be large) and is not necessarily equal to N. In fact it will sometimes be convenient to make the two numbers the same, although we shall not do that at this stage.

Now consider a formal N-particle representation for each assembly. That is, formally at least, we assume that any microstate is a solution of the N-body Schrödinger equation. We represent the microstate corresponding to a quantum number i by the symbolic notation $| i \rangle$, and associate with it an energy eigenvalue E_i, with the probability of the assembly being in this microstate denoted by p_i. Then, our aim is to obtain the probability distribution p_i. For the case of stationary equilibrium ensembles, we shall do this by maximising the entropy, so our immediate task is to generalise Boltzmann's definition of the entropy, as given in equation (1.3).

Generalizing our previous specification of an assembly, we consider the ensemble in the state

- m_1 assemblies in state $| 1 \rangle$

- m_2 assemblies in state $| 2 \rangle$

  $\vdots$

- m_i assemblies in state $| i \rangle$

We should note that the sum of all the probabilities must be unity, corresponding to dead certainty; thus we have the condition

$$\sum_i p_i = 1,$$

with the summation being over all possible values of i.

Bearing in mind that each assembly is a macroscopic object and therefore capable of being labelled, we work out the number of ways in which we can distribute the m *distinguishable* assemblies among the available states. Thus the statistical weight Ω_m of the ensemble state is readily found to be:

$$\Omega_m = \frac{m!}{m_1! m_2! \ldots m_i!}. \tag{1.6}$$

We now invoke the Boltzmann definition of the entropy and apply it to the number of ways in which the ensemble can be arranged. Denoting the entropy of the ensemble by S_m, we may use equation (1.3) to write

$$S_m = k \ln \Omega_m = k \ln m! - [k \ln m_1! + k \ln m_2! + \cdots + k \ln m_i!], \tag{1.7}$$

where we have substituted from (1.6) for the statistical weight Ω_m.

At this stage we resort to Stirling's formula:

$$\ln m! = m \ln m - m,$$

and application of this yields

$$S_m = km \ln m - km - [k \sum_i m_i \ln m_i - k \sum_i m_i.] \tag{1.8}$$

Therefore, as $\sum_i m_i = m$, we may write the total entropy of the ensemble as

$$S_m = k[m \ln m - \sum_i m_i \ln m_i] = -km \sum_i p_i \ln p_i, \tag{1.9}$$

where we have made the substitution $m_i = p_i m$. However, S_m is the total entropy of the ensemble; that is, of the m assemblies. Thus, as the entropy is, in the language of thermodynamics, an extensive quantity, it follows that the entropy of a single assembly within the ensemble is

$$S = S_m/m = -k \sum_i p_i \ln p_i, \tag{1.10}$$

where the sum, is over all possible states $|\,i\rangle$ of the assembly.

Thus the equivalent of maximizing $\ln \Omega$ for the isolated ensemble, is to maximize the entropy given by equation (1.10) for a single assembly within the ensemble. This allows us to recast the method of the most probable distribution into a much clearer, more general and more powerful form. This will be the subject of the next chapter.

Chapter 2

Stationary ensembles

In this chapter we work out mean values of quantities such as the energy, and compare them to the results obtained using thermodynamics. This allows us build a 'bridge' between the microscopic and macroscopic worlds.

In section 1.3, we introduced the idea of an ensemble of similar assemblies. Evidently the properties of the ensemble are determined by the nature of each constituent assembly. Thus, when we speak of a stationary ensemble, we mean one that is made up of assemblies which are themselves stationary or steady in time. Continuing to use the microscopic representation which we introduced in the preceding chapter, we may express mean values in terms of the probability distribution, in the usual way. For instance, the mean value of the energy may be written as

$$\overline{E} = \langle E \rangle = \sum_{i=1}^{r} p_i E_i, \tag{2.1}$$

where p_i represents the probability of the assembly being in the state $|\, i \rangle$, such that $1 \le i \le r$, with energy eigenvalue E_i, and with the probability distribution normalized to one, thus:

$$\sum_{i=1}^{r} p_i = 1. \tag{2.2}$$

(It should be noted that, strictly speaking, we have introduced a third kind of average: the expectation value. However, we shall in general treat all the methods of taking averages as being equivalent, and use the overbar or angle brackets as convenient in a given situation.) Then, by a stationary assembly, we mean one in which the mean energy, as given by equation (2.1), is constant with respect to time. Thus, the assembly (if not isolated) fluctuates between states, with its instantaneous energy E_i varying stepwise with time. That is, E_i fluctuates randomly about a constant mean value $\overline{E}$.

We know from thermodynamics that the entropy of an isolated system (in this case, the ensemble) always increases, so that any change in the entropy must satisfy the general condition

$$dS \ge 0,$$

so that at thermal (and statistical) equilibrium, the equality applies and our general condition becomes

$$dS = 0, \tag{2.3}$$

corresponding to a maximum value of the entropy. The method of finding the most probable distribution now becomes the method of choosing p_i such that the entropy, as given by equation (1.10), is a maximum. That is, if we vary the distribution by an amount δp_i from the most probable value, the corresponding change in the entropy must satisfy the equation

$$dS/dp_i = 0. \tag{2.4}$$

Thus, we find the most probable distribution by solving equation (2.4), subject to any constraints which are applied to the assembly.

2.1 Types of ensemble

As we have seen, the nature of the ensemble is determined by the nature of its constituent assemblies. A stationary ensemble is made up of stationary assemblies. The imposition of other constraints, in addition to stationarity, determines the type of ensemble, and we shall make a brief digression in order to define the three principal ensembles which will be considered this book. We list these as follows:

1. **Microcanonical ensemble (mce)**: fixed E and N
   In this case, the assembly is closed and isolated. As an example, one could think of a perfect gas at STP in a macroscopic box with insulating walls, so that heat cannot flow either in or out. This means that the assembly is constrained to have a fixed total energy and a fixed number of particles. Although the assembly will fluctuate (because of molecular collisions) through its microstates, all microstates have the same eigenvalue, the constant energy. Thus, in quantum mechanical terms, this situation is enormously degenerate, with

$$E_i = E = \overline{E}.$$

It is, of course, our old friend the isolated system.

2. **Canonical ensemble (CE)**: fixed $\overline{E}$ and N
   Here the assembly is closed but not isolated. It is free to exchange energy with its surroundings. As an example, one could again think of a perfect gas in a box, but now the walls do not impede the flow of heat in or out. Thus the energy of an individual assembly E_i fluctuates about the mean value $\overline{E}$, which is fixed.

3. **Grand canonical ensemble (GCE)**: fixed $\overline{E}$ and $\overline{N}$
   Lastly, we consider an assembly which is neither closed nor isolated. In order to continue with our specific example, we could think of a perfect gas in a box with permeable walls, so that both the total energy and the total number of particles in the assembly can fluctuate about fixed mean values. More realistically perhaps, we could imagine the grand canonical ensemble as consisting of a large volume of gas (e.g. a room full of air), notionally divided up into many small (but still macroscopic!) volumes. Then the GCE would allow us to examine fluctuations of particle number in one such volume relative to the others. However, it should be emphasized from the outset that the GCE is of immense practical importance, particularly in those quantum systems where particle number is not conserved and in chemical reactions where the number of particles of a particular chemical species will generally be variable.

In the next section, we shall carry out a general procedure for finding the probability distribution which can be applied to any one of these stationary ensembles.

2.2 Variational method for the most probable distribution

Formally we now set up our variational procedure. From equation (1.10) for the entropy and equation (2.4) for the equilibrium condition, we obtain the equation

$$dS = -k \sum_i \{\ln p_i + 1\} = 0, \tag{2.5}$$

which must be solved for p_i, subject to the various constraints imposed on the assembly. In addition to the requirement (which applies to all cases) that the distribution must be normalized to unity, we shall assume for generality that the assembly is subject to the additional constraint that two associated mean values $\overline{x}$ and $\overline{y}$, say, are invariants. Evidently x and y can stand for any macroscopic variable such as energy, pressure, or particle number. Thus, we summarize our constraints in general as:

$$\sum_i p_i = 1, \tag{2.6}$$

$$\langle x \rangle = \sum_i p_i x_i = \overline{x}, \tag{2.7}$$

and

$$\langle y \rangle = \sum_i p_i y_i = \overline{y}. \tag{2.8}$$

In order to handle the constraints, we make use of Lagrange's method of undetermined multipliers. We illustrate the general approach by considering the first constraint: the normalization requirement in (2.6). If we vary the righthand side of (2.6), it is obvious that the variation of a constant gives zero, thus:

$$d \sum_i p_i = 0. \tag{2.9}$$

On the other hand, if we make the variation $p_i \to p_i + dp_i$ inside the summation, then we have

$$\sum_i (p_i + dp_i) = 1 \Rightarrow \sum_i dp_i = 0. \tag{2.10}$$

In other words, if we make changes to the individual probabilities that specific levels will be occupied, then the sum of these changes must add up to zero in order to preserve the normalization of the distribution.

It follows then, that we are free to subtract

$$\lambda_0 d \sum_i p_i = \lambda_0 \sum_i dp_i = 0, \tag{2.11}$$

where λ_0 is a multiplier which is to be determined, from the middle term of equation (2.5) without effect.

This procedure goes through for our two general constraints as well. It should be borne in mind that varying the distribution of the way assemblies are distributed among the permitted states does not affect the eigenvalues associated with those states. Formally, therefore, we introduce the additional Lagrange multipliers λ_x and λ_y, so that equation (2.5) can be rewritten in the form

$$\sum_i \{-k(1 + \ln p_i) - \lambda_0 - \lambda_x x_i - \lambda_y y_i\} dp_i = 0. \tag{2.12}$$

As this relation holds for abitrary states $|i\rangle$, it follows that the expression in curly brackets must vanish. Which further implies that the required distribution must take the form:

$$p_i = \exp(-1 - \lambda_0/k) \exp(-[\lambda_x x_i + \lambda_y y_i]/k). \tag{2.13}$$

The prefactor is now chosen to ensure that the distribution satisfies the normalization requirement (2.6), thus:

$$\exp(-1 - \lambda_0/k) = \frac{1}{\sum_i \exp(-[\lambda_x x_i + \lambda_y y_i/k])} = \frac{1}{\mathcal{Z}}, \tag{2.14}$$

where $\mathcal{Z}$ is the partition function. Clearly this procedure is equivalent to fixing a value for the Lagrange multiplier λ_0. The other two multipliers are to be determined when we decide on a particular ensemble. At this stage, therefore, our general form of the probability of an assembly being in state $|i\rangle$ is

$$p_i = \frac{\exp(-[\lambda_x x_i + \lambda_y y_i]/k)}{\mathcal{Z}}. \tag{2.15}$$

It can be readily verified that the assembly invariants are related to their corresponding Lagrange multipliers by

$$\langle x \rangle = -k\partial \ln \mathcal{Z}/\partial \lambda_x, \tag{2.16}$$

$$\langle y \rangle = -k\partial \ln \mathcal{Z}/\partial \lambda_y. \tag{2.17}$$

2.3 Canonical ensemble

We now apply the above results to an assembly in which the mean energy is fixed but the instantaneous energy can fluctuate. Then, by considering a simple thermodynamic process and comparing the microscopic and macroscopic formulations, we show that k can be identified as the Boltzmann constant; and the general equivalence of micro and macro formulations is established.

Now the particle number is the same for every assembly in the ensemble and is therefore constant with respect to the variational process. So, it is worth observing that a constraint of this type is essentially trivial. Suppose, in general, that y is any macroscopic variable which does not depend on the state of the assembly. Then we have for its expectation value,

$$\langle y \rangle = \sum_i y p_i = y \sum_i p_i,$$

and when we make the variation in p_i this yields the condition

$$y \sum_i dp_i = 0.$$

It may be readily verified, by rederiving equation (2.14) for this case, that λ_y may be absorbed into λ_0 when we set the normalization. In effect this means, that when y is independent of the state of the assembly, we may take $\lambda_y = 0$.

In the canonical ensemble, the only nontrivial constraint is on the energy. Accordingly, we put $x = E$ and $\lambda_y = 0$ in equations (2.15) and (2.14) to obtain

$$p_i = \frac{\exp\left[-\lambda_E E_i/k\right]}{\mathcal{Z}}, \tag{2.18}$$

with partition function $\mathcal{Z}$ given by

$$\mathcal{Z} = \sum_i \exp[-\lambda_E E_i/k]. \tag{2.19}$$

Also, from equation (2.16), we have the mean energy of the assembly as

$$\overline{E} = -k\partial \ln \mathcal{Z}/\partial \lambda_E. \tag{2.20}$$

2.4   Compression of a perfect gas

As an example of a simple thermodynamical process, let us consider the compression of a perfect gas by means of a piston sliding in a cylinder, say. It is, of course, usual in thermodynamics to consider the important special cases of adiabatic and isothermal compressions. But, for our present purposes, we do not need to be so restrictive. We can describe the relationship between the macroscopic variables during such a process by invoking the combined first and second laws of thermodynamics, thus:

$$d\overline{E} = TdS - PdV. \tag{2.21}$$

It should be noted that for a compression, the volume change is negative, and so the pressure work term is positive, indicating that work is done on the gas by the movement of the piston.

Now let us use our statistical approach to derive the equivalent law from microscopic considerations. Equation (2.1) gives us our microscopic definition of the total energy of an assembly. From quantum mechanics, we know that changing the volume of the 'box' must change the energy levels and also the probability of the occupation of any level. It follows therefore that the change dV must give rise to a change in the mean energy, and from (2.1) this is

$$d\overline{E} = \sum_i E_i dp_i + \sum_i p_i dE_i. \tag{2.22}$$

Evidently we wish to get this equation into a form in which it can be usefully compared with equation (2.21). The second term on the RHS can be got into the requisite form immediately. Recalling that dV is negative, we can write (2.22) as

$$d\overline{E} = \sum_i E_i dp_i - \sum_i p_i \frac{\partial E_i}{\partial V} dV. \tag{2.23}$$

Obviously the second term now gives us a microscopic expression for the thermodynamic pressure, but we shall defer the formal comparison until we have dealt with the first term, which of course we wish to relate to TdS. We do this in a less direct way, by deriving a microscopic expression for the change in entropy dS.

Intuitively, we associate the change in entropy through equation (1.10) with the change in the probability distribution, and this may be expressed mathematically as

$$dS = \sum_i \frac{\partial S}{\partial p_i} dp_i = -k \sum_i \ln p_i dp_i, \tag{2.24}$$

where we have invoked equation (1.10) for S and the normalization condition in the form $\sum_i dp_i = 0$. By substituting from (2.18) for p_i, and again using the condition $\sum_i dp_i = 0$, we may further write our expression for the change in the entropy as

$$dS = \lambda_E \sum_i E_i dp_i, \tag{2.25}$$

which, with a little rearrangement, allows us to rewrite the first term on the RHS of (2.23), which then becomes

$$d\overline{E} = \frac{dS}{\lambda_E} + \left(\sum_i p_i \frac{\partial E_i}{\partial V} \right) dV. \tag{2.26}$$

Comparison with the thermodynamic expression for the change in mean energy, as given by equation (2.21), then yields the Lagrange multiplier as

$$\lambda_E = 1/T, \tag{2.27}$$

along with an expression for the thermodynamic pressure P in terms of the microscopic description, thus

$$P = -\sum_i p_i \partial E_i / \partial V. \tag{2.28}$$

The latter equation can be used to introduce the instantaneous pressure P_i, such that the mean pressure takes the form

$$P = \sum_i p_i P_i, \tag{2.29}$$

from which it follows that the instantaneous pressure is given by

$$P_i = -\partial E_i / \partial V. \tag{2.30}$$

2.4.1 Other thermodynamic processes

The above procedure can be generalized to any macroscopic process in which work is done such that the mean energy of the assembly remains constant. For instance, a variation in the magnetic field acting on a ferromagnet, will do work on the magnet and in the process increase its internal energy. Accordingly, we may extend the above analysis to more complicated systems by writing the combined first and second laws as

$$d\overline{E} = TdS + \sum_\alpha H_\alpha dh_\alpha, \tag{2.31}$$

where H_α is any thermodynamic force (e.g. pressure exerted on a gas, or the magnetic field) applied to a specimen of some material, and h_α is the corresponding displacement, such as volume of gas or magnetisation of a specimen.

If, for example, we take $H_1 = P$ and $h_1 = -V$, and assume that no other thermodynamic forces act on the system, then we recover equation (2.21). Evidently the analyis which led to equation (2.28), for the macroscopic pressure, can be used again to lead from equation (2.31) to the more general result

$$H_\alpha = \sum_i p_i \partial E_i / \partial h_\alpha. \tag{2.32}$$

of which equation (2.28) is a special case.

2.4.2 Equilibrium distribution and the bridge equations

With the identification of the Lagrange multiplier as the inverse absolute temperature, we may now write equation (2.18) for the equilibrium probability distribution of the canonical ensemble in the explicit form

$$p_i = \frac{\exp[-E_i/kT]}{\mathcal{Z}}, \tag{2.33}$$

with the partition function $\mathcal{Z}$ given by

$$\mathcal{Z} = \sum_i \exp[-E_i/kT]. \tag{2.34}$$

From equation (2.20), we may write the explicit form for the mean energy of the assembly

$$\overline{E} = kT^2 \partial \ln \mathcal{Z} / \partial T. \tag{2.35}$$

In the language of quantum mechanics, this is the equilibrium distribution function for the canonical ensemble 'in the energy representation', as our quantum description of an assembly is based on the energy eigenvalues available to it. We may also introduce other thermodynamic potentials in addition to the total energy $\overline{E}$, by substituting the above form for p_i into equation (1.10) to obtain an expression for the entropy in terms of the partition function and the mean energy, thus:

$$S = k \ln \mathcal{Z} + \overline{E}/T. \tag{2.36}$$

Or, introducing the Helmholtz free energy F by means of the usual thermodynamic relation $F = \overline{E} - TS$, we may rewrite the above equation as

$$F = -kT \ln \mathcal{Z}. \tag{2.37}$$

This latter result is often referred to as a 'bridge equation', as it provides a bridge between the microscopic and macroscopic descriptions of an assembly. The basic procedure of statistical physics is essentially to obtain an expression for the partition function from purely microscopic considerations, and then to use the bridge equation to obtain the thermodynamic free energy.

We finish off the work of this section by noting the convenient contraction

$$\beta = \frac{1}{kT}. \tag{2.38}$$

We shall use this abbreviation from time to time, when it is convenient to do so.

2.4.3   Fluctuations in the energy of the assembly

The energy of a specific assembly in the canonical ensemble fluctuates randomly about the fixed mean value $\overline{E}$. We are now in a position to assess the magnitude of these fluctuations, although at this stage we shall go about this in a rather indirect way. Let us at least begin directly. As before, we denote the energy of a particular assembly in the ith realization by E_i. Then the fluctuation of the ith realization from the mean is given by

$$\Delta E_i = E_i - \overline{E}. \tag{2.39}$$

If we then square the fluctuation, and take averages, we obtain the mean-square fluctuation as

$$\langle (\Delta E_i)^2 \rangle = \langle E_i^2 \rangle - \langle E_i \rangle^2. \tag{2.40}$$

Now we wish to estimate the size of the mean-square fluctuation, and this is where we take an indirect route. Let us work out the heat capacity at constant volume from our microscopic formulation. The defining relationship from thermodynamics is

$$C_V = (\partial \overline{E}/\partial T)_V = \frac{\partial}{\partial T} \sum_i p_i E_i, \tag{2.41}$$

where the second equality follows from equation (2.1). Then, substituting from equation (2.33), and performing the differentiation with respect to the absolute temperature, we obtain

$$C_V = \frac{1}{kT^2}[\langle E^2 \rangle - \langle E \rangle^2]. \tag{2.42}$$

Comparison of this result with equation (2.40) yields an explicit expression for the mean-square fluctuation, and taking the square-root of both sides leads to an expression for the root-mean-square fluctuation ΔE_{rms} as

$$\Delta E_{rms} = (kT^2 C_V)^{1/2}. \tag{2.43}$$

Evidently the relative rms fluctuation may be written as

$$\frac{\Delta E_{rms}}{\overline{E}} = \frac{\sqrt{kT^2 C_V}}{\overline{E}} \sim \frac{1}{N^{1/2}}, \tag{2.44}$$

where the last step follows from the fact that both $\langle E \rangle$ and C_V are extensive quantities and therefore depend on N. For Avogadro-sized assemblies, we have $N \sim 10^{24}$ and hence the relative fluctuation in the energy has a root-mean-square value of about $\sim 10^{-12}$.

2.5   The Grand Canonical Ensemble (GCE)

We now extend the preceding ideas to a more general case: an assembly where the number N of particles can fluctuate about a mean value $\overline{N}$. Such fluctuations are in addition to the fluctuations in energy due to exchange with the surroundings. An ensemble of such assemblies is known as the grand canonical ensemble. This concept has widespread application in statistical physics. Evidently it is of relevance in any statistical problem where the particle number is not an invariant. For example, we could visualize such an ensemble by imagining a large volume of gas (e.g. a room) divided into many imaginary subvolumes (i.e. each about a millilitre). Then each subvolume would comprise an assembly and would be free to exchange both energy and particles with other assemblies.

Clearly if an assembly gains some particles it also gains some kinetic energy, and conversely. It is usual in thermodynamics to formalize this aspect by introducing the chemical potential μ, such that

$$\mu = \left(\frac{\partial \overline{E}}{\partial N}\right)_{S,V}, \tag{2.45}$$

where the variation, as indicated, is carried out at constant entropy and volume. Once we know this quantity, then we can calculate the amount of energy brought into the assembly by an increase in the number of particles. Also, as well as transfers of this kind in a gas, the particle number in an assembly can fluctuate due to chemical reactions, which lead to a change in the number of particles of a particular chemical species in an assembly.

In order to generalize the microscopic formulation to the grand canonical ensemble, we note that for any one assembly E and N can vary, whereas $\overline{E}$ and $\overline{N}$ are fixed. Thus for an assembly containing N particles, we generalize the probability distribution p_i to take the form $p_{i,N}$, where

$p_{i,N} \equiv$ the probability that the assembly will be in the state identified by the ith eigenstate of the N-body Schrödinger equation. The actual energy of the assembly will be given by the associated eigenvalue, $E_{i,N}$.

As before, we invoke the general distribution (2.15). This time we have two constraints (in addition to the normalization). First, as in the canonical ensemble, we have the constraint on the mean energy, but this now takes the form

$$\overline{E} = \sum_{i,N} p_{i,N} E_{i,N}, \tag{2.46}$$

where the sum is over assemblies and is therefore over N as well as i. Second, we have the constraint on the mean particle number

$$\overline{N} = \sum_{i,N} p_{i,N} N. \tag{2.47}$$

With these constraints, we associate as before Lagrange multipliers, which in this case we denote by λ_E and λ_N. Thus we may take over (2.15) in the form

$$p_{i,N} = \frac{\exp(-[\lambda_E E_{i,N} + \lambda_N N]/k)}{\mathcal{Z}_{GCE}}, \tag{2.48}$$

where $\mathcal{Z}_{GCE}$ is the partition function for the grand canonical ensemble and is given by

$$\mathcal{Z}_{GCE} = \sum_{i,N} \exp(-[\lambda_E E_{i,N} + \lambda_N N]/k). \tag{2.49}$$

Now we have to identify the Lagrange multipliers and hence make the connection with macroscopic physics. Not surprisingly, we do this by a generalization of the method used in the canonical ensemble.

2.5.1 Identification of the Lagrange multipliers

Let us consider a macroscopic assembly upon which we do work by means of a compression, leading to an increase in its internal energy. We also increase its internal energy by increasing the mean number of particles present (by means of a chemical reaction, for instance). That is, we make the changes $V \to V - dV$ and $\overline{N} \to \overline{N} + d\overline{N}$. Then the thermodynamic description of this process is given by the appropriate generalization of the combined first and second laws, thus:

$$d\overline{E} = TdS - PdV + \mu d\overline{N}, \tag{2.50}$$

where the chemical potential μ is as defined by equation (2.45).

Now we work out the corresponding change in the mean energy from microscopic considerations. The reasoning involved is just a generalization of that presented in the case of the canonical ensemble. Changing the macroscopic variables V and N changes (via the Schrödinger equation) the energy eigenvalues and the probability of a particular state being occupied. Thus, differentiating equation (2.46 with respect to the changes in $p_{i,N}$ and $E_{i,N}$ leads to the result

$$d\overline{E} = \sum_{i,N} E_{i,N} dp_{i,N} + \sum_{i,N} p_{i,N} dE_{i,N}. \tag{2.51}$$

With the usual rules for differentiation in the second term on the rhs, this may be further written as

$$d\overline{E} = \sum_{i,N} E_{i,N} dp_{i,N} + \sum_{i,N} p_{i,N} \frac{\partial E_{i,N}}{\partial V} dV, \tag{2.52}$$

whereupon comparison with equation (2.50) yields an expression for the mean pressure of the assembly.

However, we shall defer this step for the moment, as we first need to deal with the first term on the rhs of (2.52). Once again, we generalise the procedures used for the canonical ensemble. From equation (1.10), we obtain an expression relating the change in entropy to the change in the probability distribution. Noting that this variation must be carried out at constant V and N, we obtain

$$dS = -k \sum_{i,N} \ln p_{i,N} \, dp_{i,N}, \tag{2.53}$$

and with the substitution of the **GCE** probability distribution from (2.48), this becomes

$$dS = \sum_{i,N} [\lambda_E E_{i,N} + \lambda_N N] dp_{i,N}. \tag{2.54}$$

We may take this further by noting that, in these circumstances, any change in the mean number of particles in an assembly must be due to a change in the probability distribution. Thus, from equation (2.47), we have

$$d\overline{N} = \sum_{i,N} N dp_{i,N}, \tag{2.55}$$

and equation (2.54) becomes

$$dS = \lambda_E \sum_{i,N} E_{i,N} dp_{i,N} + \lambda_N d\overline{N}. \tag{2.56}$$

Then, with some rearrangement of this equation, we can substitute for the second term on the rhs of equation (2.52) for $d\overline{E}$, to obtain

$$d\overline{E} = \frac{dS}{\lambda_E} - \frac{\lambda_N}{\lambda_E} d\overline{N} + \sum_{i,N} p_{i,N} \left(\frac{\partial E_{i,N}}{\partial V} \right) dV. \tag{2.57}$$

Now we compare this result with the macroscopic expression as given by equation (2.50). The result is the following set of identifications:

$$\lambda_E = 1/T; \tag{2.58}$$

$$\lambda_N = -\mu/T; \tag{2.59}$$

and

$$P = -\sum_{i,N} \left(\frac{\partial E_{i,N}}{\partial V} \right) p_{i,N}. \tag{2.60}$$

Hence, substituting for the two Lagrange multipliers in equation (2.48) for $p_{i,N}$, we obtain the explicit form of the grand canonical probability distribution as

$$p_{i,N} = \frac{\exp(-[E_{i,N} - \mu N]/kT)}{\mathcal{Z}_{GCE}}, \tag{2.61}$$

where the partition function is given by

$$\mathcal{Z}_{GCE} = \sum_{i,N} \exp(-[E_{i,N} - \mu N]/kT). \tag{2.62}$$

It is instructive to compare this result with the corresponding result for the canonical ensemble, as given by equation (2.33), and note the new presence of the potential energy term associated with the chemical potential.

2.5.2 Thermodynamic relationships

Our main aim now is to obtain the bridge equation (analogous to equation (2.37)) for the grand canonical ensemble. In the process, we shall obtain a number of useful relationships. We begin by working out an expression for the entropy. Substituting (2.61) into equation (1.10), we obtain

$$S = k \ln \mathcal{Z}_{GCE} + \overline{E}/T - \mu \overline{N}/T. \tag{2.63}$$

Then, we introduce two quantities from thermodynamics. First, we introduce the Gibbs free energy G, such that

$$G = \mu \overline{N} = \overline{E} - TS + PV. \tag{2.64}$$

It should be noted that the Gibbs free energy G in the grand canonical ensemble is analogous to the Helmholtz free energy F in the canonical ensemble. Second, we introduce the grand potential Ω, such that:

$$\Omega = \overline{E} - TS - \mu \overline{N}$$
$$= -PV. \tag{2.65}$$

Now, multiply both sides of the expression for the entropy by T and rearrange to obtain:

$$\overline{E} - TS - \mu \overline{N} = -PV, \tag{2.66}$$

and comparison with the preceding equation immediately yields

$$\Omega = -kT \ln \mathcal{Z}_{GCE}, \tag{2.67}$$

which is the required bridge equation for the grand canonical ensemble.

Lastly, expressing equation (2.65) for Ω in differential form

$$d\Omega = -SdT - PdV - \overline{N}d\mu, \tag{2.68}$$

we may immediately obtain some useful thermodynamic relationships, as follows:

$$S = -(\partial\Omega/\partial T)_{V,\mu}\,; \tag{2.69}$$

$$P = -(\partial\Omega/\partial V)_{T,\mu}\,; \tag{2.70}$$

and

$$\overline{N} = -(\partial\Omega/\partial\mu)_{T,V}\,. \tag{2.71}$$

2.5.3 Density fluctuations

As time goes on, the number of particles in each assembly in the grand canonical ensemble will fluctuate about the mean value $\overline{N}$. We can obtain an indication of the significance of such fluctuations by deriving an expression for the rms value of the fluctuation $\Delta N = N - \overline{N}$. As in the case of the energy fluctuations in the canonical ensemble, we approach this indirectly. However, intuitively, we can see that the last relationship of the previous section gives us an expression for $\overline{N}$, and logically this provides us with a line of attack.

Differentiate both sides of equation (2.71) to obtain

$$(\partial^2\Omega/\partial\mu^2)_{T,V} = -(\partial\overline{N}/\partial\mu)_{T,V} = -\sum_{i,N} N(\partial p_{i,N}/\partial\mu)_{T,V}, \tag{2.72}$$

where the last step follows from equation (2.47).

