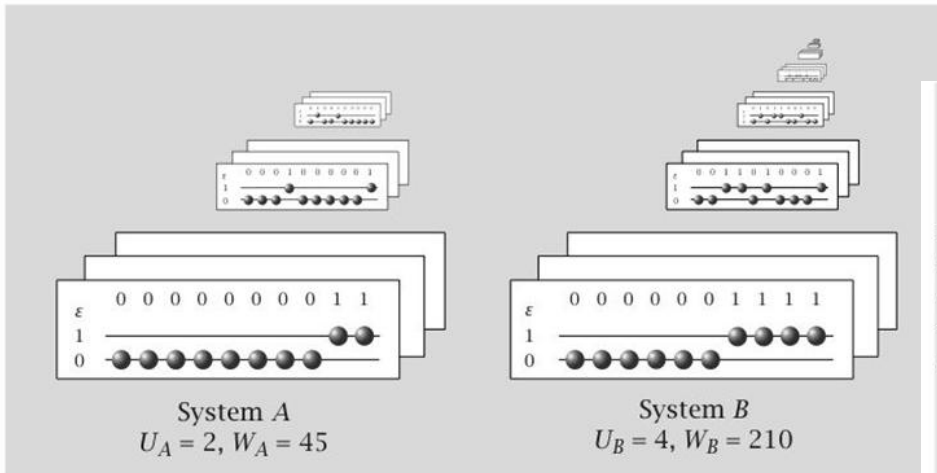# Statistical thermodynamics
2012-04-24

- Partition function
- Applications of Partition function
- What is Temperature?

Why does energy exchange?
(Economists suggest maximizing a utility function.)

Figure 3.14 Energy-level diagrams for the two different systems in Example 3.9 with 10 particles each. System A has total energy $U_A = 2$, and B has $U_B = 4$. System has the greater multiplicity of states.

The multiplicities of isolated systems A and B are

$$W_A = \frac{10!}{2!8!} = 45, \quad \text{and} \quad W_B = \frac{10!}{4!6!} = 210.$$

If A and B do not exchange energies, the total multiplicity is $W_{\text{total}} = W_A W_B = 9450$. Now suppose that you bring A and B into 'thermal contact' so that they can exchange energy. Now the system can change values of U_A and U_B subject to conservation of energy ($U_A + U_B$ will be unchanged). One possibility is $U_A = 3$ and $U_B = 3$. Then the total multiplicity W_{total} will be

$$W_{\text{total}} = \frac{10!}{3!7!}\frac{10!}{3!7!} = 14{,}400.$$

This shows that a principle of maximum multiplicity predicts that heat will flow from B to A to equalize energies in this case. Consider the alternative. Suppose A were to lower its energy to $U_A = 1$ while B wound up with $U_B = 5$. Then the multiplicity of states would be

$$W_{\text{total}} = \frac{10!}{1!9!}\frac{10!}{5!5!} = 2520.$$

A principle of maximal multiplicity predicts that this inequitable distribution is unlikely. That is, heat will not flow from the cold to the hot object.
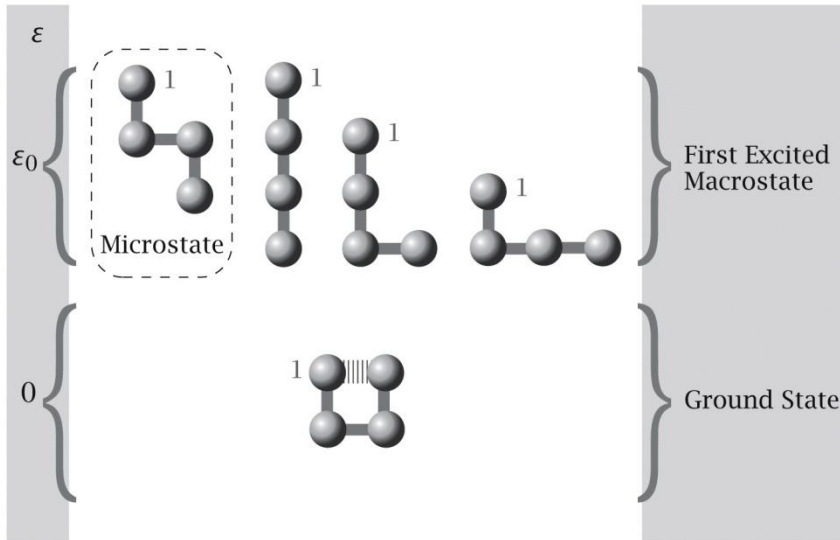
Polymer chain

Figure 10.1 Molecular Driving Forces 2/e (© Garland Science 2011)

- The system is one four-bead chain, that has two energy levels.

- Each of the five configurations is called a microstate, to distinguish it from a state or macrostate, which is a collection of microstates.

3

Boltzmann distribution

and therefore

$$\frac{\partial \ln W}{\partial n_i} = -(\ln n_i + 1) + (\ln N + 1) = -\ln \frac{n_i}{N}$$

It follows from eqn 16.49 that

$$-\ln \frac{n_i}{N} + \alpha - \beta \varepsilon_i = 0$$

and therefore that

$$\frac{n_i}{N} = e^{\alpha - \beta \varepsilon_i}$$

At this stage we note that

$$N = \sum_i n_i = \sum_i N e^{\alpha - \beta \varepsilon_i} = N e^{\alpha} \sum_i e^{\beta \varepsilon_i}$$

Because the N cancels on each side of this equality, it follows that

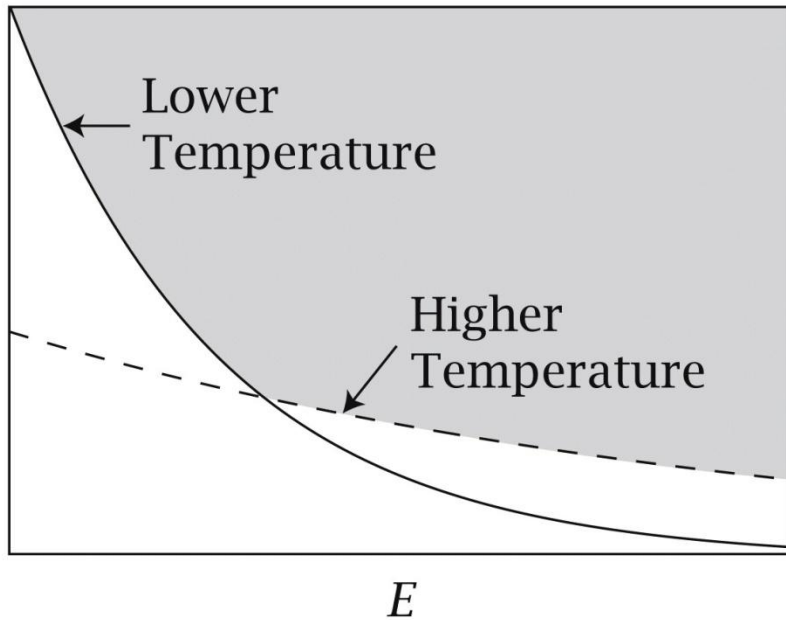$$e^{\alpha} = \frac{1}{\sum_j e^{-\beta \varepsilon_j}} \qquad (16.50)$$

and

$$\frac{n_i}{N} = e^{\alpha - \beta \varepsilon_i} = e^{\alpha} e^{-\beta \varepsilon_i} = \frac{1}{\sum_j e^{-\beta \varepsilon_j}} e^{-\beta \varepsilon_i}$$

- The Boltzmann distribution says that more particles will have low energies and fewer particles will have high energies.
- Fundamentally, all energy levels are equivalent. Rather, there are more arrangements of the system that way.
- It is extremely unlikely that one particle would have such a high energy that it would leave all the others no energy.
- There are far more arrangements in which most particles have energies that are relatively low, but nonzero. If each particle takes only a small fraction of the total energy, it leaves a great many more ways for the other particles to distribute the remaining energy.

4

What Does a Partition Function Tell You?

$p(E)$

Lower Temperature

Higher Temperature

E

Figure 10.4 Molecular Driving Forces 2/e (© Garland Science 2011)

Here's an intuitive way to think about the partition function. Think of Q as the number of states that are *effectively* accessible to the system. To see this, look at the limiting values (see Figures 10.4 and 10.5). When the energies are small, or the temperature is high, all the states become equally populated:

$$\left. \begin{array}{l} E_j \to 0 \\ \text{or} \\ T \to \infty \end{array} \right\} \quad \Longrightarrow \quad \frac{E_j}{kT} \to 0 \quad \Longrightarrow \quad p_j^* \to \frac{1}{t} \quad \Longrightarrow \quad Q \to t. \qquad (10.21)$$

In this case, all t states become accessible.

At the other extreme, as the energy intervals become large or as the temperature approaches zero, the particles occupy only the ground state:

$$\left. \begin{array}{l} E_{j \neq 1} \to \infty \\ \text{or} \\ T \to 0 \end{array} \right\} \quad \Longrightarrow \quad \frac{E_{j \neq 1}}{kT} \to \infty \quad \Longrightarrow \quad \left\{ \begin{array}{l} p_1^* \to 1 \\ \text{and} \\ p_{j \neq 1}^* \to 0 \end{array} \right. \quad \Longrightarrow \quad Q \to 1. \quad (10.22)$$

In this case, only the ground state becomes accessible.

