

CHAPTER 3

3.1) FREE ENERGY FOR TWO STATE SYSTEM

(a) By inserting (13) into (55):

$$F = -\tau \log Z = -\tau \log[1+\exp(-\varepsilon/\tau)] \quad .$$

(b) Inserted into (49),

$$\sigma = -(\partial F/\partial \tau) = \log[1+\exp(-\varepsilon/\tau)] + (\varepsilon/\tau)/[1+\exp(\varepsilon/\tau)], \quad (S1)$$

$$U = F + \tau \sigma = \varepsilon/[1+\exp(\varepsilon/\tau)] \quad ,$$

the same as (14) obtained directly from Z.

Comment. As $\tau \rightarrow 0$ and hence $\exp(-\varepsilon/\tau) \rightarrow 0$, the logarithm in (S1) may be expanded: $\log[1+\exp(-\varepsilon/\tau)] \rightarrow \exp(-\varepsilon/\tau)$. Then $\sigma \rightarrow (1+\varepsilon/\tau) \exp(-\varepsilon/\tau) \rightarrow 0$. The exponential factor goes to zero faster than any inverse power of τ goes to infinity: Both σ and all derivatives of σ vanish when $\tau \rightarrow 0$, as shown in Fig. 11. The high-temperature limit of σ is obtained by letting $\exp(-\varepsilon/\tau) \rightarrow 1$, in (S1): $\sigma \rightarrow \log 2 + \varepsilon/2\tau \rightarrow \log 2$.

3.2) MAGNETIC SUSCEPTIBILITY

(a) For a single magnet, with $\varepsilon = \bar{\mu}mB$:

$$Z_1 = \exp(mB/\tau) + \exp(-mB/\tau) = 2 \cosh(mB/\tau) \quad , \quad (S1)$$

$$\langle m \rangle = [m \exp(+mB/\tau) - m \exp(-mB/\tau)]/Z_1 = m \tanh(mB/\tau).$$

The magnetization M is obtained by multiplying by the particle concentration n:

$$M = n\langle m \rangle = nm \tanh(mB/\tau) \quad .$$

For weak fields, $mB \ll \tau$:

$$M = nm^2 B/\tau \quad . \quad (S2)$$

For strong fields, $mB \gg \tau$:

$$M = nm.$$

These two limits are seen in Fig. 3.12.

(b) Inserting (S1) into (55) and multiplying by n :

$$F = -n\tau \log Z_1 = -n\tau \log[2 \cosh(mB/\tau)] .$$

To express $\cosh(mB/\tau)$ as a function of $x = M/nm = \tanh(mB/\tau) = \tanh y$ we use the relation

$$1/\cosh^2 y = (\cosh^2 y - \sinh^2 y)/\cosh^2 y = 1 - \tanh^2 y = 1 - x^2.$$

We next write

$$\log[2 \cosh y] = -\frac{1}{2} \log(1/4 \cosh^2 y) = -\frac{1}{2} \log[(1-x^2)/4].$$

With this:

$$F = +(n\tau/2) \log[(1-x^2)/4] .$$

(c) The susceptibility is defined as

$$\chi = dM/dB.$$

In the limit $mB \ll \tau$, from (S2):

$$\chi = nm^2/\tau .$$

3.3) FREE ENERGY OF AN HARMONIC OSCILLATOR

The partition function is a geometric series:

$$Z = \sum_{s=0}^{\infty} \exp(-s\hbar\omega/\tau) = 1/[1-\exp(-\hbar\omega/\tau)].$$

(a) Inserted into (55):

$$F = -\tau \log Z = \tau \log[1-\exp(-\hbar\omega/\tau)] . \quad (87)$$

At high temperatures, $\hbar\omega/\tau \ll 1$, so that $1 - \exp(-\hbar\omega/\tau) \cong \hbar\omega/\tau$. Hence from (S1):

$$F \cong \tau \log(\hbar\omega/\tau) \quad . \quad (S2)$$

(b) The expression (88) follows directly by inserting (87) into (49), $\sigma = -(\partial F/\partial \tau)$.

Comment. The low-temperature ($\tau \ll \hbar\omega$) behavior of the harmonic oscillator is the same as for the two state system with $\varepsilon = \hbar\omega$, as is apparent from comparing Figs. 3.13 and 3.14 with Figs. 3.11 and 3.4: Only the two lowest states matter. The high-temperature behavior ($\tau \gg \hbar\omega$) is quite different, because the number of accessible states is not limited to 2. In this limit, from (S2):

$$\sigma = -(\partial F/\partial \tau) \rightarrow 1 + \log(\tau/\hbar\omega).$$

If this is inserted into (17a):

$$C_V = \tau(\partial \sigma/\partial \tau) \rightarrow 1,$$

in fundamental units.