The problem now is to find a helpful way of re-expressing the last term above, and we tackle this by means of a simple identity from the calculus, viz.,

$$\frac{1}{y}\frac{\partial y}{\partial x} = \frac{\partial \ln y}{\partial x},$$

where y is a function of x. Rewriting this in terms of $p_{i,N}$, we have

$$\frac{1}{p_{i,N}}\left(\frac{\partial p_{i,N}}{\partial \mu}\right)_{T,V} = \left(\frac{\partial \ln p_{i,N}}{\partial \mu}\right)_{T,V} = \beta N - \left(\frac{\partial \ln \mathcal{Z}_{GCE}}{\partial \mu}\right)_{T,V}, \tag{2.73}$$

where we have substituted from equation (2.61) for $p_{i,N}$, and $\beta = 1/kT$. Then, from the bridge equation (2.67), and using equation (2.71) we find

$$\frac{1}{p_{i,N}}\left(\frac{\partial p_{i,N}}{\partial \mu}\right)_{T,V} = \beta(N - \overline{N}). \tag{2.74}$$

Hence, we may write:

$$\left(\frac{\partial p_{i,N}}{\partial \mu}\right)_{T,V} = p_{i,N}\beta(N - \overline{N}), \tag{2.75}$$

and, substituting this into the extreme rhs of equation (2.72) yields

$$(\partial^2\Omega/\partial\mu^2)_{T,V} = \sum_{i,N} p_{i,N}\beta(N - \overline{N}) = -\beta\langle\Delta N^2\rangle. \tag{2.76}$$

Thus, from this result and from equation (2.71) we obtain for the relative fluctuation

$$\frac{\langle\Delta N^2\rangle^{1/2}}{\overline{N}} = \frac{-\sqrt{kT(\partial^2\Omega/\partial\mu^2)_{T,V}}}{-(\partial\Omega)/\partial\mu)_{T,V}} \sim \frac{1}{\sqrt{N}}. \tag{2.77}$$

Chapter 3

Examples of stationary ensembles

Interactions between particles can make it difficult to evaluate the partition function for an assembly, irrespective of whether it is in the canonical ensemble or the grand canonical ensemble. Indeed, in general this can only be done as an approximation and we shall look at some methods of doing this in later sections dealing with coupled particles. Here we begin with assemblies of particles which can be treated as if they do not interact with each other. Of course, in a quantum mechanical treatment, particles cannot be strictly independent, but it should be clear that what we are ruling out for the moment is any strong interaction such as a mutual coulomb potential.

3.1 Assembly of distinguishable particles

Consider N identical particles situated on a regular lattice in three dimensions. For example, we could be concerned with an array of spins making up a macroscopic piece of magnetic material. The ensemble consists of many such pieces of magnetic material and it follows that if we specify Particle 1 in Assembly 1 to be at the point (0,0,0), then we can specify Particle 1 in Assembly 2 to be at the point (0,0,0) in that lattice, Particle 1 in Assembly 3, and so on. In other words, each particle has an address within its assembly and is therefore *distinguishable*.

Under these circumstances, each particle will have access to its own spectrum of states. We can specify any particular realization of the assembly (i.e. microstate $|\,i\rangle$) as follows:

- Particle 1 is in state i_1 with energy ϵ_{i_1}

- Particle 2 is in state i_2 with energy ϵ_{i_2}
  $\vdots$

- Particle N is in state i_N with energy ϵ_{i_N}

That is, the microstate of the assembly is specified by the set of labels $\{i_1, i_2, \ldots i_N\}$. The corresponding energy eigenvalue for the assembly is therefore

$$E_i = \epsilon_{i_1} + \epsilon_{i_2} + \cdots + \epsilon_{i_N}. \tag{3.1}$$

It should be noted that this simple result depends on the fact that the particles do not interact. As we are allowing the energy of an assembly to vary, we are in effect assuming that it is a member of a canonical ensemble. Accordingly we invoke equation (2.34) for the partition function, and substituting from equation (3.1), we obtain the partition function of N distinguishable particles as

$$\mathcal{Z}_{dis} = \sum_{i_1, i_2 \ldots i_N} \exp -[\epsilon_{i_1} + \epsilon_{i_2} + \cdots + \epsilon_{i_N}]/kT. \tag{3.2}$$

Each of these summations runs over all the assemblies in the ensemble, and of course this operation is only possible because the particles are distinguishable and therefore we can identify the corresponding particle in each assembly. The subscript '*dis*' indicates that the partition function is for an assembly of distinguishable particles. Using the properties of the exponential, we can factorize this result as

$$\mathcal{Z}_{dis} = (\mathcal{Z}_1)^N, \tag{3.3}$$

where $\mathcal{Z}_1$ is the single-particle partition function and is given by

$$\mathcal{Z}_1 = \sum_j \exp\left[-\epsilon_j/kT\right]. \tag{3.4}$$

Note that the j is a dummy index and stands for any one of the set $\{i_1, i_2, \ldots i_N\}$. It may also be noted that $\mathcal{Z}_1$, as defined by equation (3.4), is sometimes referred to as the *micro-canonical* partition function.

The thermodynamic properties of the assembly now follow quite straightforwardly from the use of the bridge equation (2.37). Substituting from above for $\mathcal{Z}_{dis}$, we obtain

$$F = -kT\ln \mathcal{Z}_{dis} = -NkT\ln \mathcal{Z}_1, \tag{3.5}$$

which is of course just the result that one obtains from the microcanonical ensemble in elementary treatments of the subject.

As a corollary, we should point out that this result for the canonical ensemble contains the single-particle probability distribution. That is, if we make the definition:

$p_j \equiv$ the probability of finding a particular particle (which belongs to the assembly) in a specific state j;

then this probability is given by,

$$p_j = \frac{\exp\left[-\epsilon_j/kT\right]}{\mathcal{Z}_1}, \tag{3.6}$$

which is, of course, just the Boltzmann distribution.

3.2 Assembly of nonconserved, indistinguishable particles

As a preliminary to our general treatment of indistinguishable particles, we shall find it helpful to consider first the special case of electromagnetic radiation in a cavity. This is a well known situation where atoms in the walls of a metal cavity come into thermal equilibrium by emitting and absorbing photons. For our present purposes we can regard these photons as being particles with zero spin. Accordingly, we treat them as obeying Bose-Einstein statistics.

Obviously, when we are faced with fluctuating particle numbers, the grand canonical ensemble seems the natural choice. However, it must be understood that when particles are not conserved, the mean number of particles in an assembly cannot be specified. Accordingly, there is no Lagrange multiplier associated with a constraint on the mean number of particles, and this is equivalent to setting $\mu = 0$ in equation (2.61). It follows therefore that there is no difference for this problem between the canonical ensemble and the grand canonical ensemble. We shall simply use the former, as it will enable us to make a useful point.

In order to represent the microstate of the assembly, we shall use the occupation number representation, as discussed in Section 1.1. That is, we represent the state of the assembly by the set of numbers $\{n_j\}$, where there are n_1 particles with energy ϵ_1, n_2 particles with energy ϵ_2, and so on. The energy of the assembly in this microstate is given by

$$E = \sum_j n_j\epsilon_j. \tag{3.7}$$

The partition function for the canonical ensemble is given by equation (2.34). We note that E, as given by equation (3.7), is the energy of a particular microstate and therefore corresponds to E_i in the energy representation. The sum over all possible states of the assembly (i.e. the sum over i in (2.34)) is now got by summing each of the n_j over the ensemble. Making the appropriate replacements in equation (2.34), we obtain the partition function for the present problem as

$$\mathcal{Z} = \sum_{n_1, n_2 \ldots n_j \ldots} \exp\left\{-\beta[n_1\epsilon_1 + n_2\epsilon_2 + \ldots n_j\epsilon_j + \ldots]\right\}, \tag{3.8}$$

where the summation in the argument of the exponential has been written out explicitly, in order to make the basic structure clear.

At this point it will prove convenient to introduce a helpful relationship, which takes the form

$$\langle n_j \rangle = -\frac{1}{\beta} \frac{\partial}{\partial \epsilon_j} \ln \mathcal{Z}. \tag{3.9}$$

This relationship may be readily verified by direct substitution of equation (3.8) for the partition function.

Now let us return to the partition function. We may expand out the argument of the exponential to yield

$$\mathcal{Z} = \sum_{n_1} \exp\left[-\beta n_1 \epsilon_1\right] \times \sum_{n_2} \exp\left[-\beta n_2 \epsilon_2\right] \times \cdots \sum_{n_j} \exp\left[-\beta n_j \epsilon_j\right] \times \ldots, \tag{3.10}$$

which may be further written in terms of the product operator as

$$\mathcal{Z} = \prod_j \{\sum_{n_j} \exp\left[-\beta n_j \epsilon_j\right]\}. \tag{3.11}$$

But, for Bose-Einstein particles, we have $n_j = 0, 1, 2, \ldots$, so the term inside the curly bracket may be written as

$$\sum_{n_j} \exp[-\beta n_j \epsilon_j] = \frac{1}{1 - \exp\left[-\beta \epsilon_j\right]}, \tag{3.12}$$

hence it follows that

$$\mathcal{Z} = \prod_j \frac{1}{1 - \exp\left[-\beta \epsilon_j\right]}. \tag{3.13}$$

Then, invoking equation (3.9), we can write a neat expression for the mean number of particles on the energy level ϵ_j, thus:

$$\langle n_j \rangle = \frac{1}{\exp\left[\beta\epsilon_j\right] - 1}, \tag{3.14}$$

where we have substituted from (3.13) for $\mathcal{Z}$.

3.3   Conserved particles: general treatment for Bose-Einstein and Fermi-Dirac statistics

In this section we continue to work with quantum statistics, but we now consider nonlocalized particles, which means that we are considering either a Fermi or a Bose gas. We also continue to use the occupation number representation, as in the preceding section, but we must now recognize that in general particles will be conserved. That is, for any assembly in the ensemble, the total number of particles N is fixed. Thus, for such an assembly, the numbers of particles on the various levels are subject to the constraint that they must all add up to N, or:

$$N = \sum_j n_j. \tag{3.15}$$

The existence of this constraint immediately rules out the methods of the last section, as it makes it impossible to perform the summations which we used to evaluate the partition function. It is easily verified that the constraint on particle number leaves one with an awkward remainder term, involving the total particle number N, which cannot be summed.

An easy way around this difficulty is to consider the assembly to be part of the grand canonical ensemble, with the result that the total number of particles N becomes a variable which varies from one assembly to another. Accordingly, we wish to invoke equation (2.62) for the grand partition function, but first we have to change over from the energy to the occupation number representation. We do this as follows.

Corresponding to the N-body assembly state $\mid i \rangle$, with energy eigenvalue $E_{i,N}$, we have the set of occupation numbers $\{n_j\}$. It follows that the sum over states, becomes a sum over occupation numbers if we write the energy of state $\mid i \rangle$ as

$$E_{i,N} = \sum_j n_j \epsilon_j, \tag{3.16}$$

where, as before, the ϵ_j are the energy levels of the N-particle assembly. Hence, the grand partition function, as given by equation (2.62), takes the form

$$\mathcal{Z}_{GCE} = \sum_N \sum_{n_1, n_2 \ldots}^{(N)} \exp\{-\beta[n_1\epsilon_1 + n_2\epsilon_2 + \ldots] + \beta\mu[n_1 + n_2 + \ldots]\}, \tag{3.17}$$

where the superscript (N) on the second summation on the rhs indicates the constraint that the n_j must add up to N for each assembly. However, the first summation over N, taken over the ensemble, lifts this constraint, so that N becomes a dummy variable and the awkward remainder term mentioned above can now be treated on the same footing as all the others. Or,

$$\sum_N \sum_{n_1, n_2 \ldots}^{(N)} \equiv \sum_{n_1, n_2 \ldots}. \tag{3.18}$$

Thus, with this simplification, the partition function may be written as

$$\mathcal{Z}_{GCE} = \prod_j \mathcal{Z}_j, \tag{3.19}$$

where

$$\mathcal{Z}_j = \sum_{n_j} \exp[\beta n_j(\mu - \epsilon_j)]. \tag{3.20}$$

This result may be compared to equation (3.8) for the partition function of the canonical ensemble of nonconserved particles in the previous section. It should be noted that the conservation of particle number leads to the occurrence of the chemical potential μ.

The probability of finding the assembly in the microstate characterised by the set $\{n\}$, is just the Gibbs distribution, as given by equation (2.61),

$$p_{\{n\}} = \frac{\exp[\beta\mu \sum_j n_j - \beta \sum_j n_j \epsilon_j]}{\mathcal{Z}_{GCE}}, \tag{3.21}$$

with the appropriate changes to the occupation number representation. Correspondingly, the probability of finding exactly n_j particles of the assembly in state j is given by

$$p_{n_j} = \frac{\exp[\beta\mu n_j - \beta n_j \epsilon_j]}{\mathcal{Z}_{GCE}}. \tag{3.22}$$

It follows that the mean number of particles in a specific state j, with energy ϵ_j, is just

$$\langle n_j \rangle = \sum_{n_j} n_j p_{n_j} = kT \frac{\partial \ln \mathcal{Z}_j}{\partial \mu}, \tag{3.23}$$

where the last step follows from equations (2.17) and (2.59).

In order to make further progress, we have to consider whether our particles are Fermions or Bosons. We treat the two cases separately, as follows.

3.3.1 Fermi-Dirac (FD) statistics

In this case the particles have spin $1/2$ and the exclusion principle limits the possible occupation numbers to $n_j = 0$ or 1. Hence the single-level partition function (3.20) becomes

$$\mathcal{Z}_j = \exp 0 + \exp \beta(\mu - \epsilon_j) = 1 + \exp\left[\frac{\mu - \epsilon_j}{kT}\right]. \tag{3.24}$$

Invoking equation (3.19), and the bridge relationship in the form of equation (2.67), we obtain for the grand potential

$$\Omega = -kT \sum_j \ln\left\{1 + \exp\left[\frac{\mu - \epsilon_j}{kT}\right]\right\}, \tag{3.25}$$

and observable macroscopic properties then follow from the thermodynamic relationships contained in equations (2.69)-(2.71).

3.3.2 Bose-Einstein (BE) statistics

Bosons are those particles with integral spin, and the occupation number can take any nonnegative integer value. Thus the single-level partition function now becomes

$$\mathcal{Z}_j = \sum_{n_j=0}^{\infty} \exp \frac{n_j[\mu - \epsilon_j]}{kT}. \tag{3.26}$$

The sum of this series is of course given by the binomial theorem and takes the form

$$\mathcal{Z}_j = \left\{1 - \exp\left[\frac{\mu - \epsilon_j}{kT}\right]\right\}^{-1}. \tag{3.27}$$

The grand potential can be obtained, just as in the Fermi-Dirac case above, and is easily shown to take the form

$$\Omega = kT \sum_j \ln\left\{1 - \exp\frac{[\mu - \epsilon_j]}{kT}\right\}. \tag{3.28}$$

It should be noted that this result differs only from equation (3.25) for the Fermi-Dirac case by the sign of the rhs and also the sign of the exponential term.

3.4   The Classical Limit: Boltzmann Statistics

The classical limit is achieved at either high temperatures or low particle densities, when the *de Broglie* wavelength of a particle is much smaller than the mean interparticle separation. It can be shown that this is equivalent to the condition

$$\exp\left[\beta\mu\right] \ll 1.$$

Another criterion for the classical limit is that the probability of a given state being occupied is small. If there are many unoccupied states, then the exclusion principle for fermions becomes irrelevant as the chance of two particles trying to occupy the same state becomes vanishing small. In the previous section we derived an expression for this probability. We can obtain a combined expression for both kinds of statistics by substituting either (3.24) or (3.26) for $\mathscr{Z}_j$ into equation (3.23) for $\langle n_j \rangle$, thus:

$$\langle n_j \rangle = \frac{1}{\exp\beta[\epsilon_j - \mu] \pm 1}, \tag{3.29}$$

where the plus sign corresponds to FD statistics and the minus sign to BE statistics. For the classical limit, we have

$$\exp\left[\beta\mu\right] \ll 1 \Rightarrow \exp\left[-\beta\mu\right] \gg 1,$$

and so

$$\exp\beta[\epsilon_j - \mu] \gg 1,$$

irrespective of the value of ϵ_j. Accordingly, we can use the binomial theorem to expand out the rhs of equation (3.29) on the basis of the exponential term in the denominator being much less than unity.

At this stage it is convenient to work with the grand potential. Combining equations (3.25) and (3.28), we obtain for both kinds of statistics,

$$\Omega = \mp kT \sum_j \ln\left\{1 \pm \exp\frac{[\mu - \epsilon_j]}{kT}\right\}, \tag{3.30}$$

where the upper sign is for FD and the lower sign is for BE statistics. Now expand out the log on the basis that the exponential factor is small (note that this is the inverse of the exponential factor discussed just above!), to obtain

$$\Omega \simeq \mp kT \sum_j (\pm) \exp\frac{[\mu - \epsilon_j]}{kT} = -kT \sum_j \exp\frac{[\mu - \epsilon_j]}{kT}. \tag{3.31}$$

This is obviously consistent with our expectation that in the classical limit there is no distinction between the different kinds of particles. That is, at sufficiently high temperatures or sufficiently low densities, equation (3.31) is valid for FD, BE and Maxwell-Boltzmann statistics alike.

We can fix the chemical potential μ as follows. From equation (2.71) and equation (3.31) we can write the mean particle number as

$$\overline{N} = \sum_j \exp\beta[\mu - \epsilon_j] = \mathscr{Z}_1 \exp\left[-\beta\mu\right], \tag{3.32}$$

where $\mathscr{Z}_1$ is the single-particle partition function in the canonical ensemble, as given by equation (3.4). Rearranging this expression then yields

$$\mu = kT \ln \overline{N}/\mathscr{Z}_1. \tag{3.33}$$

Now consider the Helmholtz free energy F; viz.

$$
\begin{aligned}
F &= \overline{E} - TS \\
&= \Omega + \mu\overline{N} \\
&= \Omega + \overline{N}kT\ln\overline{N}/\mathcal{Z}_1,
\end{aligned}
\tag{3.34}
$$

where the first equality follows from the first line of equation (2.65) and the second from equation (3.33) for $\mathcal{Z}_1$. Further, assuming the equation of state of an ideal gas, and making use of Stirling's approximation we may write the free energy in the classical limit as

$$
F = -kT\ln\mathcal{Z}_1^{\overline{N}}/N!.
\tag{3.35}
$$
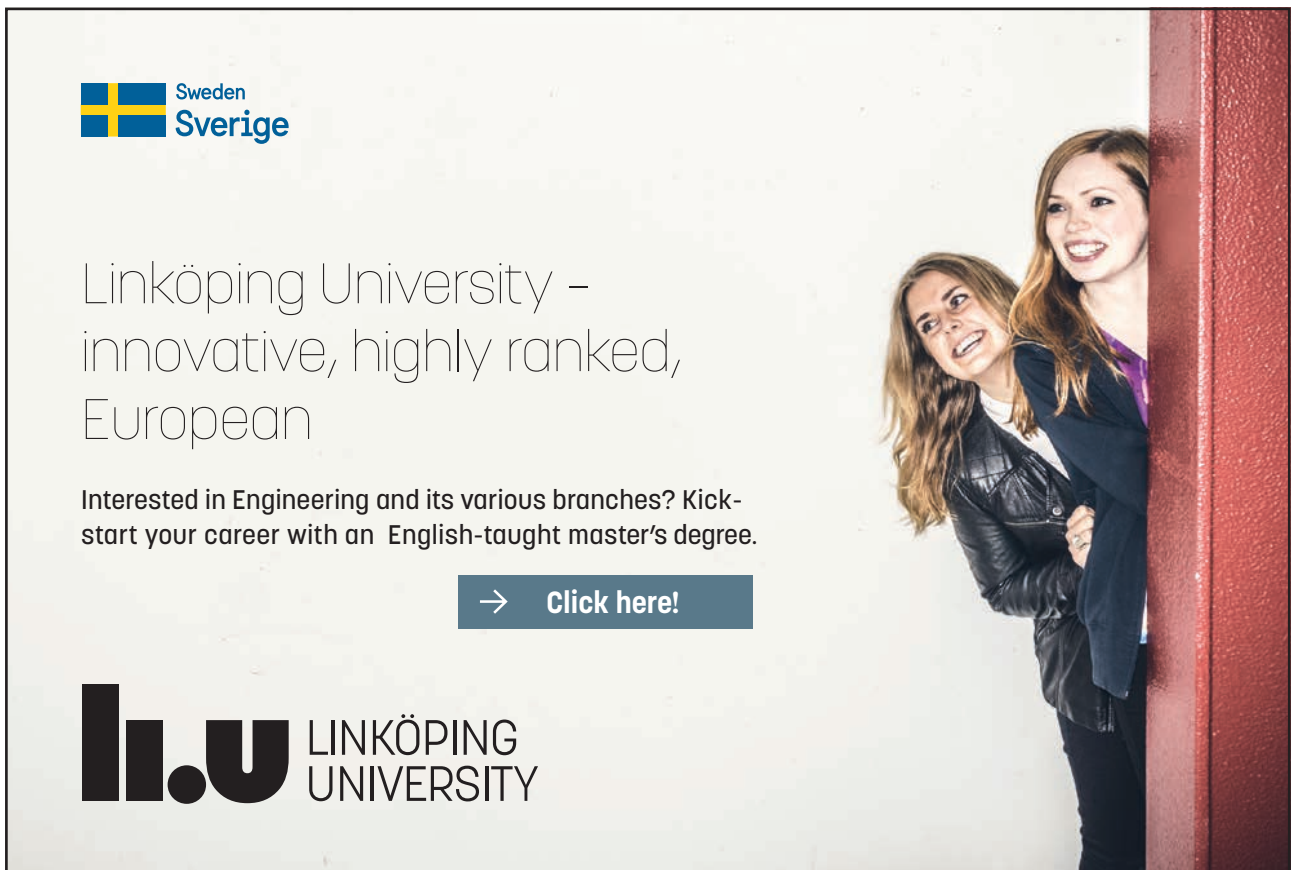
If we now compare this result with that for the free energy in the canonical ensemble, as given by equation (3.5), we can make the identification:

$$
\mathcal{Z}_{indis} = \mathcal{Z}_1^{\overline{N}}/N!,
\tag{3.36}
$$

for indistinguishable particles. So it follows, taken to the classical limit, that we have

$$
\mathcal{Z}_{indis} \to \mathcal{Z}_{dis}/N!,
\tag{3.37}
$$

where $\mathcal{Z}_{dis}$ is given by equation (3.3). That is, the factor $N!$ corrects the overcounting of actually identical microstates in a theory based on indistinguishability of identical particles.

Part II

The many-body problem

Chapter 4

The bedrock problem: strong interactions

In Part 1 we considered only cases where particles are weakly interacting. By this we mean that in the classical sense they do not interact except by localised collisions which are necessary to bring the system into equilibrium. For the quantal gases we know that the requirements of quantum mechanics have to be satisfied and that this imposes an effective interaction between particles. However, we have seen that the use of the Canonical Ensemble allows us to treat particles as being independent even although they are connected by a constraint on their total energy. Similarly, a constraint on particle number can be evaded by using the Grand Canonical Ensemble.

We now consider cases where particles are strongly interacting, through Coulomb or Lennard-Jones potentials. For sake of simplicity, we mainly opt for the classical formalism and in this Part consider only the case of stationary assemblies. In effect, we now ask the basic question: what is the many-body problem? We answer this question by considering the Hamiltonian of the system.

4.1   The interaction Hamiltonian

As before, in the classical formalism, we consider an N-body assembly of volume V with total system Hamiltonian H. For a perfect gas (no interactions), H can be written as the sum of single-particle Hamiltonians, thus:

$$H = \sum_{i=1}^{N} \frac{p_i^2}{2m} = \sum_{i=1}^{N} H_i, \tag{4.1}$$

where the index i labels any particle. However, there is no dependence on the generalised position coordinate of the ith particle $\mathbf{q}_i$.

In general this cannot be true. Suppose we consider as an example a gas of charged particles. If we take these to be electrons, then each pair of particles will experience the mutual Coulomb potential. For particles labelled 1 and 2 we may write this as

$$\phi_{12} = \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|},$$

where e is the electronic charge. More generally, for particles labelled i and j we have

$$\phi_{ij} = \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}.$$

Evidently, for a gas of charged particles we would have to add up the above contribution for every pair of particles and add it on to the free-particle form of equation (4.1) in order to obtain the system Hamiltonian. This strongly suggests that for any interacting assembly, the total Hamiltonian may be expected to take a more complicated form which may be written as

$$H = \sum_{n=1}^{N} H_n + \sum_{n,m} H_{nm} \tag{4.2}$$

where the second term represents the interactions between particles. In fact this is too general a form for our purposes here. We shall make the restriction to interactions which involve pairs of particles only and in which the potential between each pair of particles depends only on their separation, thus:

$$H = \sum_{i=1}^{N} \frac{p_i^2}{2m} + \sum_{i<j=1}^{N} \phi(|\mathbf{q}_i - \mathbf{q}_j|). \tag{4.3}$$

Note the convention on the double sum. This is to avoid counting each pair of particles twice. We shall encounter various ways of ensuring this.

The problem now is to solve for the partition function and, as we shall see later, one interesting approach is to assume that the interactions are small and look for corrections to the 'perfect gas' case. However, we begin by considering the general problem.

4.2   Diagonal forms of the Hamiltonian

The problem with (4.2) or (4.3) is that the Hamiltonian is nondiagonal: so in general it is difficult to do the 'sum over states' needed to find the partition function. An obvious approach is to try to diagonalise H, so that it takes the form of equation (4.1) for noninteracting systems, even although there are interactions present. There are some cases where this can be done exactly but more usually it can only be done approximately.

4.3   Theory of specific heats of solids

As an example of an exact method of diagonalizing the Hamiltonian, we revise a topic from elementary statistical physics.

4.3.1   Classical theory

Consider a solid as being made up from $3N$ *independent*, distinguishable oscillators, each at a different lattice site. The Hamiltonian for a simple harmonic oscillator is just

$$H(p,q) = \frac{p^2}{2m} + \frac{mw^2q^2}{2} \tag{4.4}$$

Hence we treat the problem as a canonical ensemble and obtain $\mathcal{Z}$ in order to derive the thermodynamic properties. The resultant specific heat agrees well with experimental results at large values of T.

4.3.2   Einstein theory

Make the same assumptions as in the classical case, but replace (4.4) by

$$\hat{H} = \hbar w(\hat{N} + 1/2) \tag{4.5}$$

where $\hat{H}$ is the Hamiltonian operator and $\hat{N}$ is the number operator. This gives a reasonable result for specific heat for all T, but is worst at low temperatures.

4.3.3   Debye theory

Assume that the oscillators are coupled so that the Hamiltonian for the assembly is not diagonal, thus:

$$H(\mathbf{p}, \mathbf{q}) = \sum_{i=1}^{3N} \frac{p_i^2}{2m} + \sum_{i,j}^{3N} A_{ij}q_iq_j. \tag{4.6}$$

The matrix A_{nm} depends on the nature of the interaction between the oscillators. This form of H can be diagonalised in terms of the normal coordinates and normal modes:

$$H(\mathbf{P}, \mathbf{Q}) = \sum_{i=1}^{3N} \frac{P_i^2}{2m} + \sum_{i=1}^{3N} \frac{m\omega_i^2}{2}Q_i^2, \tag{4.7}$$

where ω_n are the frequencies of the normal modes. Can then apply the Einstein approach to (4.7), with the phonon Hamiltonian

$$\hat{H} = \sum_n \hbar\omega_n(\hat{N}_n + 1/2). \tag{4.8}$$

4.4 Quasi-particles and renormalization

A very powerful *approximate* method is to diagonalise H by replacing the interaction by the *overall effect* of all the other particles on the nth particle. The result can be an approximation to (4.2) in the form:

$$H = \sum_i H_i'. \tag{4.9}$$

Here each of the N particles is replaced by a *quasi-particle* and H_i' is the *effective* Hamiltonian for the ith quasi-particle. Each quasi-particle has a portion of the interaction energy added on to its single-particle form. In order to describe this process, we borrow the term 'renormalization' from quantum field theory. A *renormalization process* is one where we make the replacement:

'bare' quantity + interactions → 'dressed' quantity.

For example, we could consider the case of conduction electrons in a metal. In this case we have:

The effect of the lattice potential → 'quasi-electron' with an effective mass.

Or, a case which we shall discuss in some detail later, that of electrons in a classical plasma. Here we have:

The effect of all the other electrons → quasi-electron with effective charge (screened potential).

A general systematic *self-consistent* approach along these lines is usually known as a *mean field theory*. We shall illustrate this approach with two examples: the Weiss theory of ferromagnetism (in Section 5) and the Debye-Hückel theory of electrolytes.

4.5 Perturbation theory for low densities

One can give a formal treatment of perturbation theory but we can cheat a little by simply expanding out the exponential form in the partition function. We can make the many-body partition function more tractable by expanding out the interaction term in powers of the density or in powers of $1/T$ (high-temperature expansions). In this context the temperature and the density are regarded as **control parameters** since they control the strength of the interaction or coupling.

In order to demonstrate the use of the density as a control parameter we consider a model for a real gas with various assumptions about the shape of the intermolecular potential. We show that it is possible to obtain 'low-density' corrections to the equation of state for an ideal gas.

For the purposes of this section we shall need the Taylor series for an exponential function, viz.,

$$e^x = 1 + x + \frac{x^2}{2!} + \frac{x^3}{3!} \dots \frac{x^s}{s!} + \dots = \sum_{s=0}^{\infty} \frac{x^s}{s!},$$

along with that for a natural logarithm, thus:

$$\ln(1 + x) = x - \frac{x^2}{2} + \frac{x^3}{3} + \dots, \tag{4.10}$$

and the binomial expansion

$$(a + x)^n = a^n + na^{n-1}x + \frac{n(n-1)}{2!}a^{n-2}x^2 + \dots. \tag{4.11}$$

4.5.1 Low-density expansions: macroscopic case

We shall consider a gas in which the molecules interact but will 'weaken' the interaction (or coupling) by restricting our attention to low densities. Accordingly we shall formulate the general theory on the assumption that interactions between particles will lead to perturbations of the 'perfect gas' solution. We shall only treat the case of the 'slightly imperfect gas' as a specific example of the method. With this in mind, it may be helpful to begin by considering the problem from the macroscopic point of view and try to anticipate the results of the microscopic theory, even if only qualitatively.

We know that the perfect gas law is consistent with the neglect of interactions between the molecules, and indeed also fails to allow for the fraction of the available volume which the molecules occupy. Thus, in general terms, we expect the perfect gas law to be a good approximation for a gas which is not too dense and not too cold. For a system of N molecules, occupying a fixed volume V, the perfect gas law, usually written as

$$PV = NkT, \tag{4.12}$$

tells us the pressure P. However, if we rewrite this in terms of the number density $n = N/V$, then we can assume that this must be the limiting form (at low densities) of some more complicated law which would be valid at larger densities. Thus,

$$P = nkT + O(n^2), \tag{4.13}$$

where for increasing values of number density we would expect to have to take into account higher-order terms in n. Formally, it is usual to anticipate that the exact form of the law may be written as the expansion

$$PV = NkT[B_1(T) + B_2(T)n + B_3(T)n^2 + \dots]. \tag{4.14}$$

This is known as the virial expansion and the coefficients are referred to as:

$B_1(T)$: the first virial coefficient, which is equal to unity;

$B_2(T)$: the second virial coefficient;

$B_3(T)$: the third virial coefficient;

and so on, to any order. It should be noted that the coefficients depend on temperature because, for a given density, the effective strength of the particle interactions will depend on the temperature. It should also be noted that the status of equation (4.14), on the basis of the reasoning given, is little more than that of a plausible guess. In the next section, we shall begin the process of seeing to what extent such a guess is supported by microscopic considerations.

