The partition function

20

The probability that a system is in some particular state α is given by the Boltzmann factor $e^{-\beta E_\alpha}$. We define the **partition function**[1] Z by a sum over all the states of the Boltzmann factors, so that

$$Z = \sum_\alpha e^{-\beta E_\alpha}$$

(20.1)

where the sum is over all states of the system (each one labelled by α). The partition function Z contains all the information about the energies of the states of the system, and the fantastic thing about the partition function is that all thermodynamical quantities can be obtained from it. It behaves like a zipped-up and compressed version of all the properties of the system; once you have Z, you only have to know how to uncompress and unzip it to get functions of state like energy, entropy, Helmholtz function, or heat capacity to simply drop out. We can therefore reduce problem-solving in statistical mechanics to two steps:

Steps to solving statistical mechanics problems:

(1) Write down the partition function Z.
(see Section 20.1)

(2) Go through some standard procedures to obtain the functions of state you want from Z.
(see Section 20.2)

We will outline these two steps in the sections that follow. Before we do that, let us pause to notice an important feature about the partition function.

- The zero of energy is always somewhat arbitrary: one can always choose to measure energy with respect to a different zero, since it is only energy differences which are important. Hence the partition function is defined up to an arbitary multiplicative constant. This seems somewhat strange, but it turns out that many physical quantities are related to the logarithm of the partition function and therefore these quantities are defined up to an additive constant (which might reflect, for example, the rest mass of particles). Other physical quantities, however, are determined by a differential of the logarithm of the partition function and therefore these quantities can be determined precisely.

[1]The partition function is given the symbol Z because the concept was first coined in German. *Zustandssumme* means 'sum over states', which is exactly what Z is. The English name 'partition function' reflects the way in which Z measures how energy is 'partitioned' between states of the system.

This point needs to be remembered whenever the partition function is obtained.

Everything in this chapter refers to what is known as the **single–particle partition function**. We are working out Z for *one* particle of matter which may well be coupled to a reservoir of other particles, but our attention is only on that single particle of matter. We will defer discussion of how to treat aggregates of particles until the next two chapters. With that in mind, we are now ready to write down some partition functions.

20.1   Writing down the partition function

The partition function contains all the information we need to work out the thermodynamical properties of a system. In this section, we show how you can write down the partition function in the first place.

This procedure is not complicated! Writing down the partition function is nothing more than evaluating eqn 20.1 for different situations. We demonstrate this for a couple of commonly encountered and important examples.
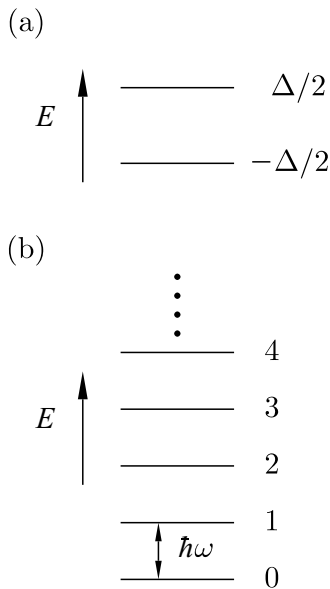
(a)

E $\dfrac{}{}$ $\Delta/2$

$\dfrac{}{}$ $-\Delta/2$

(b)

Fig. 20.1 Energy levels of (a) a two-level system and (b) a simple harmonic oscillator.

An alternative form of this result is found by multiplying top and bottom by $\mathrm{e}^{\beta\frac{1}{2}\hbar\omega}$ to obtain the result $Z = 1/(2\sinh(\beta\hbar\omega/2))$.

Example 20.1

(a) The two-level system: (see Fig. 20.1(a))
Let the energy of a system be either $-\Delta/2$ or $\Delta/2$. Then

$$Z = \sum_\alpha \mathrm{e}^{-\beta E_\alpha} = \mathrm{e}^{\beta\Delta/2} + \mathrm{e}^{-\beta\Delta/2} = 2\cosh\left(\frac{\beta\Delta}{2}\right), \qquad (20.2)$$

where the final result follows from the definition of $\cosh x \equiv \frac{1}{2}(\mathrm{e}^x + \mathrm{e}^{-x})$ (see Appendix B).

(b) The simple harmonic oscillator: (see Fig. 20.1(b))
The energy of the system is $(n+\frac{1}{2})\hbar\omega$ where $n = 0, 1, 2, \ldots$, and hence

$$Z = \sum_\alpha \mathrm{e}^{-\beta E_\alpha} = \sum_{n=0}^{\infty} \mathrm{e}^{-\beta(n+\frac{1}{2})\hbar\omega} = \mathrm{e}^{-\beta\frac{1}{2}\hbar\omega} \sum_{n=0}^{\infty} \mathrm{e}^{-n\beta\hbar\omega} = \frac{\mathrm{e}^{-\frac{1}{2}\beta\hbar\omega}}{1 - \mathrm{e}^{-\beta\hbar\omega}},$$
$$(20.3)$$

where the sum is evaluated using the standard result for the sum of an infinite geometric progress, see Appendix B.

