

## Chapter 2 Fundamentals of Statistical Mechanics

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### 2.1 Microstates and Macrostates

In classical mechanics, a **microstate** of a system is a complete description of what every particle in the system is doing. At a given instant of time, this involves specifying the position and momentum of every particle. When we observe a macroscopic system, we do not see this level of detail. Instead, we group together macroscopically indistinguishable microstates into **macrostates**. These are the states that we deal with in classical thermodynamics, and as in the previous chapter, they are specified in terms of a (relatively small) set of state variables, such as the energy, volume and particle number for an isolated, homogeneous material. Note that macrostates are defined in terms of “macroscopic indistinguishability” which is subjective to the extent that it depends on the accuracy to which we make the measurements that tell the states apart.

It turns out that a key operation in statistical mechanics is counting the number of microstates which are accessible to the system while being “consistent” with a given macrostate. This is called the **statistical weight** of the macrostate, and is denoted by  $\Omega$ . In classical mechanics, this counting process is **not** well-defined, since the dynamical values of the particles in a system can assume a continuum of values and there are no discrete microstates. By using the quantum mechanical description of a system, however, we can give a well-defined prescription for finding its thermodynamical properties, so long that the volume is finite. Later in the course, we shall treat an ideal gas, but since the quantum mechanics required to describe this is somewhat complicated, we start with a system which is much simpler to analyse from a quantum mechanical viewpoint.

#### 2.1.1 Some essential quantum mechanics

In your previous courses in quantum mechanics, you have probably considered only a **single particle**. This is not a macroscopic system, and so one of the things we shall need to learn is to how to consider systems with **many particles** in quantum mechanics, since a microstate is a state of **all** the particles which make up the system. Let us start however by considering the familiar example of a single particle confined in one dimensional “box” extending from  $x = 0$  to  $x = L$  with infinitely high walls. As we know, the particle is described by a complex-valued **wave function**  $\psi(x, t)$  which satisfies Schrödinger’s equation. This wave function is such that  $|\psi(x, t)|^2$  tells us the probability density of finding the particle at  $x$  at time  $t$ . Out of all of these wave functions, there are some special ones called the **stationary states**. These have the property that  $|\psi(x, t)|^2$  is **independent of time**. These form a **discrete** set, which we may label as  $\psi_n(x, t)$  where  $n$  is the **quantum number**. Stationary states turn out to be states of definite energy (i.e., if we look at a collection of quantum systems which are each in the  $n$ ’th stationary state and measure the energy of each, we always get the same definite answer  $E_n$ ) and are thus also called **energy eigenstates**. The wave function of the  $n$ ’th stationary state can be written as

$$\psi_n(x, t) = \phi_n(x) \exp\left(-\frac{iE_n t}{\hbar}\right) \quad (2.1)$$

where for the particle in the box of length  $L$ , the spatial part of the wave function is

$$\phi_n(x) = \begin{cases} \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right) & \text{for } 0 \leq x \leq L \\ 0 & \text{otherwise} \end{cases} \quad (2.2)$$

where  $n \in \{1, 2, 3, \dots\}$  and the **energy eigenvalues** are

$$E_n = \frac{n^2 \hbar^2 \pi^2}{2mL^2} \quad (2.3)$$

An arbitrary wave function of the system can be written as a linear combination of the  $\psi_n(x, t)$ . In statistical mechanics, we identify **microstates** with the **stationary states** of the system. Thus, we see that a **single particle** in a one dimensional box with infinitely high walls already has an infinite number of discrete microstates.

Even this apparently simple problem already has an infinite number of microstates, and is already more complicated than we would like. Fortunately, in quantum mechanics there are simpler (but perhaps less familiar) systems which have a **finite number** of discrete energy eigenstates. The simplest non-trivial single-particle system has only **two** energy eigenstates, and is (not surprisingly) called a two-level system. A physical example of a two-level system is the magnetic moment of an electron (or of any **spin-half** particle) in an applied magnetic field.

Suppose that we have a magnetic field  $\mathbf{B}$  oriented along the  $z$  direction. If we place an electron within this field, it acts like an elementary magnet with a magnetic moment  $\boldsymbol{\mu}$ . Classically, one would think that it is possible to point this magnetic moment in any direction, so that it has an energy of  $-\boldsymbol{\mu} \cdot \mathbf{B} = -\mu B \cos \theta$  in the field. Quantum mechanically, we find that this is not the case. For electrons (and other particles “spin-half” particles), measuring the energy always yields one of only two possible values, namely  $+\mu B$  or  $-\mu B$  which are the energy eigenvalues of the two energy eigenstates of the system. It is as though the elementary magnet could only point in one of two directions which we can call “spin up”, where  $\boldsymbol{\mu}$  is aligned parallel to  $\mathbf{B}$ , with energy  $-\mu B$  or “spin down”, where  $\boldsymbol{\mu}$  is anti-parallel to  $\mathbf{B}$ , with energy  $\mu B$ . A system of a single elementary magnet of spin-half in a magnetic field has only two microstates.

## 2.2 A Simple Soluble System

Let us now consider a system of  $N$  elementary magnets of spin half in an external magnetic field. We suppose the magnets to be **fixed in place** e.g., in a crystal lattice, so that they can be **distinguished** from each other by their location. We shall further suppose that the magnets do not interact with each other but only with the applied external magnetic field. Because of the assumption of no interaction, an energy eigenstate of the  $N$  particle system is one for which each of the  $N$  elementary magnets is in an energy eigenstate. This shows that the  $N$  particle system has  $2^N$  energy eigenstates, each of which counts as a microstate of the  $N$  particle system.

For example, for the case of  $N = 3$ , the table shows the eight energy eigenstates and the energy eigenvalue associated with each eigenstate

Magnet 1	Magnet 2	Magnet 3	Energy eigenvalue
up	up	up	$-3\mu B$
up	up	down	$-\mu B$
up	down	up	$-\mu B$
up	down	down	$\mu B$
down	up	up	$-\mu B$
down	up	down	$\mu B$
down	down	up	$\mu B$
down	down	down	$3\mu B$

What are the **macrostates** of this system? The obvious state variable for this system is the energy. If we use this to distinguish the macrostates, and if we assume that the resolution of our equipment is fine enough that we can distinguish the different energies, we see that there are four macrostates which have energies  $3\mu B$ ,  $\mu B$ ,  $-\mu B$  and  $-3\mu B$  respectively. Looking at this table, we see that although there is only one microstate corresponding to each of the macrostates of energy  $3\mu B$  and  $-3\mu B$ , there are three microstates corresponding to each of the macrostates of energy  $\mu B$  and energy  $-\mu B$ . We call the number of microstates corresponding to a single macrostate the **statistical weight** of the macrostate, and denote it by the symbol  $\Omega$ . For example, in this system we have  $\Omega(E = -\mu B) = 3$ .