Computing the Internal Energy from the Partition Function

Consider a system having fixed (T, V, N). To get the internal energy for a system with energies E_j, substitute Equation (10.9) for p_j^* into Equation (10.2):

$$U = \sum_{j=1}^{t} p_j^* E_j$$

$$= Q^{-1} \sum_{j=1}^{t} E_j e^{-\beta E_j}, \tag{10.31}$$

where $\beta = 1/kT$ is a useful quantity for simplifying the next few steps. Notice that the sum on the right-hand side of Equation (10.31) can be expressed as a derivative of the partition function in Equation (10.10):

$$\left(\frac{dQ}{d\beta}\right) = \frac{d}{d\beta} \sum_{j=1}^{t} e^{-\beta E_j} = -\sum_{j=1}^{t} E_j e^{-\beta E_j}. \tag{10.32}$$

Substituting Equation (10.32) into (10.31) simplifies it:

$$U = -\frac{1}{Q}\left(\frac{dQ}{d\beta}\right) = -\left(\frac{d \ln Q}{d\beta}\right). \tag{10.33}$$

Computing the Entropy Energy from the Partition Function

The entropy of a system is defined by Equation (5.2):

$$\frac{S}{k} = -\sum_{j=1}^{t} p_j \ln p_j.$$

Substituting the Boltzmann distribution $p_j^* = Q^{-1}e^{-E_j/kT}$ from Equation (10.9) into Equation (5.2) gives

$$\frac{S}{k} = -\sum_{j=1}^{t} \left(\frac{1}{Q}e^{-E_j/kT}\right)\left[\ln\left(\frac{1}{Q}\right) - \frac{E_j}{kT}\right]. \tag{10.37}$$

Substituting Equation (10.10) for Q and Equation (10.31) for U into Equation (10.37) gives

$$S = k\ln Q + \frac{U}{T} = k\ln Q + kT\left(\frac{\partial \ln Q}{\partial T}\right). \tag{10.38}$$

An unfolding or denaturation profile for a protein

Figure 10.1 Molecular Driving Forces 2/e (© Garland Science 2011)
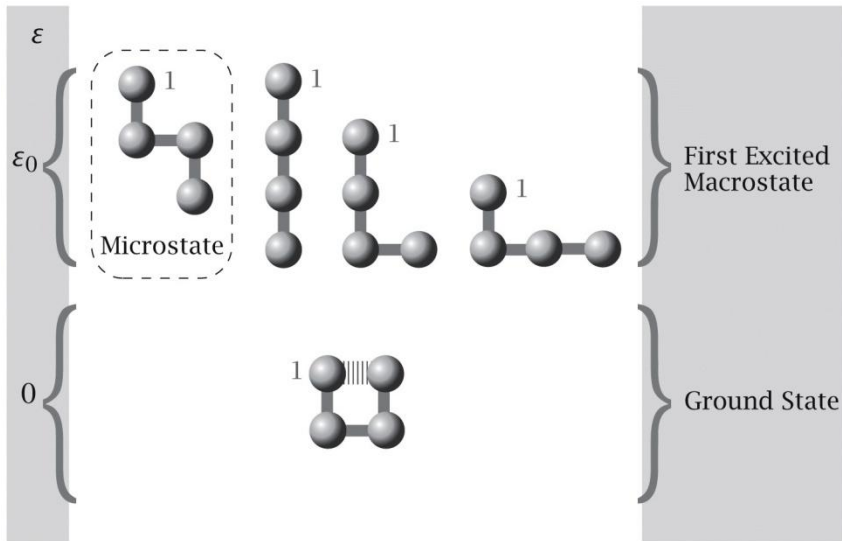

Figure 10.6 Molecular Driving Forces 2/e (© Garland Science 2011)

- For the four-bead chain, there is one compact conformation and four open conformations .

- The density of states is $W(0)=1$ and $W(\varepsilon_0) =4$.

- Since W is the number of microstates per level, the partition function can be expressed as a sum over the two levels (open and compact, in this case), rather than over the five microstates:
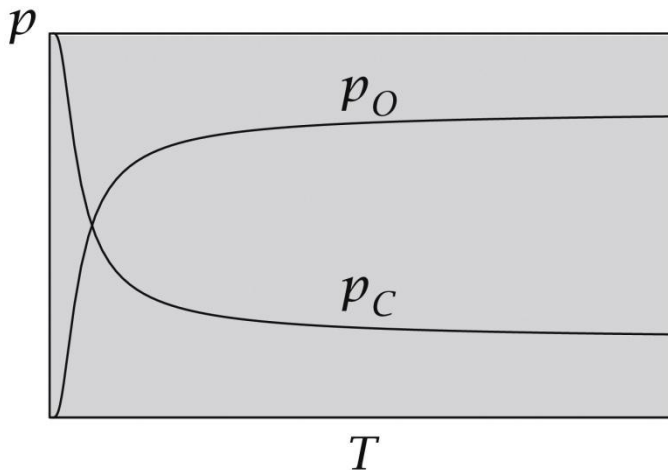
$$p_C = \frac{1}{Q} \quad \text{and} \quad p_O = \frac{4e^{-\varepsilon_0/kT}}{Q} = \frac{4e^{-\varepsilon_0/kT}}{1+4e^{-\varepsilon_0/kT}}.$$

Figure 10.6 shows how the populations change with temperature. This figure describes a series of different experiments, each one at a fixed temperature. This kind of curve is sometimes called an *unfolding* or *denaturation* profile for a polymer or protein [1]. If you define $Q_C = 1$ as the partition function for the compact state alone and $Q_O = 4\exp(-\varepsilon_0/kT)$ for the open state alone, then you can compute free energies using $F = -kT \ln Q$. At the cross-over point, where $p_C = p_O = 1/2$, the free energy of collapse is zero: $\Delta F = F_C - F_O = -kT \ln(Q_C/Q_O) = 0$.
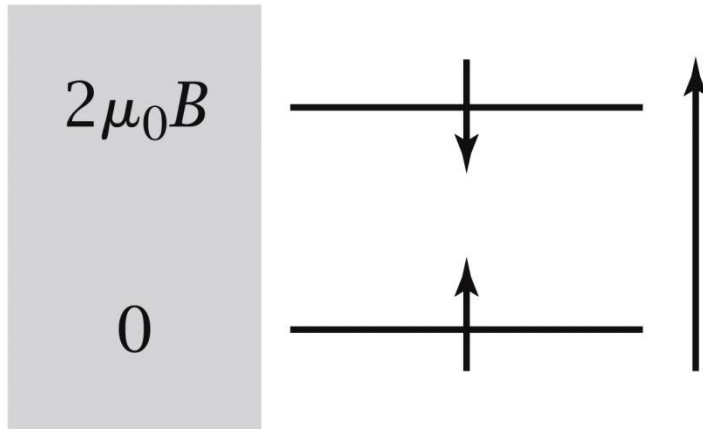
Curie's law of paramagnetism, a two-level system.

$2\mu_0 B$

0

Figure 10.10 Molecular Driving Forces 2/e (© Garland Science 2011)

$\langle\mu\rangle$

BT^{-1}
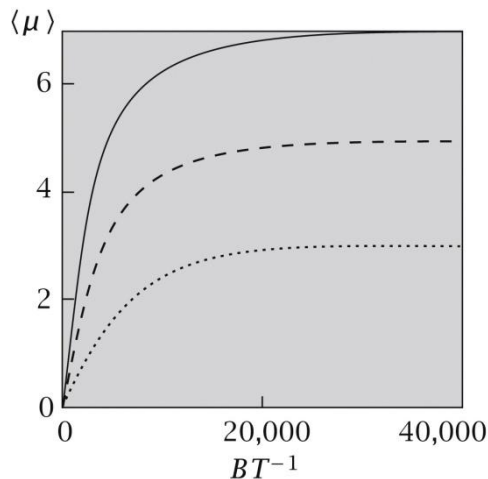
Figure 10.11 Molecular Driving Forces 2/e (© Garland Science 2011)

$$q = 1 + e^{-2\mu_0 B/kT}. \tag{10.53}$$

We want to calculate the average magnetic moment (the material's magnetization) as a function of temperature. At equilibrium, the probability that an atom's magnetic moment is parallel to B is p_1^* and the probability that it is antiparallel is p_2^*:

$$p_1^* = \frac{1}{q} \quad \text{and} \quad p_2^* = \left(\frac{1}{q}\right) e^{-2\mu_0 B/kT}. \tag{10.54}$$

Because the magnetic moment of the aligned state is $+\mu_0$ and that of the antialigned state is $-\mu_0$, the average magnetic moment is

$$\langle\mu\rangle = \sum_{j=1}^{2} \mu_j p_j^*$$

$$= \mu_0 p_1^* + (-\mu_0) p_2^* = \frac{\mu_0}{q}(1 - e^{-2\mu_0 B/kT}) = \mu_0 \frac{1 - e^{-2\mu_0 B/kT}}{1 + e^{-2\mu_0 B/kT}}. \tag{10.55}$$

The last equality follows from the definition of q in Equation (10.53). A concise way to express this relationship is through use of the hyperbolic tangent function,

$$\tanh x = \frac{1 - e^{-2x}}{1 + e^{-2x}}. \tag{10.56}$$

Using the hyperbolic tangent, the average magnetic moment is given by

$$\langle\mu\rangle = \mu_0 \tanh\left(\frac{\mu_0 B}{kT}\right). \tag{10.57}$$

In weak magnetic fields or at high temperatures, $\mu_0 B/kT \ll 1$. The Taylor series expansion for exponentials (see Appendix J, Equation (J.1)) gives $1 - e^{-2\mu_0 B/kT} \approx 2\mu_0 B/kT$ and $1 + e^{-2\mu_0 B/kT} \approx 2 - 2\mu_0 B/kT \approx 2$. At high temperatures or in weak fields, the total magnetic moment is inversely proportional to T, and Equation (10.57) becomes **Curie's law**:

$$\langle\mu\rangle = \frac{\mu_0^2 B}{kT}. \tag{10.58}$$

In contrast, at high fields ($B/kT \to \infty$), Equation (10.55) gives $\langle\mu\rangle = \mu_0$.