3.4) ENERGY FLUCTUATIONS

Note first that

$$\langle (\varepsilon - \langle \varepsilon \rangle)^2 \rangle = \langle \varepsilon^2 - 2\varepsilon \langle \varepsilon \rangle + \langle \varepsilon \rangle^2 \rangle = \langle \varepsilon^2 \rangle - \langle \varepsilon \rangle^2 \quad .$$

Next write the partition function as a function of $\beta = 1/\tau$:

$$Z = \sum_{\ell} \exp(-\beta \varepsilon_{\ell}) \quad .$$

Then

$$U = \langle \varepsilon \rangle = \frac{1}{Z} \sum_{\ell} \varepsilon_{\ell} \exp(-\beta \varepsilon_{\ell}) = - \frac{1}{Z} \frac{dZ}{d\beta} ,$$

$$\langle \varepsilon^2 \rangle = \frac{1}{Z} \sum_{\ell} \varepsilon_{\ell}^2 \exp(-\beta \varepsilon_{\ell}) = + \frac{1}{Z} \frac{d^2 Z}{d\beta^2} .$$

From these, with $d\beta/d\tau = -1/\tau^2$,

$$\begin{aligned} \tau^2 \left(\frac{\partial U}{\partial \tau} \right)_V &= \tau^2 \left(\frac{\partial U}{\partial \beta} \right)_V \frac{d\beta}{d\tau} = - \left(\frac{\partial U}{\partial \beta} \right)_V \\ &= \frac{d}{d\beta} \left(\frac{1}{Z} \frac{dZ}{d\beta} \right) = \frac{1}{Z} \frac{d^2 Z}{d\beta^2} - \frac{1}{Z^2} \left(\frac{dZ}{d\beta} \right)^2 \\ &= \langle \varepsilon^2 \rangle - \langle \varepsilon \rangle^2 . \end{aligned}$$

Comment. Manipulations involving temperature differentials of the partition functions are frequently simplified by using $\beta = 1/\tau$ rather than τ as independent variable.

3.5) OVERHAUSER EFFECT

Let U_0 be the energy of the reservoir when the energy of the system is zero. Then, when the system has the energy ε , the reservoir has, by our supposition, the energy $U_0 - \varepsilon + \alpha \varepsilon = U_0 - (1-\alpha)\varepsilon$. The probability $P(\varepsilon_s)$ to find the system in a particular state with energy ε_s is then proportional to the number of states of the reservoir with the energy $U_0 - (1-\alpha)\varepsilon_s$,

$$P(\varepsilon_s) \propto g_R[U_0 - (1-\alpha)\varepsilon_s],$$

with the same proportionality factor for all states. Hence, instead of (2) and (3):

$$\frac{P(\varepsilon_1)}{P(\varepsilon_2)} = \frac{g_R[U_0 - (1-\alpha)\varepsilon_1]}{g_R[U_0 - (1-\alpha)\varepsilon_2]} = \frac{\exp\{\sigma_R[U_0 - (1-\alpha)\varepsilon_1]\}}{\exp\{\sigma_R[U_0 - (1-\alpha)\varepsilon_2]\}} . \quad (S1)$$

If the entropy of the reservoir is expanded about $U = U_0$, as in (7):

$$\sigma_R[U_0 - (1-\alpha)\varepsilon] = \sigma_R(U_0) - (\partial\sigma_R/\partial U)(1-\alpha)\varepsilon + \dots$$

If this is inserted into (S1), one obtains, instead of (9),

$$\frac{P(\varepsilon_1)}{P(\varepsilon_2)} = \frac{\exp[-(1-\alpha)\varepsilon_1/\tau]}{\exp[-(1-\alpha)\varepsilon_2/\tau]} ,$$

which is equivalent to (91).