We can straightforwardly generalize these considerations to the case of arbitrary  $N$ . The energy eigenvalue corresponding to a particular energy eigenstate depends of the excess of up spins to down spins. If there are  $n$  up spins and  $N - n$  down spins, the energy eigenvalue is

$$E(n) = -n\mu B + (N - n)\mu B = (N - 2n)\mu B. \quad (2.4)$$

We may thus use  $n$  as a label for our macrostates. The number of microstates which correspond to a macrostate with  $n$  up spins is given by the number of ways of choosing  $n$  objects from among  $N$ . Thus the statistical weight of the macrostate  $n$  is

$$\Omega(n) = \binom{N}{n} = \frac{N!}{n!(N-n)!}. \quad (2.5)$$

Let us suppose that our system of  $N$  elementary magnets in a magnetic field  $\mathbf{B}$  is completely **isolated** from the environment so that its energy is **fixed**. In this situation, the value of  $n$  (and hence the macrostate) is determined by the energy

$$n = \frac{1}{2} \left( N - \frac{E}{\mu B} \right) \quad (2.6)$$

but of course, the **microstate** is not known. What we do know, however, is that the system is going to be in one of the  $\Omega(n)$  microstates that are consistent with the macroscopic information. The **fundamental assumption** of statistical mechanics is that it is **equally likely** that the system is in **any** of the **accessible microstates**. If we label the **microstates** by  $r$  and denote the energy of the  $r$ 'th eigenstate by  $E_r$ , we are assuming that

$$\Pr(\text{system is in microstate } r) = \begin{cases} \frac{1}{\Omega(n)} & \text{if } E_r = (N - 2n) \mu B \\ 0 & \text{otherwise} \end{cases} \quad (2.7)$$

We also claim that the quantity which corresponds to the **entropy of the macrostate**  $n$  is

$$S(n) = k \log \Omega(n) \quad (2.8)$$

where  $k$  is Boltzmann's constant and  $\log$  denotes the natural logarithm. Notice that we are assuming here that we can measure the energy accurately enough that it is possible to distinguish the energy levels. If the applied magnetic field is so weak (or the thermal isolation is so poor) that we cannot distinguish the macrostates by their energy, **all microstates** become accessible and the total statistical weight is  $2^N$ .

Recall that in classical thermodynamics, once we can write  $S$  as a function of  $E$ ,  $V$  and  $N$ , we can derive all the properties of the system. Here, the energy depends on  $n$  and the volume does not affect the system. For the system of  $N$  elementary magnets we see that

$$S(n) = k \log \frac{N!}{n!(N-n)!}. \quad (2.9)$$

This may be simplified with the help of **Stirling's approximation** which states that for large  $N$ ,

$$N! \approx \sqrt{2\pi} N^{N+1/2} \exp\left(-N + \frac{1}{12N} + \dots\right). \quad (2.10)$$

and so

$$\log N! \approx \frac{1}{2} \log(2\pi) + N \log N + \frac{1}{2} \log N - N + \frac{1}{12N} + \dots \quad (2.11)$$

Let us look at the relative importance of these terms for  $N = 10^{23}$ . Evaluating each of the above terms gives

$$\log 10^{23}! \approx 0.9 + 5.3 \times 10^{24} + 26 - 10^{23} + 8 \times 10^{-25} + \dots \quad (2.12)$$

It is apparent that to a very good approximation,

$$\log N! \approx N \log N - N. \quad (2.13)$$

Thus

$$\begin{aligned} S(n) &= k(N \log N - N - n \log n + n - (N-n) \log(N-n) + (N-n)) \\ &= k(N \log N - n \log n - (N-n) \log(N-n)). \end{aligned} \quad (2.14)$$

Let us consider graphs of  $\Omega(n)$  and  $S(n)$ , where  $n$  can range from zero to  $N$ . Since we are going to be assuming that  $N$  is large, we can consider  $n$  as being essentially a continuous variable, and replace summations over  $n$  by integrations. The function  $\Omega(n)$  is an (unnormalized) binomial distribution with its peak at  $n = N/2$ , at which  $\Omega(N/2) = \binom{N}{N/2}$ . The sum over all  $n$  gives the total number of microstates which is  $2^N$ .

The graph of  $S(n)$  also has a peak of  $N/2$  at which its maximum value is  $k \log \binom{N}{N/2}$ . Using Stirling's approximation the peak is over-estimated as  $kN \log 2$  which happens to be equal to the area under the true graph.

### 2.2.1 Gaussian Approximation to $\Omega(n)$

If we consider a binomial probability distribution in which we have  $N$  trials and a probability of success  $p$  on each trial, the probability that there are  $n$  successes is given by

$$\Pr(n) = \binom{N}{n} p^n (1-p)^{N-n} \quad (2.15)$$

The mean of this distribution is  $Np$  and the standard deviation is  $\sqrt{Np(1-p)}$ . If we consider the case in which  $p$  is not so close to 0 or 1 that the mean lies within a few standard deviations of the endpoints 0 or  $N$ , it is possible to approximate  $\Pr(n)$  by a Gaussian probability density with the same mean and standard deviation. Recall that

$$\Pr(x) = \frac{1}{\sigma\sqrt{2\pi}} \exp\left[-\frac{1}{2}\left(\frac{x-\mu}{\sigma}\right)^2\right] \quad (2.16)$$

is the general expression for a Gaussian with mean  $\mu$  and standard deviation  $\sigma$ . For large  $N$ , we may neglect the discrete nature of the variable and so

$$\Pr(n) \approx \frac{1}{\sqrt{2\pi Np(1-p)}} \exp\left[-\frac{(n-Np)^2}{2Np(1-p)}\right] \quad (2.17)$$

An important special case of this result occurs for  $p = 1/2$  whereupon

$$\binom{N}{n} \left(\frac{1}{2}\right)^N \approx \sqrt{\frac{2}{\pi N}} \exp\left[-\frac{2}{N}(n-N/2)^2\right] \quad (2.18)$$

or

$$\binom{N}{n} \approx 2^N \sqrt{\frac{2}{\pi N}} \exp\left[-\frac{2}{N}(n-N/2)^2\right] \quad (2.19)$$

This has its peak at  $x = N/2$ . We can alternatively use the true value at the peak by writing

$$\binom{N}{n} \approx \binom{N}{N/2} \exp\left[-\frac{2}{N}(n-N/2)^2\right] \quad (2.20)$$

This is very sharply peaked about the maximum. The width of the peak is  $\sigma = \sqrt{N}/2$ .

For our system of  $N$  spins,

$$\Omega(n) = \binom{N}{n} \approx \binom{N}{N/2} \exp\left[-\frac{2}{N}(n-N/2)^2\right] \quad (2.21)$$

$$S(n) \approx k \log \binom{N}{N/2} - \frac{2k}{N}(n-N/2)^2 \quad (2.22)$$

In Figure 2.1 we show graphs of the entropy for a system of  $N = 1000$  spins using expression (2.14) for the solid line and expression (2.22) for the dashed line.

The energy of the spin system is  $E(n) = (N-2n)\mu B$ . As functions of the energy, we find

$$\Omega(E) \approx \binom{N}{N/2} \exp\left[-\frac{E^2}{2N\mu^2 B^2}\right] \quad (2.23)$$

which has width  $\sigma = \mu B\sqrt{N}$  and the entropy is

$$S(E) \approx k \left[ N \log 2 + \frac{1}{2} \log \left( \frac{2}{\pi N} \right) - \frac{E^2}{2N\mu^2 B^2} \right] \quad (2.24)$$

Notice that the first two terms in the brackets are independent of the energy  $E$ . This is a quadratic approximation to the true expression for the entropy found previously.

Recall that in classical thermodynamics, knowing  $S$  as a function of  $E$ ,  $V$  and  $N$  allows one to determine all quantities of interest. For the spin system, we are assuming that the volume does not affect  $S$  and so the above gives a complete thermodynamic characterization of the system. We shall return to calculating some of these properties after establishing the definition of temperature in the context of statistical mechanics.