Peptide loop on a protein molecule

We probe the loop with fluorescence spectroscopy, which measures a distance l from a point on the loop to a point on the protein.
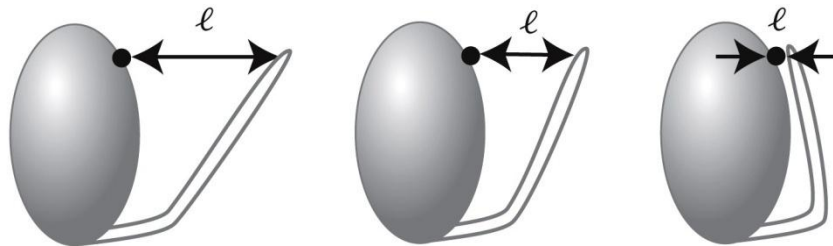
Partition function

Figure 10.12 Molecular Driving Forces 2/e (© Garland Science 2011)

$$q = 1 + e^{-\varepsilon_2/RT} + e^{-\varepsilon_3/RT} = 1 + 0.19 + 0.06 = 1.25, \qquad (10.59)$$

so the populations of the three states are

$$p_1 = \frac{1}{q} = 0.8, \qquad p_2 = \frac{e^{-\varepsilon_2/RT}}{q} = 0.15, \qquad p_3 = \frac{e^{-\varepsilon_3/RT}}{q} = 0.05. \qquad (10.60)$$

The ideal test of your model would be measurements of the three populations in the distribution. However, usually experiments measure only averages, not full distributions. So, to compare with experiments, compute averages such as

$$\langle \ell \rangle = 0.8\ell_1 + 0.15\ell_2 + 0.06\ell_3 = 1.34 \text{ Å} \qquad (10.61)$$

and

$$\langle \varepsilon \rangle = 0.8\varepsilon_1 + 0.15\varepsilon_2 + 0.06\varepsilon_3 = 0.25 \text{ kcal mol}^{-1} \qquad (10.62)$$

4A   **2A**   **1A**

1.7kCal mol^{-1}   **1**   **0**

Molecular partition function

The energy of a molecule is the sum of contributions from its different modes of motion:

$$\varepsilon_i = \varepsilon_i^T + \varepsilon_i^R + \varepsilon_i^V + \varepsilon_i^E \tag{17.10}$$

where T denotes translation, R rotation, V vibration, and E the electronic contribu-

$$q = \sum_i e^{-\beta\varepsilon_i} = \sum_{i\,(\text{all states})} e^{-\beta\varepsilon_i^T - \beta\varepsilon_i^R - \beta\varepsilon_i^V - \beta\varepsilon_i^E}$$

$$= \sum_{i\,(\text{translational})} \sum_{i\,(\text{rotational})} \sum_{i\,(\text{vibrational})} \sum_{i\,(\text{electronic})} e^{-\beta\varepsilon_i^T - \beta\varepsilon_i^R - \beta\varepsilon_i^V - \beta\varepsilon_i^E}$$

$$= \left(\sum_{i\,(\text{translational})} e^{-\beta\varepsilon_i^T}\right)\left(\sum_{i\,(\text{rotational})} e^{-\beta\varepsilon_i^R}\right)\left(\sum_{i\,(\text{vibrational})} e^{-\beta\varepsilon_i^V}\right)\left(\sum_{i\,(\text{electronic})} e^{-\beta\varepsilon_i^E}\right)$$

$$= q^T q^R q^V q^E$$

This factorization means that we can investigate each contribution separately.

Translational energy (Particle in a box)

Suppose the particle is confined within a three-dimensional box with dimensions $0 < x < a$, $0 < y < b$, and $0 < z < c$. The Schrödinger equation is

$$-\frac{h^2}{8\pi^2 m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\psi(x,y,z)+\mathcal{V}(x,y,z)\psi(x,y,z)$$
$$= \varepsilon\psi(x,y,z), \tag{11.16}$$

where $\mathcal{V}(x,y,z) = \mathcal{V}(x)+\mathcal{V}(y)+\mathcal{V}(z)$ and $\mathcal{V}(x) = \mathcal{V}(y) = \mathcal{V}(z) = 0$. Equation (11.16) can be factored into three independent equations:
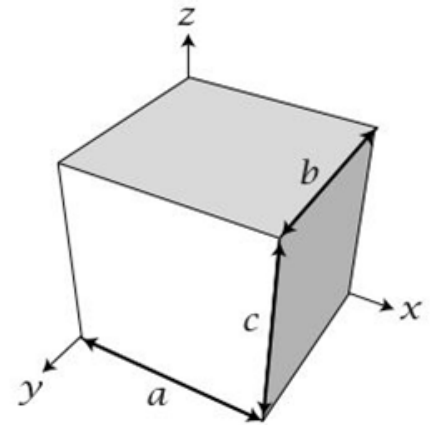
$$\mathcal{H}_x\psi_x = \varepsilon_x\psi_x,$$

$$\mathcal{H}_y\psi_y = \varepsilon_y\psi_y,$$

$$\mathcal{H}_z\psi_z = \varepsilon_z\psi_z,$$

where $\mathcal{H}_x = -(h^2/8\pi^2 m)(\partial^2/\partial x^2)$, for example. The equations are *separable*—they can be solved separately. Then $\psi(x,y,z) = \psi(x)\psi(y)\psi(z)$ and the energies can be added together. The particle energy $\varepsilon_{n_x,n_y,n_z}$ is

$$\varepsilon_{n_x,n_y,n_z} = \frac{h^2}{8m}\left(\frac{n_x^2}{a^2}+\frac{n_y^2}{b^2}+\frac{n_z^2}{c^2}\right), \tag{11.17}$$

where a, b, and c are the x, y, and z dimensions of the box (see Figure 11.6).

Partition function contributed by 1-dimensional translation

$$E_n = \frac{n^2 h^2}{8mX^2} \qquad n = 1, 2, \ldots$$

The lowest level ($n = 1$) has energy $h^2/8mX^2$, so the energies relative to that level are

$$\varepsilon_n = (n^2 - 1)\varepsilon \qquad \varepsilon = h^2/8mX^2$$

The sum to evaluate is therefore

$$q_X = \sum_{n=1}^{\infty} e^{-(n^2-1)\beta\varepsilon}$$

The translational energy levels are very close together in a container the size of a typical laboratory vessel; therefore, the sum can be approximated by an integral:

$$q_X = \int_1^{\infty} e^{-(n^2-1)\beta\varepsilon} dn \approx \int_0^{\infty} e^{-n^2\beta\varepsilon} dn$$

The extension of the lower limit to $n = 0$ and the replacement of $n^2 - 1$ by n^2 introduces negligible error but turns the integral into standard form. We make the substitution $x^2 = n^2\beta\varepsilon$, implying $dn = dx/(\beta\varepsilon)^{1/2}$, and therefore that

$$q_X = \left(\frac{1}{\beta\varepsilon}\right)^{1/2} \overbrace{\int_0^{\infty} e^{-x^2} dx}^{\pi^{1/2}/2} = \left(\frac{1}{\beta\varepsilon}\right)^{1/2} \left(\frac{\pi^{1/2}}{2}\right) = \left(\frac{2\pi m}{h^2\beta}\right)^{1/2} X$$

Partition function contributed by 3-dimensional translation

The total energy of a molecule ε is the sum of its translational energies in all three directions:

$$\varepsilon_{n_1 n_2 n_3} = \varepsilon_{n_1}^{(X)} + \varepsilon_{n_2}^{(Y)} + \varepsilon_{n_3}^{(Z)} \tag{16.16}$$

where n_1, n_2, and n_3 are the quantum numbers for motion in the x-, y-, and z-directions, respectively. Therefore, because $e^{a+b+c} = e^a e^b e^c$, the partition function factorizes as follows:

$$q = \sum_{\text{all } n} e^{-\beta\varepsilon_{n_1}^{(X)} - \beta\varepsilon_{n_2}^{(Y)} - \beta\varepsilon_{n_3}^{(Z)}} = \sum_{\text{all } n} e^{-\beta\varepsilon_{n_1}^{(X)}} e^{-\beta\varepsilon_{n_2}^{(Y)}} e^{-\beta\varepsilon_{n_3}^{(Z)}}$$

$$= \left(\sum_{n_1} e^{-\beta\varepsilon_{n_1}^{(X)}} \right) \left(\sum_{n_2} e^{-\beta\varepsilon_{n_2}^{(Y)}} \right) \left(\sum_{n_3} e^{-\beta\varepsilon_{n_3}^{(Z)}} \right) \tag{16.17}$$

$$= q_X q_Y q_Z$$

Partition function contributed by 3-dimensional translation

Equation 16.15 gives the partition function for translational motion in the x-direction. The only change for the other two directions is to replace the length X by the lengths Y or Z. Hence the partition function for motion in three dimensions is

$$q = \left(\frac{2\pi m}{h^2 \beta} \right)^{3/2} XYZ \tag{16.18}$$

The product of lengths XYZ is the volume, V, of the container, so we can write

$$q = \frac{V}{\Lambda^3} \qquad \Lambda = h \left(\frac{\beta}{2\pi m} \right)^{1/2} = \frac{h}{(2\pi m kT)^{1/2}} \tag{16.19}$$

The quantity Λ has the dimensions of length and is called the **thermal wavelength** (sometimes the *thermal de Broglie wavelength*) of the molecule.

Partition function by rotation of a nonlinear molecule

Answer From eqn 13.31, the energy levels of a linear rotor are $hcBJ(J+1)$, with $J = 0, 1, 2, \ldots$. The state of lowest energy has zero energy, so no adjustment need be made to the energies given by this expression. Each level consists of $2J + 1$ degenerate states. Therefore,

$$q = \sum_{J=0}^{\infty} \overbrace{(2J+1)}^{g_J}\overbrace{e^{-\beta hcBJ(J+1)}}^{\varepsilon_J}$$

When many rotational states are occupied and kT is much larger than the separation between neighbouring states, the sum in the partition function can be approximated by an integral, much as we did for translational motion in *Justification 16.2*:

$$q^{R} = \int_{0}^{\infty} (2J+1)e^{-\beta hcBJ(J+1)}\,dJ$$

Although this integral looks complicated, it can be evaluated without much effort by noticing that because

$$\frac{d}{dJ}e^{aJ(J+1)} = \left\{\frac{d}{dJ}aJ(J+1)\right\}e^{aJ(J+1)} = a(2J+1)e^{aJ(J+1)}$$

it can also be written as

$$q^{R} = \frac{1}{\beta hcB}\int_{0}^{\infty}\left(\frac{d}{dJ}e^{-\beta hcBJ(J+1)}\right)dJ$$

Then, because the integral of a derivative of a function is the function itself, we obtain

$$q^{R} = -\frac{1}{\beta hcB}e^{-\beta hcBJ(J+1)}\,\Big|_{0}^{\infty} = \frac{1}{\beta hcB}$$

which (because $\beta = 1/kT$) is eqn 17.14a.