4.5.2   Low-density expansion: microscopic case

Now we turn our attention to the microscopic picture, and consider N interacting particles in phase space. Although we shall base our approach on the classical picture, we shall divide phase space up into cells of volume $V_0 = h^3$. This allows us to take over the partition function for a quantum assembly to a classical description of the microstates. The partition function generalises to

$$\mathcal{Z} = \frac{1}{N!} \sum_{\text{cells}} e^{-E(\mathbf{X})/kT}, \tag{4.15}$$

where $\mathbf{X} \equiv (\mathbf{q}, \mathbf{p})$ is the usual 'system point' in phase space, the sum over discrete microstates has been replaced by a sum over cells, and the factor $1/N!$ is required for the classical limit; to take the correct form.

The cell size is small, being of the magnitude of the cube of Planck's constant h, so we can go over to the continuum limit and replace sums by integrals, thus:

$$\sum_{\text{cells}} \rightarrow \frac{1}{h^3} \int d\mathbf{p} \int d\mathbf{q}.$$

Hence equation (4.15) can be written as:

$$\mathcal{Z} = \frac{1}{N! h^{3N}} \int d\mathbf{p}_1 \dots \int d\mathbf{p}_N \int d\mathbf{q}_1 \dots \int d\mathbf{q}_N \times e^{-E(\mathbf{q}, \mathbf{p})/kT}. \tag{4.16}$$

Note that the prefactor of $1/N! h^{3N}$ guarantees that the free energy is consistent with the quantum formulation. Also note that we take the number of degrees of freedom to be determined purely by the translational velocities and exclude internal degrees of freedom such as rotations and vibrations of molecules. From now on we use Φ or ϕ for potential energy in order to avoid confusion with V for volume

We can factor out the integration with respect to $\mathbf{p}$, by writing the exponential as

$$e^{-E(\mathbf{p}, \mathbf{q})/kT} = e^{-\sum_{i=1}^{N} p_i^2/2mkT} \times e^{-\Phi(\mathbf{q})/kT},$$

and so write the total partition function for the system as the product of $\mathcal{Z}_0$, the partition function for the perfect gas, with another function Q, thus

$$\mathcal{Z} = \mathcal{Z}_0 Q, \tag{4.17}$$

where (using a well known result from elementary statistical physics)

$$\mathcal{Z}_0 = \frac{V^N}{N!} \left(\frac{2\pi mkT}{h^2} \right)^{3N/2}, \tag{4.18}$$

and the **the configurational partition function** or, more usually, **configurational integral** Q is given by

$$Q = \frac{1}{V^N} \int d\mathbf{q}_1 \ldots \int d\mathbf{q}_N e^{-\Phi(\mathbf{q})/kT}. \tag{4.19}$$

We shall restrict our attention to the important general case of two-body potentials where

$$\Phi(\mathbf{q}) = \sum_{i<j=1}^{N} \phi(|\mathbf{q}_i - \mathbf{q}_j|) \equiv \sum_{i<j=1}^{N} \phi_{ij}, \tag{4.20}$$

and hence the function $\Phi(\mathbf{q})$ will be written as the double sum over ϕ_{ij} from now on.

Evaluation of (4.19) for Q is difficult in general, and depends very much on the form of the two-body potential ϕ_{ij}. For instance, for molecules with radius $\sim b$, the hard-sphere potential is

$$\begin{aligned} \phi_{HS}(r) &= \infty \text{ for } r < 2b; \\ &= 0 \text{ for } r > 2b, \end{aligned} \tag{4.21}$$

where we have taken the interparticle separation to be r. This potential is illustrated in Figure 4.1.

Or, the more realistic Lennard-Jones (or 'six–twelve') potential is given by

$$\phi_{LJ}(r) = 4\varepsilon[(b/r)^{12} - (b/r)^6] \tag{4.22}$$

where ε is related to binding energy, and this is illustrated schematically in Figure 4.2. Evidently, if the temperature of the gas (and hence the kinetic energy of the molecules) is sufficiently low, a bound state may occur, as shown in the figure for an inter-particle energy of E_1. However, if the temperature is high
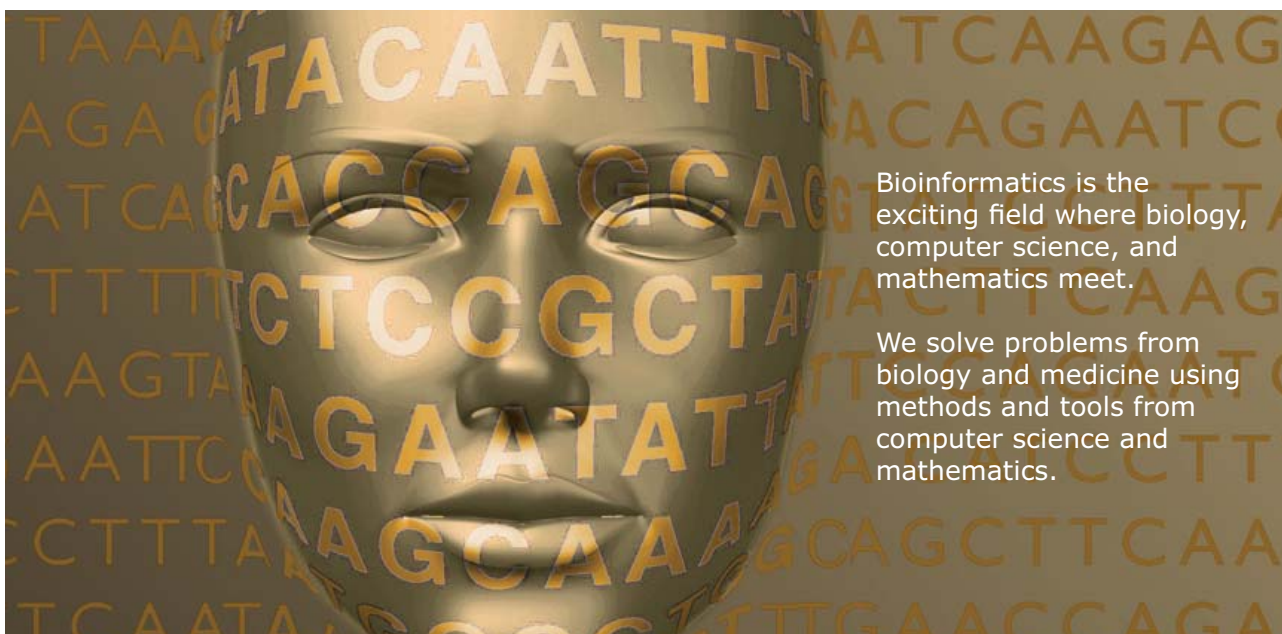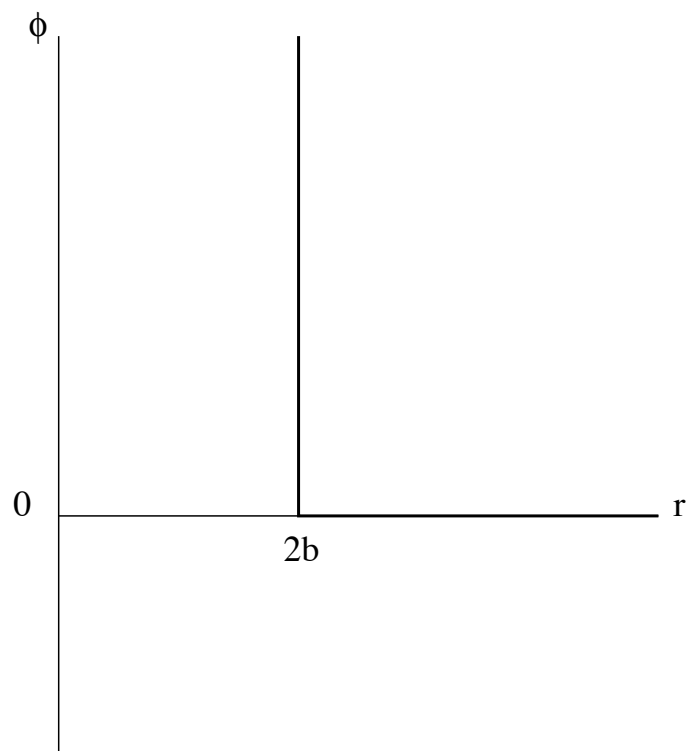
Figure 4.1: The potential equivalent to hard-sphere interactions for spheres of radius b .
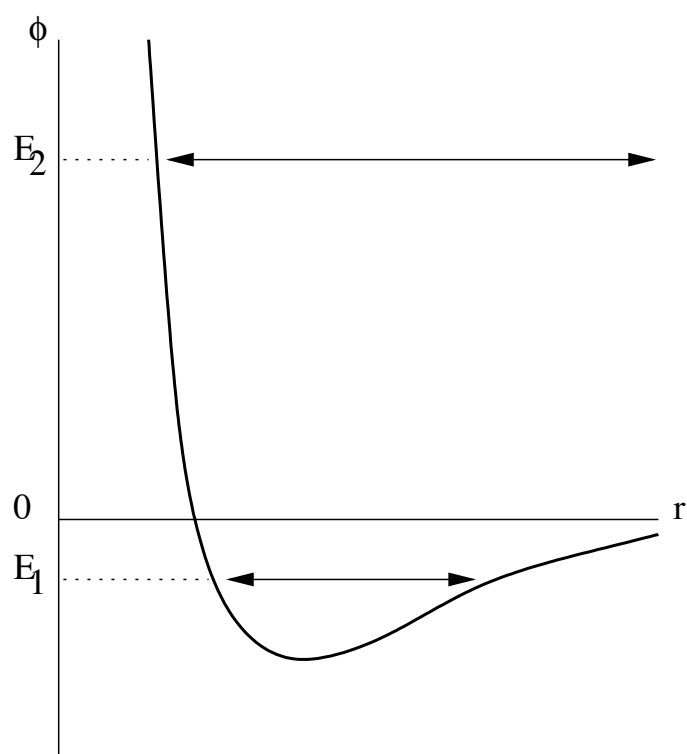
Figure 4.2: A schematic impression of the Lennard-Jones potential.

(interparticle energy labelled by E_2 in the figure), then the use of a hard-sphere potential might be a satisfactory approximation.

Other forms, such as the Coulomb potential, can be considered as required, but usually the configuration integral can only be evaluated approximately. In the next section we consider the use of the perturbation expansion in terms of a 'book-keeping' parameter. This is introduced as an arbitrary factor, just as if it were the usual 'small quantity' in perturbation theory; and, just as if it *were* the perturbation parameter, it is used to keep track of the various orders of terms during an iterative calculation. However, unlike the conventional perturbation parameter, it is not small and in fact is put equal to unity at the end of the calculation.

4.5.3 Perturbation expansion of the configuration integral

If the potential is, in some sense, weak (and we shall enlarge on what we mean by this at the end of the section), then we can expand out the exponential in (4.19) as a power series and truncate the resulting expansion at low order. In general, for any exponential we have the result given at the beginning of the section, and expanding the exponential in equation (4.19) in this way gives us

$$Q = V^{-N} \int d\mathbf{q}_1 \ldots \int d\mathbf{q}_N \sum_{s=o}^{\infty} - \left(\frac{\lambda}{kT}\right)^s \frac{1}{s!} \left(\sum_{i<j=1}^{N} \phi_{ij}\right)^s, \tag{4.23}$$

where λ is a 'book-keeping' parameter ($\lambda = 1$). Any possibility of low-order truncation depends on integrals being well-behaved and this in turn depends very much on the nature of ϕ. Also, combinatorial effects increase with order λ^s, as follows:
$s = 0 :$

$$Q_0 = V^{-N} \int d\mathbf{q}_1 \ldots \int d\mathbf{q}_N = 1, \tag{4.24}$$

where, of course,

$$\int d\mathbf{q}_1 = V \ldots \int d\mathbf{q}_N = V.$$

$s = 1:$

$$\begin{aligned}
(-kT)Q_1 &= V^{-N} \int d\mathbf{q}_1 \ldots \int d\mathbf{q}_N \left(\sum_{i<j=1}^{N} \phi_{ij}\right) \\
&= V^{-N} \int d\mathbf{q}_1 \ldots \int d\mathbf{q}_N (\phi_{12} + \phi_{13} + \phi_{23} + \phi_{14} + \ldots) \\
&= V^{-2} (\int \int d\mathbf{q}_1 d\mathbf{q}_2 \phi_{12} + \int \int d\mathbf{q}_1 d\mathbf{q}_3 \phi_{13} + \ldots).
\end{aligned} \tag{4.25}$$

And so on. Noting that Q_1 is made up of many identical terms, each of which is a double integral over the same pairwise potential, it follows that we need evaluate only one of these integrals, and may then multiply the result by the number of pairs which can be chosen from N particles. Hence

$$Q_1 = -\frac{1}{2}N(N-1)V^{-1} \int \frac{\phi_{12}}{kT} d\mathbf{r}_{12}, \tag{4.26}$$

where we have made the change of variables $\mathbf{r}_{12} = \mathbf{q}_1 - \mathbf{q}_2$, and the integration with respect to the centroid coordinate $\mathbf{R} = (\mathbf{q}_1 + \mathbf{q}_2)/2$ cancels one of the factors $1/V$.

Higher orders get more complicated and in practice diagram methods can be helpful. But the real problem is the unsatisfactory behaviour which is found when we attempt to take the thermodynamic limit:

$$Lt\ N/V \to n, \qquad \text{as} \qquad N, V \to \infty.$$

The expansion fails this test as, at any order s, there are various dependences on n, so that it does not take the form expected as in equation (4.14). (In mathematical terms, the expansion is inhomogeneous.)

This problem is not as serious as it might first appear, although our way of dealing with it may look rather like a trick. First we recall that the object of calculating the partition function is to calculate the free energy F (and hence all thermodynamical properties). To do this we use the bridge equation $F = -kT \ln \mathcal{Z}$, which tells us that $F \sim \mathcal{Z}$. Hence our trick is to work with $\ln Q$ rather than Q (in other words, with the free energy due to interactions) to get a new series. In practice this amounts to a rearrangement of the perturbation expansion such that one finds an infinite series of terms associated with n, n^2, n^3, and so on. Each of these infinite series must be summed to give a coefficient in our new expansion in powers of n.

However we close here by reconsidering what we mean by saying that the potential is 'weak'. We obtain one immediate clue from the above problems with the perturbation expansion, which is effectively (as is usual in many-body problems) in terms of the interaction strength. Intuitively, we can see that if the density is low, on average the particles will be far apart and hence the contribution of the interaction potential to the overall potential energy will be small. Also, we note that the potential energy (just like the kinetic energy) always appears divided by the factor kT, and so for large temperatures the argument of the exponentials will be small. Thus, for either low densities or high temperatures the exponentials can be expanded and truncated at low order. When we consider critical phenomena (e.g. a gas becoming a liquid), in the nature of things the density cannot realistically be treated as small. In these circumstances however, it can be useful to use the temperature as a **control parameter** and the interaction divided by kT is sometimes referred to as the **coupling**.

4.5.4   The Mayer functions and the virial coefficients

In real gases, it is postulated that higher-density corrections to the perfect gas equation take the form given by equation (4.14). Here we shall use statistical mechanics to explore the general method of calculating the virial coefficients, and although we shall not give a complete treatment, we shall highlight some of the difficulties involved. However, in the following section, we shall then calculate the second virial coefficient B_2 explicitly.

From equations (4.19) and (4.20), we may write the configurational integral as

$$Q = \frac{1}{V^N} \int d\mathbf{q}_1 \ldots \int d\mathbf{q}_N \, e^{-\sum_{i<j} \phi_{ij}/kT}$$
$$= \frac{1}{V^N} \int d\mathbf{q}_1 \ldots \int d\mathbf{q}_N \prod_{i<j} e^{-\phi_{ij}/kT}. \tag{4.27}$$

Now we introduce the **Mayer functions** f_{ij}, which are defined such that

$$f_{ij} = e^{-\phi_{ij}/kT} - 1. \tag{4.28}$$

These possess the useful property that:

as $r \to 0$, $f_{ij} \to -1$ for $\phi_{ij} \to \infty$,

and changes the product of (4.27) into a sum.

Upon substitution of (4.28), equation (4.27) for the configurational integral becomes:

$$Q = \frac{1}{V^N} \int d\mathbf{q}_1 \ldots \int d\mathbf{q}_N \prod_{i<j}(1 + f_{ij})$$
$$= \frac{1}{V^N} \int d\mathbf{q}_1 \ldots \int d\mathbf{q}_N[1 + \sum_{i<j} f_{ij} + \sum_{i<j}\sum_{k<l} f_{ij}f_{kl} + \ldots]. \tag{4.29}$$

Note three points about this:
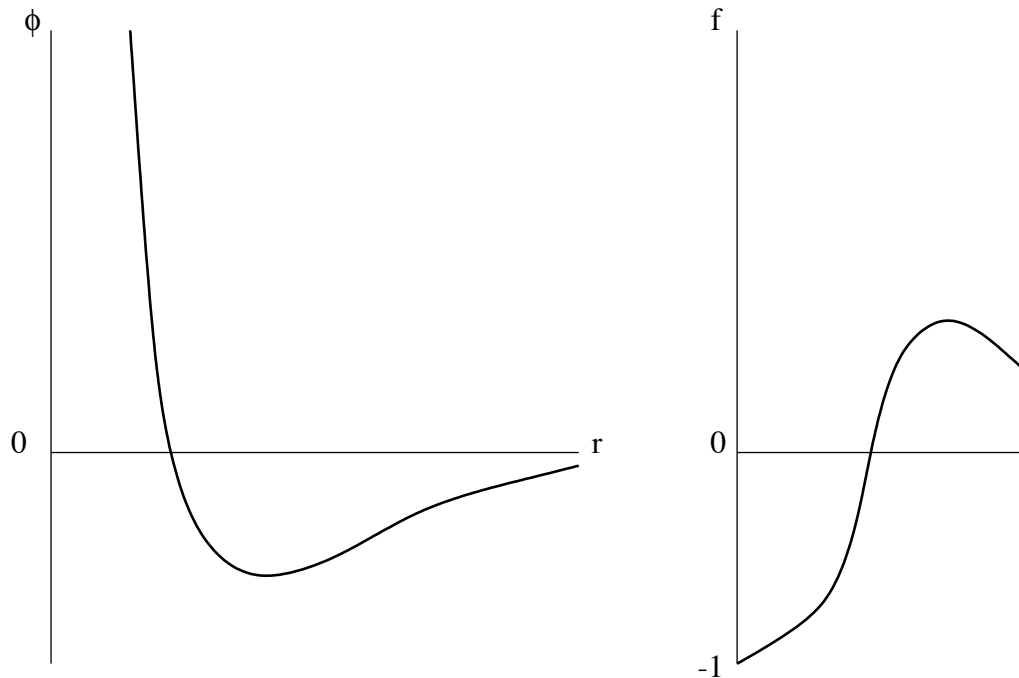
Figure 4.3: The Mayer function f corresponding to a realistic choice of interparticle potential ϕ.

1. f_{ij} is negligibly small in value unless the molecules making up the pair labelled by i and j are close together. Hence, for non-negligible values, f_{12} requires molecules 1 and 2 to collide; $f_{12}f_{34}$ requires molecules 1 and 2 to collide simultaneously with the collision between molecules 3 and 4; $f_{12}f_{23}$ requires a triple collision of molecules 1, 2 and 3; and so on.

2. The terms in equation (4.29) involve **molecular clusters**. For this reason the multiple integrals in (4.29) are known as **cluster integrals**.

3. The expansion given in equation (4.29) is known as the **virial cluster expansion**.

4.5.5 Calculation of the second virial coefficient B_2

We shall work only to first order in f_{ij}. That is,

$$Q = \frac{1}{V^N} \int d\mathbf{q}_1 \dots \int d\mathbf{q}_N [1 + \sum_{i<j} f_{ij}]. \tag{4.30}$$

Now, evidently $f_{12} = f_{13} = \dots = f_{23}$, so we shall take f_{12} as representative. Also, there are $N(N-1)/2$ pairs. Hence, to first order in the interaction potential, we have

$$Q = \frac{1}{V^N} \int d\mathbf{q}_1 \dots \int d\mathbf{q}_N \left[1 + \frac{N(N-1)}{2} f_{12}\right],$$

and so

$$\begin{aligned} Q &= \frac{1}{V^N} [V^N + V^{N-2} \int d\mathbf{q}_1 \int d\mathbf{q}_2 \frac{N(N-1)}{2} f_{12}] \\ &= 1 + V^{-2} \int d\mathbf{q}_1 \int d\mathbf{q}_2 \frac{N(N-1)}{2} f(|\mathbf{q}_1 - \mathbf{q}_2|). \end{aligned} \tag{4.31}$$
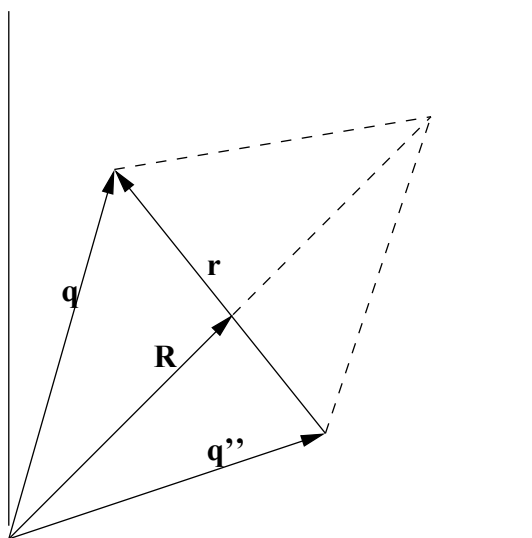
Figure 4.4: Change to centroid and difference coordinates.

Next we change variables to work in the relative and centroid coordinates, $\mathbf{r} = \mathbf{q}_1 - \mathbf{q}_2$ and $\mathbf{R} = \frac{1}{2}(\mathbf{q}_1 + \mathbf{q}_2)$, respectively: this is illustrated in Figure 4.4. Then, assuming spherical symmetry of the interaction potential, we obtain

$$
\begin{aligned}
Q &= 1 + V^{-2} \int d\mathbf{R} \frac{N(N-1)}{2} \int \mathbf{dr} f(r) \\
&= 1 + \frac{N(N-1)}{2V} \int f(r) \mathbf{dr} \\
&= 1 + \frac{N^2}{2V} I_2,
\end{aligned}
\tag{4.32}
$$

where I_2 is the cluster integral

$$
I_2 = \int d\mathbf{r} f(r) = \int \mathbf{dr}[e^{-\phi(r)/kT} - 1],
\tag{4.33}
$$

and, in the last step, we have substituted for the Mayer function to obtain our result for the second virial coefficient in terms of the interaction potential.

Now we resort to two tricks. First, we rewrite equation (4.32) for Q as the leading terms in an expansion

$$
Q = 1 + N\left(\frac{NI_2}{2V}\right) + \dots
\tag{4.34}
$$

Second, we note that the free energy $F \sim \ln Q$ must be extensive, so we must have $\ln Q \sim N$. It follows that the most likely form of the sum of the series on the righthand side of (4.35) is

$$
Q = \left(1 + \frac{NI_2}{2V}\right)^N.
\tag{4.35}
$$

So, from this result, the bridge equation for F and (4.17) for $\mathcal{Z}$ we obtain the following expression for the free energy:

$$
\begin{aligned}
F & = -kT \ln \mathcal{Z} = -kT \ln \mathcal{Z}_0 - kT \ln Q \\
& = F_0 - kT \ln Q = F_0 - NkT \ln \left(1 + \frac{NI_2}{V2}\right) \\
& = F_0 - \frac{NkT}{2}\left(\frac{N}{V}\right) I_2,
\end{aligned}
\tag{4.36}
$$

where we used the Taylor series for $\ln(1+x)$, as given at the beginning of this section. We may obtain the equation of state from the usual thermodynamic relationship $P = (-\partial F/\partial V)_{T,N}$. Thus

$$
P = \frac{NkT}{V} - \frac{NkT}{V}\left(\frac{N}{V}\right)\frac{1}{2}I_2 = \frac{NkT}{V}\left[1 - \frac{I_2}{2}\left(\frac{N}{V}\right)\right].
\tag{4.37}
$$

Then, comparison with the expansion of (4.14) yields

$$
B_2 = -\frac{1}{2}I_2,
\tag{4.38}
$$

as the second virial coefficient.

Lastly, we should note that the procedure just followed, although on the face of it *ad hoc*, nevertheless constitutes an effective *renormalization*, equivalent to a partial summation of the perturbation series.

4.6 The Debye-Hückel theory of the electron gas

We introduce the concept of the self-consistent field theory by considering the problem of a plasma or electrolyte, where the interaction between pairs of particles is the Coulomb potential.

The theory dates back to 1922 and, like the Weiss theory of ferromagnetism, is an ancient theory which is still close to the frontiers of many-body physics even today. It is not perhaps quite as important as the Weiss theory, but is of general relevance to the perturbation treatment of the electron gas at high temperatures or to electrolytes in the classical regime. It is also of relevance in rheology where it can be used to describe the mutual interactions of particles suspended in a fluid.

We state our theoretical objective here, as follows:

> We wish to calculate the electrostatic potential at a point r due to an electron at the origin while taking into account the effect of all the other electrons in the system.

4.6.1 The mean-field assumption

We shall discuss an idealized version of the problem in which N electrons are free to move in an environment with spatially uniform positive charge, chosen such that overall the system is electrically neutral. Both negative and positive charge densities are numerically equal to en_∞, where e is electronic charge and n_∞ is the number density when the electrons are spread out uniformly.

Consider the case where one electron is at $r = 0$. We wish to know the probability $p(r)$ of finding a second electron a distance r away. At thermal equilibrium, equations (2.33) and (2.34) apply, so this is given by

$$
p(r) = \frac{e^{-W(r)/kT}}{\mathcal{Z}},
\tag{4.39}
$$

where as usual $\mathcal{Z}$ is the partition function and $W(r)$ is the renormalized interaction energy, which takes into account the collective effect of all N electrons. We expect that (like the **bare** Coulomb form) the **dressed** interaction will satisfy

$$
W(r) \to 0 \text{ as } r \to \infty.
\tag{4.40}
$$

It will be seen later that $W(r)$ is analogous to the molecular field introduced in the Weiss theory and that (4.39) and (4.40) together amount to a **mean-field approximation**. Then, the probability P_r (say) of finding a second electron in the spherical shell between r and $r + dr$ around the first electron is just

$$P_r = P(r) \times 4\pi r^2 dr = \frac{1}{\mathcal{Z}} e^{-W(r)/kT} \times 4\pi r^2 dr, \qquad (4.41)$$

and so the number of electrons in the shell is

$$N_r = NP_r = \frac{N}{\mathcal{Z}} e^{-W(r)/kT} \times 4\pi r^2 dr. \qquad (4.42)$$

Hence, the **number density** $n(r)$ of electrons in the shell is given by

$$n(r) = \frac{NP_r}{4\pi r^2 dr} = \frac{N}{\mathcal{Z}} e^{-W(r)/kT}. \qquad (4.43)$$

Now consider the ratio of this density to that at some other $r = R$, thus:

$$\frac{n(r)}{n(R)} = \frac{e^{-W(r)/kT}}{e^{-W(R)/kT}}. \qquad (4.44)$$

Further, let us take $R \to \infty$, and using (4.40), we have

$$e^{-W(R)/kT} \to 1,$$

and so equation(4.44) may be written as

$$\frac{n(r)}{n(\infty)} = e^{-W(r)/kT}. \qquad (4.45)$$

Or, in terms of the uniform number density introduced at the beginning of this section, viz., $n_\infty = n(\infty)$, we may rearrange this result into the form:

$$n(r) = n_\infty e^{-W(r)/kT}. \qquad (4.46)$$

4.6.2 The self-consistent approximation

Debye and Hückel (1923) proposed that ϕ should be determined *self-consistently* by making a '**continuum approximation**' and solving Poisson's equation (from electrostatics), thus:

$$\nabla^2 \phi = -4\pi \rho(r), \qquad (4.47)$$

where $\rho(r)$ is the electron charge density. In this case, the electron charge density may be taken as

$$\rho(r) = en(r) - en_\infty,$$

and the Poisson equation becomes

$$\nabla^2 \phi(r) = -4\pi e n_\infty \{ e^{-e\phi(r)/kT} - 1 \}, \qquad (4.48)$$

where we substituted

$$W = e\phi(r), \qquad (4.49)$$

into the right-hand side of equation (4.46) for $n(r)$ and $\phi(r)$ is the self-consistent field potential.
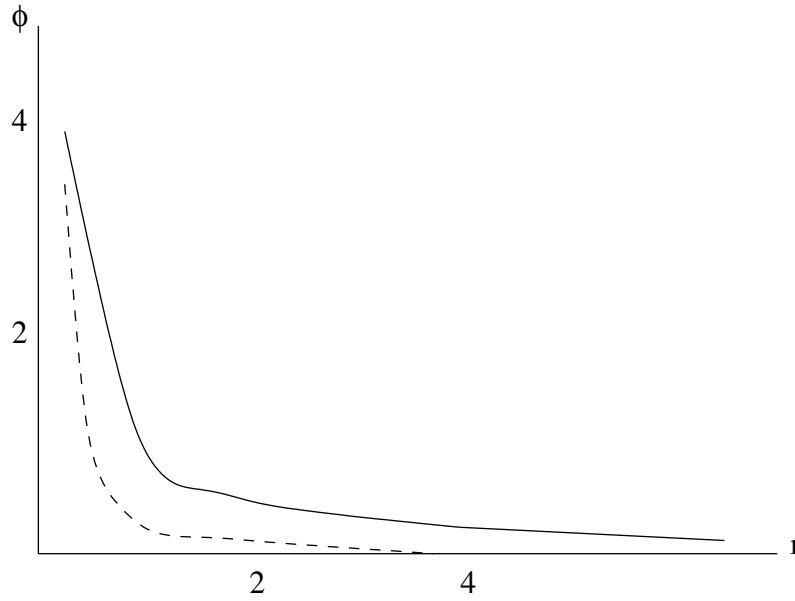
Figure 4.5: Comparison of the Coulomb potential (full line) with a screened potential (dashed line .