Two further, slightly more complicated, examples are the set of N equally spaced energy levels and the energy levels appropriate for the rotational states of a diatomic molecule.

Example 20.2

(c) The N-level system: (see Fig. 20.2(c))
Let the energy levels of a system be 0, $\hbar\omega$, $2\hbar\omega$, ..., $(N-1)\hbar\omega$. Then

$$Z = \sum_\alpha e^{-\beta E_\alpha} = \sum_{j=0}^{N-1} e^{-j\beta\hbar\omega} = \frac{1 - e^{-N\beta\hbar\omega}}{1 - e^{-\beta\hbar\omega}}, \qquad (20.4)$$

where the sum is evaluated using the standard result for the sum of a finite geometric progress, see Appendix B.

(d) Rotational energy levels: (see Fig. 20.2(d))
The rotational kinetic energy of a molecule with moment of inertia I is given by $\hat{J}^2/2I$, where $\hat{J}$ is the total angular momentum operator. The eigenvalues of $\hat{J}^2$ are given by $\hbar^2 J(J+1)$, where the angular momentum quantum number, J, takes the values $J = 0, 1, 2, \ldots$ The energy levels of this system are given by

$$E_J = \frac{\hbar^2}{2I} J(J+1), \qquad (20.5)$$

and have degeneracy $2J+1$. Hence the partition function is

$$Z = \sum_\alpha e^{-\beta E_\alpha} = \sum_{J=0}^{\infty} (2J+1) e^{-\beta\hbar^2 J(J+1)/2I}, \qquad (20.6)$$

where the factor $(2J+1)$ takes into account the degeneracy of the level.
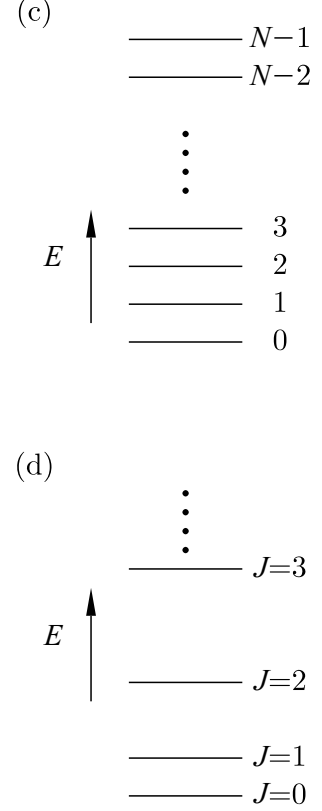
Fig. 20.2 Energy levels of (c) an N-level system and (d) a rotational system.

20.2 Obtaining the functions of state

Once Z has been written down, we can place it in our mathematical sausage machine (see Fig. 20.3) which processes it and spits out fully-fledged thermodynamical functions of state. We now outline the derivations of the components of our sausage machine so that you can derive all these functions of state for any given Z.

- *Internal energy U*
  The internal energy U is given by

$$U = \frac{\sum_i E_i e^{-\beta E_i}}{\sum_i e^{-\beta E_i}}. \qquad (20.7)$$

Now the denominator of this expression is the partition function $Z = \sum_i e^{-\beta E_i}$, but the numerator is simply

$$-\frac{\mathrm{d}Z}{\mathrm{d}\beta} = \sum_i E_i e^{-\beta E_i}. \qquad (20.8)$$
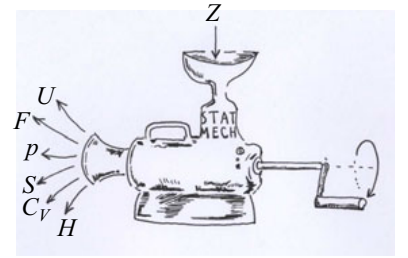
Fig. 20.3 Given Z, it takes only a turn of the handle on our 'sausage machine' to produce other functions of state.