Partition function by rotation of a nonlinear molecule

The calculation for a nonlinear molecule is along the same lines, but slightly trickier. First, we note that the energies of a symmetric rotor are

$$E_{J,K,M_J} = hcBJ(J+1) + hc(A-B)K^2$$

with $J = 0, 1, 2, \ldots$, $K = J, J-1, \ldots, -J$, and $M_J = J, J-1, \ldots, -J$. Instead of considering these ranges, we can cover the same values by allowing K to range from $-\infty$ to ∞, with J confined to $|K|, |K|+1, \ldots, \infty$ for each value of K (Fig. 17.2). Because the energy is independent of M_J, and there are $2J+1$ values of M_J for each value of J, each value of J is $2J+1$-fold degenerate. It follows that the partition function

$$q = \sum_{J=0}^{\infty} \sum_{K=-J}^{J} \sum_{M_J=-J}^{J} e^{-E_{JKM_J}/kT}$$
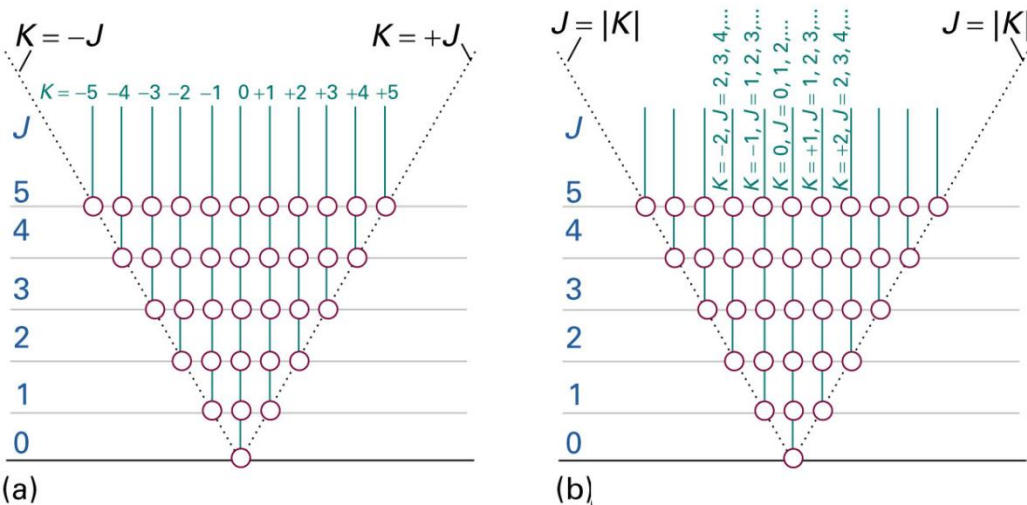
Fig. 17.2 (a) The sum over $J = 0, 1, 2, \ldots$ and $K = J, J-1, \ldots, -J$ (depicted by the circles) can be covered (b) by allowing K to range from $-\infty$ to ∞, with J confined to $|K|$, $|K|+1, \ldots, \infty$ for each value of K.

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Partition function by rotation of a nonlinear molecule

$$q = \sum_{J=0}^{\infty} \sum_{K=-J}^{J} \sum_{M_J=-J}^{J} e^{-E_{JKM_J}/kT}$$

with $J = 0, 1, 2, \ldots$, $K = J, J-1, \ldots, -J$, and $M_J = J, J-1, \ldots, -J$. Instead of considering these ranges, we can cover the same values by allowing K to range from $-\infty$ to ∞, with J confined to $|K|, |K|+1, \ldots, \infty$ for each value of K (Fig. 17.2). Because the energy is independent of M_J, and there are $2J+1$ values of M_J for each value of J, each value of J is $2J+1$-fold degenerate. It follows that the partition function

$$q = \sum_{J=0}^{\infty} \sum_{K=-J}^{J} \sum_{M_J=-J}^{J} e^{-E_{JKM_J}/kT}$$

can be written equivalently as

$$q = \sum_{K=-\infty}^{\infty} \sum_{J=|K|}^{\infty} (2J+1) e^{-E_{JKM_J}/kT}$$

$$= \sum_{K=-\infty}^{\infty} \sum_{J=|K|}^{\infty} (2J+1) e^{-hc[BJ(J+1)+(A-B)K^2]/kT}$$

$$= \sum_{K=-\infty}^{\infty} e^{-\{hc(A-B)/kT\}K^2} \sum_{J=|K|}^{\infty} (2J+1) e^{-hcBJ(J+1)/kT}$$

Partition function contributed by the rotation of a nonlinear molecule

Now we assume that the temperature is so high that numerous states are occupied and that the sums may be approximated by integrals. Then

$$q = \int_{-\infty}^{\infty} e^{-\{hc(A-B)/kT\}K^2} \int_{|K|}^{\infty} (2J+1)e^{-hcBJ(J+1)/kT} dJ dK$$

As before, the integral over J can be recognized as the integral of the derivative of a function, which is the function itself, so

$$\int_{|K|}^{\infty} (2J+1)e^{-hcBJ(J+1)/kT} dJ = \int_{|K|}^{\infty} \left(-\frac{kT}{hcB}\right)\frac{d}{dJ} e^{-hcBJ(J+1)/kT} dJ$$

$$= \left(-\frac{kT}{hcB}\right) e^{-hcBJ(J+1)/kT} \Big|_{|K|}^{\infty} = \left(\frac{kT}{hcB}\right) e^{-hcB|K|(|K|+1)/kT}$$

$$\approx \left(\frac{kT}{hcB}\right) e^{-hcBK^2/kT}$$

In the last line we have supposed that $|K| \gg 1$ for most contributions. Now we can write

$$q = \frac{kT}{hcB} \int_{-\infty}^{\infty} e^{-\{hc(A-B)/kT\}K^2} e^{-hcBK^2/kT} dK$$

$$= \frac{kT}{hcB} \int_{-\infty}^{\infty} e^{-\{hcA/kT\}K^2} dK = \left(\frac{kT}{hcB}\right)\left(\frac{kT}{hcA}\right)^{1/2} \overbrace{\int_{-\infty}^{\infty} e^{-x^2} dx}^{\pi^{1/2}}$$

$$= \left(\frac{kT}{hc}\right)^{3/2} \left(\frac{\pi}{AB^2}\right)^{1/2}$$

Partition function by vibration

If the vibrational excitation is not too great, the harmonic approximation may be made, and the vibrational energy levels written as

$$E_v = (v + \tfrac{1}{2})hc\tilde{v} \qquad v = 0, 1, 2, \ldots \tag{17.17}$$

If, as usual, we measure energies from the zero-point level, then the permitted values are $\varepsilon_v = vhc\tilde{v}$ and the partition function is

$$q^V = \sum_v e^{-\beta vhc\tilde{v}} = \sum_v (e^{-\beta hc\tilde{v}})^v \tag{17.18}$$

Evaluate the partition function for a molecule with an infinite number of equally spaced nondegenerate energy levels (Fig. 16.3). These levels can be thought of as the vibrational energy levels of a diatomic molecule in the harmonic approximation.

Method We expect the partition function to increase from 1 at $T=0$ and approach infinity as T to ∞. To evaluate eqn 16.8 explicitly, note that

$$1 + x + x^2 + \cdots = \frac{1}{1-x}$$

Answer If the separation of neighbouring levels is ε, the partition function is

$$q = 1 + e^{-\beta\varepsilon} + e^{-2\beta\varepsilon} + \cdots = 1 + e^{-\beta\varepsilon} + (e^{-\beta\varepsilon})^2 + \cdots = \frac{1}{1 - e^{-\beta\varepsilon}}$$

This expression is plotted in Fig. 16.4: notice that, as anticipated, q rises from 1 to infinity as the temperature is raised.

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Overall Partition function

(e) The overall partition function

The partition functions for each mode of motion of a molecule are collected in Table 17.3 at the end of the chapter. The overall partition function is the product of each contribution. For a diatomic molecule with no low-lying electronically excited states and $T \gg \theta_R$,

$$q = g^E \left(\frac{V}{\Lambda^3} \right) \left(\frac{T}{\sigma \theta_R} \right) \left(\frac{1}{1 - e^{-T/\theta_v}} \right) \qquad (17.23)$$

Mean translational energy

the mean energy of each mode M (from eqn 16.29) is

$$\langle \varepsilon^M \rangle = -\frac{1}{q^M}\left(\frac{\partial q^M}{\partial \beta}\right)_V \qquad M = T, R, V, \text{ or } E$$

(a) The mean translational energy

To see a pattern emerging, we consider first a one-dimensional system of length X, for which $q^T = X/\Lambda$, with $\Lambda = h(\beta/2\pi m)^{1/2}$. Then, if we note that Λ is a constant times $\beta^{1/2}$,

$$\langle \varepsilon^T \rangle = -\frac{\Lambda}{X}\left(\frac{\partial}{\partial \beta}\frac{X}{\Lambda}\right)_V = -\beta^{1/2}\frac{d}{d\beta}\left(\frac{1}{\beta^{1/2}}\right) = \frac{1}{2\beta} = \tfrac{1}{2}kT \qquad (17.25a)$$

For a molecule free to move in three dimensions, the analogous calculation leads to

$$\langle \varepsilon^T \rangle = \tfrac{3}{2}kT \qquad (17.25b)$$

Both conclusions are in agreement with the classical equipartition theorem (see *Molecular interpretation 2.2*) that the mean energy of each quadratic contribution to the energy is $\tfrac{1}{2}kT$. Furthermore, the fact that the mean energy is independent of the size of the container is consistent with the thermodynamic result that the internal energy of a perfect gas is independent of its volume (*Molecular interpretation 2.2*).