4.6.3 The screened potential

If we restrict ourselves to $W << kT$ (that is, the high-temperature case), and expand out the exponential to first order, Poisson's equation further becomes

$$\nabla^2 \phi = \frac{4\pi e^2 n_\infty \phi}{kT} \tag{4.50}$$

with solution readily found to be

$$\phi = \left(\frac{e}{r}\right) exp\{-r/l_D\}, \tag{4.51}$$

where l_D is the Debye length and is given by

$$l_D = \left[\frac{4\pi e^2 n_\infty}{kT}\right]^{-1/2}. \tag{4.52}$$

Equation (4.51) represents a **'screened potential'**. Physically, the Debye length is interpreted as the radius of the *screening cloud* of electrons about any one electron. This can also be interpreted as 'charge renormalization', in the following sense

$$e \to e \times \exp\{-r/l_D\}.$$

Note that it is necessary to consider the circumstances under which the cloud of discrete electrons can be regarded as a continuous charge density.

4.6.4 Validity of the continuum approximation

The continuum approximation should be valid for the case where the distance between particles is much smaller than the Debye length. That is

$$l_D \gg N^{-1/3}; \quad \text{or} \quad l_D^3 \gg N^{-1},$$

and from equation (4.52)

$$8\pi^{3/2} e^3 N^{1/2} \beta^{3/2} \ll 1,$$

where $\beta \equiv 1/kT$.

Chapter 5

Phase transitions

In this chapter we are concerned with changes of state such as gas-liquid and ferro-paramagnetic transformations.

5.1 Critical exponents

Critical points occur in a great variety of systems. The value of T_c depends on the details of the atomic or molecular interactions of the system and hence will vary widely from one system to another. However there is a considerable degree of similarity in the way systems approach a critical point: macroscopic variables like specific heat or magnetic susceptibility either diverge or go to zero as $T \to T_c$. We can characterise this behaviour by the introduction of critical exponents.

We may represent any macroscopic variable by $F(T)$ and introduce the reduced temperature θ_c by

$$\theta_c = \frac{T - T_c}{T_c}. \tag{5.1}$$

Then a critical exponent s can be defined for $\theta_c \approx 0$ (i.e $T \approx T_c$) by

$$F(\theta_c) = A\theta_c^{-s}, \tag{5.2}$$

where A is a constant. We note that there are two broad cases as follows, depending only on the sign of the critical exponent:

1. Critical exponent s is positive, $F(\theta_c)$ diverges as $T \to T_c$.

2. Critical exponent s is negative, $F(\theta_c) \to 0$ as $T \to T_c$.

Actually F may be expected to behave analytically away from the fixed point. With this in mind, we can write it with greater range of validity as

$$F(\theta_c) = A\theta_c^{-s}(1 + B\theta_c^y + ...),\tag{5.3}$$

where $y > 0$ for analytic behaviour at large θ_c and B is a constant.

More formally, the critical exponent s of $F(\theta_c)$ is defined to be:

$$s = -\lim_{\theta_C \to 0} \frac{\ln F(\theta_c)}{\ln \theta_c}.\tag{5.4}$$

Lastly, we should mention at this stage the idea of *universality*. The critical exponents are to a large extent universal, depending only on the symmetry of the Hamiltonian and its dimension, provided the interatomic forces are short range.

5.2   The ferro-paramagnetic transition

When a piece of ferromagnetic material is placed in a magnetic field $\mathbf{B}$, a mean magnetization $\mathbf{M}$ is induced in the material which is proportional[1] to $\mathbf{B}$. Then, taking one coordinate axis along $\mathbf{B}$, we can work with the scalars B and M (assumed to be in the same direction!).

The relationship between the applied magnetic field and the resulting magnetization is given by the isothermal susceptibility, as defined by the relation:

$$\chi_T \equiv \left(\frac{\partial M}{\partial B}\right)_T.\tag{5.5}$$

Note this is an example of an **response function**. For a fluid, the analogous response function would be the isothermal compressibility.

5.2.1   The microscopic picture

The basic model is that the magnetic material consists of N spins on a lattice and each has magnetic moment μ_0 (up or down), corresponding to the spin s_i at the lattice site labelled by i taking its permitted values of $S_i = \pm 1$. The instantaneous state at one lattice site is therefore given by

$$\mu = \pm\mu_0.$$

We may define the magnetisation M,

$$M = N\bar{\mu},$$

where $\bar{\mu}$ is the average value of the magnetic moment at a lattice site.

It is helpful to consider two extreme cases, as follows:

- If all spins are oriented at random then $\bar{\mu} = 0$ and so $M = 0$, and hence there is no net magnetization.

- If all spins are lined up then $\bar{\mu} = \mu_0$ and so the net magnetization is $M_\infty = N\mu_0$, which is the largest possible value and is often referred to as the saturation value.

---

[1]We are assuming here that the magnetic material is isotropic

In between these extremes there is an average magnetisation appropriate to the temperature of the system, thus:

$$\bar{\mu} = \sum_{states} P(\mu)\mu. \tag{5.6}$$

This dependence on temperature is illustrated qualitatively in Figure 5.1.

5.3 The Weiss theory of ferromagnetism

The Weiss theory dates from 1907, before the formulation of quantum mechanics, so we shall present a slightly modernized version which acknowledges the existence of quantum physics.

5.3.1 The ferro-paramagnetic transition: theoretical aims

As mentioned in Section 2.4, when a piece of ferromagnetic material is placed in a magnetic field **B**, a mean magnetization **M** is induced in the material which is proportional to **B**. Then, taking one coordinate axis along **B**, we can work with the scalars B and M which we assume to be in the same direction.

Our general theoretical aim will be to obtain an expression relating the magnetization to the applied field. However in order to have a specific objective, we will seek a value of the critical temperature T_c, above which spontaneous magnetization cannot exist.
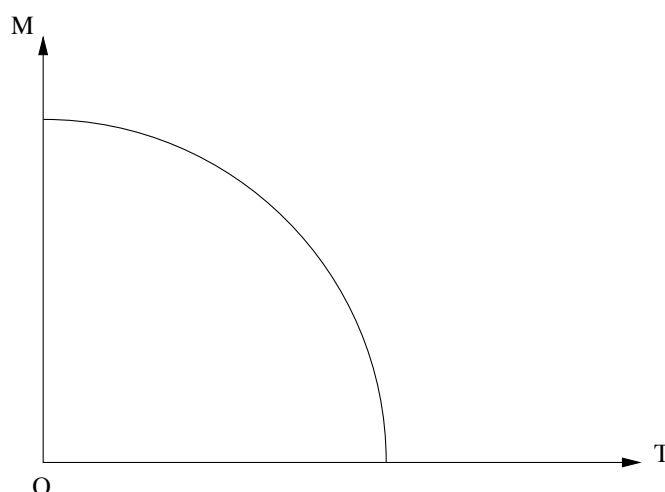
Figure 5.1: Magnetization as a function of temperature.

5.3.2 The molecular field B'

We assume that any spin experiences an effective magnetic field B_E, which is made up of an externally applied field B and a molecular field B' due to spin-spin interactions.

This is the mean-field approximation.

That is, identifying the 'magnetic energy' as

$$H = -\mu B_E, \tag{5.7}$$

the effective field is given by

$$B_E = B + B'. \tag{5.8}$$

At thermal equilibrium the probability of any value of the magnetic moment is given by equations (2.33) and (2.34), suitably adapted to the magnetic case, thus;

$$P(\mu) = e^{\mu B_E/kT} / \sum_{states} e^{\mu B_E/kT}. \tag{5.9}$$

Hence the mean value of the individual magnetic moments is

$$\bar{\mu} = \sum_{states} \mu e^{\mu B_E/kT} / \sum_{states} e^{\mu B_E/kT}. \tag{5.10}$$

The possible states of the individual magnetic moments are given by $\mu = \pm\mu_0$, hence the expression for the mean magnetization becomes

$$\bar{\mu} = \frac{\mu_0 e^{\mu_0 B_E/kT} - \mu_0 e^{-\mu_0 B_E/kT}}{e^{\mu_0 B_E/kT} + e^{-\mu_0 B_E/kT}}, \tag{5.11}$$

and so

$$\bar{\mu} = \mu_0 \tanh\left[\frac{\mu_0}{kT}(B + B')\right]. \tag{5.12}$$

Or, in terms of the total magnetisation of the specimen, we may write this as

$$M = N\bar{\mu} = N\mu_0 \tanh\left[\frac{\mu_0}{kT}(B + B')\right]. \tag{5.13}$$

But $N\mu_0 = M_\infty$ is the saturation value and hence we have

$$M = M_\infty \tanh\left[\frac{\mu_0}{kT}(B + B')\right], \tag{5.14}$$

which gives the magnetisation at any temperature T as a fraction of the saturation magnetisation, in terms of the applied field B and the unknown molecular field B'. This means, of course, that we only have one equation for two unknowns, M and B'.

5.3.3   The self-consistent assumption: $B' \propto M$

We are interested in the case where there is permanent magnetization which can be detected even when the external field B has been set to zero. Under these circumstances, the molecular field and the magnetization must be related to each other in some way. The self-consistent step which can close equation (5.14) is to assume that B' is a function of M, and the simplest such assumption is $B' \propto M$. This is such an important step that we highlight it as:

self-consistent assumption: $B' \propto M$.

We can identify the constant of proportionality in such a relationship as follows. For any one spin at a lattice site,

- Let z be the number of neighbouring spins;

- Let z_+ be the number of neighbouring spins up;

- Let z_- be the number of neighbouring spins down.

Hence we may write

$$\frac{z_+ - z_-}{z} = \frac{M}{M_\infty},$$

and so

$$z_+ - z_- = z\frac{M}{M_\infty}. \tag{5.15}$$

On this picture the average energy of interaction of one spin with its neighbours is

$$\Delta E = \pm \mu_0 B'$$

and, from a microscopic point of view, we can express this in terms of the quantum-mechanical exchange interaction as

$$\Delta E = J(z_+ - z_-).$$

where J is sometimes called the **exchange coupling constant** and has the dimension of an energy. Equating these two expressions gives us

$$\mu_0 B' = J(z_+ - z_-). \tag{5.16}$$

From this result, and using equation (5.15) for $(z_+ - z_-)$, we obtain an expression for the molecular field as

$$B' = \frac{J}{\mu_0}(z_+ - z_-) = \frac{J}{\mu_0}z\frac{M}{M_\infty}. \tag{5.17}$$
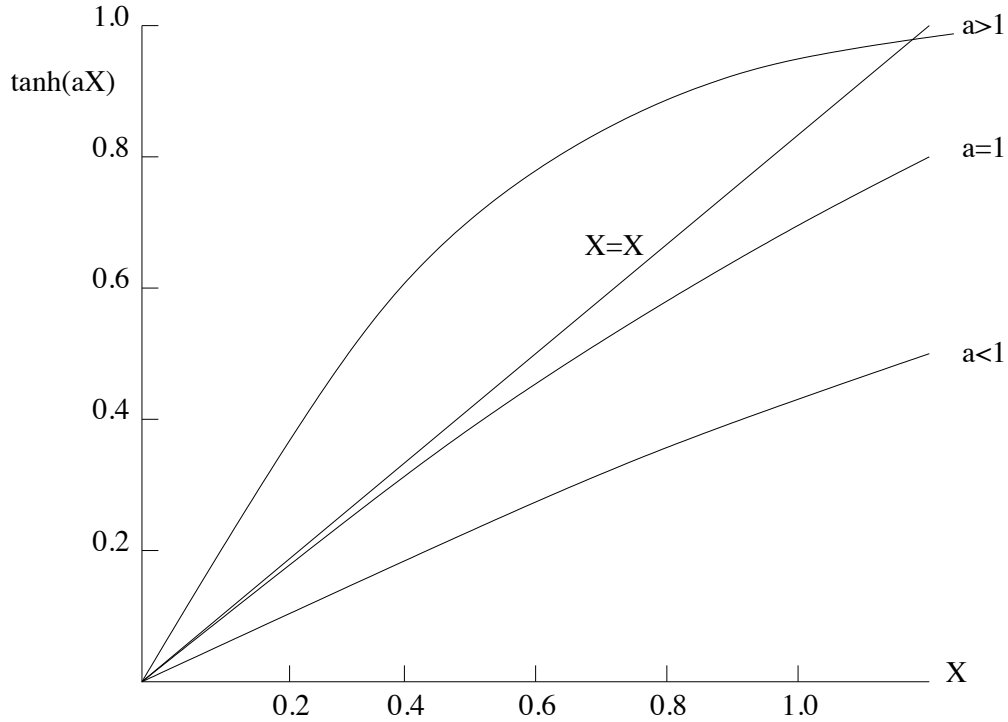
Figure 5.2: Graphical solutions of equation (5.19). Note that here $a = T_c/T$.

Lastly, we substitute for B' into equation for M:

$$\frac{M}{M_\infty} = \tanh\left[\frac{\mu_0}{kT}\left(B + \frac{Jz}{\mu_0}\cdot\frac{M}{M_\infty}\right)\right],\tag{5.18}$$

and obtain a closed equation for the magnetisation of the system. For spontaneous magnetization, we have $B = 0$, and so

$$\frac{M}{M_\infty} = \tanh\left[\frac{Jz}{kT}\cdot\frac{M}{M_\infty}\right].\tag{5.19}$$

We may solve this for the critical temperature for spontaneous magnetization. We note that the result depends on the coupling strength J and the number of nearest neighbours (in other words, the lattice type) but not on μ_0. The simplest method is graphical. The spontaneous magnetisation is given by plotting the graph of

$$X = \tanh\left(\frac{zJ}{kT}X\right)\tag{5.20}$$

and looking for the intersection with the straight line

$$X = M_s/M_\infty,$$

where M_s is the spontaneous magnetisation.

5.3.4 Graphical solution for the critical temperature T_c

Let us anticipate the fact that equation (5.19) can be solved for the critical temperature T_c and rewrite it as:

$$X = \tanh\left(\frac{T_c}{T}X\right)\tag{5.21}$$

where

$$T_c = \frac{zJ}{k}. \tag{5.22}$$

We note that in general T_c depends on the lattice type (simple cubic, body-centered cubic etc.,) through the parameter z, the strength of the interaction J and the Boltzmann constant k.

Now, for the case $T = T_c$, equation (5.16) reduces to

$$X = \tanh X,$$

and for small values of X, this becomes

$$X = X$$

and the only possible solution is $X = 0$, corresponding to there being no mean magnetization. In general this is true for $T_c/T \leq 1$ and the only possibility of an intersection at non-zero X is for $T_c/T > 1$, as shown in Figure 5.2. We can summarize the situation as follows:

- $T > T_c$ $X = 0$, $M = 0$: disordered phase;

- $T < T_c$ $X \neq 0$, $M \neq 0$: ordered phase.

As the transition from a disordered to an ordered phase is from a more symmetric to a less symmetric state, such transitions are often referred to as **symmetry-breaking**.

5.4 Macroscopic mean field theory: the Landau model for phase transitions

As a preliminary to the Landau model, we introduce the theoretical aims: we wish to calculate the **critical exponents** of the system.

5.4.1 The theoretical objective: critical exponents

We have met the concept of critical exponents in Section 5.1. Here we shall introduce four critical exponents, viz., those associated respectively with the heat capacity C_B, the magnetization M, the susceptibility χ and the equation of state, which is the relationship between the applied field B and the magnetization. The defining relationships, which are no more than an arbitrary way of correlating experimental data, may be listed as follows:

$$C_B \sim \left| \frac{T - T_c}{T_c} \right|^{-\alpha} ; \tag{5.23}$$

$$M \sim - \left(\frac{T - T_c}{T_c} \right)^{\beta} ; \tag{5.24}$$

$$\chi_T \sim \left| \frac{T - T_c}{T_c} \right|^{-\gamma} ; \tag{5.25}$$

and

$$B \sim |M|^{\delta} \,\mathrm{sgn} M, \tag{5.26}$$

where sgn is the signum, or sign, function. These relationships define the exponents α, β, γ and δ.
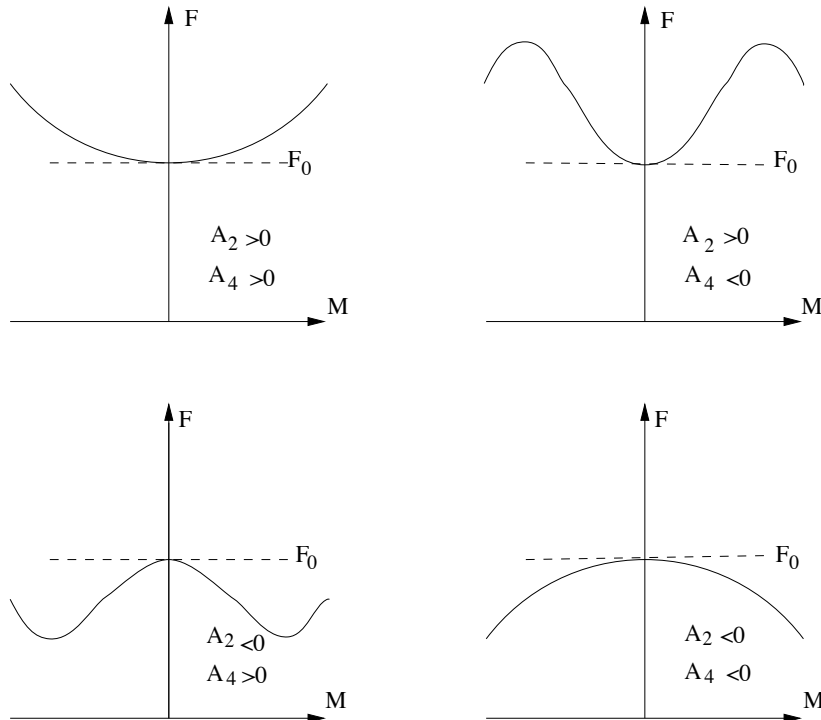
Figure 5.3: Possible variations of the free energy F with the magnetization M.

5.4.2 Approximation for the free energy F

This theory is restricted to symmetry-breaking transitions, where the free energy F and its first derivatives vary continuously through the phase transition. We shall consider a ferromagnet in zero external field as an example. Let us assume that F is analytic in $\mathbf{M}$ near the transition point, so that we may expand the free energy in powers of the magnetization, as follows:

$$F(T, \mathbf{M}) = F_0(T) + A_2(T)M^2 + A_4(T)M^4 + \ldots \tag{5.27}$$

We note that only even terms occur in the expansion, as F is a scalar and can only depend on scalar products of $\mathbf{M}$. Referring to Figure 5.3, we see that in broad qualitative terms, there are only four possible 'shapes' for the variation of F with M, depending on the signs of the coefficients $A_2(T)$ and $A_4(T)$.

We may reject two of these cases immediately on purely physical grounds. That is, both cases with $A_4 < 0$ show decreasing F with increasing M. This is unstable behaviour, thus, for *global stability*, we have the requirement:
$$A_4 > 0.$$

Refer now to the two left hand graphs, where in both cases we have $A_4 > 0$. We shall consider the two cases separately:

Case 1. $A_2 > 0$: Here F has a minimum F_0 at $M = 0$. There is no permanent magnetization, so this can be interpreted as the paramagnetic phase, hence we may assume that this case corresponds to $T > T_c$.

Case 2. $A_2 < 0$: Here F has a maximum at $M = 0$, but two minima at $\pm M$, corresponding to permanent magnetization in one or other direction. Therefore we may interpret this as being the ferromagnetic phase and assume that this case corresponds to $T < T_c$.

Thus we conclude that $T = T_c$ corresponds to $A_2 = 0$.

Now let us reconsider these two cases from a mathematical point of view. The conditions for F to be minimised are:
$$\left.\frac{\partial F}{\partial M}\right)_T = 0; \qquad \partial^2 F/\partial M^2)_T > 0.$$

Accordingly, we differentiate the expression for F, as given by (5.27) to obtain:
$$\left.\frac{\partial F}{\partial M}\right)_T = 2A_2(T)M + 4A_4(T)M^3, \tag{5.28}$$

and re-examine our two cases:

Case 1. Here we have $A_2 > 0$, $T > T_c$ and clearly,
$$\left.\frac{\partial F}{\partial M}\right)_T = 0, \text{ if and only if, } M = 0,$$

as M and M^3 have the same sign, and A_2 and A_4 are both positive, therefore no cancellations are possible.

Case 2. Here we have $A_2 < 0$, $T < T_c$ and it follows that
$$\partial F/\partial M)_T = 0;$$

if
$$-2A_2\mathbf{M} + 4A_4M^2\mathbf{M} = 0,$$

or
$$\mathbf{M} = \pm(-A_2/2A_4)^{1/2}\widehat{\mathbf{M}},$$

where $\widehat{\mathbf{M}}$ is a unit vector in the direction of $\mathbf{M}$. The change of sign of A_2 at $T = T_c$, implies that an expansion of the coefficient $A_2(T)$ in powers of the temperature should take the form
$$A_2(T) = A_{20}(T - T_c) + \text{higher order terms.} \tag{5.29}$$

We may summarise all this as follows:

For $T \geq T_c$:
$$F(T, M) = F_0(T),$$
and this corresponds to $M = 0$ which is the paramagnetic phase.

For $T \leq T_c$:

$$F(T, M) = F_0(T) + A_2(T)M^2 + \ldots,$$

and this corresponds to

$$M^2 = -A_2/2A_4,$$

with

$$A_2 = A_{20}(T - T_c).$$

Evidently this is the ferromagnetic phase.

Equation (5.27) for the free energy may now be written as

$$F(T, M) = F_0(T) - (A_{20}^2/2A_4)(T - T_c)^2 + \ldots \tag{5.30}$$

Note that the equation of state may be obtained from this result by using the relationship $B = -\partial F/\partial M)_T$.

5.4.3 Values of critical exponents

Equilibrium magnetization corresponds to minimum free energy. From equations (5.29) and (5.30):

$$\begin{aligned}
\frac{dF}{dM} &= 2A_2M + 4A_4M^3 = 0 \\
&= 2A_{20}(T - T_c)M + 4A_4M^3,
\end{aligned}$$

and so

$$M = 0 \text{ or } M^2 \sim (T - T_c).$$

Hence

$$M \sim (T - T_c)^{1/2} \sim \theta_c^{1/2},$$

and from (5.24) we identify the exponent β as:

$$\beta = 1/2.$$

To obtain γ and δ, we add a magnetic term due to an external field B; thus:

$$F = F_0 + A_{20}(T - T_c)M^2 + A_4M^4 - BM,$$

and hence

$$\frac{dF}{dM} = -B + 2A_{20}(T - T_c)M + 4A_4M^3 = 0.$$

For the critical isotherm, $T = T_c$ and so $B \sim M^3$; or:

$$\delta = 3.$$

Lastly, as

$$\chi = \left.\frac{\partial M}{\partial B}\right)_T,$$

we differentiate both sides of the equation for equilibrium magnetization with respect to B:

$$1 = 2A_{20}(T - T_c)\left.\frac{\partial M}{\partial B}\right)_T + 12A_4M^2 \left.\frac{\partial M}{\partial B}\right)_T,$$

and so,

$$\chi = \left(2A_2T_c\theta_c + 12A_4M^2\right)^{-1} = 1,$$

and from (5.25):

$$\gamma = 1.$$

These values may be compared with the experimental values: $\beta = 0.3 - 0.4, \delta = 4 - 5,$ and $\gamma = 1.2 - 1.4$.

5.5 Theoretical models

We have previously introduced the idea of models for magnetic systems in an informal way. Now we introduce the idea more formally. This includes the use of the term 'Hamiltonian', although we shall still mean by this the energy. Remember that for quantum systems, the Hamiltonian is an operator and the energy is its eigenvalue.

We begin by noting that the microscopic behaviour of assemblies can often be regarded as 'classical' rather than 'quantum mechanical' for the following reasons:

- Thermal fluctuations are often much larger than quantum fluctuations.

- Classical uncertainty in the large-N limit overpowers the quantum uncertainty.

- The complexity of the micro-structure of the assembly introduces its own uncertainty.

We can set up theoretical models which should be:

(a) physically representative of the system to some reasonable degree of approximation;

(b) soluble.

But, usually (b) is incompatible with (a) and attempting to reconcile the two usually involves some form of perturbation theory. In practice, one sacrifices some degree of physical 'correctness' in order to be able to solve the model. Invariably, by 'solve', we mean that we can obtain a good approximation to the partition function.

5.6 The Ising model

This is the most widely studied model in statistical field theory, including both the theory of critical phemomena and particle theory. So naturally it is the one which we shall concentrate on here. The Hamiltonian can be written for the generic Ising model as

$$H = -\sum_{\langle i,j \rangle} J_{ij} S_i S_j - \sum_i B_i S_i, \tag{5.31}$$

$$\text{such that} \quad S_i = \pm 1,$$

where the restriction to nearest-neighbour pairs of spins in the double sum is indicated by the use of angle brackets to enclose the indices i and j. As we shall see later, there are other ways in which this restriction can be indicated.

The Ising model is really a family of models, the individual members being determined by our choice of the dimensionality d. We begin by summarising a few features of the model for each value of d.

- $d = 1$ In this case we envisage a line of spins each either up or down. It presents a very simple problem and can be solved exactly. But, although its solution is of considerable pedagogical importance, the model does not exhibit a phase change[2].

- $d = 2$ In two dimensions, the Ising model can be thought of as an array of spins on a square lattice, with each lattice site having an associated spin vector up or down at right angles to the plane of the array. This model is more realistic in that a phase transition appears in the thermodynamic limit. It was solved exactly by Onsager (1944) and this work is still regarded as a theoretical *tour de force.*

- $d \geq 3$ These cases are more difficult to draw but at least the three-dimensional problem is easily visualized. One simply imagines a cubic lattice with the three main coordinate directions corresponding to the cartesian coordinate axes x, y, and z. Then we assume that unit spin vectors at each lattice site can point in the directions of $\pm z$. The Ising models for $d \geq 3$ cannot be solved exactly but they can be treated numerically, and numerical simulation of Ising models is a very active area of statistical physics. It turns out that mean-field theory gives a reasonable approximation to the partition function for $d = 3$ and a very good approximation for $d \geq 4$.

5.7 Mean-field theory with a variational principle

This is a more modern version of the Weiss theory and has the advantage that it can be used to work out correlations, although we shall not do that in the present book.

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[2]It is sometimes said that there is a phase change at $T = 0$, but in any model the spins will be aligned at zero temperature, so arguably this is a rather trivial example of a phase transition.

$$H = \sum_{i=1}^N H_i + \sum_{i,j} H_{i,j}. \tag{5.32}$$

Let us *choose* a model Hamiltonian of the form

$$H(\lambda) = H_0 + \lambda H_I, \tag{5.33}$$

---

such that

$$0 \leq \lambda \leq 1,$$

where H is exact, H_0 is soluble, H_I is the correction term and λ is a variable control parameter. The **Bogoliubov theorem** can be stated in terms of the Helmholtz free energy F as:

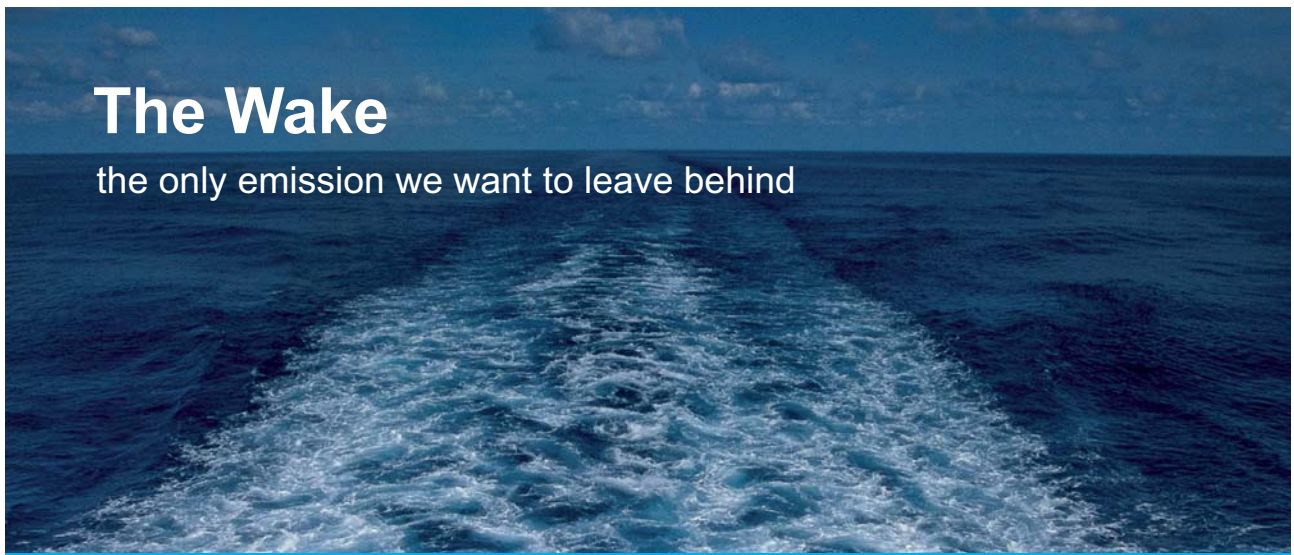$$F \leq F_0 + \langle H_I \rangle_0, \tag{5.34}$$

where F_0 is the free energy of the soluble system with Hamiltonian H_0, and the ground-state expectation value of the correction term is given by

$$\langle H_I \rangle_0 = \frac{tr \ H_I e^{-\beta H_0}}{tr \ e^{-\beta H_0}}. \tag{5.35}$$

(Note those unfamiliar with the 'density matrix' notation, may just interpret 'tr' as standing for 'sum over levels'.)

This procedure may be interpreted as follows:

1. We are evaluating our estimate of the exact free energy F using the full Hamiltonian $H = H_0 + \lambda H_I$, but only the ground-state (i.e. non-interacting) probability distribution associated with the soluble model Hamiltonian H_0.

2. Then equation (5.35) gives us a rigorous upper bound on our *estimate* of the free energy corresponding to the exact Hamiltonian.

Our strategy now involves the following steps:

- Choose a trial Hamiltonian H_0 which is soluble.

- Use our freedom to vary the control parameter λ in order to minimise the quantity on the right hand side of the Bogoliubov inequality, as given in (5.35).

Then, in this way, we obtain our best estimate of the exact free energy F for a given choice of soluble model Hamiltonian H_0.