Thus $U = -(1/Z)(\mathrm{d}Z/\mathrm{d}\beta)$, or more simply,

$$U = -\frac{\mathrm{d}\ln Z}{\mathrm{d}\beta}. \tag{20.9}$$

This is a useful form since Z is normally expressed in terms of β. If you prefer things in terms of temperature T, then using $\beta = 1/k_{\mathrm{B}}T$ (and hence $\mathrm{d}/\mathrm{d}\beta = -k_{\mathrm{B}}T^2(\mathrm{d}/\mathrm{d}T)$) one obtains

$$U = k_{\mathrm{B}}T^2 \frac{\mathrm{d}\ln Z}{\mathrm{d}T}. \tag{20.10}$$

- *Entropy S*
  Since the probability P_j is given by a Boltzmann factor divided by the partition function (so that the sum of the probabilities is one, as can be shown using eqn 20.1), we have $P_j = \mathrm{e}^{-\beta E_j}/Z$ and hence

$$\ln P_j = -\beta E_j - \ln Z. \tag{20.11}$$

Equation 14.48 therefore gives us an expression for the entropy as follows:

$$\begin{aligned} S &= -k_{\mathrm{B}}\sum_i P_i \ln P_i \\ &= k_{\mathrm{B}}\sum_i P_i(\beta E_i + \ln Z) \\ &= k_{\mathrm{B}}(\beta U + \ln Z), \end{aligned} \tag{20.12}$$

where we have used $U = \sum_i P_i E_i$ and $\sum_i P_i = 1$. Using $\beta = 1/k_{\mathrm{B}}T$ we have that

$$S = \frac{U}{T} + k_{\mathrm{B}}\ln Z. \tag{20.13}$$

- *Helmholtz function F*
  The Helmholtz function is defined via $F = U - TS$, so using eqn 20.13 we have that

$$F = -k_{\mathrm{B}}T \ln Z. \tag{20.14}$$

This can also be cast into the memorable form

$$\boxed{Z = \mathrm{e}^{-\beta F}.} \tag{20.15}$$

Once we have an expression for the Helmholtz function, a lot of things come out in the wash. For example, using eqn 16.19 we have that

$$S = -\left(\frac{\partial F}{\partial T}\right)_V = k_{\mathrm{B}}\ln Z + k_{\mathrm{B}}T\left(\frac{\partial \ln Z}{\partial T}\right)_V, \tag{20.16}$$

which, using eqn 20.10, is equivalent to eqn 20.13 above. This expression then leads to the heat capacity, via (recall eqn 16.68)

$$C_V = T\left(\frac{\partial S}{\partial T}\right)_V, \tag{20.17}$$

or one can use

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V .$$
(20.18)

Either way,

$$C_V = k_B T \left[2 \left(\frac{\partial \ln Z}{\partial T}\right)_V + T \left(\frac{\partial^2 \ln Z}{\partial T^2}\right)_V \right] .$$
(20.19)

- *Pressure p*
  The pressure can be obtained from F using eqn 16.20, so that

$$p = -\left(\frac{\partial F}{\partial V}\right)_T = k_B T \left(\frac{\partial \ln Z}{\partial V}\right)_T .$$
(20.20)

Having got the pressure we can then write down the enthalpy and the Gibbs function.

- *Enthalpy H*

$$H = U + pV = k_B T \left[T \left(\frac{\partial \ln Z}{\partial T}\right)_V + V \left(\frac{\partial \ln Z}{\partial V}\right)_T \right]$$
(20.21)

- *Gibbs function G*

$$G = F + pV = k_B T \left[-\ln Z + V \left(\frac{\partial \ln Z}{\partial V}\right)_T \right]$$
(20.22)

Function of state		Statistical mechanical expression
U		$-\dfrac{d \ln Z}{d\beta}$
F		$-k_B T \ln Z$
S	$= -\left(\frac{\partial F}{\partial T}\right)_V = \frac{U-F}{T}$	$k_B \ln Z + k_B T \left(\frac{\partial \ln Z}{\partial T}\right)_V$
p	$= -\left(\frac{\partial F}{\partial V}\right)_T$	$k_B T \left(\frac{\partial \ln Z}{\partial V}\right)_T$
H	$= U + pV$	$k_B T \left[T \left(\frac{\partial \ln Z}{\partial T}\right)_V + V \left(\frac{\partial \ln Z}{\partial V}\right)_T \right]$
G	$= F + pV = H - TS$	$k_B T \left[-\ln Z + V \left(\frac{\partial \ln Z}{\partial V}\right)_T \right]$
C_V	$= \left(\frac{\partial U}{\partial T}\right)_V$	$k_B T \left[2 \left(\frac{\partial \ln Z}{\partial T}\right)_V + T \left(\frac{\partial^2 \ln Z}{\partial T^2}\right)_V \right]$

Table 20.1 Thermodynamic quantities derived from the partition function Z.

These relations are summarized in Table 20.1. In practice, it is easiest to only remember the relations for U and F, since the others can be derived (using the relations shown in the left column of the table). Now that we have described how the process works, we can set about practising this for different partition functions.