Mean rotational energy

The mean rotational energy of a linear molecule is obtained from the partition function given in eqn 17.13. When the temperature is low ($T < \theta_R$), the series must be summed term by term, which gives

$$q^R = 1 + 3e^{-2\beta hcB} + 5e^{-6\beta hcB} + \cdots$$

Hence

$$\langle \varepsilon^R \rangle = \frac{hcB(6e^{-2\beta hcB} + 30e^{-6\beta hcB} + \cdots)}{1 + 3e^{-2\beta hcB} + 5e^{-6\beta hcB} + \cdots} \qquad (17.26a)$$

This function is plotted in Fig. 17.8. At high temperatures ($T \gg \theta_R$), q^R is given by eqn 17.15, and

$$\langle \varepsilon^R \rangle = -\frac{1}{q^R}\frac{dq^R}{d\beta} = -\sigma hc\beta B \frac{d}{d\beta}\frac{1}{\sigma hc\beta B} = \frac{1}{\beta} = kT \qquad (17.26b)$$

(q^R is independent of V, so the partial derivatives have been replaced by complete derivatives.) The high-temperature result is also in agreement with the equipartition theorem, for the classical expression for the energy of a linear rotor is $E_K = \frac{1}{2}I_\perp\omega_a^2 + \frac{1}{2}I_\perp\omega_b^2$. (There is no rotation around the line of atoms.) It follows from the equipartition theorem that the mean rotational energy is $2 \times \frac{1}{2}kT = kT$.
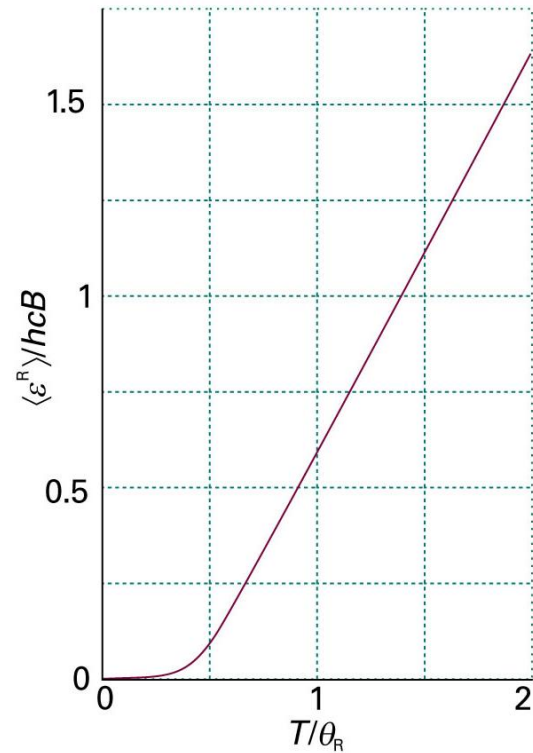
Mean vibrational energy

The vibrational partition function in the harmonic approximation is given in eqn 17.19. Because q^V is independent of the volume, it follows that

$$\frac{dq^V}{d\beta} = \frac{d}{d\beta}\left(\frac{1}{1-e^{-\beta hc\tilde{\nu}}}\right) = -\frac{hc\tilde{\nu}e^{-\beta hc\tilde{\nu}}}{(1-e^{-\beta hc\tilde{\nu}})^2} \qquad (17.27)$$

and hence from

$$\langle \varepsilon^V \rangle = -\frac{1}{q^V}\frac{dq^V}{d\beta} = -(1-e^{-\beta hc\tilde{\nu}})\left\{-\frac{hc\tilde{\nu}e^{-\beta hc\tilde{\nu}}}{(1-e^{-\beta hc\tilde{\nu}})^2}\right\} = \frac{hc\tilde{\nu}e^{-\beta hc\tilde{\nu}}}{1-e^{-\beta hc\tilde{\nu}}}$$

that

$$\langle \varepsilon^V \rangle = \frac{hc\tilde{\nu}}{e^{\beta hc\tilde{\nu}} - 1} \qquad (17.28)$$

The zero-point energy, $\frac{1}{2}hc\tilde{\nu}$, can be added to the right-hand side if the mean energy is to be measured from 0 rather than the lowest attainable level (the zero-point level). The variation of the mean energy with temperature is illustrated in Fig. 17.9. At high temperatures, when $T \gg \theta_V$, or $\beta hc\tilde{\nu} \ll 1$, the exponential functions can be expanded ($e^x = 1 + x + \cdots$) and all but the leading terms discarded. This approximation leads to

$$\langle \varepsilon^V \rangle = \frac{hc\tilde{\nu}}{(1+\beta hc\tilde{\nu}+\cdots)-1} \approx \frac{1}{\beta} = kT \qquad (17.29)$$
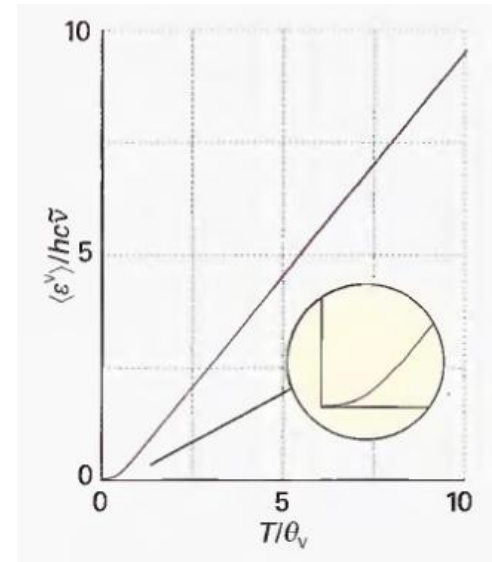
Heat capacity

The constant-volume heat capacity is defined as $C_V = (\partial U/\partial T)_V$. The derivative with respect to T is converted into a derivative with respect to β by using

$$\frac{d}{dT} = \frac{d\beta}{dT}\frac{d}{d\beta} = -\frac{1}{kT^2}\frac{d}{d\beta} = -k\beta^2\frac{d}{d\beta} \tag{17.30}$$

It follows that

$$C_V = -k\beta^2\left(\frac{\partial U}{\partial \beta}\right)_V \tag{17.31a}$$

Because the internal energy of a perfect gas is a sum of contributions, the heat capacity is also a sum of contributions from each mode. The contribution of mode M is

$$C_V^M = N\left(\frac{\partial \langle \varepsilon^M \rangle}{\partial T}\right)_V = -Nk\beta^2\left(\frac{\partial \langle \varepsilon^M \rangle}{\partial \beta}\right)_V \tag{17.31b}$$

The temperature is always high enough (provided the gas is above its condensation temperature) for the mean translational energy to be $\frac{3}{2}kT$, the equipartition value. Therefore, the molar constant-volume heat capacity is

$$C_{V,m}^T = N_A\frac{d(\frac{3}{2}kT)}{dT} = \frac{3}{2}R \tag{17.32}$$

Heat capacity of diatomic molecule
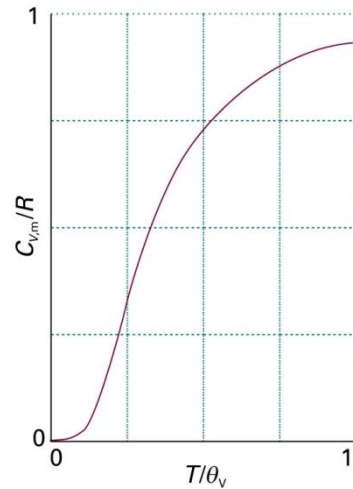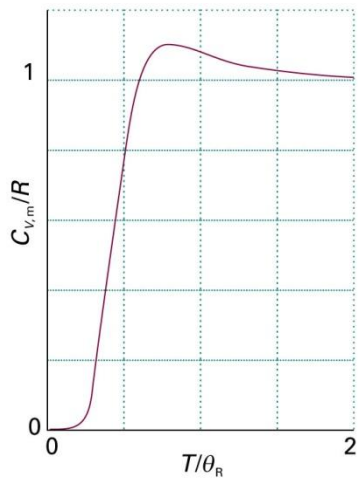
Fig. 17.10 The temperature dependence of the rotational contribution to the heat capacity of a linear molecule.
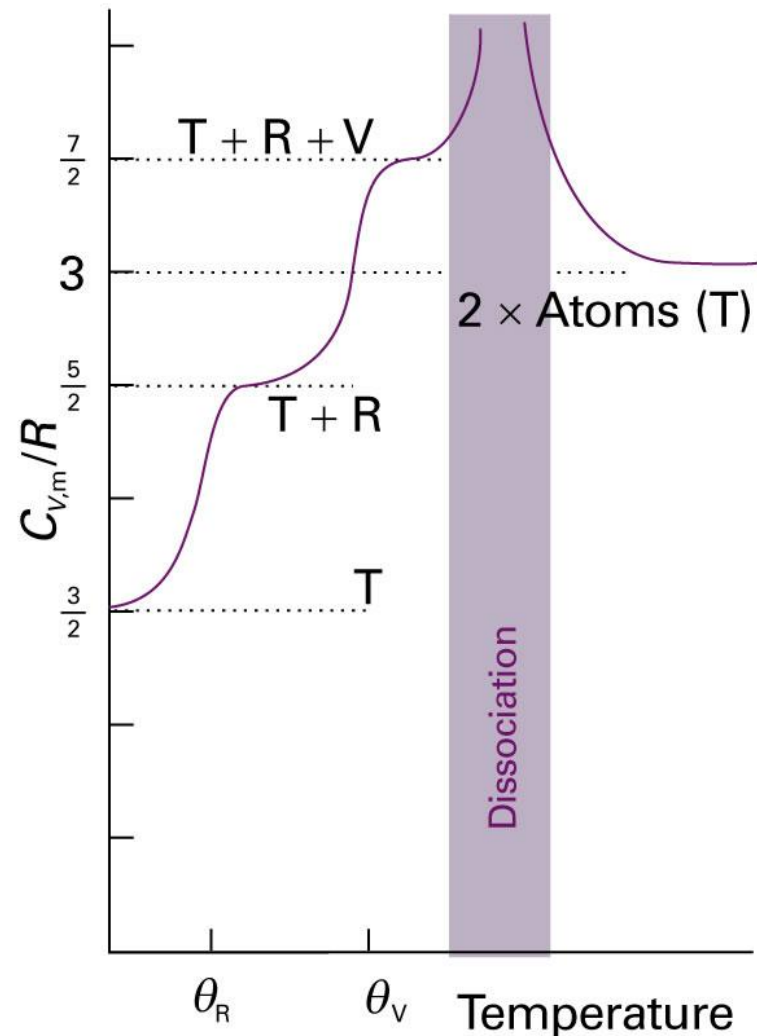
Partition Functions for Independent and Distinguishable Particles