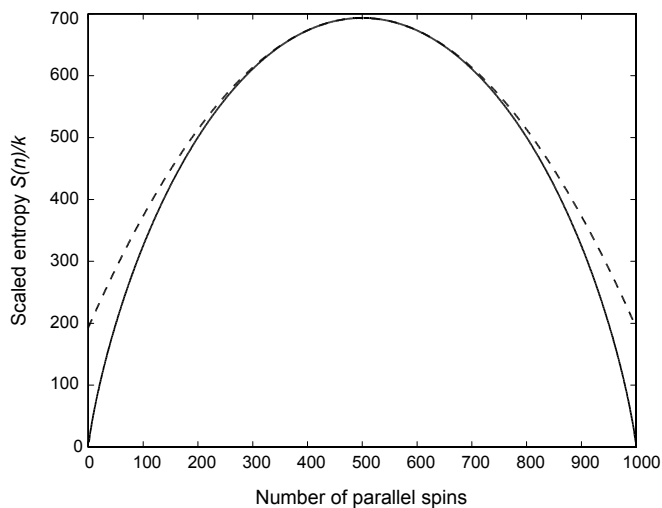


Figure 2.1 Entropy  $S(n)$  of a system of  $N = 1000$  spins (solid line) together with the Gaussian approximation (dashed line).

## 2.3 Thermal Equilibrium of two Systems

Suppose we have two systems, the first with energy  $E_1^{(0)}$ , volume  $V_1^{(0)}$  and with  $N_1^{(0)}$  particles, and the second with energy  $E_2^{(0)}$ , volume  $V_2^{(0)}$  and with  $N_2^{(0)}$  particles. At some time, these systems are placed in **thermal contact**, so that they can exchange energy with each other via heat flow. Given that they are isolated from the rest of the universe, we want to find out how the composite system behaves, and what is the equilibrium state of the composite system.

Let us write  $\Omega_1(E_1)$  for the statistical weight of the first system when its energy is  $E_1$  and  $\Omega_2(E_2)$  for the statistical weight of the second system when its energy is  $E_2$ . The entropies are then given by  $S_i(E_i) = k \log \Omega_i(E_i)$ . While the systems are separated, the microstates (energy eigenstates) of the composite system are found by supposing that each system is individually in an energy eigenstate, and adding the energies of the components. If the energy of the first system is  $E_1$  and that of the second is  $E_2$ ; for each microstate of the first system, the second can be in any one of  $\Omega_2(E_2)$  microstates. The number of microstates of the composite system associated with this distribution of energy is  $\Omega_{\text{tot}}(E_1, E_2) = \Omega_1(E_1) \Omega_2(E_2)$ .

In this problem, the volumes and particle numbers of the individual systems are fixed. However, after thermal contact is established, the energies  $E_1$  and  $E_2$  can in principle have any values which satisfy

$$E_1 + E_2 = E_{\text{tot}} = E_1^{(0)} + E_2^{(0)}, \quad (2.25)$$

since the composite system is isolated. In Figure 2.2, this means that the systems must lie somewhere on the constraint line shown. By the fundamental assumption, all *microstates* along this line are equally likely. However, this does **not** mean that any combination of energies along the line is equally likely, since the microstates are **unevenly distributed** on the  $E_1 E_2$  plane, and in particular along the constraint line. The statistical weight  $\Omega_1(E_1) \Omega_2(E_2)$  tells us the **density** of microstates on the plane. For a macroscopic system, this weighting function is very highly peaked, so that given a random microstate along the constraint line, it is overwhelmingly probable that the energy distribution between the systems for this state is very close to the most probable values of  $E_1$  and  $E_2$  shown in the figure.

It is straightforward to compute the most probable energies for this problem. We need to **maximize**  $\Omega_1(E_1) \Omega_2(E_2)$  subject to the **constraint**  $E_1 + E_2 = E_{\text{tot}}$ . This requires

$$\begin{aligned} 0 &= \frac{d}{dE_1} \Omega_1(E_1) \Omega_2(E_{\text{tot}} - E_1) \\ &= \Omega_2(E_{\text{tot}} - E_1) \Omega_1'(E_1) - \Omega_1(E_1) \Omega_2'(E_{\text{tot}} - E_1) \end{aligned} \quad (2.26)$$

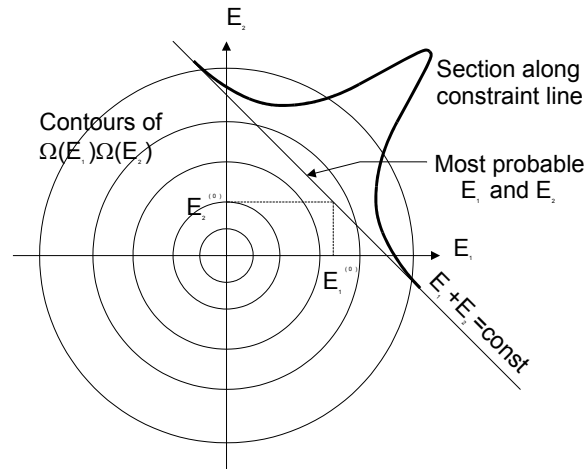


Figure 2.2 Statistical weights as a function of energy for two systems brought into thermal contact. The most probable state is where the statistical weight is a maximum along the energy constraint line.

Dividing by  $\Omega_1(E_1)\Omega_2(E_{\text{tot}} - E_1)$  and identifying  $E_2 = E_{\text{tot}} - E_1$ , we see that

$$0 = \frac{\Omega'_1(E_1)}{\Omega_1(E_1)} - \frac{\Omega'_2(E_2)}{\Omega_2(E_2)} \quad (2.27)$$

or

$$\frac{\partial}{\partial E_1} \log \Omega_1(E_1) = \frac{\partial}{\partial E_2} \log \Omega_2(E_2). \quad (2.28)$$

Since the entropy is defined as  $S = k \log \Omega$ , the condition for thermal equilibrium can also be written as

$$\frac{\partial S_1}{\partial E_1} = \frac{\partial S_2}{\partial E_2} \quad (2.29)$$

or, recalling that

$$\frac{1}{T} = \frac{\partial S}{\partial E} \quad (2.30)$$

we see that  $T_1 = T_2$  at thermal equilibrium. Note that in statistical mechanics, we regard 2.30 as the **definition** of temperature.

The similarities and differences between this statistical mechanics argument and the classical thermodynamics argument for this result should be noted. In statistical mechanics, the energies of the two systems are each not absolutely precisely defined when thermal equilibrium is reached, since energy can still flow between the systems. Despite this, for a macroscopic system, the fluctuations away from the most probable values are usually extremely small indeed, and so for practical purposes, we **can** assign an energy to each system. In classical thermodynamics, the tendency for a system to reach a state of maximum entropy is postulated as a law of thermodynamics. In the statistical mechanics context, this is seen simply as a probabilistic result following from the assumption of equal probabilities for the accessible microstates together with the way the microstates are distributed, as given by the statistical weights of the various macrostates.