Example 20.3

(a) Two-level system:
The partition function for a two-level system (whose energy is either $-\Delta/2$ or $\Delta/2$) is given by eqn 20.2, which states that

$$Z = 2 \cosh\left(\frac{\beta\Delta}{2}\right). \qquad (20.23)$$

Having obtained Z, we can immediately compute the internal energy U and find that

$$U = -\frac{\mathrm{d}\ln Z}{\mathrm{d}\beta} = -\frac{\Delta}{2}\tanh\left(\frac{\beta\Delta}{2}\right). \qquad (20.24)$$

Hence the heat capacity C_V is

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = k_\mathrm{B}\left(\frac{\beta\Delta}{2}\right)^2 \mathrm{sech}^2\left(\frac{\beta\Delta}{2}\right). \qquad (20.25)$$

The Helmholtz function is

$$F = -k_\mathrm{B}T\ln Z = -k_\mathrm{B}T\ln\left[2\cosh\left(\frac{\beta\Delta}{2}\right)\right], \qquad (20.26)$$

and hence the entropy is

$$S = \frac{U-F}{T} = -\frac{\Delta}{T}\tanh\left(\frac{\beta\Delta}{2}\right) + k_\mathrm{B}\ln\left[2\cosh\left(\frac{\beta\Delta}{2}\right)\right]. \qquad (20.27)$$

These results are plotted in Fig. 20.4(a). At low temperature, the system is in the lower level and the internal energy U is $-\Delta/2$. The entropy S is $k_\mathrm{B}\ln\Omega$, where Ω is the degeneracy and hence $\Omega = 1$ and so $S = k_\mathrm{B}\ln 1 = 0$. At high temperature, the two levels are each occupied with probability $\frac{1}{2}$, U therefore tends to 0 (which is half-way between $-\Delta/2$ and $\Delta/2$), and the entropy tends to $k_\mathrm{B}\ln 2$ as expected. The entropy rises as the temperature increases because it reflects the freedom of the system to exist in different states, and at high temperature the system has more freedom (in that it can exist in either of the two states). Conversely, cooling corresponds to a kind of 'ordering' in which the system can only exist in one state (the lower), and this gives rise to a reduction in the entropy.
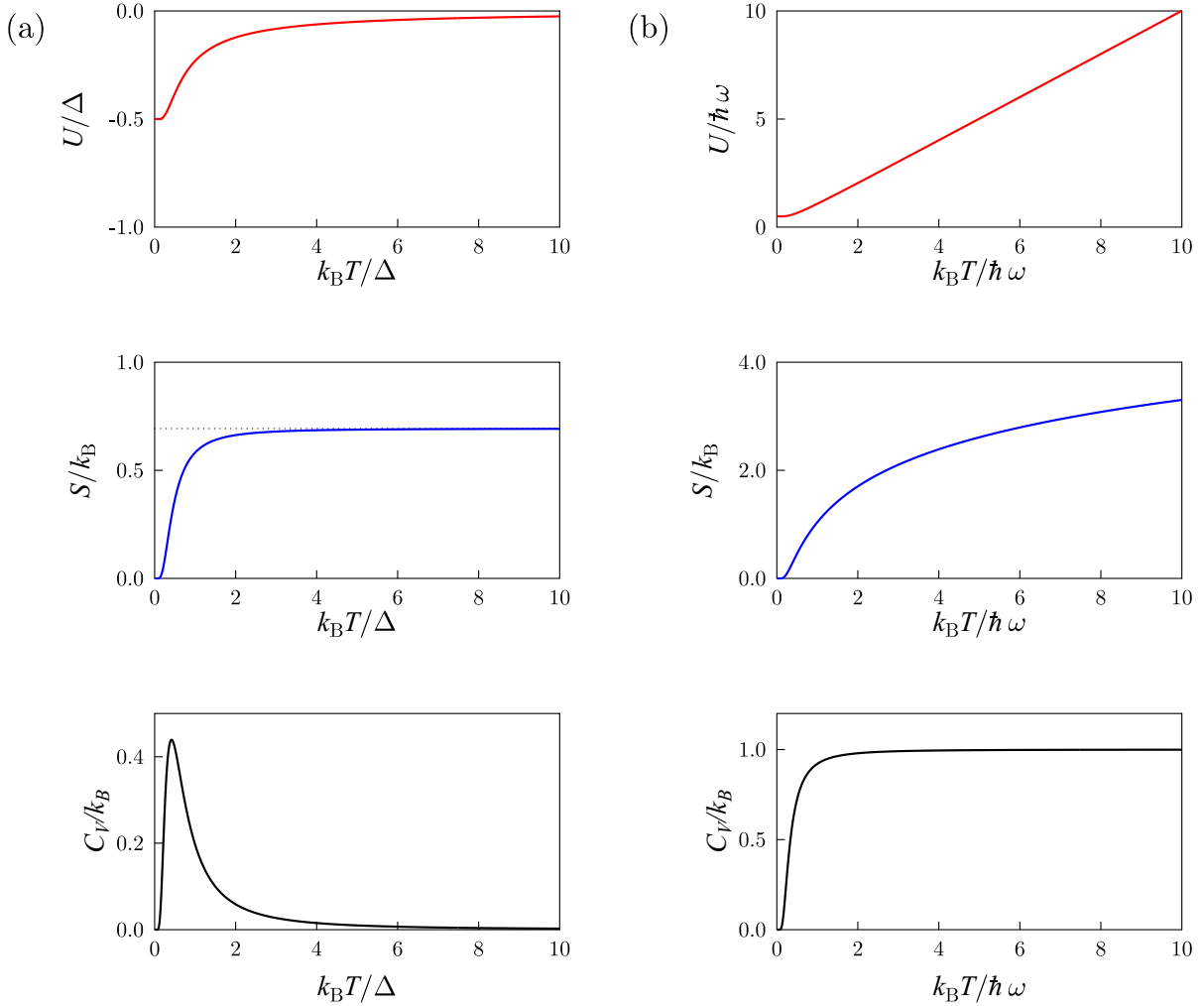
Fig. 20.4 The internal energy U, the entropy S and the heat capacity C_V for (a) the two-state system (with energy levels $\pm\Delta/2$) and (b) the simple harmonic oscillator.