First, consider distinguishable particles in a system with energy levels E_j. Suppose the system has two independent subsystems (e.g., two particles), distinguishable by labels A and B, with energy levels ε_i^A and ε_m^B, respectively, $i = 1, 2, \ldots, a$ and $m = 1, 2, \ldots, b$. The system energy is

$$E_j = \varepsilon_i^A + \varepsilon_m^B.$$

Because the subsystems are independent, you can write partition functions q_A for subsystem A and q_B for subsystem B according to Equation (10.10):

$$q_A = \sum_{i=1}^{a} e^{-\varepsilon_i^A/kT} \quad \text{and} \quad q_B = \sum_{m=1}^{b} e^{-\varepsilon_m^B/kT}. \tag{10.25}$$

The partition function Q for the entire system is the sum of Boltzmann factors $e^{-E_j/kT}$ over all $j = ab$ energy levels:

$$Q = \sum_{j=1}^{t} e^{-E_j/kT} = \sum_{i=1}^{a} \sum_{m=1}^{b} e^{-(\varepsilon_i^A + \varepsilon_m^B)/kT} = \sum_{i=1}^{a} \sum_{m=1}^{b} e^{-\varepsilon_i^A/kT} e^{-\varepsilon_m^B/kT}. \tag{10.26}$$

Because the subsystems are independent and distinguishable by their labels, the sum over the i levels of A has nothing to do with the sum over the m levels of B. The partition function Q in Equation (10.26) can be factored into subsystem partition functions q_A and q_B:

$$Q = \sum_{i=1}^{a} e^{-\varepsilon_i^A/kT} \sum_{m=1}^{b} e^{-\varepsilon_m^B/kT} = q_A q_B. \tag{10.27}$$

Partition Functions for Independent and Indistinguishable Particles

- For distinguishable independent molecules: $Q = q^N$ (16.45a)

- For indistinguishable independent molecules: $Q = q^N/N!$ (16.45b)

For molecules to be indistinguishable, they must be of the same kind: an Ar atom is never indistinguishable from a Ne atom. Their identity, however, is not the only criterion. Each identical molecule in a crystal lattice, for instance, can be 'named' with a set of coordinates. Identical molecules in a lattice can therefore be treated as distinguishable because their sites are distinguishable, and we use eqn 16.45a. On the other hand, identical molecules in a gas are free to move to different locations, and there is no way of keeping track of the identity of a given molecule; we therefore use eqn 16.45b.

Ideal gas law

Derive an expression for the pressure of a gas of independent particles.

Method We should suspect that the pressure is that given by the perfect gas law. To proceed systematically, substitute the explicit formula for Q for a gas of independent, indistinguishable molecules (see eqn 16.45 and Table 17.3 at the end of the chapter) into eqn 17.3.

Answer For a gas of independent molecules, $Q = q^N/N!$ with $q = V/\Lambda^3$:

$$p = kT\left(\frac{\partial \ln Q}{\partial V}\right)_T = \frac{kT}{Q}\left(\frac{\partial Q}{\partial V}\right)_T = \frac{NkT}{q}\left(\frac{\partial q}{\partial V}\right)_T$$

$$= \frac{NkT\Lambda^3}{V} \times \frac{1}{\Lambda^3} = \frac{NkT}{V} = \frac{nRT}{V}$$

To derive this relation, we have used

$$\left(\frac{\partial q}{\partial V}\right)_T = \left(\frac{\partial(V/\Lambda^3)}{\partial V}\right)_T = \frac{1}{\Lambda^3}$$

and $NkT = nN_A kT = nRT$. The calculation shows that the equation of state of a gas of independent particles is indeed the perfect gas law.

Schottky two-state model

- a system that has N distinguishable particles with two energy levels for each particle

- a ground state with energy zero and an excited state with energy $\varepsilon = \varepsilon_0 > 0$.

$$q = 1 + e^{-\beta \varepsilon_0}. \tag{10.45}$$

The partition function approaches 1 at low temperatures and 2 at high temperatures. The relative populations of the two states are given by the Boltzmann distribution, Equation (10.9):

$$p_1^* = \frac{1}{q} \quad \text{and} \quad p_2^* = \frac{e^{-\beta \varepsilon_0}}{q}. \tag{10.46}$$
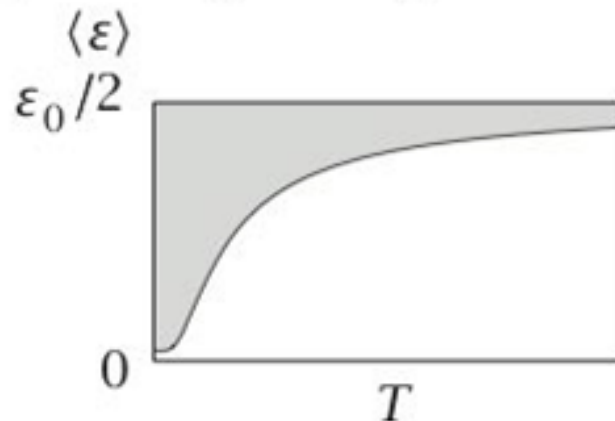
Average energy of two-state model

The average energy is given by Equation (10.36):

$$\langle \varepsilon \rangle = \sum p_j^* \varepsilon_j = 0 p_1^*(0) + \varepsilon_0 p_2^* = \frac{\varepsilon_0 e^{-\varepsilon_0/kT}}{1 + e^{-\varepsilon_0/kT}} \qquad (10.47)$$

(or you can get this by taking the derivative $\langle \varepsilon \rangle = -q^{-1}(\partial q/\partial \beta)$). Figure 10.9(a) shows the energy of the two-state system as a function of temperature. At low temperatures, most molecules are in the ground state, so the system has low energy. As the temperature increases, the energy of the system increases and approaches the value $\varepsilon_0/2$ per particle because energy levels 0 and ε_0 become equally populated.

(a) Average Energy

$\langle \varepsilon \rangle$

Heat capacity of two-state model

To compute the heat capacity, use the definition $C_V = (\partial U / \partial T)$ from thermodynamics. Using Equation (10.36) to convert the total energy to the average energy per particle, $U = N\langle\varepsilon\rangle$, you have

$$C_V = N \left(\frac{\partial\langle\varepsilon\rangle}{\partial T}\right)_{V,N} = N \left(\frac{\partial\langle\varepsilon\rangle}{\partial\beta}\right)\left(\frac{d\beta}{dT}\right) = -\frac{N}{kT^2}\left(\frac{\partial\langle\varepsilon\rangle}{\partial\beta}\right), \qquad (10.48)$$

where the right-hand expressions convert from T to β to make the next step of the differentiation simpler. Take a derivative of the form $d(u/v) = (vu' - uv')/v^2$, where $u = \varepsilon_0 e^{-\beta\varepsilon_0}$ and $v = 1 + e^{-\beta\varepsilon_0}$, to get

$$\left(\frac{\partial\langle\varepsilon\rangle}{\partial\beta}\right) = \frac{(1+e^{-\beta\varepsilon_0})(-\varepsilon_0^2 e^{-\beta\varepsilon_0}) - \varepsilon_0 e^{-\beta\varepsilon_0}(-\varepsilon_0 e^{-\beta\varepsilon_0})}{(1+e^{-\beta\varepsilon_0})^2}$$

$$= \frac{-\varepsilon_0^2 e^{-\beta\varepsilon_0}}{(1+e^{-\beta\varepsilon_0})^2}. \qquad (10.49)$$

Substitute Equation (10.49) into the right side of Equation (10.48) to find the heat capacity C_V in terms of the energy level spacing ε_0:
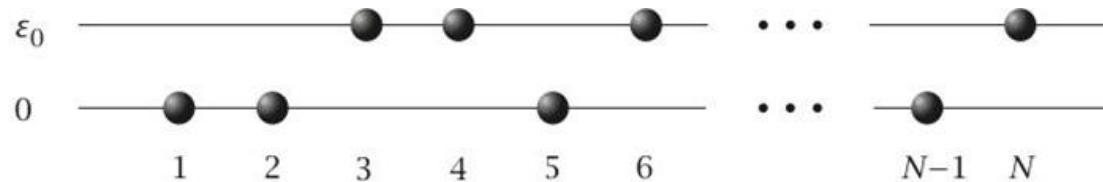
$$C_V = \frac{N\varepsilon_0^2}{kT^2}\frac{e^{-\beta\varepsilon_0}}{(1+e^{-\beta\varepsilon_0})^2}. \qquad (10.50)$$