Let us now compute the **direction** of heat flow as the composite system moves towards the most probable (maximum entropy) state. The change of entropy  $\Delta S$  associated with an amount of energy  $\Delta E$  being transferred **from** system 1 **to** system 2 is

$$\begin{aligned} \Delta S &= \Delta S_1 + \Delta S_2 = \frac{\partial S_1}{\partial E_1} (-\Delta E) + \frac{\partial S_2}{\partial E_2} (\Delta E) \\ &= \left( \frac{1}{T_2} - \frac{1}{T_1} \right) \Delta E \end{aligned}$$

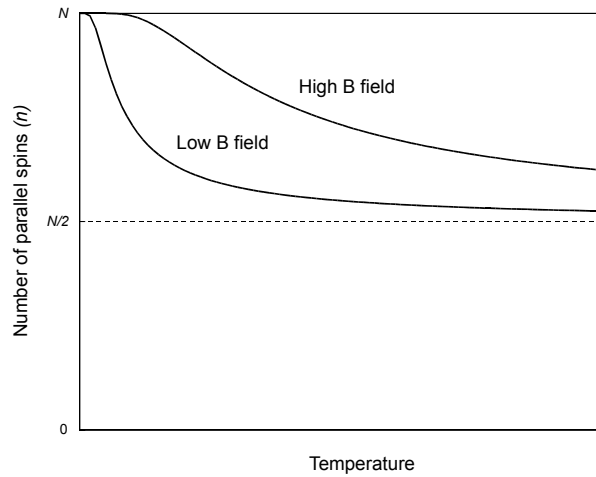


Figure 2.3 Number of parallel spins as a function of temperature for the system of  $N$  spins in a magnetic field.

In the process of approaching equilibrium  $\Delta S > 0$ . In order for  $\Delta E$  to be positive  $T_2^{-1} > T_1^{-1}$  or  $T_2 < T_1$ . Thus our definition of temperature is consistent with the idea that heat flows spontaneously from hot objects to cold objects.

**Example: Temperature of the spin system.**

In the system of  $N$  elementary spin-half magnets of magnetic moment  $\mu$  in a magnetic field  $B$ , find the temperature of the system if  $n$  of the spins are up (i.e., aligned with the magnetic field).

We have from (2.14) that

$$\left(\frac{\partial S}{\partial n}\right)_N = k \log\left(\frac{N-n}{n}\right) \quad (2.31)$$

Since the energy is related to  $n$  via  $E(n) = (N - 2n)\mu B$ , we see that

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_N = \frac{k}{2\mu B} \log\left(\frac{n}{N-n}\right) = \frac{k}{2\mu B} \ln\left(\frac{N\mu B - E}{N\mu B + E}\right) \quad (2.32)$$

Similarly we can write  $n$  as a function of  $T$ , yielding

$$n = \frac{N}{1 + \exp\left(-\frac{2\mu B}{kT}\right)} \quad (2.33)$$

where  $x = \mu B/(kT)$ . This graph is shown in Figure 2.3. At low temperatures  $x \rightarrow \infty$  and  $n \rightarrow N$ , whereas at high temperatures,  $x \rightarrow 0$  and  $n \rightarrow N/2$ . This is as we would expect intuitively. At low temperatures, the elementary magnets align parallel with the external field in order to minimize the energy, while at high temperatures, the elementary magnets are pointing randomly up or down, giving an average of half pointing upwards. When the magnetic field is high, the spins tend to be aligned even at higher temperatures, since the “energy cost” of flipping to an antiparallel state is large.

**Example: Adiabatic magnetic cooling**

For a reversible (quasi-static) adiabatic change, we know from classical thermodynamics that the **entropy** remains constant. Let us suppose that we prepare a system of spins in a magnetic field at a given temperature, thermally isolate the system and then slowly reduce the magnetic field. From the expression (2.14), it is apparent that the entropy depends only on the number of up spins  $n$ . This means that during the reversible adiabatic process, the number of up pointing spins does not change. Since we know that

$$\frac{1}{T} = \frac{k}{2\mu B} \log\left(\frac{n}{N-n}\right), \quad (2.34)$$

it is apparent that  $T \propto B$  if  $n$  is fixed. Thus during the reduction of the magnetic field from  $B_i$  to  $B_f$  say, the temperature will also be reduced from  $T_i$  to  $T_f$  where

$$T_f = T_i \left( \frac{B_f}{B_i} \right) \quad (2.35)$$

## 2.4 Thermal and Mechanical Equilibrium of two Systems

We can extend the above considerations to a situation where two systems are placed in thermal and mechanical contact so that they can not only exchange heat energy but are also able to change their volumes so as to satisfy the constraints

$$E_1 + E_2 = E_{\text{tot}} = E_1^{(0)} + E_2^{(0)} \quad (2.36)$$

$$V_1 + V_2 = V_{\text{tot}} = V_1^{(0)} + V_2^{(0)} \quad (2.37)$$

If the entropy functions of the two systems are  $S_1(E_1, V_1, N_1)$  and  $S_2(E_2, V_2, N_2)$ , the microstates of the composite system can explore any states consistent with the above constraints. However, the overwhelming majority of these will lie in the most probable macrostate which is the one which maximizes

$$S = S_1(E_1, V_1, N_1^{(0)}) + S_2(E_2, V_2, N_2^{(0)}) \quad (2.38)$$

subject to the constraints. In order to find the condition(s) for this maximum,

$$\begin{aligned} 0 &= \frac{\partial S}{\partial E_1} = \frac{\partial S_1}{\partial E_1} + \frac{\partial S_2}{\partial E_2} \frac{\partial E_2}{\partial E_1} \\ &= \frac{\partial S_1}{\partial E_1} - \frac{\partial S_2}{\partial E_2} \end{aligned} \quad (2.39)$$

which is the usual condition for the equality of the temperatures. We also need to satisfy

$$0 = \frac{\partial S}{\partial V_1} = \frac{\partial S_1}{\partial V_1} - \frac{\partial S_2}{\partial V_2}. \quad (2.40)$$

From our previous discussion of the fundamental thermodynamic relation, we know that

$$\frac{P}{T} = \frac{\partial S}{\partial V} \quad (2.41)$$

and so, we obtain the result that for systems in thermal and mechanical equilibrium, the temperatures are equal and the pressures are equal. We shall give a statistical mechanics argument for (2.41) later.

## 2.5 Equilibrium of a System in Thermal Contact with a Heat Bath

Instead of considering an **isolated system**, we now consider a system in thermal contact with a heat bath of temperature  $T$ . The heat bath is supposed to be so large that its temperature does not change when heat flows into or out of it. In order to make our previous considerations apply, we consider the system and heat bath together as a composite system which is **isolated** from the rest of the universe.

In this situation, although the **total** energy of system and heat bath is a constant, the energy of the system alone can fluctuate due to heat exchange between it and the bath. Thus it is no longer the case that the microstates of the system can be classified as being accessible (and occurring with equal probabilities) if they have the correct energy and inaccessible if they have the wrong energies. Instead, there is a certain **probability** that the system is in a particular microstate, and this is what we want to compute.

### 2.5.1 Probability of each system microstate

Let us label the **system microstates** by the index  $r$ . Each system microstate is an energy eigenstate of the system, and let us suppose that the energy eigenvalues are ordered such that

$$E_1 \leq E_2 \leq E_3 \leq \dots \leq E_r \leq \dots \quad (2.42)$$

What is the probability that the system is in the microstate  $r$ ? It is simply the fraction of all microstates of the **composite system** which have this property. All that we know about the heat bath when we are told that the system is in state  $r$  is that the energy of the heat bath is

$$E_B = E_{\text{tot}} - E_r. \quad (2.43)$$

If  $\Omega_B(E_B)$  is the statistical weight of the **bath** when its energy is  $E_B$ , then the probability  $p_r$  that the system is in **microstate**  $r$  is

$$p_r = \frac{\text{No. of microstates of composite system in which system is in microstate } r}{\text{Total number of microstates of composite system}} \quad (2.44)$$

$$= \frac{\Omega_B(E_{\text{tot}} - E_r)}{\sum_{r'} \Omega_B(E_{\text{tot}} - E_{r'})} \quad (2.45)$$

where the sum in the denominator is over **all** the system microstates. This simply acts as a normalizing constant.