The heat capacity is very small both (i) at low temperature ($k_{\mathrm{B}}T \ll \Delta$) and (ii) at very high temperature ($k_{\mathrm{B}}T \gg \Delta$), because changes in temperature have no effect on the internal energy when (i) the temperature is so low that only the lower level is occupied and even a small change in temperature won't alter that, and (ii) the temperature is so high that both levels are occupied equally and a small change in temperature won't alter this. At very low temperature, it is hard to change the energy of the system because there is not enough energy to excite transitions from the ground state and therefore the system is 'stuck'. At very high temperature, it is hard to change the energy of the system because both states are equally occupied. In between, roughly around a temperature $T \approx \Delta/k_{\mathrm{B}}$, the heat capacity rises to a maximum, known as a **Schottky anomaly**,[2] as shown in the lowest panel of Fig. 20.4(a).

[2]Walter Schottky (1886–1976).

This arises because at this temperature, it is possible to thermally excite transitions between the two states of the system. Note, however, that the Schottky anomaly is not a sharp peak, cusp or spike, as might be associated with a phase transition (see Section 28.7), but is a smooth, fairly broad maximum.

(b) Simple harmonic oscillator:

The partition function for the simple harmonic oscillator (from eqn 20.3) is

$$Z = \frac{e^{-\frac{1}{2}\beta\hbar\omega}}{1 - e^{-\beta\hbar\omega}}. \tag{20.28}$$

Hence (referring to Table 20.1), we find that U is given by

$$U = -\frac{d\ln Z}{d\beta} = \hbar\omega\left(\frac{1}{2} + \frac{1}{e^{\beta\hbar\omega} - 1}\right) \tag{20.29}$$

and hence that C_V is

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = k_B(\beta\hbar\omega)^2 \frac{e^{\beta\hbar\omega}}{(e^{\beta\hbar\omega} - 1)^2}. \tag{20.30}$$

At high temperature, $\beta\hbar\omega \ll 1$ and so $(e^{\beta\hbar\omega} - 1) \approx \beta\hbar\omega$ and so $C_V \to k_B$ (the equipartition result). Similarly, $U \to \frac{\hbar\omega}{2} + k_B T \approx k_B T$. The Helmholtz function is (referring to Table 20.1)

$$F = -k_B T \ln Z = \frac{\hbar\omega}{2} + k_B T \ln(1 - e^{-\beta\hbar\omega}), \tag{20.31}$$

and hence the entropy is (referring again to Table 20.1)

$$S = \frac{U - F}{T} = k_B\left(\frac{\beta\hbar\omega}{e^{\beta\hbar\omega} - 1} - \ln(1 - e^{-\beta\hbar\omega})\right). \tag{20.32}$$

These results are plotted in Fig. 20.4(b). At absolute zero, only the lowest level is occupied, so the internal energy is $\frac{1}{2}\hbar\omega$ and the entropy is $k_B \ln 1 = 0$. The heat capacity is also zero. As the temperature rises, more and more energy levels in the ladder can be occupied, and U rises without limit. The entropy also rises (and follows a dependence which is approximately $k_B \ln(k_B T/\hbar\omega)$ where $k_B T/\hbar\omega$ is approximately the number of occupied levels). Both functions carry on rising because the ladder of energy levels increases without limit. The heat capacity rises to a plateau at $C_V = k_B$, which is the equipartition result (see eqn 19.13).