5.7.2 Mean-field theory of the Ising model

We consider the Ising model with external magnetic field B. The Hamiltonian may be written in the slightly different form:

$$H = -\sum_{i,j} J_{ij} S_i S_j - B \sum_j S_j, \tag{5.36}$$

where

- $J_{ij} = J$ if i, j are nearest neighbours

- $J_{ij} = 0$ if i, j are NOT nearest neighbours.

Note that this is yet another way of specifying the sum over nearest-neighbour pairs of spins!

In order to reduce the Hamiltonian to a diagonal form, we choose the unperturbed model for H to be

$$H_0 = -\sum_j B' S_j - B \sum_j S_j, \tag{5.37}$$

where B' is the 'collective field' representing the effect of all the other spins with labels $i \neq j$ on the spin at the lattice site j. Sometimes it is convenient to lump the two magnetic fields together as an 'effective field' B_E, viz.,

$$B_E = B' + B. \tag{5.38}$$

Now we can work out our upper bound for the system free energy F, using the statistics of the model system. First we obtain the partition function Z_0 for the ground-state case, thus:

$$Z_0 = tre^{-\beta H_0} = [e^{\beta B_E} + e^{-\beta B_E}]^N, \tag{5.39}$$

where we have summed over the two spin states of $S = \pm 1$. This may be further written as

$$Z_0 = [2\cosh(\beta B_E)]^N. \tag{5.40}$$

The free energy F_0 follows immediately from the bridge equation, as

$$F_0 = -\frac{N}{\beta} \ln[2\cosh(\beta B_E)]. \tag{5.41}$$

Now from (5.35) the Bogoliubov inequality may be written in the form

$$F \leq F_0 + \langle H_I \rangle_0 \ \leq F_0 + \langle H - H_0 \rangle_0, \tag{5.42}$$

where we have simply re-expressed the correction term as the difference between the exact and model system Hamiltonians. Then, in terms of equation (5.37) we may further rewrite this condition on the free energy as:

$$F \leq F_0 - \sum_{i,j} J_{ij} \langle S_i S_j \rangle_0 + B' \sum_j \langle S_j \rangle_0. \tag{5.43}$$

We now work out averages over the *model* assembly, thus:

$$\sum_j \langle S_j \rangle_0 = N \langle S \rangle_0, \tag{5.44}$$

and

$$\sum_{ij} J_{ij} \langle S_i S_j \rangle_0 = \sum_{ij} J_{ij} \langle S_i \rangle_0 \langle S_j \rangle_0 = \frac{JNz}{2} \langle S \rangle_0^2, \tag{5.45}$$

where we have made use of the statistical independence of S_i and S_j, which is consistent with the statistics of the zero-order (non-interacting) model, and z is the number of nearest neighbours. Then, substituting these results into equation (5.43), we have

$$F \leq F_0 - \frac{N}{2} zJ \langle S \rangle_0^2 + B'N \langle S \rangle_0. \tag{5.46}$$

We already know F_0 from equation (5.41), while $\langle S \rangle_0$ is easily worked out as:

$$\langle S \rangle_0 = \frac{tr\ S \exp(-\beta H_0)}{tr\ \exp(-\beta H_0)} = \frac{tr\ S \exp(+\beta B_E S)}{tr\ \exp(\beta B_E S)}, \tag{5.47}$$

and the permissible spin states of the Ising model are $S = \pm 1$, hence:

$$\langle S \rangle_0 = \frac{\exp(\beta B_E) - \exp(-\beta B_E)}{\exp(\beta B_E) + \exp(-\beta B_E)} = \tanh(\beta B_E). \tag{5.48}$$

5.7.3   The variational method

Our next step is to differentiate F (as given by (5.46) with the equality) with respect to B' and set the result equal to zero. Noting that B' occurs as part of B_E, the condition for an extremum can be written as

$$\frac{\partial F}{\partial B_E} = 0, \tag{5.49}$$

which becomes

$$\frac{\partial F}{\partial B_E} = \frac{\partial F_0}{\partial B_E} - NzJ \langle S \rangle_0 \frac{\partial \langle S \rangle_0}{\partial B_E} + (B_E - B)N \frac{\partial \langle S \rangle_0}{\partial B_E} + N \langle S \rangle_0. \tag{5.50}$$

From equation (5.41) for F_0, we have:

$$\frac{\partial F_0}{\partial B_E} = -N \langle S \rangle_0, \tag{5.51}$$

which cancels the last term on the right hand side of equation (5.51), hence

$$\frac{\partial F}{\partial B_E} = (B_E - B)N \frac{\partial \langle S \rangle_0}{\partial B_E} - NzJ \langle S \rangle_0 \frac{\partial \langle S \rangle_0}{\partial B_E} = 0, \tag{5.52}$$

and so

$$(B_E - B) = zJ \langle S \rangle_0; \tag{5.53}$$

or, with some rearrangement,

$$B_E = B + zJ \langle S \rangle_0. \tag{5.54}$$

In this model, the magnetisation is just the mean value of the spin, thus:

$$\langle S \rangle_0 = \tanh(\beta B_E) = \tanh(\beta B + zJ \beta \langle S \rangle_0). \tag{5.55}$$

In order to identify a phase transition, we put $B = 0$, and (8.30) becomes

$$\langle S \rangle_0 = \tanh(zJ \beta \langle S \rangle_0), \tag{5.56}$$

which is the same as our previous mean-field result as given by equation (5.14), with the replacement of M/M_∞ by $\langle S \rangle_0$. We have therefore shown that the optimum value of the free energy with an F_0 corresponding to independent spins is exactly that of mean-field theory.

5.8 Mean-field critical exponents for the Ising model

The exponents for the thermodynamic quantities can be obtained quite easily from our present results. However, to get the exponents associated with the correlation function η and the correlation length ν we need to obtain expressions for these quantities. We begin with the easier ones!

5.8.1 α, β, γ and δ

<div align="center">

CASE 1: α

</div>

For $B = 0$, we have $H = -J \sum_{\langle i,j \rangle} S_i S_j$ where $\sum_{\langle i,j \rangle}$ is the sum over nearest neighbours. The mean energy of the system is given by

$$\overline{E} = \langle H \rangle = -J \sum_{\langle i,j \rangle} \langle S_i S_j \rangle.$$

In lowest-order mean field approximation, the spins are independent and so we may factorize as:

$$\langle S_i S_j \rangle = \langle S_i \rangle \langle S_j \rangle.$$

Hence

$$\overline{E} = -J \sum_{\langle i,j \rangle} \langle S_i \rangle \langle S_j \rangle = -Jz\frac{N}{2}M^2,$$

where $M = \langle S \rangle \equiv$ order parameter. From the thermodynamic definition of the heat capacity, C_B at constant magnetic field, we have

$$C_B = \left. \frac{\partial \overline{E}}{\partial T} \right)_B = -2Jz\frac{N}{2}M\frac{dM}{dT} = -JzNM\frac{dM}{dT}.$$

Now, for:

$T > T_c :\qquad M = 0 \quad$ therefore $\quad C_B = 0;$

$T \leq T_c :\qquad M = (-3\theta_c)^{1/2}.$

Thus

$$\frac{\partial M}{\partial T} = \frac{1}{2}\left(-3\theta_c\right)^{-1/2} \times -\frac{d\theta_c}{dT} = \frac{-3}{2}M^{-1}\frac{d\theta_c}{dt} = \frac{-3}{2}M^{-1}T_c^{-1},$$

and so

$$\left. \frac{\partial \overline{E}}{\partial T} \right)_B = \frac{3}{2}JzNMM^{-1}T_c^{-1} = \frac{3}{2}\frac{JzN}{c}, \text{from equation (5.17).}$$

$$= \frac{3}{2}Nk \quad \text{as} \quad Jz = kT_c.$$

Hence C_B is discontinuous at $T = T_c$ and so $\alpha = 0$.

CASE 2: β

The mean magnetization $M = \langle S \rangle_0$, and from mean field theory:

$$\langle S \rangle_0 = \tanh(\beta B + 2zJ\beta\langle S \rangle_0).$$

Hence we can write:

$$M = \tanh(\beta zJM + b) \text{ where } b \equiv \beta B.$$

Now mean field theory gives $z\beta_c J = 1$ or $zJ = 1/\beta_c$, thus it follows that

$$M = \tanh\left[\frac{\beta M}{\beta_c} + b\right] = \tanh\left[M\frac{T_c}{T} + b\right] = \tanh\left[\frac{M}{(1+\theta_c)} + b\right].$$

Set $B = 0$ and expand for $T \sim T_c$, in which case θ_c is small:

$$M = \frac{M}{1+\theta_c} - \frac{1}{3}\frac{M^3}{(1+\theta_c)^3},$$

and re-arranging:

$$M\left(1 - \frac{1}{1+\theta_c}\right) = -\frac{1}{3}\frac{M^3}{(1+\theta_c)^3},$$

hence, either:

$$M = 0$$

or

$$M^2 = -3\theta_c\frac{(1+\theta_c)^3}{(1+\theta_c)} = -3\theta_c(1+\theta_c)^2.$$

Taking the nontrivial case,

$$M \sim |-3\theta_c|^{1/2},$$

and by comparison with the equation which defines the critical exponent:

$$\beta = 1/2.$$

CASE 3: γ and δ

From the definition of the isothermal susceptibility χ_T, we have:

$$\chi_T = \frac{\partial M}{\partial B} = \beta \frac{\partial M}{\partial b},$$

and also

$$M = \tanh\left(\frac{M}{1 + \theta_c} + b\right) \simeq \frac{M}{1 + \theta_c} + b \quad \text{for} \quad T > T_c.$$

Now, with some re-arrangement,

$$M - \frac{M}{1 + \theta_c} = b,$$

to this order of approximation and, re-arranging further, we have:

$$M = \left(\frac{1 + \theta_c}{\theta_c}\right) b.$$

Hence

$$\chi_T \sim \frac{\partial M}{\partial b} \sim \frac{1}{\theta_c} \quad \text{as} \quad \theta_c \to 0$$

and so

$$\chi_T \sim \theta_c^{-1}, \qquad \gamma = -1,$$

which follows from the definition of γ. Next, consider the effect of an externally imposed field at $T = T_c$, where $\theta_c = 0$, and so $1 + \theta_c = 1$. We use the identity:

$$M = \tanh(M + b) = (\tanh M + \tanh b)(1 + \tanh M \tanh b),$$

which leads to

$$M \simeq \left(M - \frac{M^3}{3} + b - \frac{b^3}{3}\right)(1 + \tanh M \tanh b).$$

Cancel the factor of M on both sides and rearrange, to obtain:

$$b \sim \frac{M^3}{3} + \frac{b^3}{3} - \left(M - \frac{M^3}{3} + b - \frac{b^3}{3}\right)\left(Mb - \frac{Mb^3}{3} - \frac{Mb^3}{3} + \ldots\right).$$

Therefore $b \sim M^3/b$ for small b, M and by comparison with the defining relation, $\delta = 3$.

If we set $b \sim M^3$ on the right hand side, we can verify all terms of order higher than $\mathcal{O}(M^3)$ are neglected.

Part III

The arrow of time

Chapter 6

Classical treatment of the Hamiltonian N-body assembly

In this section we discuss the behaviour of the assembly as a function of time. To do this, we formulate the microscopic description of an assembly in a way that is completely rigorous and fundamental yet which leads to some surprising results which do not appear to accord with everyday experience. Although we should note that our theory here is fundamental only insofar as that property is compatible with a classical description, we should emphasise two points. First, we shall as usual maintain contact with the quantum description, which should ensure that we do not do anything which is actually wrong. Second, the paradoxes which will arise do not depend on a quantum description for their resolution.

We may foreshadow the later paradoxical behaviour of the theoretical predictions by first discussing a simple, qualitative version of the reversibility paradox. Let us consider a box with an internal partition which divides it into two equal volumes, one of which contains a gas at (say) STP, and the other which is empty. The situation is illustrated in Fig. 6.1. Let us now imagine that the partition is broken in such a way that the gas can escape to the empty half of the box. Obviously this is just what will happen and the process will stop when the amount of gas in each half of the box is the same.

Yet when we try to describe this process at the macroscopic level, we run into a difficulty. The motion of each particle is governed by Newton's laws and these are reversible in time. If we know the *state* of any one particle at any time t_0 (say), then we know its past history $t < t_0$ and its future behaviour $t > t_0$ for all time. This is the **deterministic picture**. We can equally well run the clock backwards and the description of the particle motion will still be valid. Thus on a microscopic level, there would appear to be no reason to predict that a system would evolve irreversibly from a non-equilibrium state to an equilibrium one. Indeed, as we shall see, at this level of description it may not be possible to even say what we mean by an equilibrium state.

In the classical description, by 'state of a particle' we mean its instantaneous position and velocity. The quantum description is, in this context, more difficult to envisage, because we have to think of the individual particles as undergoing transitions from one quantum state to another. These quantum states are the relevant solutions of the Schroedinger equation and this equation (which is equivalent to a statement of conservation of energy) is, like Newton's laws, reversible in time. Thus, irrespective of whether we adopt a classical or a quantum description, at the microscopic level it is not immediately obvious why a system will evolve in one direction rather than another. This is the fundamental problem of statistical physics: what determines the direction of **time's arrow**? We shall consider this aspect further as we develop the theory in this chapter.

6.1   Hamilton's equations and phase space

The treatment of this chapter will be based on Hamilton's equations. It is assumed that the reader has met both the Lagrangian and Hamiltonian formulations of classical mechanics and so only the briefest of introductions will be given here.
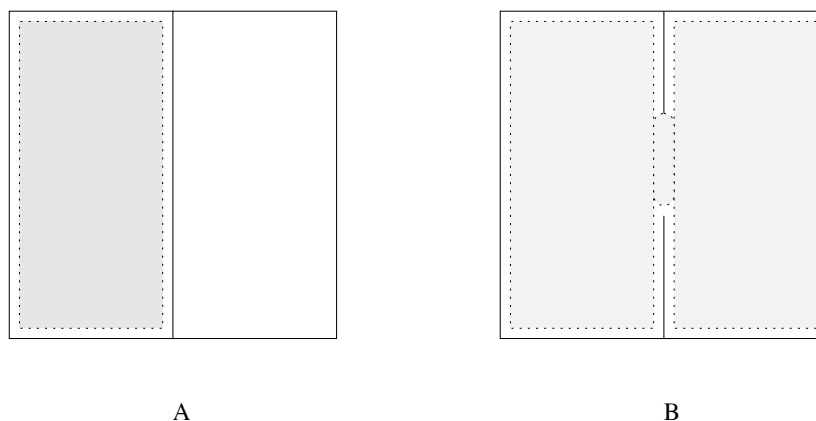
Figure 6.1: Illustration of the reversibility paradox.

From our present point of view, we note that we can recast Newton's laws of motion in the form of Hamilton's equations. If we specify the state of the ith particle in the assembly by its generalised position coordinate $\mathbf{q}_i$ and its conjugate momentum $\mathbf{p}_i$, then we have six scalar coordinates to describe each particle state and Hamilton's equations of motion take the form:

$$\dot{\mathbf{q}}_i = \frac{\partial H}{\partial \mathbf{p}_i}, \tag{6.1}$$

$$\dot{\mathbf{p}}_i = -\frac{\partial H}{\partial \mathbf{q}_i}. \tag{6.2}$$

Formally, one obtains the Hamiltonian from the Lagrangian; but, provided any constraints on the system are independent of time and that any potentials do not depend on velocities, the Hamiltonian is just the total energy. That is,

$$H = T + U,$$

where T is the kinetic energy of the system and U is its potential energy. This will be the case for the simple system consisting of N point masses in a box with rigid impermeable walls, which we consider here.

In this formalism, the evolution of the particle 'state' with time can be represented by a **trajectory** in **phase space**. This terminology was first coined in statistical mechanics by Gibbs, but it is perhaps most easily understood in the context of oscillatory motion where the term 'phase' is normally first encountered.

As an example, let us consider a simple pendulum, which is a realization of simple harmonic motion in one dimension. In Fig. 6.2, we show the phase space trajectory corresponding to the simple pendulum. We note that in this representation the oscillatory motion of the pendulum in real space is translated into an elliptical orbit in phase space. The 'state' of the pendulum at any time corresponds to the value of the phase as plotted on the diagram.

In the case of the ideal simple pendulum, the motion is undamped and the phase space trajectory (or locus of points) corresponds to constant total energy. In general, for higher dimensional problems, we talk about a constant energy surface in phase space. However, if we consider the motion of a damped pendulum, the amplitude decays with time and ultimately the pendulum comes to rest with its bob at the point of equilibrium. In this case the phase space trajectory is no longer a closed orbit but instead spirals into the origin where the bob is ultimately at rest. This sort of behaviour is illustrated in Fig. 6.3.
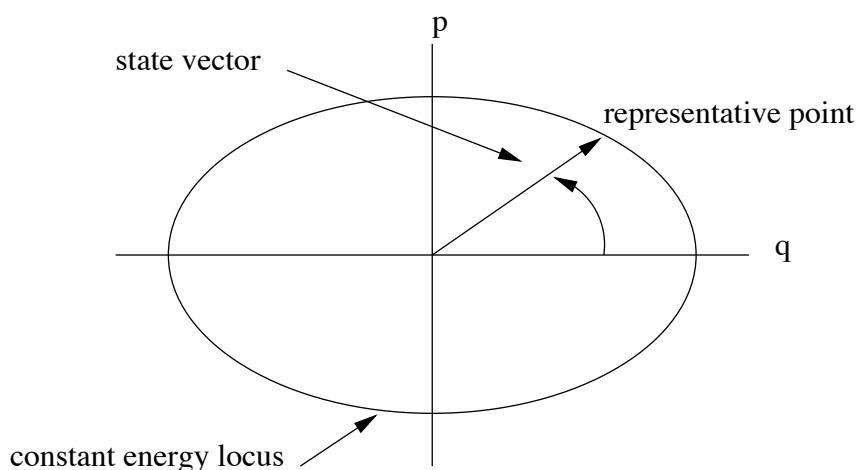
Figure 6.2: Phase space representation of the motion of a simple pendulum.

constant energy locus
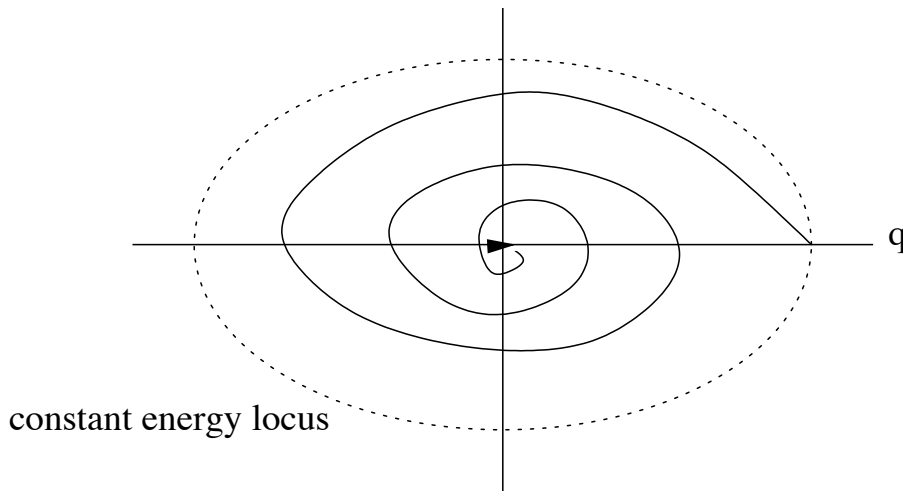
Figure 6.3: Phase space trajectory of the motion of a damped pendulum.

6.2 Hamilton's equations and $6N$-dimensional phase space

The use of Hamilton's formalism is a natural one for problems where the energy is conserved. However, we have another motivation. If we set up our classical treatment using Hamilton's equations then it facilitates the transfer to a quantum mechanical formulation.

In order to see this, we extend the present formalism by introducing the Poisson bracket (PB) notation. If F and G are arbitrary functions of the set of coordinates $\{\mathbf{q}, \mathbf{p}\}$, then their PB is defined by:

$$[F, G] = \sum_i \left(\frac{\partial F}{\partial \mathbf{q}_i} \frac{\partial G}{\partial \mathbf{p}_i} - \frac{\partial F}{\partial \mathbf{p}_i} \frac{\partial G}{\partial \mathbf{q}_i} \right). \tag{6.3}$$

The usefulness of this lies in way in which it allows us to make the transition to the quantum mechanical formalism:

$$[F, G]_{PB} \rightarrow [F, G]_{\text{commutator}},$$

along with multiplicative factors involving Planck's constant and $i = \sqrt{-1}$.

Let us now choose $F = q_i$ and $G = H$; and then $F = p_i$ and $G = H$. It immediately follows that Hamilton's equations can be written as

$$[\mathbf{q}_i, H] = \frac{\partial H}{\partial \mathbf{p}_i} = \dot{\mathbf{q}}_i, \tag{6.4}$$

$$[\mathbf{p}_i, H] = -\frac{\partial H}{\partial \mathbf{q}_i} = \dot{\mathbf{p}}_i. \tag{6.5}$$

In general, it can be shown that the time derivative of any arbitrary function $u \equiv u(\mathbf{q}, \mathbf{p}, t)$ is given by:

$$\frac{du}{dt} = \frac{\partial u}{\partial t} + [u, H], \tag{6.6}$$

and this is a result which will be useful later on.

Let us now consider a closed classical assembly with $3N$ degrees of freedom. It is quite simple to extend this to larger numbers of degrees of freedom such as might arise with molecules which can vibrate or rotate; but we shall not pursue such complications here. It follows that the state of an assembly is specified by $6N$ real, scalar variables q, p, such that (in a contracted notation):

$$\mathbf{q} \equiv \mathbf{q}_1, \mathbf{q}_2, ..., \mathbf{q}_N \tag{6.7}$$

and
$$\mathbf{p} \equiv \mathbf{p}_1, \mathbf{p}_2, ..., \mathbf{p}_N. \tag{6.8}$$

It is also helpful to introduce an even more contracted notation in the form of the state vector $\mathbf{X}$, such that:
$$\mathbf{X} \equiv \{\mathbf{q}, \mathbf{p}\}, \tag{6.9}$$

and $\mathbf{X}$ specifies the complete state of the assembly at time t. If we define the Hamiltonian for the assembly as $H(\mathbf{X}, t)$, then the variation of its state with time is governed by Hamilton's equations in the form:

$$\dot{\mathbf{q}} \equiv \frac{\partial \mathbf{q}}{\partial t} = \frac{\partial H(\mathbf{X}, t)}{\partial \mathbf{p}}, \tag{6.10}$$

$$\dot{\mathbf{p}} \equiv \frac{\partial \mathbf{p}}{\partial t} = -\frac{\partial H(\mathbf{X}, t)}{\partial \mathbf{q}}. \tag{6.11}$$

Now we introduce a $6N$ dimensional phase space, which is often referred to as $\boldsymbol{\Gamma}$ **space**, spanned by vectors $\{\mathbf{p}, \mathbf{q}\}$. Then the state vector $\mathbf{X}(\mathbf{q}, \mathbf{p})$ represents the state of the assembly as a point in Γ-space. As the assembly evolves with time, $\mathbf{X}$ traces out a trajectory in Γ space. At any instant, the ensemble is represented by a cloud of points in Γ space.

As time goes on, the ensemble is represented by a swarm of trajectories. Obviously, any region where the trajectories lie most densely, indicates the region of phase space where one is most likely to find an assembly state. This intuitive idea about probability can be expressed in terms of a **density distribution** $\rho(\mathbf{X}, t)$, which is defined by
$$dN = \rho(\mathbf{X}, t)d\mathbf{X}, \tag{6.12}$$

where

dN = the number of assemblies with state vector inside the interval $\mathbf{X}, \mathbf{X} + d\mathbf{X}$;

and

$d\mathbf{X}$ $\equiv$ $6N$-dimensional volume element.

It is conventional to assume that the number of assemblies in the ensemble is so large that ρ and dN can be regarded as continuous functions of $\mathbf{X}$ and t. In fact this number is somewhat arbitrary, but it is often convenient to choose the total number of assemblies to be N, the same as the number of particles in an assembly.

If we integrate the density distribution $\rho(\mathbf{X}, t)$ over the volume of Γ-space, then it follows that we obtain
$$N = \int_\Gamma \rho(\mathbf{X}, t)d\mathbf{X}, \tag{6.13}$$

$\equiv$ the total number of assemblies in the ensemble;

$\equiv$ the total number of representative points in Γ-space.

This allows us to define the normalized density distribution ρ_N as follows:

$$\rho_N(\mathbf{X}, t) = \frac{\rho(\mathbf{X}, t)}{N} \equiv \frac{\rho(\mathbf{X}, t)}{\int_\Gamma \rho(\mathbf{X}, t)d\mathbf{X}}, \tag{6.14}$$

where the normalized density distribution can be interpreted in words, as follows:

$\rho_N(\mathbf{X}, t) \equiv$ the probability that the state point of an assembly, chosen at random from the ensemble, will lie in a volume element between $\mathbf{X}$ and $\mathbf{X} + d\mathbf{X}$ at time t.

It follows from equations (6.13) and (6.14) that ρ_N is correctly normalized, thus:

$$\int_\Gamma \rho(\mathbf{X}, t) d\mathbf{X} = 1. \tag{6.15}$$

6.3 Liouville's theorem for N particles in a box

Liouville's theorem states that the density of points in the neighbourhood of some given point in phase space remains constant in time. Consider an elementary volume of Γ space dV, containing dN points. From equation (6.12) the density of points is:

$$\rho = \frac{dN}{dV}, \tag{6.16}$$

and Liouville's **theorem** may be restated as

$$\frac{d\rho}{dt} = 0, \tag{6.17}$$

which is often referred to as Liouville's **equation**.

We can prove this theorem in two parts by showing that dN and dV are separately independent of time.

A. Show that dN=constant.

Consider the motion of the elementary volume dV in phase space from t_0 to t. Each point within the volume corresponds to a dynamical system, evolving with time according to Hamilton's equations. Thus, as time goes on, the dynamical system representative points contained in dV move about in phase space and the shape of dV must change with time.

However the number of points dN cannot change with time. If any point were to cross the boundary then it would occupy at some time the same point in Γ space as one of the dynamical systems defining the boundary of dV. Since the subsequent motion of a dynamical system is uniquely determined by its location in Γ space at a given time, the two systems would thereafter travel together.

As a result, we come to the following conclusions:

- No system point can leave dV;

- No system point can join dV;

- No two distinct trajectories in Γ space can intersect.

B. Show that dV=constant.

Using our state vector notation, we may write

$$dV = \{d\mathbf{q}_1 d\mathbf{q}_2...d\mathbf{q}_N d\mathbf{p}_1 d\mathbf{p}_2...d\mathbf{p}_N\} \equiv d\mathbf{X}.$$

Now consider the change in the volume element with time $t_0 \to t$, thus:

$$d\mathbf{X}_t = J_N(t,t_0)d\mathbf{X}_{t_0}, \tag{6.18}$$

where $J_N(t,t_0)$ is the Jacobian of the transformation. That is, the determinant of the $6N \times 6N$ matrix, written symbolically as:

$$J_N(t,t_0) = \det \begin{vmatrix} \frac{\partial \mathbf{p}_t}{\partial \mathbf{p}_{t_0}} & \frac{\partial \mathbf{p}_t}{\partial \mathbf{q}_{t_0}} \\ \frac{\partial \mathbf{q}_t}{\partial \mathbf{p}_{t_0}} & \frac{\partial \mathbf{q}_t}{\partial \mathbf{q}_{t_0}} \end{vmatrix} \tag{6.19}$$

It is a standard mathematical result that the product of the determinants of two matrices is equal to the determinant of the product. Hence, the Jacobean has the transitive property

$$J_N(t,t_0) = J_N(t,t_1)J_N(t_1,t_0), \tag{6.20}$$

where $t \geq t_1 \geq t_0$. We take the time of evolution to be small and write $t - t_0 = \Delta t$. Then the coordinates of the state point at t can be related to the coordinates of the state point at t_0 by:

$$\mathbf{q}_t = \mathbf{q}_{t_0} + \dot{\mathbf{q}}_{t_0}\Delta t + O(\Delta t^2); \tag{6.21}$$

$$\mathbf{p}_t = \mathbf{p}_{t_0} + \dot{\mathbf{p}}_{t_0}\Delta t + O(\Delta t^2). \tag{6.22}$$

Next, substitute into (6.16) and multiply out:

$$J_N(t,t_0) = 1 + \left(\frac{\partial \dot{\mathbf{q}}_{t_0}}{\partial \mathbf{q}_{t_0}} + \frac{\partial \dot{\mathbf{p}}_{t_0}}{\partial \mathbf{p}_{t_0}}\right)\Delta t + O(\Delta t^2). \tag{6.23}$$

However, from Hamilton's equations (6.4) and (6.5) we have

$$\partial \dot{\mathbf{q}}_{t_0}/\partial \mathbf{q}_{t_0} + \partial \dot{\mathbf{p}}_{t_0}\partial \mathbf{p}_{t_0} = 0, \tag{6.24}$$

and so

$$J_N(t,t_0) = 1 + O(\Delta t^2). \tag{6.25}$$

Now, from (6.20) we have:

$$J_N(t,0) = J_N(t,t_0)J_N(t_0,0) = [1 + O(\Delta t^2)]J_N(t_0,0). \tag{6.26}$$

So, if we divide across by Δt and take the limit $\lim \Delta t \to 0$ we obtain

$$\frac{dJ_N}{dt} = \lim_{\Delta t \to 0} \frac{J_N(t_0 + \Delta t, 0) - J_N(t_0, 0)}{\Delta t} = 0, \tag{6.27}$$

and hence

$$J_N(t, 0) = J_N(0, 0) = 1. \tag{6.28}$$

So, in all, it follows from equation (6.18) that,

$$d\mathbf{X}_t = d\mathbf{X}_{t_0} \tag{6.29}$$

or equivalently, $dV = $ constant and equation (6.17) is proved.