In order to evaluate the numerator, we express  $\Omega_B$  in terms of the entropy of the bath  $S_B$  and carry out a Taylor expansion about  $E_{\text{tot}}$ .

$$\begin{aligned} \Omega_B(E_{\text{tot}} - E_r) &= \exp \left[ \frac{S_B(E_{\text{tot}} - E_r)}{k} \right] \\ &\approx \exp \left[ \frac{1}{k} \left\{ S_B(E_{\text{tot}}) - E_r \left( \frac{\partial S_B}{\partial E} \right)_{E_{\text{tot}}} \right\} \right] \end{aligned} \quad (2.46)$$

By definition of the temperature of the bath,

$$\frac{\partial S_B}{\partial E} \equiv \frac{1}{T} \quad (2.47)$$

and so

$$p_r \propto \Omega_B(E_{\text{tot}} - E_r) \propto \exp \left( -\frac{E_r}{kT} \right) = \exp(-\beta E_r) \quad (2.48)$$

where  $\beta \equiv 1/(kT)$ .

The constant of proportionality may be found by **normalization**, since we must have  $\sum_r p_r = 1$ . We write

$$p_r = \frac{\exp(-\beta E_r)}{Z} \quad (2.49)$$

where

$$Z = \sum_r \exp(-\beta E_r) \quad (2.50)$$

is called the **partition function**. The relationship (2.49) for the probability that the system is in a given **microstate** when it is in **thermal contact** with a **heat bath** at temperature  $T$  is known as the **Boltzmann distribution**.

**Note:** In the above derivation, it would have been unhelpful to try to expand  $\Omega_B$  (instead of  $S_B$ ) as a Taylor series in  $E$ . This is because  $\Omega_B$  changes very rapidly with  $E$ , and taking only the linear term in the expansion as we did for the entropy  $S_B$  would not have given a good approximation. More precisely, it is

found that for a macroscopic system of  $N$  particles, the dependence of  $\Omega$  on  $E$  is of the form  $\Omega = cE^\nu$  where  $\nu$  is of the order of  $N$ . If we try to carry out a Taylor series expansion on  $\Omega$ , we have

$$\begin{aligned}\Omega(E - dE) &\approx \Omega(E) - \Omega'(E)(dE) + \frac{1}{2}\Omega''(E)(dE)^2 - \dots \\ &= cE^\nu - c\nu E^{\nu-1}(dE) + \frac{1}{2}c\nu(\nu-1)E^{\nu-2}(dE)^2 - \dots\end{aligned}\quad (2.51)$$

In order for the quadratic term to be much less than the linear term, we require

$$dE \ll \frac{2E}{\nu-1}$$

which is of order of the energy of a single molecule. The energy fluctuations we need to consider due to heat exchange between system and bath are much larger than this.

On the other hand, when we expand  $S \approx k\nu \log E$ , we have

$$\begin{aligned}S(E - dE) &\approx S(E) - S'(E)(dE) + \frac{1}{2}S''(E)(dE)^2 - \dots \\ &= k\nu \log E - k\nu \frac{dE}{E} - \frac{k}{2}\nu \left(\frac{dE}{E}\right)^2 - \dots\end{aligned}\quad (2.52)$$

The condition for the quadratic term to be much less than the linear term is now

$$dE \ll 2E \quad (2.53)$$

Since we need to apply this to the bath which is so large that the energy exchanged with the system is very small compared to the total energy of the bath, this condition is easily fulfilled.

Once we know the probabilities for each of the system microstates, we can (in principle) work out **all** the properties of the system since we can find the probability distribution of **any** function of the system microstates.

## 2.5.2 Alternative forms for probabilities and the partition function

### 2.5.2.1 Grouping Microstates by Energy

In the above, we consider each **microstate** of the system separately, and so all the summations are indexed by the individual microstates. As we know, the microstates are often degenerate in energy, and we may have, for instance  $E_1 < E_2 = E_3 = E_4 < E_5 = E_6 < E_7 \dots$ . We may choose to focus on the **distinct energies** rather than on the individual microstates, and label the **degeneracy** of the microstate with energy  $E_r$  by  $g(E_r)$ . (This is the same as the statistical weight of a macrostate which we denoted by  $\Omega$  if we classify macrostates according to their energy and have an energy resolution which is fine enough to distinguish the energies of the various microstates). In this case the partition function may be written

$$Z = \sum_{E_r} g(E_r) \exp(-\beta E_r) \quad (2.54)$$

where the sum is over only the **distinct energies**. Similarly, the probability that the system has a certain energy is

$$p(E_r) = \frac{g(E_r) \exp(-\beta E_r)}{Z}. \quad (2.55)$$

If the energy levels are closely spaced, we may often approximate the discrete levels by a continuum and define a **density of states**  $f(E)$  such that

$$f(E) \delta E = \text{No. of system energy eigenstates with energy between } E \text{ and } E + \delta E \quad (2.56)$$

We then have

$$Z = \int dE f(E) \exp(-\beta E) \quad (2.57)$$

and

$$p(E) \delta E = \frac{f(E) \exp(-\beta E)}{Z} \delta E \quad (2.58)$$

where  $p(E)$  is the probability density of the system energy, so that  $p(E) \delta E$  is the probability that the system energy lies between  $E$  and  $E + \delta E$ .

### 2.5.2.2 Alternative Groupings of Microstates

The key idea in the definition of the partition function is that  $Z$  is a sum over system **microstates**  $r$ . We can choose to group these microstates however we like. For example, it may be more appropriate to group the microstates so that each macrostate corresponds to some (narrow range of) momentum, labelled by  $p_s$ . We can then write  $Z$  as

$$Z = \sum_{p_s} \Omega(p_s) \exp[-\beta E(p_s)] \quad (2.59)$$

where the sum is over the macrostate labels and the statistical weight  $\Omega(p_s)$  counts the number of microstates associated with the macrostate labelled by  $p_s$ . Note that the Boltzmann factor always involves the **energy**. The probability that the system is in the macrostate labelled by  $p_s$  is then

$$\text{Pr}(p_s) = \frac{\Omega(p_s) \exp[-\beta E(p_s)]}{Z}. \quad (2.60)$$

Again if the labels are in some sense closely-spaced, we can often approximate the sum by an integral over a density of states

$$\sum_{p_s} \Omega(p_s) \rightarrow \int dp f(p) \quad (2.61)$$

where  $f(p) \delta p$  is the number of states in the range  $p$  to  $p + \delta p$ .