The results for two further examples are plotted in Fig. 20.5 and are shown without derivation. The first is an N-level system and is shown in Fig. 20.5(a). At low temperature, the behaviour of the thermodynamic functions resembles that of the simple harmonic oscillator, but at higher temperature, U and S begin to saturate and C_V falls, because the system has a limited number of energy levels.
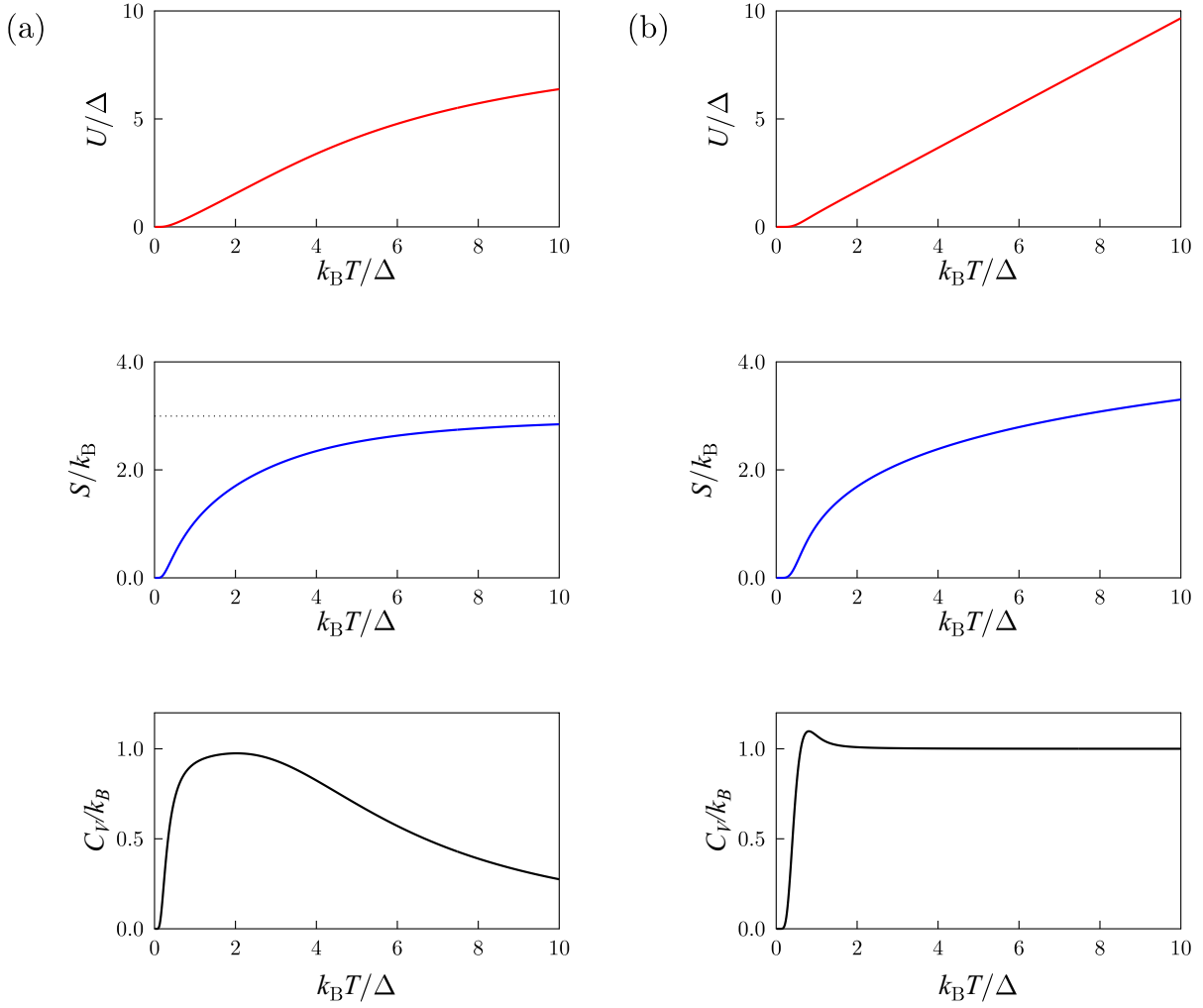
Fig. 20.5 The internal energy U, the entropy S and the heat capacity C_V for (a) the N-level system (the simulation is shown for $N = 20$) and (b) the rotating diatomic molecule (in this case $\Delta = \hbar^2/2I$ where I is the moment of inertia).