6.4   Probability density as a fluid.

If we regard the points in phase space as making up a fluid, in some continuum limit, then we may identify the fluid velocity as $\dot{\mathbf{X}} = \{\dot{\mathbf{q}}, \dot{\mathbf{p}}\}$. That is, it is the velocity of a state point. We can rewrite equation (6.24) as

$$div\,\dot{\mathbf{X}} = 0 \tag{6.30}$$

so the probability density is in effect an *incompressible* fluid. It should be borne in mind that here 'div' is an operator in Γ space:

$$\nabla \equiv \left\{ \frac{\partial}{\partial \mathbf{q}_1}, \frac{\partial}{\partial \mathbf{q}_2} \cdots \frac{\partial}{\partial \mathbf{q}_N}; \frac{\partial}{\partial \mathbf{p}_1}, \frac{\partial}{\partial \mathbf{p}_2} \cdots \frac{\partial}{\partial \mathbf{p}_N} \right\}.$$

We shall work in terms of the normalised probability density ρ_N, which satisfies

$$\int_\Gamma \rho_N(\mathbf{X}, t) d\mathbf{X} = 1.$$

From equation (6.14) which defines this distribution, it follows that the probability of finding the state point in a finite region R of Γ space is given by

$$P(R) = \int_R \rho_N(\mathbf{X}, t) d\mathbf{X}. \tag{6.31}$$

It can be shown that, by considering the rate of change of probability in a fixed volume V_0 with surface area S_0 in Γ space, and using equation (6.30), that

$$\frac{\partial \rho_N}{\partial t} + \dot{\mathbf{X}}.\nabla \rho_N = 0. \tag{6.32}$$

In the language of fluid mechanics, $\dot{\mathbf{X}}.\nabla$ is a convective derivative in Γ space. Hence we may combine this with the partial derivative with respect to time to make up the usual total time derivative and rewrite the above equation as

$$\frac{d\rho_N}{dt} = 0, \tag{6.33}$$

in agreement with (6.17) which is Liouville's equation.

6.5   Liouville's equation: operator formalism.

We can re-express these results in terms of the Poisson Bracket formalism, as given in equations (6.3)-(6.5). If we invoke equation (6.6) to write (6.33) as:

$$\frac{d\rho_N}{dt} = \frac{\partial \rho_N}{\partial t} + [\rho_N, H] = 0, \tag{6.34}$$

then we can put this in terms of the **Liouvillian** L_N, which is defined by:

$$L_N\rho_N = -i[\rho_N, H],\qquad(6.35)$$

and (6.34) can be written as

$$\frac{i\partial\rho_N}{\partial t} = L_N\rho_N,\qquad(6.36)$$

with general solution:

$$\rho_N(\mathbf{X}, t) = e^{iL_N t}\rho_N(\mathbf{X}, 0).\qquad(6.37)$$

A probability density which is independent of time must satisfy the condition

$$L_N\rho_N(\mathbf{X}, 0) = 0,\qquad(6.38)$$

and in this case, $\rho_N(\mathbf{X}, 0)$ is called a stationary state of the Liouville equation.

Two general points should be noted:

- The formulation in terms of the Liouvillian is very general and can be used for ensembles where the Hamiltonian does not exist.

- L_N is Hermitian and has real eigenvalues. Thus the solution given by (6.37) will oscillate in time, rather than decay to a unique equilibrium state.

We may expand upon the latter point as follows. If we reverse the time in (6.37), we do not change the equation. L_N changes sign as $t \to -t$ and so the product $L_N t$ is time-reversal symmetric. It is an everyday observation that processes are often irreversible and decay with time to an equilibrium or stationary state. Yet Liouville's equation - although rigorous - cannot apparently predict irreversible processes. The resolution of this apparent contradiction poses one of the fundamental problems of statistical mechanics.

However, from ensemble theory, we actually know a great deal about the stationary states of Liouville's equation. For these cases, H does not depend explicitly on time and so is a constant of the motion:

$$H_N(\mathbf{X}) = E, \tag{6.39}$$

where E is the total energy of the assembly.

6.6 The generalised H-theorem (due to Gibbs).

We begin by introducing a 'coarse-grained' probability density $\overline{\rho}(\mathbf{X}, t)$, which we shall discuss presently, and use this to define the quantity

$$H = \int \overline{\rho}(\mathbf{X}, t) \ln \overline{\rho}(\mathbf{X}, t) d\mathbf{X}. \tag{6.40}$$

Then, the generalised H-theorem due to Gibbs is equivalent to the statement:

$$\frac{dH}{dt} \leq 0, \tag{6.41}$$

where the equality corresponds to equilibrium.
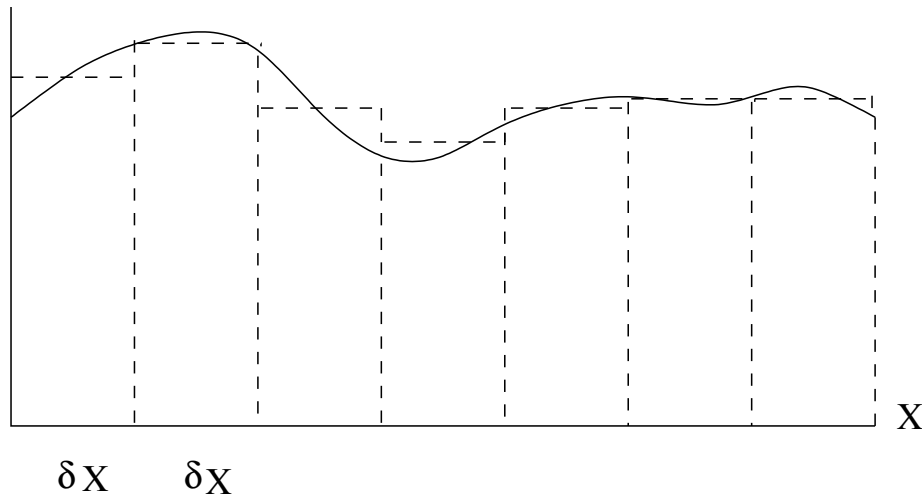
Figure 6.4: Illustration of a coarse-graining operation. The histogram is the coarse-grained version of the distribution ρ.

The Liouville description

The probability of finding a member of the ensemble in the range $(\mathbf{X}, \mathbf{X} + d\mathbf{X})$ is

$$\frac{dN}{N} = \rho_N(\mathbf{X}, t) d\mathbf{X}, \tag{6.42}$$

such that

$$\int_\Gamma \rho_N(\mathbf{X}, t) d\mathbf{X} = 1. \tag{6.43}$$

The coarse-grained description

The probability of finding a member of the ensemble in the *small* but *finite* volume $\delta\mathbf{X}$ is

$$\frac{\delta N}{N} = \overline{\rho}(\mathbf{X}, t) \delta\mathbf{X}, \tag{6.44}$$

such that

$$\int_{\Gamma} \overline{\rho}(\mathbf{X}, t) d\mathbf{X} = 1. \tag{6.45}$$

That is. $\overline{\rho}$ is just ρ_N averaged over $\delta\mathbf{X}$. This concept is illustrated for a one-dimensional distribution in Fig. 6.4. Or, equivalently,

$$\overline{\rho}(\mathbf{X}, t) = \int_{\delta\mathbf{X}} \rho_N(\mathbf{X}, t) d\mathbf{X}. \tag{6.46}$$

We now define a new quantity H, for any ensemble, thus:

$$H = \int_{\Gamma} \overline{\rho}(\mathbf{X}, t) \ln \overline{\rho}(\mathbf{X}, t) d\mathbf{X}. \tag{6.47}$$

At this stage, we should note the following points:

1. H will depend on the number and form of the regions $\delta\mathbf{X}$;

2. $\int \overline{\rho} \ln \overline{\rho} d\mathbf{X}$ is *not* in general equal to $\int \rho_N \ln \rho_N d\mathbf{X}$;

3. We can generalise H to the form $H = \int \rho_N \ln \overline{\rho} d\mathbf{X} \equiv \langle \ln \overline{\rho} \rangle$. This step is well justified because $\ln \overline{\rho}$ is constant over each $\delta\mathbf{X}$ and hence integration of ρ_N over any such interval would just give $\overline{\rho}\delta\mathbf{X}$.

Next we state two important lemmas.

Lemma 1

$$\int \rho_N(t_1) \ln \rho_N(t_1) d\mathbf{X} = \int \rho_N(t_2) \ln \rho_N(t_2) d\mathbf{X}. \tag{6.48}$$

This follows immediately from Liouville's theorem.

Lemma 2 There exists Q as a combination of ρ_N and $\overline{\rho}$, such that Q is positive definite $\forall \rho_N$, $\overline{\rho}$, where

$$Q = \rho_N \ln \rho_N - \rho_N \ln \overline{\rho} - \rho_N + \overline{\rho} \geq 0. \tag{6.49}$$

It should be emphasised that this is a specially chosen initial case and, as pointed out in Note 2 above, is not true in general.

The development of the theory now proceeds as follows. Let us consider the change in H with time from t_1 to t_2, where $(t_1 < t_2)$.

Time $t = t_1$

We choose our initial conditions for the ensemble such that ρ_N is uniform in regions $\delta\mathbf{X}$ that correspond to possible initial states of our assembly. That is, we choose

$$\rho_N(t_1) = \overline{\rho}(t_1), \tag{6.50}$$

and so

$$H_1 = \int \overline{\rho}(t_1) \ln \overline{\rho}(t_1) d\mathbf{X} = \int \rho_N(t_1) \ln \rho_N(t_1) d\mathbf{X}. \tag{6.51}$$

Time $t = t_2$

As time goes on, there will be a mixing effect in phase space, in which the *shape* of each $\delta\mathbf{X}$ will change, but the volume of $\delta\mathbf{X}$ will remain the same. Thus

$$\rho_N(t_2) \neq \overline{\rho}(t_2).$$

The H-function is given by

$$H_2 = \int \overline{\rho}(t_2) \ln \overline{\rho}(t_2) d\mathbf{X} = \int \rho_N(t_2) \ln \overline{\rho}(t_2) d\mathbf{X}, \tag{6.52}$$

where the second equality follows by Note 3 above. Now consider $H_1 - H_2$. From equations (6.51) and (6.52) we have:

$$H_1 - H_2 = \int \rho_N(t_1) \ln \rho_N(t_1) d\mathbf{X} - \int \rho_N(t_2) \ln \overline{\rho}(t_2) d\mathbf{X}. \tag{6.53}$$

Then, by Lemma 1
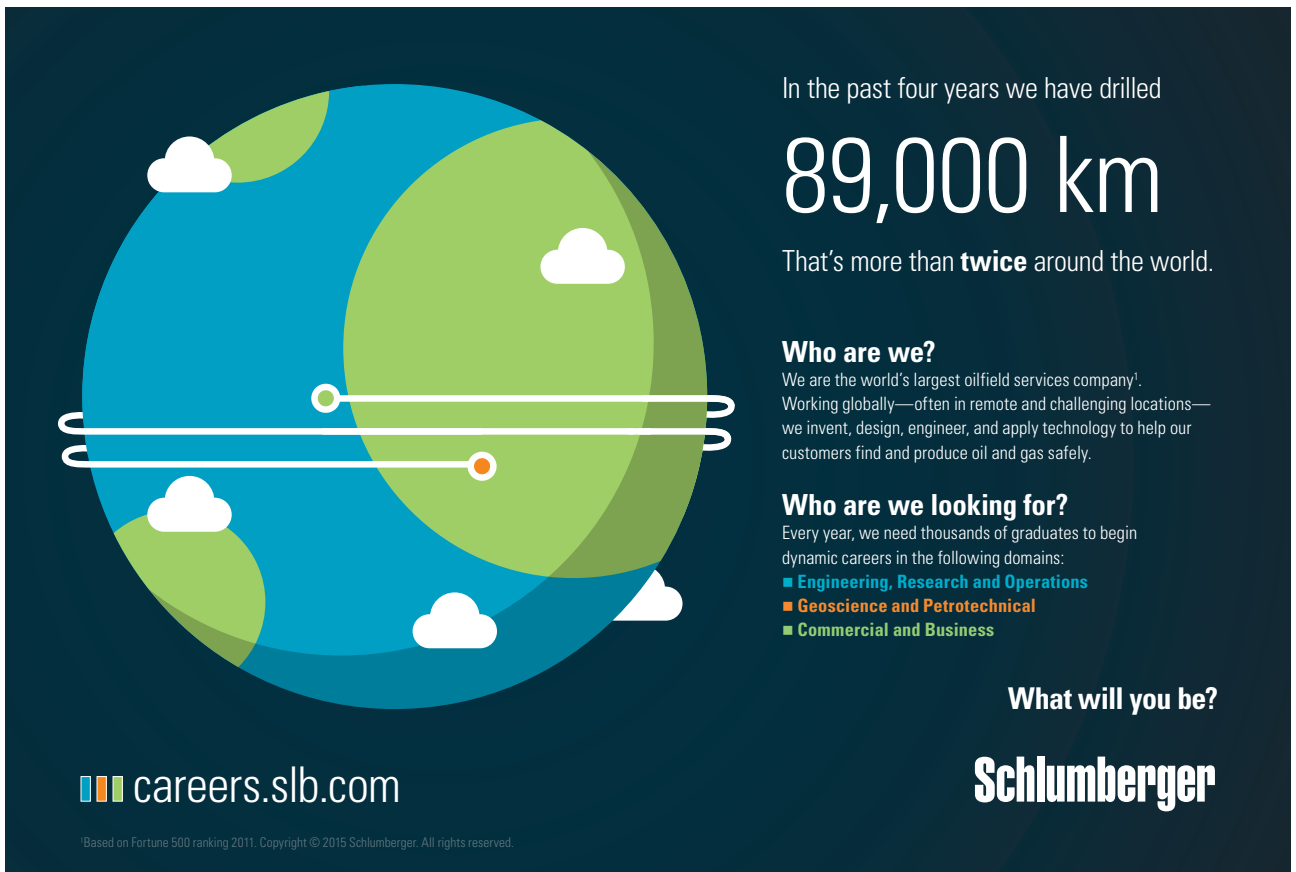
$$\begin{aligned}
H_1 - H_2 &= \int \rho_N(t_2) \ln \rho_N(t_2) d\mathbf{X} - \int \rho_N(t_2) \ln \overline{\rho}(t_2) d\mathbf{X}, \\
&= \int \{\rho_N(t_2) \ln \rho_N(t_2) - \rho_N(t_2) \ln \overline{\rho}(t_2)\} d\mathbf{X}. \tag{6.54}
\end{aligned}$$

Now, normalization of both distributions gives us

$$\int [\overline{\rho}(t_2) - \rho_N(t_2)] d\mathbf{X} = 0, \tag{6.55}$$

so we can add $\overline{\rho}(t_2) - \rho_N(t_2)$ to the integrand, without affecting anything, and obtain

$$H_1 - H_2 = \int \{\rho_N(t_2) \ln \rho_N(t_2) - \rho_N(t_2) \ln \overline{\rho}(t_2) - \rho_N(t_2) + \overline{\rho}(t_2)\} d\mathbf{X}. \tag{6.56}$$

Lastly, by Lemma 2,

$$H_1 - H_2 \geq 0, \tag{6.57}$$

and so

$$\frac{dH}{dt} \leq 0. \tag{6.58}$$

Note that this decrease in the value of H with time corresponds to the decrease with time of the amount of information that we have about the ensemble, due to mixing in phase space.

6.7   Reduced probability distributions

We have seen that Liouville's equation is rigorous and contains complete information about an assembly, yet it cannot give us any indication of whether or not the assembly is in equilibrium. One is led to the conclusion that, despite possessing complete information about microscopic behaviour, it cannot tell us anything about macroscopic behaviour. However, from the Gibbs H-theorem, we see that any form coarse-graining (however little) is sufficient to yield a microscopic description which will reveal the trend to equilibrium. The overall conclusion is that one **must** coarse-grain $\rho_N(\mathbf{X}, t)$. In fact there are various useful ways of doing this, and we shall meet some of these later on, but in this section we shall introduce the important concept of the reduced probability distribution.

We begin by noting that the probability density $\rho_N(\mathbf{X}, t)$ contains information about all the particles in the assembly. In practice we can often obtain macroscopic (average) quantities from one-body or two-body densities. In order to introduce these reduced densities, let us consider the state vector of an assembly as having N components as follows:

$$\mathbf{X} = \{\mathbf{X}_1, \mathbf{X}_2, \dots \mathbf{X}_N\}, \tag{6.59}$$

where $\mathbf{X}_1 \equiv (\mathbf{q}_1, \mathbf{p}_1)$ and so on. Further, consider any one particle such that at any time t its state vector takes the value $\mathbf{X}_1(t) = \mathbf{x}_1$. That is:

The probability of $\mathbf{X}_1$ lying in the elementary volume bounded by $\mathbf{x}_1$ and $\mathbf{x}_1 + \mathbf{dx}_1$ is $\delta[\mathbf{X}_1(t) - \mathbf{x}_1]$.

By considering the average of all such particles (in the vicinity of $\mathbf{x}_1$) over all the assemblies in the ensemble, we can smooth out the delta function and obtain

$$\rho_1(\mathbf{X}_1, t) = \langle \delta[\mathbf{X}_1(t) - \mathbf{x}_1] \rangle. \tag{6.60}$$

Clearly, by the properties of the delta function, this form satisfies the normalisation condition:

$$\int \rho_1(\mathbf{X}_1, t) d\mathbf{X}_1 = 1. \tag{6.61}$$

Similarly, the two-body density is obtained as:

$$\rho_2(\mathbf{X}_1, \mathbf{X}_2; t) = \langle \delta[\mathbf{X}_1(t) - \mathbf{x}_1]\delta[\mathbf{X}_2(t) - \mathbf{x}_2] \rangle, \tag{6.62}$$

with

$$\int \rho_2(\mathbf{X}_1, \mathbf{X}_2; t) d\mathbf{X}_2 = \rho_1(\mathbf{X}_1, t) \tag{6.63}$$

And in general we can consider the s-body density (for $s < N$)

$$\rho_s(\mathbf{X}_1, \mathbf{X}_2, \dots \mathbf{X}_s) = \int d\mathbf{X}_{s+1} \dots \int d\mathbf{X}_N \rho_N(\mathbf{X}_1, \mathbf{X}_2, \dots \mathbf{X}_N). \tag{6.64}$$

As $\rho_N(\mathbf{X}, t)$ contains all possible information about position and momentum of particles in the assembly, the introduction of reduced densities is a systematic way of providing a more coarse-grained description of the system. It is a way of eliminating information. However, formally, the complete state of the assembly can still be specified by the set of reduced densities, thus:

$$\mathbf{f} \equiv \{\rho_1(\mathbf{X}_1), \rho_2(\mathbf{X}_1, \mathbf{X}_2), \dots \rho_N(\mathbf{X} \dots X_N)\} \tag{6.65}$$

where $\mathbf{f}$ is called the distribution vector.

6.7.1 *Example*: The perfect gas at equilibrium

Later on we shall make use of reduced probability densities when we consider interacting systems. Here we give a simple introduction to their use in the case of a perfect gas. As an application it is trivial, but it has the merit of letting some of the main ideas stand out and showing how we may make contact with the earlier theory of stationary ensembles.

We begin by noting that at equilibrium there is no explicit time dependence in the distribution; and in statistical terms we have a stationary state. Also, the energy of the particles does not depend on their position in the box. Thus, from elementary probability considerations, we have:

The probability distribution of a particle with $\mathbf{q}$ is uniform $\equiv 1/V$.

For N particles, and assuming statistical independence, we have

The probability distribution of N particles with $\mathbf{q}$ is uniform $\equiv 1/V^N$,

and so we may write the density distribution as

$$\rho_N(\mathbf{q}, \mathbf{p}, t) = \frac{1}{V^N} \rho_N(\mathbf{p}). \tag{6.66}$$

In order to obtain a reduced distribution, we integrate over coordinates and in this particular case we shall begin by integrating ρ_N over the position coordinates for all the particles,

$$\int \rho_N(\mathbf{q}, \mathbf{p}, t) d\mathbf{q}_1 \dots d\mathbf{q}_N = \frac{1}{V^N} \int d\mathbf{q}_1 \dots \int d\mathbf{q}_N \rho_N(\mathbf{p}). \tag{6.67}$$

However, the normalizations are

$$\int_V d\mathbf{q}_1 = \int_V d\mathbf{q}_2 = \dots \int_V d\mathbf{q}_N = V, \tag{6.68}$$

and thus

$$\int \rho_N(\mathbf{q}, \mathbf{p}, t) d\mathbf{q}_1 \dots d\mathbf{q}_N = \frac{1}{V^N} \cdot V^N \rho_N(\mathbf{p}) = \rho_N(\mathbf{p}_1, \mathbf{p}_2, \dots \mathbf{p}_N). \tag{6.69}$$

For the classical Boltzmann case, each single particle has the distribution

$$\frac{1}{\mathcal{Z}_1} e^{-p_1^2/2mkT},$$

hence we may write

$$\rho_N = \frac{1}{\mathcal{Z}_1} e^{-p_1^2/2mkT} \times \frac{1}{\mathcal{Z}_1} e^{-p_2^2/2mkT} \times \dots \frac{1}{\mathcal{Z}_1} e^{-p_N^2/2mkT} \tag{6.70}$$

as the individual particles do not interact. Next we integrate out $(N-1)$ momentum coordinates, thus

$$\int \frac{e^{-p_2^2/2mkT}}{\mathcal{Z}_1} d\mathbf{p}_2 = \dots \int \frac{e^{-p_N^2/2mkT}}{\mathcal{Z}_1} d\mathbf{p}_N = 1. \tag{6.71}$$

From the general definition given in equation (6.64), we identify the 1-body distribution as

$$\rho_1(\mathbf{p}_1) = \int d\mathbf{p}_2 \ldots \int d\mathbf{p}_N \rho_N(\mathbf{p}_1, \mathbf{p}_2, \ldots \mathbf{p}_N) \Rightarrow \rho_1(\mathbf{p}_1) = \frac{e^{-p_1^2/2mkT}}{\mathcal{Z}_1}. \tag{6.72}$$

As *all* particles are representative, $\rho_1(\mathbf{p}_1)$ is the probability of finding *any* particle with momentum between $\mathbf{p}_1$ and $\mathbf{p}_1 + d\mathbf{p}_1$. It should be noted that for this special case there are no interactions, so for any order we have:

$$\rho_2 = \rho_1^2\,;$$
$$\rho_3 = \rho_1^3\,;$$
$$\vdots$$
$$\rho_N = \rho_1^N.$$

However, we should emphasise that in general, this is not so. But, in principle at least, one can still obtain the reduced densities by integrating out coordinates.

6.8   Basic cells in Γ space

Another way of smoothing out the delta-function structure of probability densities is by dividing up Γ space into small cells, each of volume v_0, say. Then the probability of a particle being in v_0 is given by

$$\int_{v_0} \rho_1(\mathbf{X}_1)d\mathbf{X}_1 \;\;=\;\; 1 \text{ if } \mathbf{X}_1 \text{ in } v_0;$$
$$=\;\; 0 \text{ if } \mathbf{X}_1 \text{ not in } v_0. \tag{6.73}$$

So we can specify the state of the assembly by saying whether each cell of size v_0 is occupied or not. Clearly, if v_0 is small enough, then the probability of there being two occupants can be neglected.

In order to get the correct asymptotic result from quantum theory, we must choose:

$$v_0 = h^3, \tag{6.74}$$

where h is Planck's constant. Note that as this is a volume in phase space, we must have $v_0 \sim (qp)^3$. Thus v_0 has dimensions of $(angular\ momentum)^3$ or $(action)^3$, as required by the above equation.

Chapter 7

Derivation of transport equations

In this chapter we consider the most general problem in statistical many-body physics. We consider an assembly where the individual particles interact with each other and where the assembly itself is not in equilibrium. By which we mean that, at a macroscopic level, it is possible to detect nonuniformity such as temperature or density gradients. If we wish to think of a specific instance, then we could consider a metal rod which is heated at one end and the source of heat removed, as shown in Fig. 7.1. At the macroscopic level, this produces a temperature gradient in the rod which in turn produces a flow of heat until the temperatures even out over the length of the metal rod. In this sense, we have produced a nonequilibrium system (the differentially heated rod) which then returns to equilibrium. The flow of heat which accompanies the return to equilibrium is mediated by the interactions between the particles (atoms at lattice sites) which make up the system.

Of course, there is other nonequilibrium behaviour present. In the real world the metal rod would also return to the ambient temperature. But, as we are only interested in the interactions inside the assembly at this stage, we shall ignore interactions with the outside world.

In general it is a characteristic feature of nonequilibrium systems that, once the origin of the nonuniformity is removed, equilibrium is restored by macroscopic flow processes such as mass flow, heat conduction, macroscopic diffusion and so on. This is perfectly straightforward and familiar phenomenology. However, in this chapter we shall examine these processes from a microscopic point of view and it will be seen that certain paradoxes arise. Our objective here is to start from Liouville's equation, which is both rigorous and exact (and hence in the context of many-body physics can be regarded as a 'theory of everything'), and derive the macroscopic conservation equations of heat and mass flow.

7.1 BBGKY hierarchy (Born, Bogoliubov, Green, Kirkwood, Yvon)

From equation (6.35), we have Liouville's equation in operator form as

$$\frac{\partial \rho_N}{\partial t} = L_N \rho_N \equiv -[\rho_N, H],$$

T_1 T_2

$Q \longrightarrow$
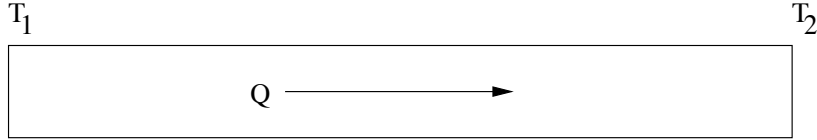
Figure 7.1: A temperature gradient in a metal bar as an example of a nonequilibrium system. Here Q is the flow of heat from the higher temperature T_1 to the lower temperature T_2.

where the square brackets stand for either a Poisson bracket or a commutator, according to whether we are using a classical or quantum description respectively.

If we generalise the Hamiltonian H to the form given by (4.2), viz.,

$$H = \sum_{1=1}^{N} H_i + \sum_{i,j} H_{i,j},$$

then we use equations (6.34)–(6.36) to show that Liouville's equation becomes

$$\frac{\partial \rho_N}{\partial t} = \sum_{n=1}^{N} L_i \rho_N + \sum_{i<j=1}^{N} L_{ij} \rho_N \tag{7.1}$$

where the precise forms of L_i, L_{ij} can be deduced from (6.32) and (4.2). We note that we have in fact introduced an 'interaction Liouvillian', L_{ij}.

We use this to derive an equation for the reduced density ρ_s $(s \leq N)$. Noting equation (6.64), which defines ρ_s, we integrate both sides of (7.1), obtaining:

$$\int \ldots \int d\mathbf{X}_{s+1} \quad \ldots \quad d\mathbf{X}_N \frac{\partial \rho_N}{\partial t} = \sum_{i=1}^{N} \int \ldots \int d\mathbf{X}_{s+1} \ldots d\mathbf{X}_N L_i \rho_N$$

$$+ \sum_{i<j=1}^{N} \int \ldots \int d\mathbf{X}_{s+1} \ldots d\mathbf{X}_N L_{ij} \rho_N. \tag{7.2}$$

The left hand side is straightforward, but the right hand side needs some elementary results from probability theory, as follows. For all time, we have the conservation relation

$$\int \ldots \int d\mathbf{X}_1 \ldots d\mathbf{X}_N \, \rho_N(\mathbf{X}_1 \ldots \mathbf{X}_N, t) = \text{constant},$$

and so it follows immediately that

$$\frac{\partial}{\partial t} \int d\mathbf{X}_1 \ldots d\mathbf{X}_N \, \rho_N(\mathbf{X}_1 \ldots \mathbf{X}_N, t) = 0.$$

Taking this, with (7.1), we can write

$$\int d\mathbf{X}_i L_i \rho_N(\mathbf{X}_1 \ldots \mathbf{X}_N) = 0, \quad \text{if } 1 \leq i \leq N, \tag{7.3}$$

and

$$\int\int d\mathbf{X}_i d\mathbf{X}_j L_{ij}\rho_N(\mathbf{X}_1\dots\mathbf{X}_N) = 0, \quad \text{if } 1 \le i \text{ and } j \le N. \tag{7.4}$$

As $\partial/\partial t$ is unaffected by $\int d\mathbf{X}_{s+1}\dots\int d\mathbf{X}_N$, the lefthand side of (7.2) becomes

$$\text{LHS of equation (7.2)} \equiv \frac{\partial}{\partial t}\int d\mathbf{X}_{s+1}\dots\int d\mathbf{X}_N\rho_N(\mathbf{X}_1\dots\mathbf{X}_N) = \partial\rho_s/\partial t.$$

The righthand side of (7.2) is more complicated: we deal with this by dividing up the summations and consider various cases of the noninteracting and interacting terms in turn:

$$\text{RHS of equation (7.2)} \equiv \int d\mathbf{X}_{s+1}\dots\int d\mathbf{X}_N[\underbrace{\sum_{n=1}^{N}L_i\rho_N}_{A} + \underbrace{\sum_{i<j=1}^{N}L_{ij}\rho_N}_{B}].$$

Now we consider the two terms A and B in turn.

Term A

Case 1 For $1 \le i \le s$, L_i is unaffected by the integrations, so $\rho_N \to \rho_s$;

Case 2 For $s+1 \le i \le N$, this term vanishes by (7.3).

Term B

Case 1 For $1 \le i, j \le s$, L_{ij} is unaffected by the integrations, therefore $\rho_N \to \rho_s$

Case 2 For $s+1 \le i$ and $j \le N$, this term vanishes by (7.4)

Case 3 For $1 \le i \le s; s+1 \le j \le N$ the situation is more complicated and we need to consider two points, as follows:

One, as the particles are identical, it follows that ρ_N is symmetric in its arguments, thus:

$$\rho_N(\mathbf{X}_1\dots\mathbf{X}_A\dots\mathbf{X}_B\dots\mathbf{X}_N) = \rho_N(\mathbf{X}_1\dots\mathbf{X}_B\dots\mathbf{X}_A\dots\mathbf{X}_N).$$

Two, X_j is a dummy variable of integration as $\int d\mathbf{X}_{s+1}\dots\int d\mathbf{X}_N$ and $s+1 \le j \le N$, hence

$$\sum_{j=s+1}^{N}L_{ij}\rho_N \to (N-s)L_{i,s+1}\rho_N.$$

Continuing with Term B, Case 3, we note that $L_{i,s+1}$ is unaffected by $\int d\mathbf{X}_{s+2}\dots\int d\mathbf{X}_N$ and hence

$$(N-s)\sum_{i=1}^{s}\int d\mathbf{X}_{s+1}\dots\int d\mathbf{X}_N L_{i,s+1}\ \rho_N(\mathbf{X}_1\dots X_N)$$

$$= (N-s)\sum_{i=1}^{s}\int d\mathbf{X}_{s+1}L_{i,s+1}\int d\mathbf{X}_{s+2}\dots\int d\mathbf{X}_N\ \rho_N(\mathbf{X}_1\dots X_N)$$

$$= (N-s)\sum_{i=1}^{s}\int d\mathbf{X}_{s+1}L_{i,s+1}\rho_{s+1}(\mathbf{X}_1\dots\mathbf{X}_{s+1}). \tag{7.5}$$

Thus, in all, equation (7.2) becomes

$$\frac{\partial\rho_s}{\partial t} = \sum_{i=1}^{s}L_i\rho_s(\mathbf{X}_1\dots\mathbf{X}_s) + \sum_{i\le j=1}^{s}L_{ij}\rho_s(\mathbf{X}_1\dots\mathbf{X}_s)$$

$$+ \quad (N-s) \sum_{i=1}^{s} \int d\mathbf{X}_{s+1} L_{i,s+1} \rho_{s+1}(\mathbf{X}_1 \dots \mathbf{X}_{s+1}). \tag{7.6}$$

Two points should be noted about this result.