### 2.5.3 Mean energy, heat capacity and energy fluctuations

First, let us consider the **mean (internal) energy** while the system is in contact with the bath. This is

$$\bar{E} = \sum_r p_r E_r = \frac{\sum_r E_r \exp(-\beta E_r)}{Z} \quad (2.62)$$

Remarkably, we can write this entirely in terms of  $Z$ . From the definition, differentiation with respect to  $\beta$  yields

$$\frac{\partial Z}{\partial \beta} = - \sum_r E_r \exp(-\beta E_r) \quad (2.63)$$

and so

$$-\frac{1}{Z} \frac{\partial Z}{\partial \beta} = \frac{\sum_r E_r \exp(-\beta E_r)}{Z} \quad (2.64)$$

Thus,

$$\bar{E} = -\frac{1}{Z} \frac{\partial Z}{\partial \beta} = -\frac{\partial (\log Z)}{\partial \beta} \quad (2.65)$$

From this, we can find the **heat capacity at constant volume**, which is

$$\begin{aligned} C_V &= \left( \frac{\partial \bar{E}}{\partial T} \right)_V = -k\beta^2 \left( \frac{\partial \bar{E}}{\partial \beta} \right)_V \\ &= k\beta^2 \left( \frac{\partial^2 (\log Z)}{\partial \beta^2} \right)_V. \end{aligned} \quad (2.66)$$

Since we actually know the **probability distribution** of the microstates, we can also find the **variance** of the energy when the system is in thermal contact with a heat bath.

$$(\Delta E)^2 = \overline{E^2} - \bar{E}^2 \quad (2.67)$$

We have already obtained an expression for  $\bar{E}$ . Following an analogous procedure for  $\overline{E^2}$ ,

$$\overline{E^2} = \sum_r p_r E_r^2 = \frac{\sum_r E_r^2 \exp(-\beta E_r)}{Z} \quad (2.68)$$

and we notice that

$$\frac{\partial^2 Z}{\partial \beta^2} = \sum_r E_r^2 \exp(-\beta E_r) \quad (2.69)$$

so that

$$\overline{E^2} = \frac{1}{Z} \frac{\partial^2 Z}{\partial \beta^2} \quad (2.70)$$

Using the result (2.65), we find that

$$(\Delta E)^2 = \overline{E^2} - \bar{E}^2 = \frac{1}{Z} \frac{\partial^2 Z}{\partial \beta^2} - \left( \frac{1}{Z} \frac{\partial Z}{\partial \beta} \right)^2 \quad (2.71)$$

$$= \frac{\partial}{\partial \beta} \left( \frac{1}{Z} \frac{\partial Z}{\partial \beta} \right) = \frac{\partial^2 (\log Z)}{\partial \beta^2} \quad (2.72)$$

By comparing this with (2.66), we obtain the interesting result that the size of the **energy fluctuations** is related to the **heat capacity** at constant volume. In fact,

$$\Delta E = \left( \frac{C_V}{k\beta^2} \right)^{1/2} \quad (2.73)$$

What does this tell us? For one thing, we can look at the **relative size** of the fluctuations compared to the mean:

$$\frac{\Delta E}{\bar{E}} = \left( \frac{C_V}{k\beta^2 \bar{E}^2} \right)^{1/2} \quad (2.74)$$

Now consider how this scales with the number of molecules in the system. The temperature (and hence  $\beta$ ) is an **intensive** quantity and does not change with the size of the system. On the other hand, both  $C_V$  and  $\bar{E}$  are **extensive** quantities which scale with  $N$ . Thus  $(\Delta E/\bar{E})$  scales as  $N^{-1/2}$ , and for large  $N$ , the fluctuations become negligible. For such macroscopic systems, we can imagine the internal energy to be essentially well-defined when the system is in thermal contact with a heat bath even though, of course, it is only absolutely precisely determined for an **isolated** system.

There is a caveat to the above conclusion, since we implicitly assumed in the argument that  $C_V$  was finite, so that the fractional fluctuations would be reduced by the factor  $N^{-1/2}$ . There are important cases where this is not true. For example, if we consider ice and water in contact with each other at the melting point, we know that as we add heat to this system, the ice melts but the temperature remains constant. This corresponds to an infinite heat capacity, and according to the equation, we expect the energy fluctuations to be very large in this case, even though the system is in contact with a heat bath at constant temperature. This is indeed the case, since at such a phase change, fixing the temperature does **not** specify how much of the system is in each of the phases, and the internal energy depends critically on the fraction in the two phases. (Recall that the internal energy of water exceeds that of ice at the same temperature by the latent heat).

## 2.5.4 Entropy

For the case of an isolated system, microstates of the system were either accessible or inaccessible, and the entropy was given by (Boltzmann's constant multiplied by) the logarithm of the number of accessible microstates. When the system is in contact with a heat bath, different microstates occur with different probabilities and we need to **generalize** the definition of the entropy to accommodate this.

In the isolated system, in which we know that the total energy is  $E$ , the probabilities of the various microstates may be written as

$$p_r = \begin{cases} \frac{1}{\Omega(E_r)} & \text{if } E_r = E \\ 0 & \text{if } E_r \neq E \end{cases} \quad (2.75)$$

The expression for the entropy is

$$S = k \log \Omega(E) = -k \log p_r \quad (2.76)$$

where  $p_r$  is the probability of any of the accessible microstates. In Figure 2.4(a), we show schematically how the microstates can be classified into accessible and inaccessible when the system is thermally isolated.

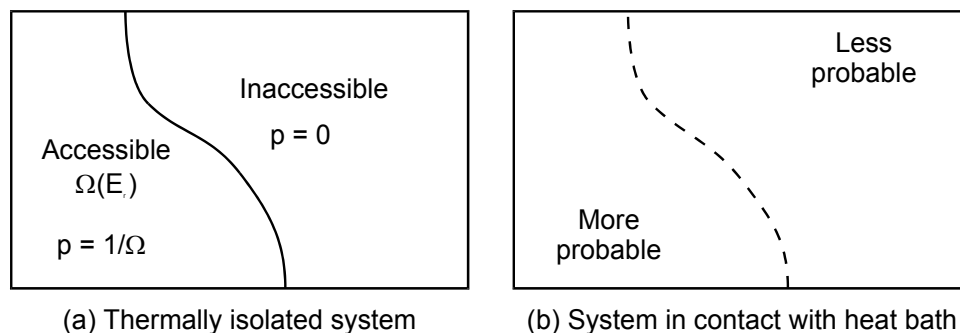


Figure 2.4 Schematic diagram showing that for a thermally isolated system (a), there is a clean division between accessible and inaccessible microstates, whereas for a system at a fixed temperature (b), microstates occur with different probabilities. We wish to generalize the concept of entropy to allow the latter situation.

In Figure 2.4(b) on the other hand, which represents the system in thermal contact with a heat bath, there is a smooth gradation from probable microstates to improbable ones as given by the Boltzmann distribution. If we think of each microstate as making a contribution to the entropy of the system, when the probabilities of the microstates are no longer equal, we can take the expectation value of the above over all possible microstates. This suggests that a plausible generalization for the entropy is

$$S = \langle -k \log p_r \rangle = -k \sum_r p_r \log p_r \quad (2.77)$$

where the sum is over the microstates. This is in fact correct, and is called the Gibbs' expression for the entropy for an arbitrary probability distribution for the microstates. It is possible to derive this formula more formally, but we shall not do so in this course.

For the system in thermal contact with a bath, we can substitute the Boltzmann distribution (2.49) for  $p_r$  into the expression (2.77) to obtain

$$\begin{aligned} S &= -k \sum_r \frac{e^{-\beta E_r}}{Z} \log \frac{e^{-\beta E_r}}{Z} \\ &= k \sum_r \frac{e^{-\beta E_r}}{Z} (\beta E_r + \log Z) \\ &= k\beta \bar{E} + k \log Z \end{aligned} \quad (2.78)$$

Writing  $\beta = 1/(kT)$ , we see that

$$S = \bar{E}/T + k \log Z \quad (2.79)$$

which may be rearranged as

$$-kT \log Z = \bar{E} - TS. \quad (2.80)$$

Comparing this with the expression for the **free energy**  $F$  in classical thermodynamics, we see that

$$F = -kT \log Z. \quad (2.81)$$

This connection allows us to calculate all thermodynamic variables starting from the partition function, once this is expressed as a function of  $T$ ,  $V$  and  $N$ .