The second plot in Fig. 20.5(b) is for the rotating diatomic molecule. This resembles the simple harmonic oscillator at higher temperature (the heat capacity saturates at $C_V = k_B$) but differs at low temperature owing to the detailed difference in the structure of the energy levels. At high temperature, the heat capacity is given by the equipartition result (see eqn 19.13). This can be verified directly using the partition function which, at high temperature, can be represented by the following integral:

$$Z = \sum_{J=0}^{\infty}(2J+1)e^{-\beta\Delta J(J+1)} \approx \int_{0}^{\infty}(2J+1)e^{-\beta\Delta J(J+1)}\,\mathrm{d}J, \quad (20.33)$$

where $\Delta = \hbar^2/2I$. Using

$$\frac{\mathrm{d}}{\mathrm{d}J}e^{-\beta\Delta J(J+1)} = -(2J+1)\beta\Delta\,e^{-\beta\Delta J(J+1)}, \qquad (20.34)$$

we have that

$$Z = -\left[\frac{1}{\beta\Delta}e^{-\beta\Delta J(J+1)}\right]_0^\infty = \frac{1}{\beta\Delta}. \tag{20.35}$$

This implies that $U = -\mathrm{d}\ln Z/\mathrm{d}\beta = 1/\beta = k_BT$ and hence $C_V = (\mathrm{d}U/\mathrm{d}T)_V = k_B$.

20.3 The big idea

The examples above illustrate the 'big idea' of statistical mechanics: you *describe* a system by its energy levels E_α and *evaluate* its properties by following the prescription given by the two steps:

(1) Write down $Z = \sum_\alpha e^{-\beta E_\alpha}$.

(2) Evaluate various functions of state using the expressions in Table 20.1.

And that's really all there is to it![3]

You can *understand* the results by comparing the energy k_BT to the spacings between energy levels.

- If k_BT is much less than the spacing between the lowest energy level and the first excited level then the system will sit in the lowest level.

- If there are a finite set of levels and k_BT is much larger than the energy spacing between the lowest and highest levels, then each energy level will be occupied with equal probability.

- If there are an infinite ladder of levels and k_BT is much larger than the energy spacing between adjacent levels, then the mean energy rises linearly with T and one obtains a result consistent with the equipartition theorem.

[3]Well, almost. The Schrödinger equation can only be solved for a few systems, and if you don't know the energy levels of your system, you can't write down Z. Fortunately, there are quite a number of systems for which you can solve the Schrödinger equation, some of which we are considering in this chapter, and they describe lots and lots of important physical systems, enough to keep us going in this book!

20.4 Combining partition functions

Consider the case when the energy E of a particular system depends on various independent contributions. For example, suppose it is a sum of two contributions a and b, so that the energy levels are given by $E_{i,j}$ where

$$E_{i,j} = E_i^{(a)} + E_j^{(b)}, \tag{20.36}$$

and where $E_i^{(a)}$ is the ith level due to contribution a and $E_j^{(b)}$ is the jth level due to contribution b, so the partition function Z is

$$Z = \sum_i \sum_j e^{-\beta(E_i^{(a)} + E_j^{(b)})} = \sum_i e^{-\beta E_i^{(a)}} \sum_j e^{-\beta E_j^{(b)}} = Z_a Z_b, \tag{20.37}$$

so that the partition functions of the independent contributions *multiply*. Hence also $\ln Z = \ln Z_a + \ln Z_b$, and the effect on functions of state which depend on $\ln Z$ is that the independent contributions *add*.

Example 20.4

(i) The partition function Z for N independent simple harmonic oscillators is given by

$$Z = Z_{\text{SHO}}^N, \qquad (20.38)$$

where $Z_{\text{SHO}} = e^{-\frac{1}{2}\beta\hbar\omega}/(1 - e^{-\beta\hbar\omega})$, from eqn 20.3, is the partition function for a single simple harmonic oscillator.

(ii) A diatomic molecule with *both* vibrational and rotational degrees of freedom has a partition function Z given by

$$Z = Z_{\text{vib}} Z_{\text{rot}}, \qquad (20.39)$$

where Z_{vib} is the vibrational partition function $Z_{\text{vib}} = e^{-\frac{1}{2}\beta\hbar\omega}/(1 - e^{-\beta\hbar\omega})$, from eqn 20.3, and Z_{rot} is the rotational partition function

$$Z_{\text{rot}} = \sum_{\alpha} e^{-\beta E_\alpha} = \sum_{J=0}^{\infty} (2J+1) e^{-\beta\hbar^2 J(J+1)/2I}. \qquad (20.40)$$

from eqn 20.6. For a gas of diatomic molecules, we would also need a factor in the partition function corresponding to translational motion. We will derive this in the following chapter.

Chapter summary

- The partition function $Z = \sum_{\alpha} e^{-\beta E_\alpha}$ contains the information needed to find many thermodynamic properties.
- The equations $U = -\mathrm{d}\ln Z/\mathrm{d}\beta$, $F = -k_{\text{B}}T\ln Z$, $S = (U - F)/T$, $p = -\left(\frac{\partial F}{\partial V}\right)_T$, $H = U + pV$, $G = H - TS$ can be used to generate the relevant thermodynamic properties from Z.