(b) **Heat Capacity**

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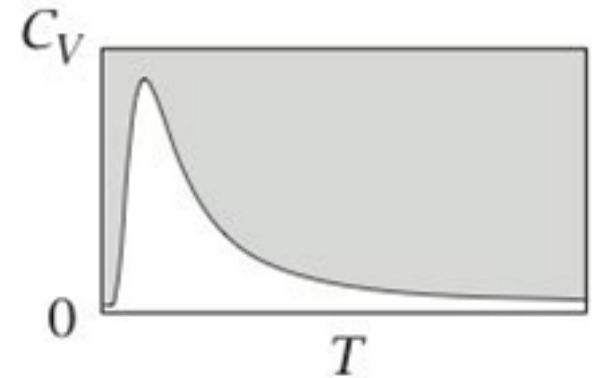
A two-state system with N particles

Figure 12.1 A two-state system with N particles, n of which are in the excited state. Each particle has ε_0 or zero energy.

the excited state and $N-n$ of which are in the ground state (see Figure 12.1). When energy enters the system as heat, it excites particles to move from the ground state to the excited state. The energy U of the system is proportional to the number n of molecules in the excited state, so

$$U = n\varepsilon_0 \quad \Longrightarrow \quad n = \frac{U}{\varepsilon_0}. \tag{12.1}$$

Coin-flip statistics, Equation (1.22), gives the multiplicity of states:

$$W = \frac{N!}{n!(N-n)!},$$

so (see Example 6.1)

$$\frac{S}{k} = \ln W = -n\ln\left(\frac{n}{N}\right) - (N-n)\ln\left(\frac{N-n}{N}\right). \tag{12.2}$$

What is (1/Temperature)?

$$\frac{S}{k} = \ln W = -n \ln\left(\frac{n}{N}\right) - (N-n)\ln\left(\frac{N-n}{N}\right). \tag{12.2}$$

To get $S(U)$, replace n by U/ε_0 in Equation (12.2). A simple way to get $1/T$ is to express Equation (6.6) as
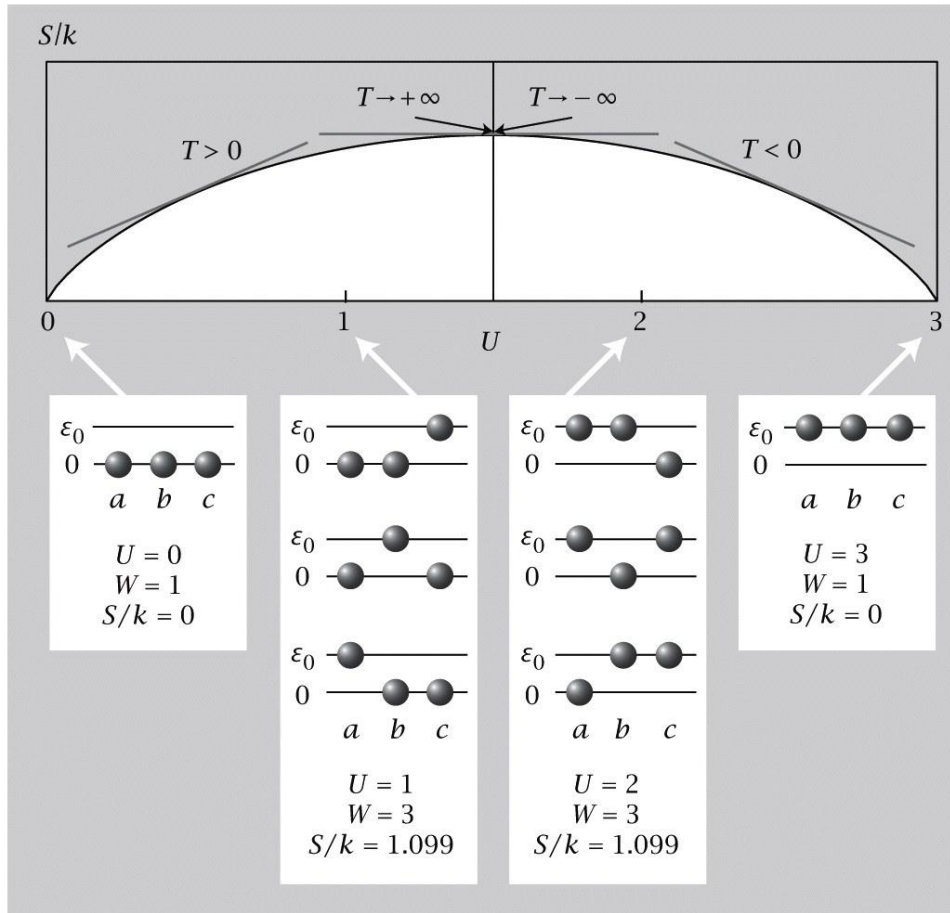
$$\frac{1}{T} = k\left(\frac{\partial \ln W}{\partial U}\right)_{V,N} = k\left(\frac{\partial \ln W}{\partial n}\right)_{V,N}\left(\frac{dn}{dU}\right). \tag{12.3}$$

Since $dn/dU = 1/\varepsilon_0$, Equation (12.3) becomes

$$\frac{1}{T} = \frac{k}{\varepsilon_0}\left[-1 - \ln\left(\frac{n}{N}\right) + 1 + \ln\left(\frac{N-n}{N}\right)\right]$$

$$= -\frac{k}{\varepsilon_0}\ln\left(\frac{n/N}{1-(n/N)}\right) = -\frac{k}{\varepsilon_0}\ln\left(\frac{U/N\varepsilon_0}{1-U/N\varepsilon_0}\right)$$

$$= \frac{k}{\varepsilon_0}\ln\left(\frac{f_{\text{ground}}}{f_{\text{excited}}}\right), \tag{12.4}$$

where $f_{\text{excited}} = (n/N)$ is the fraction of particles in the excited state and $f_{\text{ground}} = 1-(n/N)$ is the fraction in the ground state.

What is Temperature?

Positive temperature, $T > 0$. For a two-state system that has low energy U (see the left side of Figure 12.2), most of the particles are in the ground state. As a consequence, $f_{ground}/f_{excited} > 1$, so $\ln(f_{ground}/f_{excited}) > 0$. According to Equation (12.4), the temperature of such a system is positive. If an external source of energy (a bath) is available, the system will tend to absorb energy from it. Particles will be excited from the ground state to the excited state because of the fundamental principle (the Second Law) that systems tend toward their states of maximum entropy. The system can increase its multiplicity of states by taking up energy. Systems having positive temperature absorb energy to gain entropy.

Figure 12.2 Molecular Driving Forces 2/e (© Garland Science 2011)

What is Negative Temperature?

Figure 12.2 Molecular Driving Forces 2/e (© Garland Science 2011)

Infinite temperature, $T = \infty$. For a two-state system having intermediate energy U (middle of Figure 12.2), with equal populations in the ground and excited states, $f_{ground}/f_{excited} = 1$, and $\ln(f_{ground}/f_{excited}) = 0$. According to Equation (12.4), this implies $1/T = 0$, which means that the temperature is infinite. This is the point at which $S(U)$ is maximal. Just as with coin flips, the maximum multiplicity occurs when half the particles are in each of the two states. Two-state systems at infinite temperature cannot gain additional entropy by absorbing more energy, so they have no tendency to take up energy from a bath.

Negative temperature, $T < 0$. For a two-state system that has high energy U (right side of Figure 12.2), most of the particles are in the excited state, so $f_{ground}/f_{excited} < 1$, and therefore $\ln(f_{ground}/f_{excited}) < 0$. It follows from Equation (12.4) that $T < 0$. In this condition, if the system were to absorb additional energy, shifting the last few particles from the ground state to the excited state would lead to a *lower* multiplicity of states. The Second Law says that systems tend toward higher entropy, so systems at negative temperatures will tend to *give off* energy, not absorb it. In that regard, a system at negative temperature is *hotter* than a system at positive temperature, since 'hotness' corresponds to a tendency to give up energy.
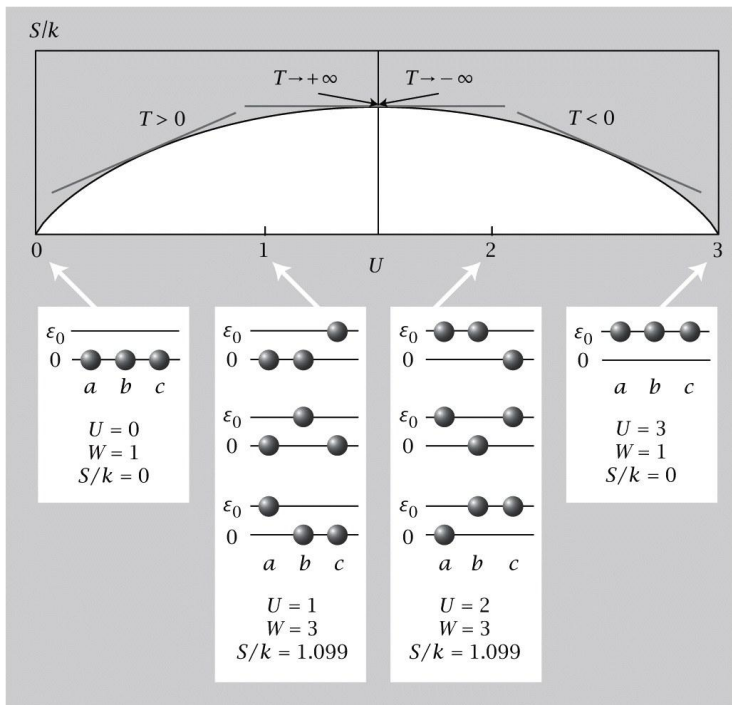
1/T