## 2.6 Derivation of the Fundamental Thermodynamic Relation

The fundamental relation relates the change in internal energy of a system when the system undergoes an infinitesimal process which changes the entropy and the volume. In this section we derive this relationship using statistical mechanics and show the microscopic origin of each of the terms.

Consider a fluid with a fixed number of particles and suppose that a process occurs which changes its temperature  $T$  and volume  $V$  from  $(\beta, V)$  to  $(\beta + d\beta, V + dV)$  where, as usual,  $\beta = 1/(kT)$ . In statistical mechanics, we identify the microstates of the system as the energy eigenstates which we label by the indices  $r$ . We have seen that when the system is in thermal equilibrium with a heat bath, the probability  $p_r$  for being in state  $r$  is given by the Boltzmann distribution and the average energy is

$$\bar{E} = \sum_r p_r E_r \quad (2.82)$$

where  $E_r$  is the energy of the  $r$ 'th eigenstate. During the change from  $(\beta, V)$  to  $(\beta + d\beta, V + dV)$ , both  $p_r$  and  $E_r$  will change, and the average energy changes by

$$d\bar{E} = \sum_r dp_r E_r + \sum_r p_r dE_r \quad (2.83)$$

Let us consider how the entropy changes. Using Gibbs' expression,

$$\begin{aligned} dS &= d \left( -k \sum_r p_r \log p_r \right) = -k \left( \sum_r p_r \frac{1}{p_r} dp_r + \log p_r dp_r \right) \\ &= -k \sum_r dp_r - k \sum_r \log p_r dp_r \end{aligned} \quad (2.84)$$

Since the probabilities of the various microstates always add up to one, the sum of the changes  $\sum_r dp_r = 0$  for any process.

We can use the Boltzmann distribution to find  $p_r$ . This is

$$p_r = \frac{\exp(-\beta E_r)}{Z} \quad (2.85)$$

and so

$$\log p_r = -\beta E_r - \log Z \quad (2.86)$$

Substituting this into (2.84) and using  $\sum_r dp_r = 0$  we see that

$$dS = \frac{1}{T} \sum_r E_r dp_r \quad (2.87)$$

and so the first term on the right-hand side of (2.83) is just  $T dS$ .

It remains to calculate  $\sum_r p_r dE_r$  which involves the change in the **energy eigenvalues**. From quantum mechanics, the energy eigenvalues depends on the external parameters of the system, such as the volume, **not** on the temperature. If during the process, the system starts in eigenstate  $r$  and remains in this eigenstate, the change in volume produces a change of energy

$$dE_r = \frac{\partial E_r}{\partial V} dV = -P_r dV \quad (2.88)$$

where  $P_r$  is the pressure of the system in state  $r$ . The assumption that a system initially in an eigenstate remains in that state as the process takes place is the microscopic version of the process being **quasistatic**. Taking the average over the probability to be in each of the eigenstates, we see that

$$\sum_r p_r dE_r = - \sum_r p_r P_r dV = -P dV \quad (2.89)$$

where  $P$  is the average pressure.

Substituting (2.87) and (2.89) into (2.83) leads to the fundamental relation

$$dE = TdS - PdV \quad (2.90)$$

For a **reversible** change, we see that

$$\sum_r p_r dE_r = -PdV = dW \quad (2.91)$$

so work changes the energy levels, not the probabilities of being in the levels. Also

$$\sum_r dp_r E_r = TdS = dQ \quad (2.92)$$

so heat changes the probability of being in the various levels, without affecting the levels themselves.

## 2.7 Spin System in Thermal Contact with Heat Bath

We illustrate the theory for the system of  $N$  spin-half particles considered earlier, but we now suppose them to be in thermal contact with a heat bath at temperature  $T$ . If the spin-half particles are each localized at fixed positions within a crystal lattice, this is a simple model for a **paramagnetic solid** (see Chapter 3 of Mandl). The important features of the model are that the particles are **distinguishable** by their positions and that each is supposed to interact directly with the applied magnetic field and not with each other.

### 2.7.1 System consisting of a single spin

Let us first consider a **single particle** with dipole moment  $\mu$ . This can be in one of two energy levels, denoted  $+$  for spin up (parallel with  $\mathbf{B}$  field) or  $-$  for spin down (antiparallel with  $\mathbf{B}$  field). The energies are

$$E_+ = -\mu B \quad \text{and} \quad E_- = \mu B. \quad (2.93)$$

The partition function for one particle involves a sum over its energy eigenstates,

$$\begin{aligned} Z_1 &= \exp(-\beta E_+) + \exp(-\beta E_-) \\ &= 2 \cosh x \end{aligned} \quad (2.94)$$

where  $x = \mu B \beta = \mu B / (kT)$ .

We find from the partition function that

- The probability for the particle to be in each of the two states is

$$p_{\pm} = \frac{\exp(-\beta E_{\pm})}{Z} = \frac{\exp(\pm x)}{2 \cosh x}, \quad (2.95)$$

- The mean dipole moment is

$$\bar{\mu}_1 = \mu p_+ + (-\mu) p_- = \mu \tanh x, \quad (2.96)$$

- The mean energy is

$$\bar{E}_1 = E_+ p_+ + E_- p_- = -\mu B \tanh x \quad (2.97)$$

Notice that we could have also worked this out using

$$\begin{aligned} \bar{E}_1 &= -\frac{\partial}{\partial \beta} (\log Z_1) = -\frac{\partial \log (2 \cosh x)}{\partial x} \frac{\partial x}{\partial \beta} \\ &= -\mu B \tanh x \end{aligned} \quad (2.98)$$

In Figure 2.5, we plot the probability for being in each of the two states as a function of  $x$ , which is proportional to the ratio of the magnetic field to the temperature.

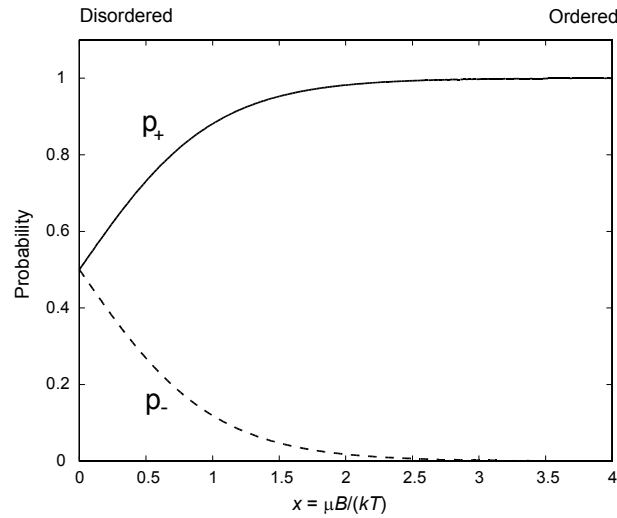


Figure 2.5 Probability of a spin being aligned parallel  $p_+$  or antiparallel  $p_-$  with a magnetic field as a function of  $x = \mu B/(kT)$ .

### 2.7.2 System consisting of $N$ spins

If we consider  $N$  spins which are **distinguishable** and **independent**, the partition function is simply given by the  $N$ 'th power of  $Z_1$ , i.e.,

$$Z_N = (Z_1)^N = 2^N \cosh^N x \quad (2.99)$$

Let us consider in more detail why this should be so. With  $N$  independent spins, there are  $2^N$  energy levels, each of which is labelled by a string of  $N$  symbols such as  $r \equiv (+, +, -, -, +, \dots, +)$  where each symbol represents the state of each of the  $N$  distinguishable spins.