Exercises

(20.1) Show that at high temperature, such that $k_{\text{B}}T \gg \hbar\omega$, the partition function of the simple harmonic oscillator is approximately $Z \approx (\beta\hbar\omega)^{-1}$. Hence find U, C, F and S at high temperature. Repeat the problem for the high temperature limit of the rotational energy levels of the diatomic molecule for which $Z \approx (\beta\hbar^2/2I)^{-1}$ (see eqn 20.35).

(20.2) Show that

$$\ln P_j = \beta(F - E_j). \qquad (20.41)$$

(20.3) Show that eqn 20.29 can be rewritten as

$$U = \frac{\hbar\omega}{2} \coth \frac{\beta\hbar\omega}{2}, \qquad (20.42)$$

and eqn 20.32 can be rewritten as

$$S = k_B \left[\frac{\hbar\omega}{2} \coth \frac{\beta\hbar\omega}{2} - \ln\left(2\sinh\frac{\beta\hbar\omega}{2} \right) \right].$$
(20.43)

(20.4) Show that the zero-point energy of a simple harmonic oscillator does not contribute to its entropy or heat capacity, but does contribute to its energy and Helmholtz function.

(20.5) A spin-$\frac{1}{2}$ paramagnet in a magnetic field B can be modelled as a set of independent two-level systems with energy $-\mu_B B$ and $\mu_B B$ (where $\mu_B \equiv e\hbar/2m$ is the Bohr magneton).
(a) Show that for one magnetic ion, the partition function is
$$Z = 2\cosh(\beta\mu_B B).$$
(20.44)
(b) For N independent magnetic ions, the partition function Z_N is $Z_N = Z^N$. Show that the Helmholtz function is given by
$$F = -Nk_B T \ln[2\cosh(\beta\mu_B B)].$$
(20.45)
(c) Eqn 17.32 implies that the magnetic moment m is given by $m = -(\partial F/\partial B)_T$. Hence show that
$$m = N\mu_B \tanh(\beta\mu_B B).$$
(20.46)
Sketch m as a function of B.
(d) Show further that for small fields, $\mu_B B \ll k_B T$,
$$m \approx N\mu_B^2 B/k_B T.$$
(20.47)
(e) The magnetic susceptibility is defined as $\chi \approx \mu_0 M/B$ (see Blundell (2001)) for small B. Hence show that $\chi \propto 1/T$, which is Curie's law.

(20.6) A certain magnetic system contains n independent molecules per unit volume, each of which has four energy levels given by 0, $\Delta - g\mu_B B$, Δ, $\Delta + g\mu_B B$ (g is a constant). Write down the partition function, compute the Helmholtz function and hence compute the magnetization M. Hence show that the magnetic susceptibility χ is given by
$$\chi = \lim_{B \to 0} \frac{\mu_0 M}{B} = \frac{2ng\mu_B^2}{k_B T(3 + e^{\Delta/k_B T})}.$$
(20.48)

(20.7) The energy E of a system of three independent harmonic oscillators is given by
$$E = (n_x + \frac{1}{2})\hbar\omega + (n_y + \frac{1}{2})\hbar\omega + (n_z + \frac{1}{2})\hbar\omega.$$
(20.49)
Show that the partition function Z is given by
$$Z = Z_{SHO}^3,$$
(20.50)
where Z_{SHO} is the partition function of a simple harmonic oscillator given in eqn 20.3. Hence show that the Helmholtz function is given by
$$F = \frac{3}{2}\hbar\omega + 3k_B T \ln(1 - e^{-\beta\hbar\omega}),$$
(20.51)
and that the heat capacity tends to $3k_B$ at high temperature.

(20.8) The internal levels of an isolated hydrogen atom are given by $E = -R/n^2$ where $R = 13.6\,\text{eV}$. The degeneracy of each level is given by $2n^2$.
(a) Sketch the energy levels.
(b) Show that
$$Z = \sum_{n=1}^{\infty} 2n^2 \exp\left(\frac{R}{n^2 k_B T} \right).$$
(20.52)
Note that when $T \neq 0$, this expression for Z diverges. This is because of the large degeneracy of the hydrogen atom's highly excited states. If the hydrogen atom were to be confined in a box of finite size, this would cut off the highly excited states and Z would not then diverge.
By approximating Z as follows:
$$Z \approx \sum_{n=1}^{2} 2n^2 \exp\left(\frac{R}{n^2 k_B T} \right),$$
(20.53)
i.e. by ignoring all but the $n = 1$ and $n = 2$ states, estimate the mean energy of a hydrogen atom at $300\,\text{K}$.