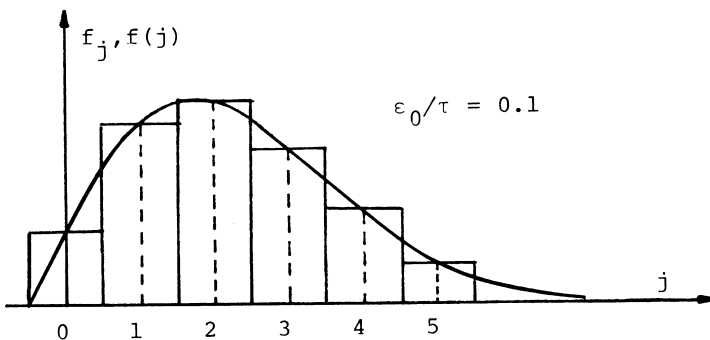
3.6) ROTATION OF DIATOMIC MOLECULE

(a) There are $2j+1$ states at energy $j(j+1)\varepsilon_0$, hence

$$Z_R = \sum_s \exp(-\varepsilon_s/\tau) = \sum_j (2j+1) \exp[-j(j+1)\varepsilon_0/\tau] ,$$

where the sum over all states has been converted into a sum over all energy levels.

(b) The sum may be viewed as a sum over the areas of rectangles with the width $\Delta j = 1$ and with the height $f_j = (2j+1) \exp[-j(j+1)\varepsilon_0/\tau]$, as shown below. Also shown is the curve $f(j)$, with j treated as a continuous rather than discrete variable. Note that this curve goes through the middle of the upper edge of each rectangle.



When $\tau \gg \varepsilon_0$, the slope of the continuous curve $f(j)$ varies only very little within each rectangle, and the sum can be approximated by the integral

$$Z = \int_{-1/2}^{\infty} f(j) dj \quad .$$

Note that the lower integration limit is not zero; this is important. Substitute new variable: $x = j(j+1)\varepsilon_0/\tau$, $dx = (2j+1)(\varepsilon_0/\tau)dj$:

$$Z = \frac{\tau}{\varepsilon_0} \int_{x_0}^{\infty} \exp(-x) dx = \frac{\tau}{\varepsilon_0} [1 - \exp(-x_0)] \quad , \quad (S1)$$

where $x_0 = -\varepsilon_0/4\tau$ is the value of x corresponding to $j = -1/2$. When $\tau \gg \varepsilon_0$, $x_0 \ll 1$, and the exponential may be expanded: $\exp(-x_0) \cong 1 - x_0 + \dots$. If this is inserted into (S1),

$$Z \cong \tau/\varepsilon_0 + 1/4 + \dots \quad , \quad (S2)$$

where all omitted terms decrease at least as rapidly as $1/\tau$ when $\tau \rightarrow \infty$.

A more careful treatment of the sum (see below) yields the slightly different result

$$Z = \tau/\varepsilon_0 + 1/3 + \dots \quad . \quad (S3)$$

This is the form we will use in what follows.

$$(c) \quad Z = 1 + 3 \exp(-2\varepsilon_0/\tau) + \dots \quad , \quad (S4)$$

where the omitted terms vanish more rapidly than the second term when $\tau \rightarrow 0$.

(d) Insert Z into (12), $U(\tau) = \tau^2(\partial Z/\partial \tau)/Z$:

$$\begin{aligned} \tau \gg \varepsilon_0: \quad U(\tau) &= \tau^2 \varepsilon_0 Z = \tau / (1 + \varepsilon_0 / 3\tau) \\ &\cong \tau \times (1 - \varepsilon_0 / 3\tau) = \tau - \varepsilon_0 / 3 \quad . \end{aligned} \quad (S5)$$

$$C(\tau) \cong 1 \quad .$$

$$\begin{aligned} \tau \ll \varepsilon_0: \quad U(\tau) &= 6\varepsilon_0 \exp(-2\varepsilon_0/\tau) / Z \\ &\cong 6\varepsilon_0 \exp(-2\varepsilon_0/\tau) \ll 6\varepsilon_0 \quad . \end{aligned} \quad (S6)$$