The **energy** of the state  $r$  is

$$E_r = (-\mu B)n + (\mu B)(N - n) = (N - 2n)\mu B \quad (2.100)$$

where  $n$  is the number of up spins (+ signs) in  $r$ .

The **degeneracy** of the energy  $E_r$  is the number of ways of getting  $n$  spins pointing upwards, which is

$$g(E_r) = \binom{N}{n}. \quad (2.101)$$

The partition function is thus given by

$$\begin{aligned} Z_N &= \sum_{E_r} g(E_r) \exp(-\beta E_r) \\ &= \sum_{n=0}^N \binom{N}{n} \exp[-\beta(N - 2n)\mu B] \\ &= e^{-N\beta\mu B} \sum_{n=0}^N \binom{N}{n} e^{2n\beta\mu B} \end{aligned} \quad (2.102)$$

By the binomial theorem, the sum is simply  $[1 + \exp(2x)]^N$  and so we recover the result that  $Z_N = (e^{-x} + e^x)^N = 2^N \cosh^N x$ .

We can find various properties of interest, either from the  $N$  particle partition function or from the single particle results together with statistical independence.

- The probability for the  $N$  particles to be in a particular state  $r \equiv (+, +, -, -, +, \dots, +)$  is the product of the probabilities for the individual particles to be in these states, i.e.,

$$p_r = \underbrace{p_+ p_+ p_- p_- p_+ \dots p_+}_{\text{single particle probs}} = \frac{\exp(+nx) \exp[-(N-n)x]}{(2 \cosh x)^N} \quad (2.103)$$

$$= \frac{\exp[-(N-2n)x]}{(2 \cosh x)^N} \quad (2.104)$$

where  $n$  is the number of up spins in the state  $r$ .

- The mean energy is

$$\bar{E}_N = -\frac{\partial}{\partial \beta} (\log Z_N) = -N\mu B \tanh x \quad (2.105)$$

This result is simply  $N\bar{E}_1$  as might be expected due to the assumption of independence.

- The mean dipole moment is

$$\bar{\mu}_N = N\bar{\mu}_1 = N\mu \tanh x \quad (2.106)$$

- The mean number of up spins when the temperature is  $T$  may be readily found from the mean energy, since  $E = (N - 2n) \mu B$

$$\begin{aligned} \bar{n} &= \frac{N}{2} - \frac{\bar{E}_N}{2\mu B} = \frac{N}{2} (1 + \tanh x) = \frac{N}{1 + \exp(-2x)} \\ &= \frac{N}{1 + \exp\left(-\frac{2\mu B}{kT}\right)} \end{aligned} \quad (2.107)$$

Comparing this equation with (2.33), we see that the mean number of up-spins when the temperature is maintained at  $T$  by an external heat bath is consistent with the temperature of an **isolated** system when the number of upwards pointing spins is fixed at  $n$ .

- The **magnetic susceptibility** of a material is the ratio of the net magnetization of the system (i.e., the magnetic moment per unit volume) to the applied magnetic field. It measures how well the internal magnetic dipoles in a material are aligned by the presence of an external field. Intuitively, we expect that at high temperatures, the dipoles in the material will be randomized leading to a small magnetization for a given field whereas at low temperatures, the magnetization will be higher since more alignment will occur.

If  $\bar{n}$  is the mean number of up spins, the net magnetic moment is  $(2\bar{n} - N) \mu$  (since there are also  $N - \bar{n}$  spins pointing down on average) and the magnetization  $\mathcal{I}$  is  $(2\bar{n} - N) \mu/V$ . The susceptibility is thus

$$\chi = \frac{(2\bar{n} - N) \mu/V}{(B/\mu_0)} \quad (2.108)$$

Note that in the denominator we have  $H = B/\mu_0$  which is the quantity which is properly called the magnetic field strength. ( $B$  is more properly called the magnetic induction, but we shall often lapse into calling it the field strength). From (2.107) we find that

$$\chi = \frac{N\mu\mu_0}{VB} \tanh\left(\frac{\mu B}{kT}\right) \quad (2.109)$$

In the limit of weak field and high temperature, the argument of the hyperbolic tangent is small and we can use  $\tanh x \approx x$  for small  $x$  to conclude that

$$\chi = \frac{N\mu^2\mu_0}{VkT} \quad (2.110)$$

At high temperatures, it is more difficult to align the magnetic moments against the tendency towards randomization, and the susceptibility falls. This inverse relationship is known as **Curie's law**, and this effect is used to measure temperatures as low as 0.01 K (which is nevertheless "high" in this context,

since  $\mu B \ll kT$ ) using paramagnetic salts such as cerium magnesium nitrate  $\text{Ce}_2\text{Mg}_3(\text{NO}_3)_{12} \cdot 24\text{H}_2\text{O}$ . At low temperatures, the argument of the hyperbolic tangent is large and the magnetization saturates as essentially all the dipoles align with the field.

This expression (and its generalization to include elementary magnets of spins greater than one half) gives results which are in excellent agreement with experiment (see Mandl).

- The **heat capacity** of the system (at fixed volume) is

$$C = \frac{\partial \bar{E}}{\partial T} = k\beta^2 \left( \frac{\partial^2 (\log Z)}{\partial \beta^2} \right)_V = Nkx^2 (\text{sech } x)^2$$

This is shown as the solid line in Figure 2.6 and the mean energy is shown as the dashed line. Notice that the heat capacity has quite a large peak over a relatively narrow range of temperatures. Over this range of temperatures, the system goes essentially from an ordered state to a disordered state. This feature of the specific heat of a collection of two-state systems is called the **Schottky anomaly**.

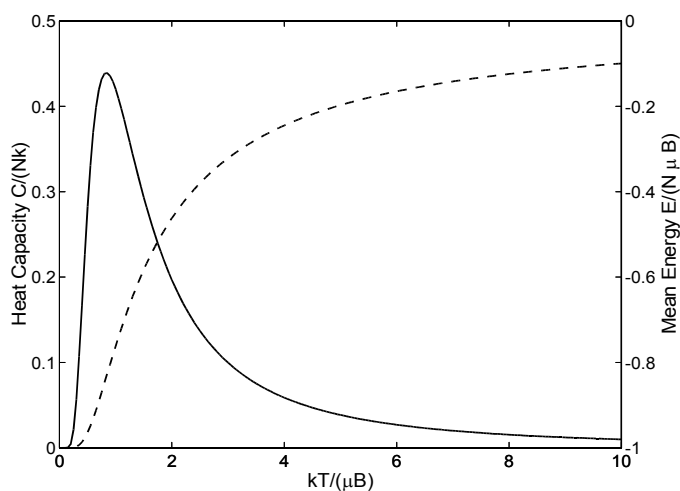


Figure 2.6 Heat capacity (solid line) and mean energy (dashed line) of the system of  $N$  spins in a magnetic field.

- The **entropy** of the spin system when in thermal equilibrium with a heat bath is given by

$$S = -k\beta^2 \frac{\partial}{\partial \beta} \left( \frac{\log Z}{\beta} \right) = Nk (\log 2 + \log \cosh x - x \tanh x) \quad (2.111)$$

Note that at high temperatures,  $x \rightarrow 0$  and  $S \rightarrow k \log 2^N$  so all  $2^N$  states are effectively accessible, whereas for low temperatures,  $x \rightarrow \infty$  and  $S \rightarrow 0$ , indicating that only one state is effectively accessible.