The two-state model shows that the quantity $1/T$ represents the inclination of a system to absorb energy. When $1/T > 0$, a system tends to absorb energy. When $1/T < 0$, it tends to give off energy. When $1/T = 0$, the system has neither tendency. These inclinations result from the drive to maximize entropy.
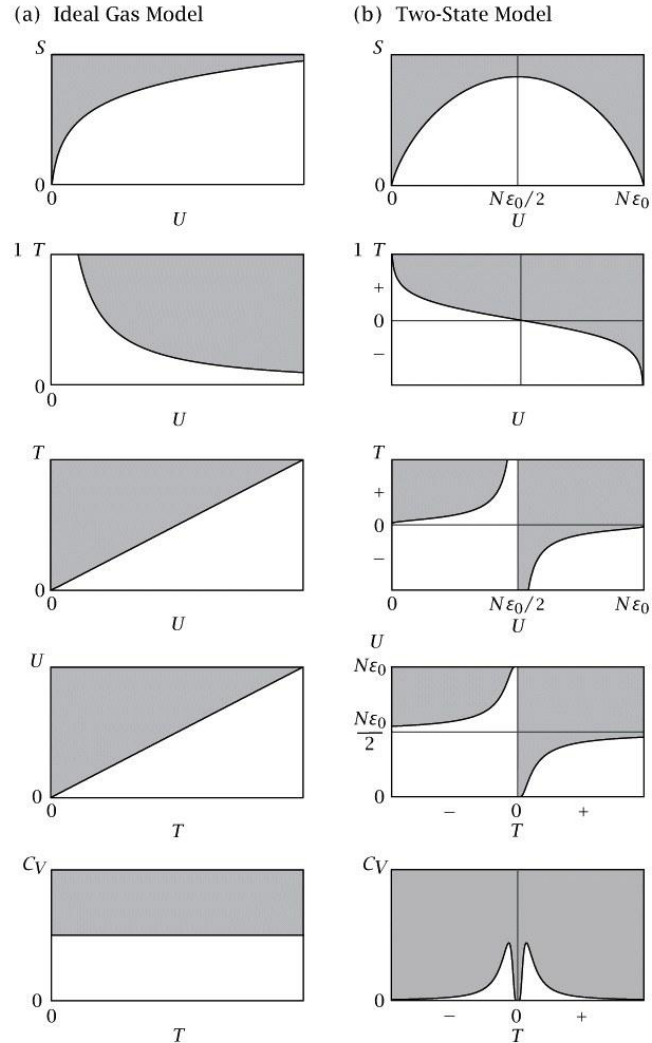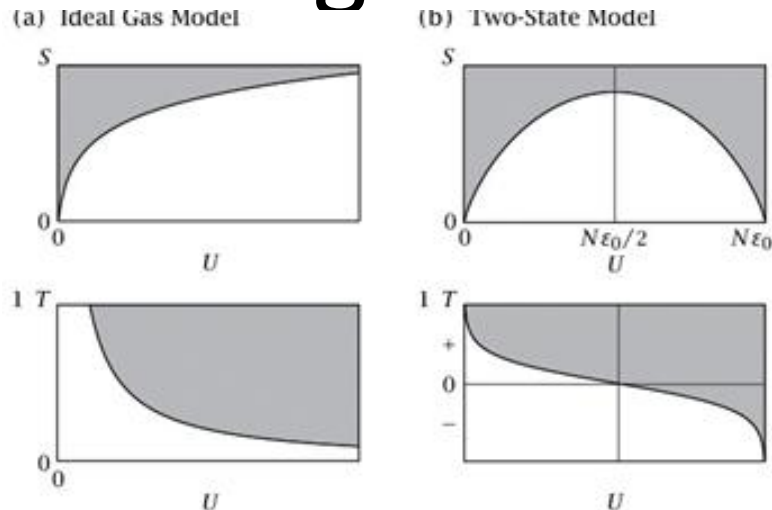
Driving force

Figure 12.3 Molecular Driving Forces 2/e (© Garland Science 2011)

Driving force

(a) Ideal Gas Model   (b) Two-State Model

First row: S versus U. For an ideal gas at constant volume, $S = (3Nk/2) \ln U$ (Figure 12.3(a)). (To see this, you can invert the logic here, start with the fourth row of this figure, $U(T) = 3NkT/2$, which results from equipartition, and work up. Note, incidentally, that you shouldn't trust this expression for small T or U, near $U = 0$ on the figures, where equipartition doesn't hold.) S is a monotonically increasing function of U because such systems have infinite ladders of energy levels. In contrast, for a two-state system (Figure 12.3(b)), $S(U)$ increases, reaches a maximum, then decreases, as described in Figure 12.2. The first row of Figure 12.3 gives the most fundamental description of either system in terms of the driving force, the entropy.

Second row: $1/T$ versus U. To get the second row of Figure 12.3 from the first row, take the slope $1/T = (\partial S / \partial U)$. This curve represents the driving force to absorb heat. For the ideal gas (Figure 12.3(a)), the driving force to take up heat is always positive: $1/T = 3Nk/(2U)$. For the two-state system (Figure 12.3(b)), the driving force changes sign if the energy U is large.

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Temperature is related with the population density

(a) Ideal Gas Model
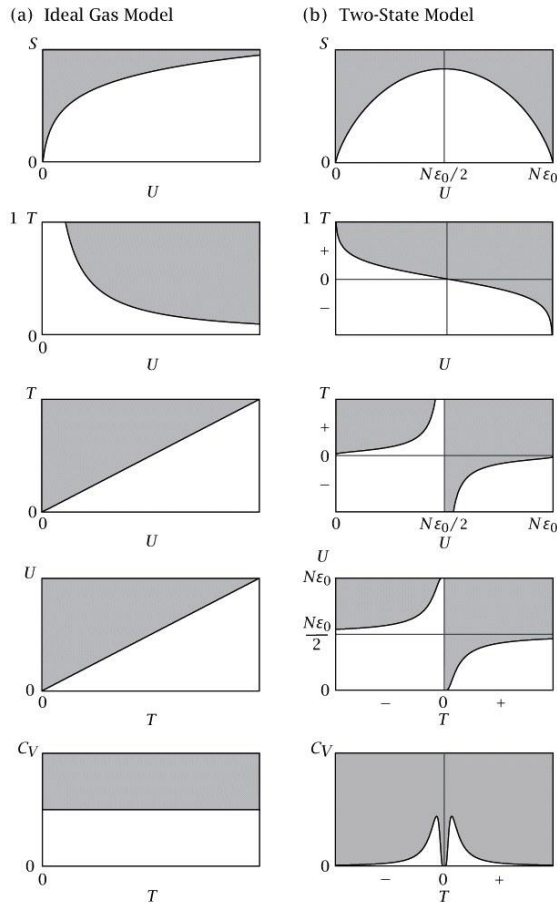
(b) Two-State Model

from Figure 12.3(b) that in general the temperature need not be proportional to energy. In general, temperature is simply a measure of the relative populations of energy levels: T is inversely proportional to $\ln(f_{\text{ground}}/f_{\text{excited}})$ in the two-state model (Equation (12.4)).

Fourth Row: U versus T. To get the fourth row of Figure 12.3, interchange the x and y axes, to convert $T(U)$ into $U(T)$, a familiar function. For the ideal gas, the energy increases linearly with temperature (see Equation (11.37), $U = (3/2)NkT$). It shows why you can normally speak of 'putting thermal energy into' a system. The ideal gas absorbs energy in linear proportion to the temperature of the surrounding bath, at all temperatures.

On the other hand, the two-state system behaves differently: (1) it has negative temperatures and (2) at high temperatures, the two-state system cannot 'take up' heat from the bath, because the system is already saturated. The energy of a two-state system can never exceed $N\varepsilon_0/2$, as long as the temperature is positive. At most, the two-state system can reach equal populations of the two states. To reach higher energies requires negative temperatures.

Figure 12.3 Molecular Driving Forces 2/e (© Garland Science 2011)

What drives heat exchange?

Now let's use the two-state model to revisit thermal equilibrium. System A has energy U_A, energy spacing ε_A, and particle number N_A. System B has U_B, ε_B, and N_B.

At low positive temperatures, $U/N\varepsilon_0 \ll 1$, and Equation (12.4) becomes

$$\frac{1}{T} = \frac{k}{\varepsilon_0} \ln\left(\frac{N\varepsilon_0}{U}\right).$$

Thermal equilibrium between two two-state systems A and B leads to

$$\frac{1}{T_A} = \frac{1}{T_B} \quad \Longrightarrow \quad \frac{1}{\varepsilon_A} \ln\left(\frac{N_A\varepsilon_A}{U_A}\right) = \frac{1}{\varepsilon_B} \ln\left(\frac{N_B\varepsilon_B}{U_B}\right). \tag{12.5}$$

Here are some of the implications of Equation (12.5). Sometimes heat exchange equalizes energies. If the two objects are made of the same material ($\varepsilon_A = \varepsilon_B$), and have the same total number of particles ($N_A = N_B$), the tendency to maximize entropy and to equalize temperatures is a tendency to equalize their energies U_A and U_B, according to Equation (12.5).

But thermal equilibrium isn't a tendency of high-energy objects to unload their energy into low-energy objects. A large heat bath can have more energy than a system in a small test tube, but this doesn't force the small system to take up energy from the heat bath. If two two-state objects are made of identical material, $\varepsilon_A = \varepsilon_B$, but their sizes are different, $N_A \neq N_B$, Equation (12.5) tells us that thermal equilibrium will occur when $U_A/N_A = U_B/N_B$, not when $U_A = U_B$. At equilibrium, the objects will share energies in proportion to their sizes. In general, equilibrium is defined by the equality of *intensive* properties (U/N in this case), not extensive properties.

Summary

- $1/T$ is the driving force for the uptake of energy. For two bodies A and B in thermal contact, energy will flow from one to the other until the driving forces are equal: $1/T_A = 1/T_B$.

- Thermal equilibrium is not a tendency of high-energy objects to unload their energy to low-energy object.