- Essentially this is a s-particle Liouville equation *plus* a term coupling ρ_s to ρ_{s+1}.

- It follows that equation (7.6) defines an *open* statistical hierarchy of equations for the reduced densities. That is, if we wish to calculate the single-body reduced density ρ_1, then solving equation (7.6) depends on our knowing the two-body reduced density ρ_2. If we seek to solve for ρ_2, then we need to know ρ_3; and so on. The equations of motion for the reduced densities form an open statistical hierarchy. This is the well known BBGKY hierarchy.

The problem of how to close the BBGKY hierarchy is the fundamental problem of many-body physics.

7.2 Equations for the reduced distribution functions

Although the formal analysis has so far been in terms of reduced probability densities, our progress towards the real (macroscopic) world is aided by the introduction of probability distributions, which we denote by f_s and relate to the reduced densities in terms of the system volume V, such that

$$f_s(\mathbf{X}_1 \dots \mathbf{X}_s) \equiv V^s \rho_s(\mathbf{X}_1 \dots \mathbf{X}_s). \tag{7.7}$$
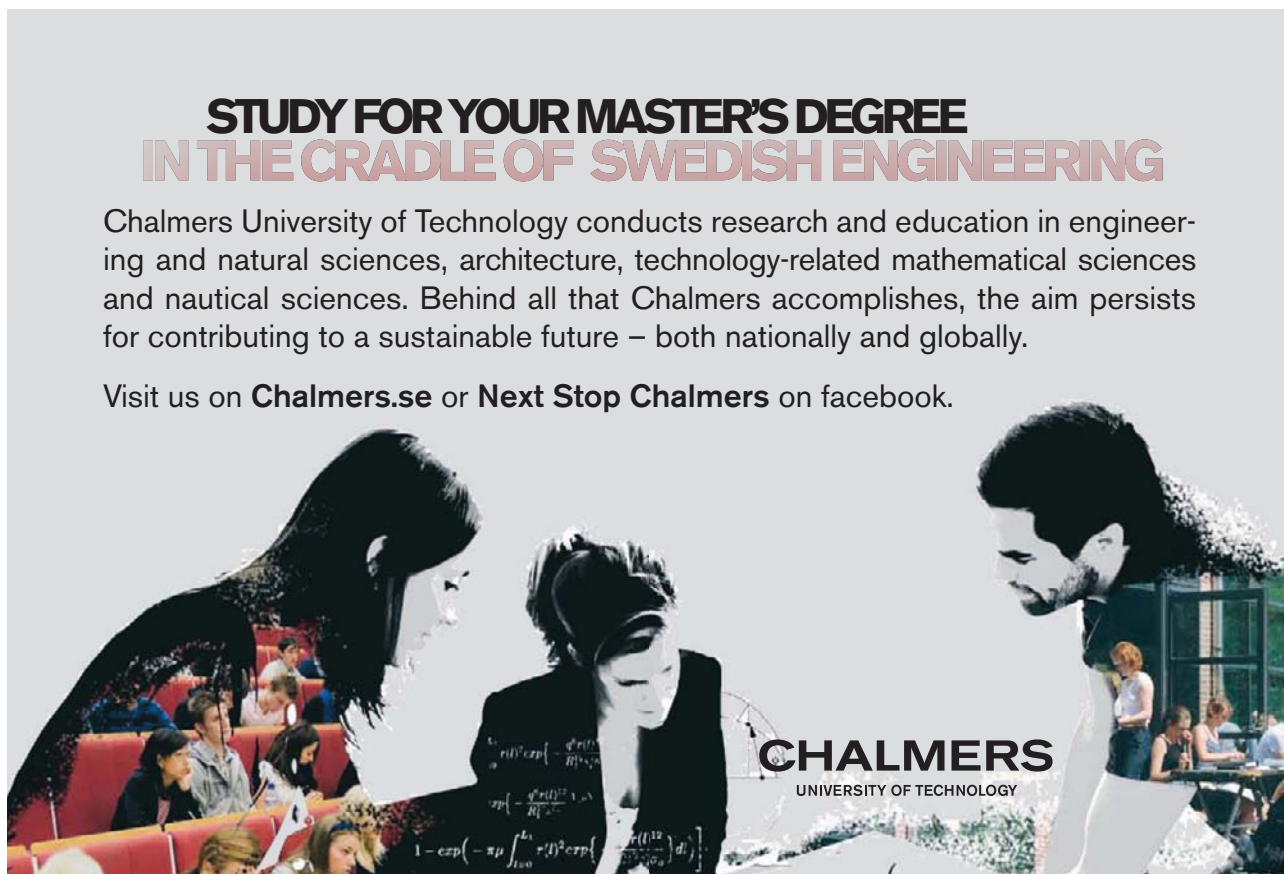
In order to derive evolution equations for the reduced distributions, we introduce a compact form of Liouville's equation, thus

$$\frac{\partial \rho_N}{\partial t} = -\hat{H}_N \, \rho_N, \tag{7.8}$$

(where the hat on H means it is an operator) and from (6.32), (4.2), (4.3), and (7.1) we can write

$$\hat{H}_N = \sum_{i=1}^N \frac{p_i}{m} \frac{\partial}{\partial q_i} - \sum_{i<j=1}^N \Theta_{ij}, \tag{7.9}$$

where the assembly is assumed to be Hamiltonian and to be made up of from identical particles of mass m. In the interests of a compact formulation, we have introduced the operator

$$\Theta_{ij} = \frac{\partial \phi_{ij}}{\partial q_j} \frac{\partial}{\partial p_j} + \frac{\partial \phi_{ij}}{\partial q_i} \frac{\partial}{\partial p_i} \tag{7.10}$$

where $\phi(|q_i - q_j|) \equiv \phi_{ij}$ is the two-body interaction potential. Then it can be shown that the reduced distribution function f_s satisfies the equation:

$$\frac{\partial f_s}{\partial t} = -\hat{H}_s f_s + \frac{(N-s)}{V} \sum_{i=1}^s \int d\mathbf{X}_{s+1} \Theta_{i,s+1} f_{s+1}(\mathbf{X}_1 \dots \mathbf{X}_{s+1}). \tag{7.11}$$

If we now take the thermodynamic limit:

$N \to \infty, V \to \infty$ such that $v \equiv V/N$=constant,

where v is often referred to as the specific volume, then the equation for the reduced distribution functions takes the form

$$\frac{\partial f_s}{\partial t} + \hat{H}_s f_s = \frac{1}{v} \sum_{i=1}^s \int d\mathbf{X}_{s+1} \hat{\Theta}_{i,s+1} f_{s+1}(\mathbf{X}_1 \dots \mathbf{X}_{s+1}, t). \tag{7.12}$$

(When taking the thermodynamic limit, it should be borne in mind the N is normally of the order of Avogadro's number, whereas s takes a value of only one or two and hence can be neglected by comparison.) The most important case is that of the single-body distribution, when $s = 1$:

$$\frac{\partial f_1(\mathbf{X}_1, t)}{\partial t} + \hat{H}_1 f_1 = \frac{1}{v} \int d\mathbf{X}_2 \Theta_{12} f_2(\mathbf{X}_1, \mathbf{X}_2, t), \tag{7.13}$$

which is known as the **the kinetic equation**. Equations of this kind are the basis of **balance equations** for mass, momentum, energy; and so on, for an assembly which is not at equilibrium. The resulting equations, governing, as they do, the **transport** of quantities like mass or momentum are often referred to as **transport equations**.

7.3   The kinetic equation

At this stage we will find it helpful to unpack our symbolic notation and we begin by reverting to the canonical phase space coordinates, thus we have $f_1(\mathbf{X}_1, t) = f_1(\mathbf{q}_1, \mathbf{p}_1; t)$. Now, going back to the definitions of the probability density and the probability distribution, we may interpret this as:

$f_1(\mathbf{q}_1, \mathbf{p}_1, t)d\mathbf{q}_1 d\mathbf{p}_1 \equiv$ the probability of finding a particle at time t with its coordinates in the range $(\mathbf{q}_1, \mathbf{q}_1 + d\mathbf{q}_1; \mathbf{p}_1, \mathbf{p}_1 + d\mathbf{p}_1) \times$ the volume of the assembly.

Thus we have

$nf_1(\mathbf{q}_1, \mathbf{p}_1 t) \equiv$ the number of particles at time t with their phase space coordinates in the shell $(\mathbf{q}_1, \mathbf{q}_1 + d\mathbf{q}_1; \mathbf{p}_1, \mathbf{p}_1 + d\mathbf{p}_1)$,

where $n = N/V$ is the number density.

Next, we change back to the usual cartesian coordinates, thus:

$$\mathbf{q}_1, \mathbf{q}_2 \to \mathbf{x}, \mathbf{x}', \qquad \mathbf{p}_1, \mathbf{p}_2 \to m\mathbf{u}, m\mathbf{u}', \tag{7.14}$$

and hence

$$\int d\mathbf{q} \int d\mathbf{p} \; n f_1(\mathbf{q}, m\mathbf{u}; t) = \int d\mathbf{x} \int m^3 d\mathbf{u} \; n f_1(\mathbf{x}, m\mathbf{u}; t)$$
$$= \int d\mathbf{x} \int d\mathbf{u} \; f(\mathbf{x}, \mathbf{u}; t) = N, \tag{7.15}$$

where we have introduced

$$f(\mathbf{x}, \mathbf{u}; t) \equiv n m^3 f_1(\mathbf{x}, m\mathbf{u}; t). \tag{7.16}$$

This quantity is what we shall mean when we refer to the single-body distribution from now on. Its normalization is given by equation (7.15) and we may readily derive its governing equation from (7.13), the result being

$$\frac{\partial f_1(\mathbf{X}_1, t)}{\partial t} + \frac{\mathbf{p}_1}{m} \cdot \frac{\partial}{\partial \mathbf{q}_1} f_1 = n \int d\mathbf{X}_2 \hat{\Theta}_{12} f_2(\mathbf{X}_1, \mathbf{X}_2; t), \tag{7.17}$$

where it should be noted that we have excluded any effects due to external forces.

It should also be noted that, for sufficiently small density (n), the interaction term on the righthand side becomes unimportant, except during discrete collisions. Also, we shall restrict our attention to a dilute ideal gas where, the duration of collisions is very much less than the time between collisions.

Next, we proceed as follows: multiply (7.13) across by $n m^3$, change variables according to (7.14)-(7.16), and obtain

$$\frac{\partial f(\mathbf{x}, \mathbf{u}; t)}{\partial t} + \mathbf{u}.\nabla f(\mathbf{x}, \mathbf{u}; t) = \int d\mathbf{x}' \int d\mathbf{u}' \hat{\Theta}_{12} \; g(\mathbf{x}, \mathbf{x}'; \mathbf{u}, \mathbf{u}'; t), \tag{7.18}$$

where we have introduced the function

$$g \equiv n^2 m^6 f_2(\mathbf{x}, \mathbf{x}'; m\mathbf{u}, m\mathbf{u}'; t). \tag{7.19}$$

It can be shown (using methods which are beyond the scope of this book) that g may be expressed in terms of f, in the form:

$$g(\mathbf{x}, \mathbf{x}'; \mathbf{u}, \mathbf{u}') = f(\mathbf{x}, \mathbf{u}) f(\mathbf{x}', \mathbf{u}') - \overline{f}(\mathbf{x}, \mathbf{u}) \overline{f}(\mathbf{x}', \mathbf{u}'), \tag{7.20}$$

where the first pairing is due to collisions and the overbars on the second pairing indicate 'inverse collisions'. These terms will be explained in the next section where we consider the Boltzmann theory.
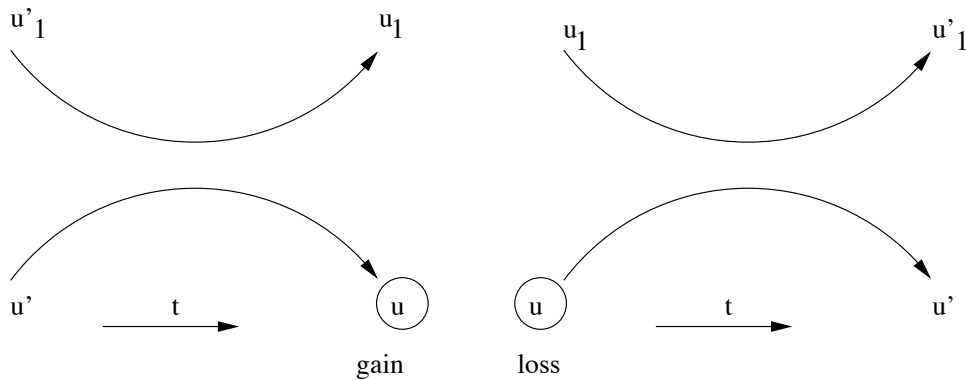
Figure 7.2: Reconstituting and inverse two-body collisions.

7.4 The Boltzmann equation

The idea (stated at the end of the previous section) that g could be factored in terms of f was originally due to Boltzmann: it is his famous assumption of molecular chaos or *'Stosszahlansatz'*. Essentially it states that particles only interact during collisions: before and after, their motion is uncorrelated.

As eqn.(7.18) gives the rate of change of $f(\mathbf{x}, \mathbf{u}; t)$ with time, we may make the following identifications:

- $\partial f / \partial t$: the local time-derivative of f;

- $\mathbf{u}.\nabla f$: the convective time-derivative of f;

- $\int d\mathbf{x}' \int d\mathbf{u}' \hat{\Theta}_{12}\, g$: the rate of change with time of f due to two-body collisions.

On this basis, we may interpret the righthand side of equation (7.18) as

$$\int d\mathbf{x}' \int d\mathbf{u}' \hat{\Theta}_{12}\, g(\mathbf{x}, \mathbf{x}'; \mathbf{u}, \mathbf{u}'; t) \equiv \left(\frac{\partial f}{\partial t} \right)_{\text{coll}}, \tag{7.21}$$

where the subscript 'coll' stands for collisions. This term may be further interpreted as

$$\left(\frac{\partial f}{\partial t} \right)_{\text{coll}} = \text{ gain to state } \mathbf{u} - \text{ loss from state } \mathbf{u}, \tag{7.22}$$

as illustrated in Fig. 7.2.

It can be shown, using elementary scattering theory and the assumption of molecular chaos that

$$\left(\frac{\partial f}{\partial t} \right)_{\text{coll}} = \int d\mathbf{u} \int d\omega\, \sigma_d(\omega) |\mathbf{u} - \mathbf{u}_1|$$
$$\times \quad \{ f(\mathbf{x}, \mathbf{u}'; t) f(\mathbf{x}, \mathbf{u}'_1; t) - f(\mathbf{x}, \mathbf{u}; t) f(\mathbf{x}, \mathbf{u}_1; t) \}, \tag{7.23}$$

where ω is the solid angle through which a particle is scattered and $\sigma_d(\omega)$ is the differential scattering cross-section.

Substituting (7.23) and (7.21) into (7.18) yields the Boltzmann equation:

$$\frac{\partial f(\mathbf{x}, \mathbf{u}; t)}{\partial t} + (\mathbf{u}.\nabla) f(\mathbf{x}, \mathbf{u}; t) = \int d\mathbf{u}_1 \int d\omega \, \sigma_d(\omega) |\mathbf{u} - \mathbf{u}_1|$$
$$\times \quad \{ f(\mathbf{x}, \mathbf{u}'; t) f(\mathbf{x}, \mathbf{u}_1'; t) - f(\mathbf{x}, \mathbf{u}; t) f(\mathbf{x}, \mathbf{u}_1; t) \}.$$

(7.24)

Or, in a more compact notation:

$$\frac{\partial f}{\partial t} + (\mathbf{u}.\nabla) f = \int d\mathbf{u}_1 \int d\omega \, \sigma_d \, |\mathbf{u} - \mathbf{u}_1| \times \{ f' f_1' - f f_1 \},$$

(7.25)

where $f \equiv f(\mathbf{x}, \mathbf{u}; t)$, $f' \equiv f(\mathbf{x}, \mathbf{u}'; t)$; and so on.

7.5 The Boltzmann H-theorem

In order to work in Boltzmann's original notation, we write the expression for the entropy S as:

$$S = -kH,$$

(7.26)

where k is the Boltzmann constant and the function H is defined by

$$H = \int d\mathbf{u} f(\mathbf{u}, t) \ln f(\mathbf{u}, t).$$

(7.27)

Note that this is still the same general form for the Boltzmann entropy, but now it is based on the distribution f, rather than ρ, which was the solution of the Liouville equation. Also, for simplicity, we ignore spatial variations: that is, we shall drop the $\mathbf{u}.\nabla$ term in (7.25).

Now we want to show that the entropy increases or remains constant. We begin by differentiating both sides of (7.27) with respect to the time. The result is

$$\frac{dH}{dt} = \int d\mathbf{u} \frac{\partial f}{\partial t} [1 + \ln f].$$

(7.28)

Then we substitute for $\partial f / \partial t$ on the righthand side, from (7.25), with $(\mathbf{u}.\nabla) = 0$, and (7.28) becomes

$$\frac{dH}{dt} = \int d\mathbf{u} \int d\mathbf{u}_1 \int d\omega \, \sigma \, d|\mathbf{u} - \mathbf{u}_1| \{ f' f_1' - f f_1 \}(1 + \ln f).$$

(7.29)

Now, we can interchange $\mathbf{u}$ and $\mathbf{u}_1$: this leaves everything unchanged, as they are dummy variables, so that we have:

$$\frac{dH}{dt} = \int d\mathbf{u} \int d\mathbf{u}_1 \int d\omega \, \sigma \, d|\mathbf{u}_1 - \mathbf{u}| \{ f_1' f' - f_1 f \}(1 + \ln f),$$

(7.30)

which is equivalent to equation (7.29), so that we may add (7.29) and (7.30), and divide across by a factor of two, to obtain:

$$\frac{dH}{dt} = \frac{1}{2} \int d\mathbf{u} \int d\mathbf{u}_1 \int d\omega \sigma_d |\mathbf{u}_1 - \mathbf{u}| \{ f_1' f' - f_1 f \}[2 + \ln(f f_1)].$$

(7.31)

Now this integrand is invariant under the interchange of $\{\mathbf{u}, \mathbf{u}_1\}$ and $\{\mathbf{u}', \mathbf{u}_1'\}$, as this merely interchanges reconstituting collisions and inverse collisions. Hence (7.31) implies

$$\frac{dH}{dt} = \frac{1}{2} \int d\mathbf{u}' \int d\mathbf{u}_1' \int d\omega' \sigma_d' |\mathbf{u}_1' - \mathbf{u}'| \{ f f_1 - f' f_1' \}[2 + \ln(f' f_1')]$$
$$= -\frac{1}{2} \int d\mathbf{u}' \int d\mathbf{u}_1' \int d\omega' \sigma_d' |\mathbf{u}_1' - \mathbf{u}'| \{ f' f_1' - f f_1 \}[2 + \ln(f' f_1')].$$

(7.32)

At this stage we note that:

$$d\mathbf{u}\,d\mathbf{u}_1 = d\mathbf{u}'\,d\mathbf{u}_1',$$

$$|\mathbf{u} - \mathbf{u}_1| = |\mathbf{u}' - \mathbf{u}_1'|,$$

and

$$\sigma_d(\omega) = \sigma_d(\omega');$$

so we add (7.31) to (7.32), and again divide across by a factor two to obtain:

$$\frac{dH}{dt} = \frac{1}{4} \int d\mathbf{u} \int d\mathbf{u}' \int d\omega \, \sigma_d \, |\mathbf{u}_1 - \mathbf{u}| \{f_1'f' - f_1 f\} [\ln(f f_1) - \ln(f' f_1')].$$

The integrand on the righthand side is *never* positive: thus we conclude that

$$\frac{dH}{dt} \leq 0, \tag{7.33}$$

and, from (7.26),

$$\frac{dS}{dt} \geq 0. \tag{7.34}$$

Thus the entropy increases as the assembly moves *irreversibly* towards equilibrium.

This result is the Boltzmann H-theorem. It may usefully be considered in the context of the generalised H-theorem due to Gibbs, which we discussed in Chapter 5. There we found that the entropy constructed from the solution to the Liouville equation did not change with time. But, if that solution was coarse-grained in some way (which amounts to giving up some information about the microstate of the system), then the entropy was found to increase with time. Here, in the Boltzmann result, the coarse-graining has been quite extensive, as we have moved from the N-body density ρ_N (or its corresponding distribution) to the single-body distribution, which is governed by the Boltzmann equation. Evidently the Boltzmann H-theorem is a consequence of the form of the Boltzmann equation; and its correspondence with experience amounts to a rather fundamental check on that equation.

7.6   Macroscopic balance equations

In any individual collision, a quantity b may be conserved (for example, b can stand for any one of mass or momentum or energy; and so on) and the associated microscopic conservation law for a two-body collision may be written as

$$b + b_1 = b' + b_1'. \tag{7.35}$$

That is, the total amount of property b possessed by the two particles before the collision is the same as the total amount of b afterwards, although the relative proportion possessed by each particle will normally be changed. It can be shown (and is probably intuitively obvious) that the collision term in the Boltzmann equation must satisfy

$$\int d\mathbf{u}\, b(\mathbf{x}, u) \left(\frac{\partial f}{\partial t} \right)_{\text{coll}} = 0. \tag{7.36}$$

Accordingly, the *macroscopic* conservation law corresponding to equation (7.35) may be found from (7.24), with the righthand side set equal to zero, and we do this as follows.

First we multiply each term on the lefthand side of (7.24) by $b(\mathbf{x}, \mathbf{u})$; and, integrating with respect to $\mathbf{u}$, we obtain the general macroscopic relation

$$\int d^3 u\, b(\mathbf{x}, \mathbf{u}) \left[\frac{\partial}{\partial t} + u_i \frac{\partial}{\partial x_i} \right] f(\mathbf{x}, \mathbf{u}; t) = 0, \tag{7.37}$$

where we have rewritten $\mathbf{u}.\nabla$ in cartesian tensor notation and the index i takes the values 1, 2 or 3. Then, as b is independent of t, we can rewrite this as:

$$\frac{\partial}{\partial t} \int d^3 u\, bf + \frac{\partial}{\partial x_i} \int d^3 u\, b u_i f - \int d^3 u\, \frac{\partial b}{\partial x_i} u_i f = 0. \tag{7.38}$$

Next, if we denote the average of any property A against f by $\langle A \rangle$, we may write

$$\langle A \rangle = \frac{\int d^3 u\, Af}{\int d^3 u f} = \frac{\int d^3 u Af}{n}, \tag{7.39}$$

where

$$n = n(\mathbf{x}, t) \equiv \int d^3 u\, f(\mathbf{x}, \mathbf{u}; t). \tag{7.40}$$

As the number density n does not depend on $\mathbf{u}$, we can rewrite (7.39) as

$$\langle nA \rangle = \int d^3 u\, Af. \tag{7.41}$$

Lastly, in view of all this, equation (7.38) can now be rewritten in the neat form:

$$\frac{\partial}{\partial t}\langle nb \rangle + \frac{\partial}{\partial x_i}\langle nu_i b \rangle - n\langle u_i \frac{\partial b}{\partial x_i}\rangle = 0. \tag{7.42}$$

Now, if we choose b to be mass or momentum (say), equation (7.42) will lead to the corresponding macroscopic conservation law. In the next section, we shall consider conservation of mass as an example.

7.6.1   The continuity equation as an example

In the macroscopic study of fluids, conservation of mass is seen as a consequence of the continuous nature of the fluid, and hence the statement of conservation of mass is often referred to as the 'continuity equation'.

Our procedure is now quite straightforward. We choose $b = m$, the mass of a particle, and substitute accordingly in equation (7.42). If we take the mass of the particle to be constant, then the last term on the lefthand side vanishes and we obtain

$$\frac{\partial (nm)}{\partial t} + \frac{\partial nm\langle u_i \rangle}{\partial x_i} = 0. \tag{7.43}$$

The macroscopic velocity field may be written as

$$\mathbf{U}(\mathbf{x}, t) \equiv \langle u_i \rangle, \tag{7.44}$$

and we define the mass density ρ to be

$$\rho(\mathbf{x}, t) \equiv mn(\mathbf{x}, t). \tag{7.45}$$

Hence, with substitutions from (7.44) and (7.45), equation (7.43) becomes the usual continuity equation as encountered in the subject of continuum mechanics:

$$\frac{\partial \rho}{\partial t} + div(\rho \mathbf{U}) = 0. \tag{7.46}$$

It may be of interest to note that this equation is normally derived in continuum mechanics by entirely macroscopic arguments. We can derive the Euler equation (which expresses conservation of momentum in an inviscid fluid) in much the same way as we have done here by taking $b = mu_i$. However, in order to include viscous effects (that is, to derive the Navier-Stokes equation) we must take the righthand side of the Boltzmann equation into account. We shall not pursue that here, except to remark that the Navier-Stokes equation can be derived both by microscopic methods (as here) and by macroscopic methods based on conservation of momentum examined with respect to a fixed control volume in the fluid continuum. Both methods essentially rely on an **assumption** of a linear relationship between viscous shear stress and the rate of strain tensor (in effect, Newton's law of viscosity).

Chapter 8

Dynamics of Fluctuations

We have previously discussed energy fluctuations in the canonical ensemble and fluctuations in particle number in the grand canonical ensemble. We now consider time-dependent behaviour in assemblies which are at thermal equilibrium. Some examples of nonstationary equilibrium systems are:

- Brownian motion of colloidal particles floating in a liquid.

- movement of a small mirror suspended in a rarefied gas.

- thermal noise in electronic or optical systems.

We shall take the case of Brownian motion as a specific example.

8.1   Brownian motion and the Langevin equation

Consider the motion of large particles (e.g. pollen grains) floating in water. The particles move about in an irregular fashion due to molecular collisions. Take one-dimensional motion (i.e. a one-dimensional projection of the actual motion) for simplicity. If we plot the displacement $X(t)$ against the elapsed time t then we obtain the graph shown in Fig. 8.1.

If we adopt a macroscopic view, then we note that a particle moving with velocity u, experiences Stokes drag with coefficient η (per unit mass). Applying Newton's second law of motion then yields the macroscopic equation of motion in the form

$$\dot{u} = -\eta u, \tag{8.1}$$

where the dot denotes time differentiation.

At the microscopic level, the particle experiences the molecular impacts as a random force. If the *mean* response of the particle is given by equation (8.1), then the microscopic equation of motion may be written as:

$$\dot{u} = -\eta u + F(t), \tag{8.2}$$

where $F(t)$ is a random force per unit mass due to collisions with fluid molecules. This equation is usually known as the Langevin equation.

Essentially we have to model the effect of the molecular impacts and the next step is to specify F in such a way that it provides a physically plausible model. To begin with, it is clear that the average effect of impacts must be zero and hence the random force must satisfy the condition

$$\langle F(t) \rangle = 0, \tag{8.3}$$

which ensures that the microscopic and macroscopic laws are consistent, when we average equation (8.2) term by term to obtain (8.1).

In choosing a form for $F(t)$, we may express the idea of the irregularity of molecular collisions by assuming that $F(t)$ is only correlated with itself at very short times $t \leq t_c$, where t_c is the duration of
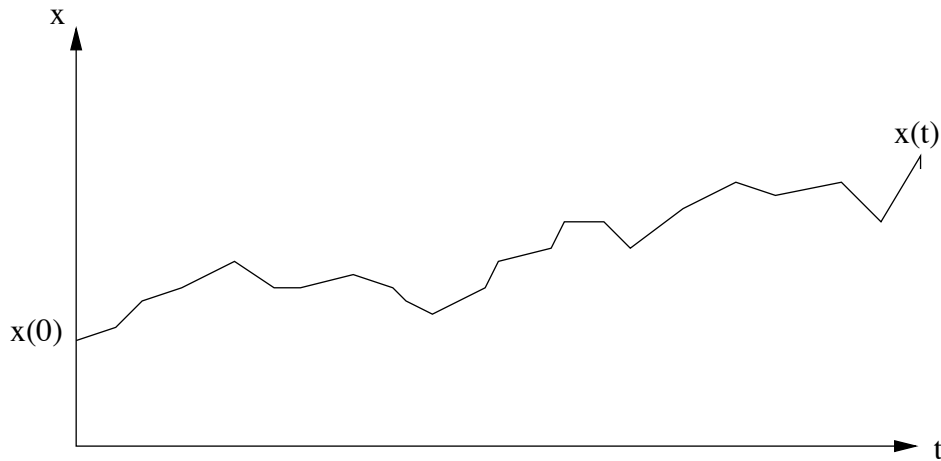
Figure 8.1: Variation of displacement x with time t in a one-dimensional random walk.

a collision. This idea may be put in more quantitative form, by considering the autocorrelation of the random force at two different times t_1 and t_2. Let

$$\langle F(t_1)F(t_2) \rangle = w(t_1 - t_2), \tag{8.4}$$

and

$$W(t) = \int_0^t w(\tau)d\tau, \tag{8.5}$$

where

$$W(t) \to W = \text{a constant},$$

for values of t very much greater than t_c. This behaviour is illustrated in Figures 8.2 and 8.3.

Now we solve the Langevin equation as given by (8.2), taking as initial conditions that $u = u_0$ at $t = 0$, to obtain

$$u = u_0 e^{-\eta t} + e^{-\eta t} \int_0^t dt' e^{\eta t'} F(t'), \tag{8.6}$$

for the velocity of a pollen grain at any time t.

We may make a consistency check by averaging this solution over the ensemble, using equation (8.3), to find

$$\langle u \rangle = u_0 e^{-\eta t}, \tag{8.7}$$

which is, as required, the solution to the macroscopic equation of motion (8.1).

However, we can find a solution which depends on the random force F, if we first square each side of equation (8.6), and then average, to obtain

$$\langle u^2 \rangle = u_0^2 e^{-2\eta t} + e^{-2\eta t} J(t), \tag{8.8}$$

where

$$J(t) = \int_0^t dt_1 \int_0^t dt_2 e^{\eta(t_1 + t_2)} \langle F(t_1) F(t_2) \rangle. \tag{8.9}$$

Note that the 'cross terms', which are linear in $F(t)$, vanish as a consequence of (8.3). Now substitute from (8.4) for the autocorrelation, and make the change of variables,

$$\tau = t_1 - t_2; \qquad T = t_1 + t_2, \tag{8.10}$$
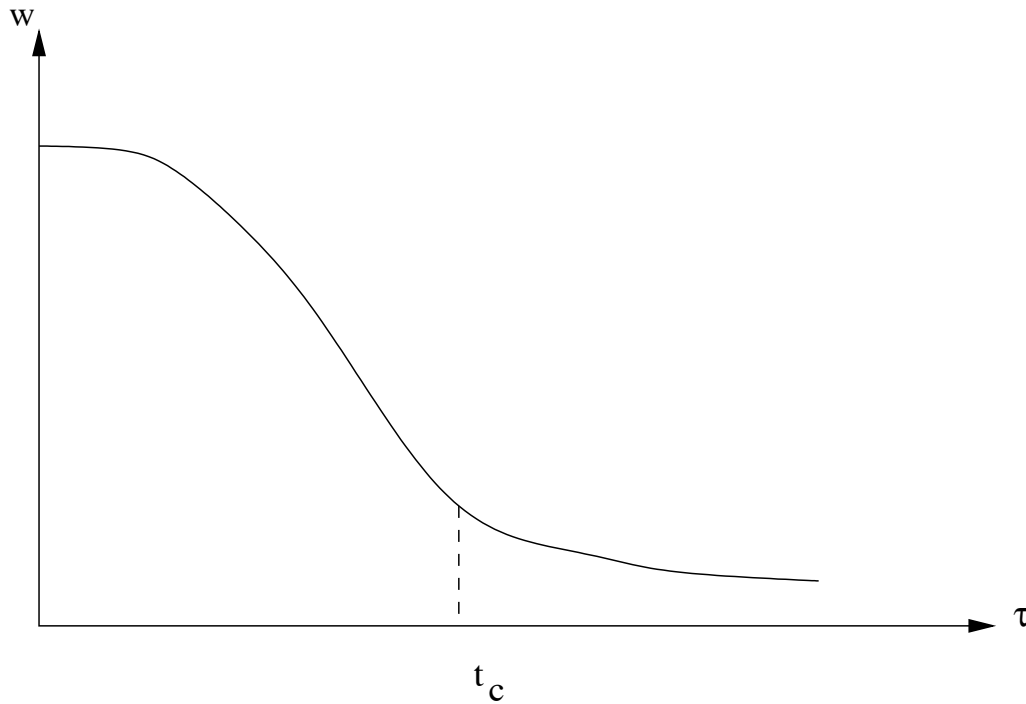
Figure 8.2: Autocorrelation w of the random force.
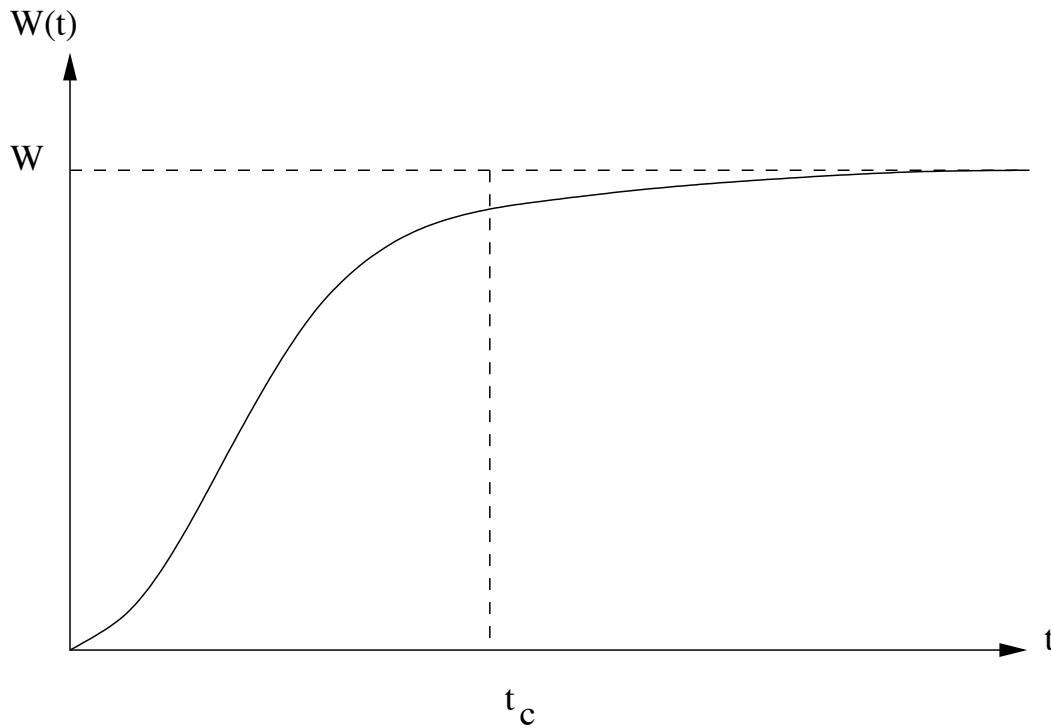
Figure 8.3: Saturation of the force correlation at long times.
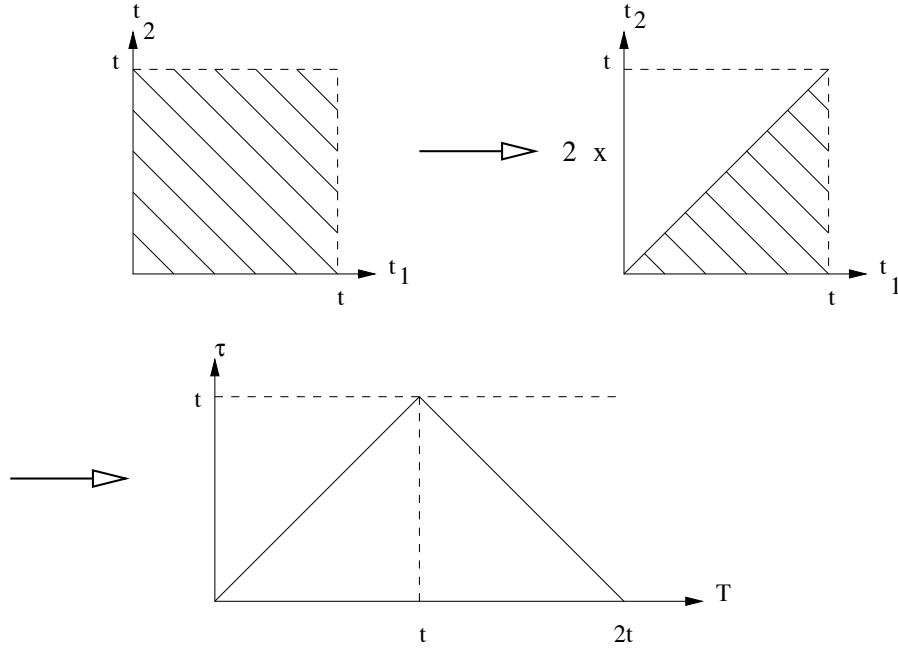
Figure 8.4: Change of field of integration with change of time variable.

to obtain

$$J(t) = \int_0^t dt_1 \int_0^t dt_2 e^{\eta T} w(\tau) = 2 \int_{A'} dT d\tau e^{\eta T} w(\tau), \tag{8.11}$$

where we have used

$$\left| \frac{\partial(t_1, t_2)}{\partial(\tau, T)} \right| = 2.$$

To find the new field of integration A', consider the old field of integration A. We have

$$\int_0^t dt_1 \int_0^t dt_2 f(t_1, t_2) \Rightarrow 2\{ \int_0^t dT \int_0^T d\tau + \int_t^{2t} dT \int_0^{2t-T} d\tau \} g(\tau, T).$$

This procedure is illustrated in Fig. 8.4. With these changes, equation (8.11) yields

$$
\begin{aligned}
J(t) &= 2 \int_0^t dT e^{\eta T} \int_0^T d\tau w(\tau) + 2 \int_t^{2t} dT \int_0^{2t-T} d\tau w(\tau) \\
&= 2 \int_0^t dT e^{\eta T} W(T) + 2 \int_t^{2t} dT e^{\eta T} W(2t - T).
\end{aligned}
\tag{8.12}
$$

However, for long diffusion times $t >> t_c$, $W(t)$ tends to the constant value W. Therefore,

$$J(t) \approx 2 \int_0^{2t} dT e^{\eta T} W \approx \frac{2W}{\eta} \left[e^{2\eta t} - 1 \right] \tag{8.13}$$

and, substituting back into (8.8),

$$\langle u^2 \rangle = u_o^2 e^{-2\eta t} + \frac{2W}{\eta} \left[1 - e^{-2\eta t} \right] \tag{8.14}$$

Now let us consider two cases. First, for short diffusion times (i.e. small t), equation (8.14) reduces to

$$\langle u^2 \rangle \approx u_o^2.$$

Second, for large t,

$$e^{-2\eta t} \to 0,$$

and

$$\langle u^2 \rangle = 2W/\eta$$

That is, for long diffusion times, the motion is determined by fluctuations and the initial velocity is forgotten.

As the host fluid is in thermal equilibrium, the large particles come into equilibrium with it, due to collisions, as time goes on. We can demonstrate this approach to equilibrium by rearranging equation (8.14) and substituting the equilibrium value of $\langle u^2 \rangle = kT/m$, thus we can show that

$$\langle u^2 \rangle = \frac{kT}{m} + \left[u_0^2 - \frac{kT}{m} \right] e^{-2\eta t}. \tag{8.15}$$

Coming to equilibrium requires a coarse-grained description in which fine details for $t < t_c$ are smoothed out.

8.2   Fluctuation-dissipation relations

We now generalise the work of the previous section to the more general topic of fluctuation-dissipation relations. Moreover, we now extend our interest to two classes of phenomena. First, as in the preceding section, we are interested in Brownian motion or thermal noise. That is, phenomena which are driven by the fluctuations and with their mean response also controlled by them. Such systems are characterized by their two-time equilibrium correlation functions: $\langle F(t_1)F(t_2) \rangle$, $\langle u(t_1)u(t_2) \rangle$, $\langle x(t_1)x(t_2) \rangle$ and so on.

Second, we will also be interested in the effect of external fields. Equilibrium systems have high symmetry. If we apply an external field, such as electric, magnetic or pressure fields, then we break some of the symmetries, leading to new observables, such as the electric current (or polarization), magnetization and fluid flow.

The general subject, which embraces both topics, is *linear response theory* (note that the restriction to linearity rules out nonlinear optics or turbulence) and can be envisaged by treating the system as a 'black box', in which the response function can be related to the pair-correlation of relevant fluctuating variables at thermal equilibrium. The general result is known as a fluctuation-dissipation relation.

8.3   The response (or Green) function

In thermodynamics, the response functions of systems are macroscopic quantities such as the heat capacity or the magnetic susceptibility. However, in a microscopic description, the response function of a system is related to the Green function as encountered in the theory of differential equations. In the final section of this chapter, we shall show how to calculate the macroscopic response function from the microscopic form. In this section we introduce the concept of the Green function.

We begin by remarking that the Green function is of great importance in theoretical physics and that a proper introduction to it can be found in various texts on mathematical methods. However, for our present purposes, it will be sufficient to give a rather informal and pragmatic introduction to it here.

The idea arises in connection with the solution of the linear differential equations which are important in mathematical physics. Essentially, one can think of it either as a labour saving device or as a very powerful method of carrying out symbolic manipulations.

Suppose we consider, as a specific example, Laplace's equation for the electrostatic potential ϕ in a region where there are no sinks or sources. This may be written as

$$\nabla^2 \phi = 0, \tag{8.16}$$

INPUT

Response function

OUTPUT

External field

Response

Example:

External field B

Susceptibility χ

Magnetization   M
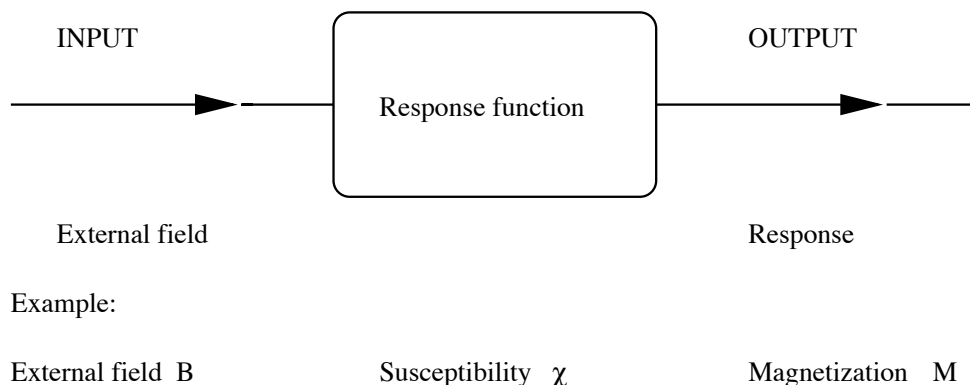
Figure 8.5: Schematic view of system response.

where we take the one-dimensional case for simplicity, with $\nabla^2 = d^2/dx^2$. This is known as the homogeneous form of the equation. If there are sources present—in the form of a continuous charge density $\rho(x)$, say—then the equation becomes

$$\nabla^2 \phi = \rho(x), \tag{8.17}$$

which is the inhomogeneous form and is known as Poisson's equation.

Now, Laplace's equation can be solved for a particular geometry and boundary conditions and the resulting solution is unique. In contrast, there are as many solutions of the Poisson equation as one can invent or envisage different charge distributions $\rho(x)$.

Exactly the same considerations would arise in other situations in mathematical physics. For instance, in the case of simple harmonic motion, the solution to the homogeneous equation will represent a sinusoidal oscillation (which is damped, if friction is included in the problem). However, if we connect a signal generator to the system, then there will be as many possible solutions (sine waves, square waves, sawtooth waves . . .) as the generator has output waveforms.

The labour saving aspect arises because we can often solve an 'almost homogeneous' equation and use the resulting unique solution (known as the Green function) to find the solution of the inhomogeneous cases in a straightforward way. To see this, let us write a general homogeneous differential equation in the form:

$$L\phi = 0, \tag{8.18}$$

where L stands for some combination of differential operators. For example, in the case of Laplace's equation, the operator L would be the Laplacian. Clearly L should be linear, that is it should not depend on ϕ.

Now, keeping to one dimension for simplicity, we rewrite this equation as

$$LG(x, x') = \delta(x - x'), \tag{8.19}$$

where $G(x, x')$ is the Green function and $\delta(x - x')$ is the Dirac delta function. There are many representations of the delta function, but the simplest is probably obtained from the use of the unit step function $\Theta(x - x')$, which is defined by:

$$\Theta(x - x') = \begin{cases} 1 & \text{for} \quad x > x' \\ 0 & \text{for} \quad x < x'. \end{cases}$$

Then we define the delta function to be the derivative of the unit step function, thus:

$$\delta(x - x') \equiv \frac{d\Theta(x - x')}{dx}. \tag{8.20}$$

We note that this implies that the delta function is zero everywhere except where $x = x'$, when it is infinite in value.

If we now consider the general form of the corresponding inhomogeneous equation, we may write this as

$$L\phi = \rho(x), \tag{8.21}$$

with the general solution

$$\phi(x) = \int G(x, x')\rho(x')dx'. \tag{8.22}$$

We can see how this comes about, as follows. Formally we may write the solution of the general inhomogeneous equation (8.22) as:

$$\phi(x) = L^{-1}\rho(x), \tag{8.23}$$

where the inverse of L is defined by the relationship $LL^{-1} = 1$. Now we wish to find the inverse of the operator L, and there are various methods of doing this. But for the purposes of our present informal treatment, we note that the inverse of L may be expressed in terms of the Green function and the delta function by means of equation (8.19), thus:

$$G(x, x') = L^{-1}\delta(x - x'), \tag{8.24}$$

where we have operated on each side of (8.19) from the left with L^{-1}. Now, we multiply each side of this equation by $\rho(x')$ and integrate with respect to x':

$$\phi(x) = \int G(x, x')\rho(x')dx' = \int L^{-1}\delta(x - x')\rho(x')dx' = L^{-1}\rho(x). \tag{8.25}$$

Then, when this result is taken in conjunction with equation (8.24), equation (8.23) for the general solution follows.

8.4   General derivation of the fluctuation-dissipation theorem

This is a generalization of our treatment of Brownian motion. The Langevin equation, in the form of (8.2) is now written as

$$\frac{du}{dt} + \eta u(t) = F(t). \tag{8.26}$$

As before, the random force is chosen such that

$$\langle F(t) \rangle = 0, \tag{8.27}$$

so that the molecular force is then specified in terms of its autocorrelation:

$$\langle F(t)F(t') \rangle = w(t - t') \tag{8.28}$$

The correlation function of the force satisfies

$$W(t) = \int_0^t w(\tau)d\tau, \tag{8.29}$$

where $W(t) \to W$ as $t \to \infty$ and W is a constant.

The Green function of the Langevin equation is

$$G(t, t') = e^{-\eta(t-t')}, \quad \text{for} \quad t \geq t'. \tag{8.30}$$

This may be verified by direct substitution into the Langevin equation with a delta function input. To simplify the mathematics, we choose the special case of 'white noise'. That is, the random force correlation takes the form

$$w(t - t') = W\delta(t - t'). \tag{8.31}$$

As before, we take the general solution of the Langevin equation to be given by equation (8.6), and we rewrite this in terms of a new dummy time variable s as

$$u(t) = u_0 e^{-\eta t} + e^{-\eta t} \int_0^t ds e^{\eta s} F(s). \tag{8.32}$$

Now we form the general two-time correlation of velocities at times t and t' as

$$
\begin{aligned}
\langle u(t) u(t') \rangle &= u_0^2 e^{-\eta(t+t')} \\
&+ e^{-\eta(t+t')} \int_0^t ds \int_0^{t'} ds' e^{\eta(s+s')} \langle F(s) F(s') \rangle,
\end{aligned} \tag{8.33}
$$

where we have substituted from (8.33) with appropriate amendments to give $u(t')$ as well as $u(t)$. Thus, invoking (8.32) for the case of white noise, we have

$$
\begin{aligned}
\langle u(t) u(t') \rangle &= u_0^2 e^{-\eta(t+t')} \\
&+ e^{-\eta(t+t')} \int_0^t ds \int_0^{t'} ds' e^{\eta(s+s')} W \delta(s - s'),
\end{aligned} \tag{8.34}
$$

and, using the sifting property of the delta function to eliminate s, we obtain

$$
\begin{aligned}
\langle u(t) u(t') \rangle &= u_0^2 e^{-\eta(t+t')} \\
&+ e^{\eta(t+t')} W \int_0^{t'} e^{2\eta s'} ds'.
\end{aligned} \tag{8.35}
$$

Then, doing the integral over s',

$$
\begin{aligned}
\langle u(t) u(t') \rangle &= u_0^2 e^{-\eta(t+t')} \\
&+ e^{-\eta(t+t')} \frac{W}{2\eta} \left[e^{2\eta t'} - 1 \right],
\end{aligned} \tag{8.36}
$$

re-arranging

$$
\begin{aligned}
\langle u(t) u(t') \rangle &= \frac{W}{2\eta} e^{-\eta t + \eta t'} \\
&+ \left[u_0^2 - \frac{W}{2\eta} \right] e^{-\eta t - \eta t'},
\end{aligned} \tag{8.37}
$$

and setting $t = t'$, we obtain

$$\langle u^2(t') \rangle = \frac{W}{2\eta} + \left[u_0^2 - \frac{W}{2\eta} \right] e^{-2\eta t'}. \tag{8.38}$$

Now if we multiply equation (8.39) through on the left-hand side by $G(t, t')$, and on the right-hand side by the explicit form of the Green function as given by equation (8.31), it is easily seen that we obtain $\langle u(t) u(t') \rangle$, as given by equation (8.38). Hence the general relationship is

$$\langle u(t) u(t') \rangle = G(t, t') \langle u^2(t') \rangle. \tag{8.39}$$

This is the most general form of the fluctuation–dissipation theorem. The significance of this result is that the response (or Green) function of the system is determined by the correlation of the fluctuations about equilibrium.

Chapter 9

Quantum dynamics

We have seen that Liouville's equation can be expressed in an operator (Poisson bracket) formalism which goes over naturally into a quantum formalism. We conclude this book with a brief look at the subject of quantum dynamics.

Although the introduction of a probability density ρ involves a form of coarse-graining in quantum mechanics, in that the phase information contained in the wave function is lost, the formalism still preserves the invariants of the Liouville equation. Accordingly, the general formalism is still not compatible with the second law of thermodynamics and a further coarse-graining is needed.

9.1 Fermi's master equation

Coarse-graining implies the discarding of information from our description of the system. Fermi suggested that this could be done by describing the system in terms of a set of approximate eigenstates $|i\rangle$. These are the eigenstates of a model Hamiltonian $\hat{H}_0$ which differs from the true Hamiltonian $\hat{H}$ by a small perturbation $\hat{h}$ (say). Thus:

$$\hat{H} = \hat{H}_0 + \hat{h}. \tag{9.1}$$

In other words, the $|i\rangle$ are **exact** for $\hat{H}_0$ but only approximate for $\hat{H}$.

The matrix elements in this basis are:

$$h_{ij} = \langle i|\hat{h}|j\rangle = h_{ji}^*, \tag{9.2}$$

and the last step follows from the fact that h is Hermitian.

This perturbation $\hat{h}$ induces quantum jumps between approximate states $|i\rangle$.

9.1.1 Fermi's golden rule

Fermi assumed that the system could jump from a state $|i\rangle$ with energy E_i into some narrow **band** of other states $|j\rangle$ having energy within δE of E_i. Using time-dependent perturbation theory, he showed that the probability per unit time of a jump from an initial state $|i\rangle$ to a final state $|j\rangle$ is given by:

$$\nu_{ij} = \frac{2\pi}{\hbar \delta E}|h_{ij}|^2. \tag{9.3}$$

This is: **Fermi's golden rule**.

Note:

1. According to the golden rule, ν_{ij} cannot be negative.

2. Because $h_{ij} = h_{ji}^*$, the jump rates obey the rule:

$$\nu_{ij} = \nu_{ji}. \tag{9.4}$$

This is the: **principle of jump rate symmetry**.

9.1.2 The master equation

This involves the same idea as in the Boltzmann equation but now applied to quantum jumps.

Note that ν_{ij} is:

1. a conditional probability;

2. a probability per unit time.

We can write down an analogue of the Boltzmann equation as:

The change of probability of the system being in state $|i\rangle$ = The probability of the system jumping into state $|i\rangle$ from all other states $|j\rangle-$ the probability of the system jumping out of state $|i\rangle$ into any other state $|j\rangle$.

Bearing all the above points in mind, we can write this as an equation:

$$dp_i = \left[\sum_j \nu_{ji}p_j - p_i \sum_j \nu_{ij}\right]dt, \tag{9.5}$$

or using jump rate symmetry

$$\frac{dp_i}{dt} = \sum_j \left(\nu_{ij}\left(p_j - p_i\right)\right). \tag{9.6}$$

This is the **master equation**.

It is first order in time and hence does not possess time-reversal symmetry.

9.2 Applications of the master equation

9.2.1 Diffusion

Consider diffusion on a lattice in one dimension. This could be the motion of a vacancy in a crystal that moves by changing places with atoms at lattice sites. Take the lattice sites to be labelled by positive or negative integer values of x, where $-N/2 \leq x \leq N/2$.

Suppose that the probability of the vacancy moving one step to the left or right in time interval dt is Ddt, then the jump rate is given by:

$$
\begin{aligned}
\nu_{ij} &= D \quad \text{if} \quad i = x \quad \text{and} \quad j = x \pm 1; \qquad &(9.7) \\
&= 0 \quad \text{otherwise.} &(9.8)
\end{aligned}
$$

Thus the master equation becomes

$$
\dot{p}_x = \sum_y \nu_{xy}\left(p_y - p_x\right) = D\left(p_{x-1} - p_x\right) + D\left(p_{x+1} - p_x\right). \qquad (9.9)
$$

This is the master equation for a random walk: specifically, a continuous time random walk on a discrete lattice.

Once the walk has gone on for a sufficiently large number of steps, we can replace p_i by the continuous $p(x,t)dx$ and the right hand side is the difference of two finite differences which turns into the Laplacian. Hence the master equation turns into the usual diffusion equation.

9.2.2 Macroscopic systems

The concept of the master equation can be applied directly to macroscopic systems provided that they are *Markovian* in nature. This means that probabilities only depend on current values and not on the history of the process.

Chapter 10

Consequences of time-reversal symmetry

We have seen that coarse-graining ensures that the statistical description of the system complies with the second law and is not reversible in time.

Nevertheless, the underlying microphysics is still time-reversal symmetric and paradoxically this has deep consequences for non-equilibrium thermodynamics.

10.1 Detailed balance

In equilibrium we can write

$$\nu_{ij} p_i^{eq} = \nu_{ji} p_j^{eq}, \tag{10.1}$$

which is known as the **principle of detailed balance**. This follows from the principle of equal *a priori* probabilities, which in this case takes the form

$$p_i^{eq} = p_j^{eq}, \tag{10.2}$$

and from the principle of jump rate symmetry.

The principle of detailed balance states that, on average, the actual rate of quantum jumps from i to j is the same as from j to i. This is a stronger statement than the master equation which only says that there is overall balance (in equilibrium) between the rates of jumping into and out of state i. The result is very powerful, because it applies not only to individual states but to any grouping of them.

For example, for two *groups* of states A and B, the overall rate of transitions from group A to group B is balanced, in equilibrium, by those from B to A:

$$\nu_{AB} p_A^{eq} = \nu_{BA} p_B^{eq}. \tag{10.3}$$

Hence detailed balance arguments can be used for subsystems within a large isolated system; and, by extension, for systems which are not isolated. In these cases, the principle is far from obvious, since once states are grouped together in this fashion:

$$\nu_{AB} \neq \nu_{BA} \quad \text{and} \quad p_A \neq p_B. \tag{10.4}$$

Nevertheless, detailed balance holds, in equilibrium, in the general form eqn (10.1).

10.2 Dynamics of fluctuations

Consider some fluctuating thermodynamic variable x of zero mean. For example, this could be local magnetization or local density. It follows that x satisfies:

$$\langle x \rangle = 0; \qquad \langle x^2 \rangle^{1/2} \neq 0,$$

and hence it is usual to characterize any fluctuation about a mean value by its root-mean-square value. In addition, it can be important to know to what extent fluctuations at different times are correlated.

For this reason, we introduce the *correlation function* for different times t and t',

$$\langle x(t) x(t') \rangle \equiv \langle x(t) x(t + \tau) \rangle, \tag{10.5}$$

where τ is referred to as the *lag time*, and is given by $\tau = t' - t$.

In equilibrium (steady or stationary state) this must be independent of the initial time t and hence:

$$\langle x(t)x(t+\tau)\rangle = M_{xx}(\tau). \tag{10.6}$$

Different fluctuating variables can be correlated with each other, for example the magnetization at two nearby places is correlated. To study this we can define similarly

$$\langle x(t)y(t')\rangle = M_{xy}(t'-t), \tag{10.7}$$

for any pair of variables x and y. Here M_{xy} is the *dynamic correlation matrix*, of which $M_{xx}(\tau)$ is a diagonal element.

Time reversal symmetry of the microphysics implies that

$$\langle x(t)y(t')\rangle = \langle x(t')y(t)\rangle \tag{10.8}$$

or

$$M_{xy}(\tau) = M_{xy}(-\tau). \tag{10.9}$$

However, $M_{xy}(-\tau)$ satisfies

$$
\begin{aligned}
M_{xy}(-\tau) &= M_{xy}(t-t') = \langle x(t)y(t')\rangle \\
&= \langle y(t')x(t)\rangle = M_{yx}(t'-t) \\
&= M_{yx}(\tau).
\end{aligned}
\tag{10.10}
$$

Hence, combining these two results, we have

$$M_{xy}(\tau) = M_{yx}(\tau). \tag{10.11}$$

Thus the dynamic correlation matrix is symmetric in the indices x and y.

10.2.1 Linear response theory

Let us now consider the effect of a small perturbation on an equilibriun system. We represent this by a 'thermodynamic force' F_x which leads to a 'displacement' x. In practice, F_x could be a mechanical force and x would be a particle displacement. Or, for instance, F_x could be a locally applied magnetic field and x would be the magnetization.

In either case the work done on the system leads to a change in system energy and formally one adds $-F_x x$ to the Hamiltonian.

Let us suppose that F_x was applied to the system at $t = -\infty$ and then turned off at $t = 0$. Then the resulting mean response of $y(t)$ decays away irreversibly according to:

$$\langle y(t)\rangle = R_{yx}(t)F_x. \tag{10.12}$$

This defines the response function matrix $R_{yx}(t)$ where $t \geq 0$.

10.2.2 The fluctuation-dissipation theorem

We have met the general form of the fluctuation-dissipation relation as equation (8.40), which we derived from the Langevin equation. It is also possible to obtain this result from linear response theory and, in the notation of this chapter, we have:

$$M_{xx}(0)R_{yx}(t) = M_{yx}(t), \tag{10.13}$$

and it is readily verified that this is the same form as (8.40). In other words, the fluctuation induced by a perturbation will on average decay just as if it were a spontaneous fluctuation from equilibrium.

For microscopic systems in equilibrium we have $M_{xx}(0) \equiv \langle x^2(0) \rangle \equiv kT$ and the fluctuation-dissipation equation may be written as:

$$kTR_{yx}(t) = M_{yx}(t). \tag{10.14}$$

Thus the 'response' to perturbations is determined by the correlation of fluctuations about equilibrium.

10.3 Onsager's theorem

Finally, if we combine the fluctuation-dissipation relation, in the form of equation (10.14), with equation (10.11) which expresses the symmetry, with respect to its indices, of the correlation function, we obtain:

$$R_{xy}(t) = R_{yx}(t). \tag{10.15}$$

This is Onsager's theorem and states that the response function matrix is symmetric in its indices. As we have seen that (10.11) follows directly from time reversal symmetry of the microphysics, we have the interesting result that this underlying time reversal symmetry constrains the irreversible behaviour of a macroscopic system perturbed away from equilibrium.

The surprising aspect is that Onsager's theorem states that the mean response of a variable x to a force F_y is entirely determined by the mean response of y to F_x.

There are many applications for this theorem but we shall just mention that Onsager's result can be used to predict the magnitude of the Peltier effect from measurements of the thermoelectric effect.

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