$$C(\tau) \cong (12\varepsilon_0/\tau^2) \exp(-2\varepsilon_0/\tau) \quad .$$

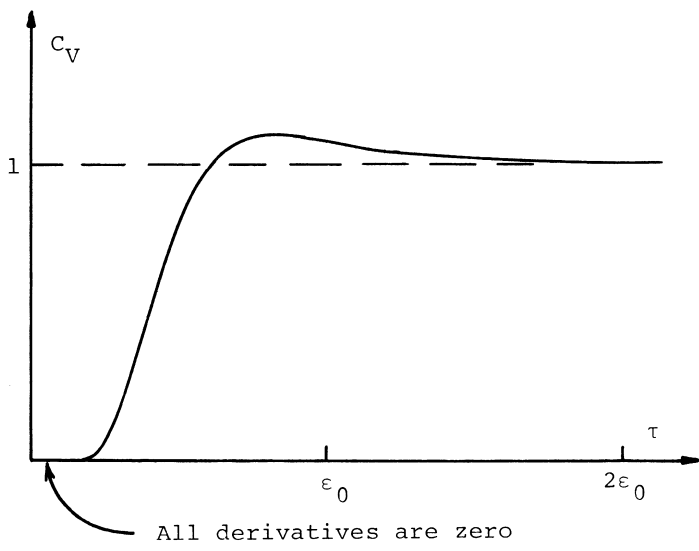
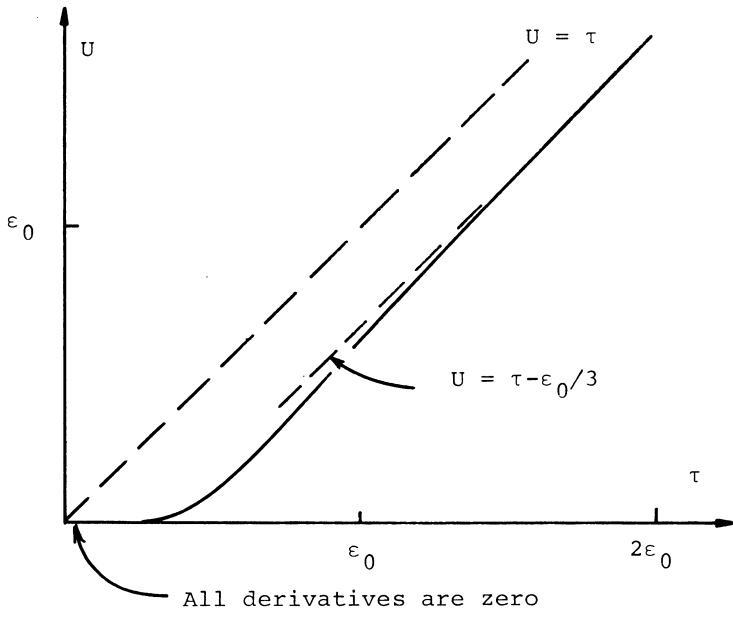
Note that, as in Problems 3.1 and 3.3, the exponential factor goes to zero much faster than $1/\tau^2$ goes to infinity, when $\tau \rightarrow 0$.

(e) See drawings on next page. The approximation (S6) dips below (S5), suggesting that $U(\tau)$ approaches the asymptote (S5) from below. This means that $C = \partial U / \partial \tau > 1$ above some temperature, that is, the heat capacity goes through a maximum. An accurate calculation confirms this prediction.

The instructor should check that the student drawings show correctly the vanishing slope of both $U(\tau)$ and $C(\tau)$ as $\tau \rightarrow 0$, rather than exhibiting a non-descript behavior.

Discussion and Elaborations. Unless forewarned, many students are likely to replace the sum by an integral with a lower integration limit of zero. As the graphs of f_j and $f(j)$ show, this is invalid. This pitfall may be taken as the point of departure for a classroom discussion on several mathematical points concerning the summation of series, starting with a warning against the purely formal replacement of sums by integrals without a graphical visualization of the difference between the two.

The difference between (S2) and (S3) arises from the non-zero second derivative of the continuous function $f(j)$, which integrates to a finite error in (S2). The formal tool for a more systematic accurate replacement of



sums by integrals is the Euler-McLaurin summing formula. The Supplementary Material to this Chapter gives a simple derivation that does not draw on the properties of the Euler polynomials, which are commonly utilized in the proofs found in most textbooks.

If the Euler-McLaurin expansion is applied to our partition function, one can obtain an expansion of Z by powers of $\eta = \varepsilon_0/\tau$,

$$Z = \frac{1}{\eta} + \frac{1}{3} + \frac{\eta}{15} + O(\eta^2) \quad , \quad (S7)$$

where $O(\eta^2)$ stands for omitted terms of order η^2 or higher. To obtain all contributions of order η , the Euler-McLaurin expansion must be carried up to the term $(1/720)f^{(3)}(0)$.

From (S7) one obtains, by standard methods,

$$U(\tau) = -\varepsilon_0 \frac{d(\log Z)}{d\eta} = \tau - \varepsilon_0/3 - \varepsilon_0^2/45\tau + O(1/\tau^2) \quad ,$$

$$C(\tau) = 1 + (1/45)(\varepsilon_0/\tau)^2 + O(1/\tau^3) \quad .$$

The details are left to the reader.

These results do indeed indicate that $U(\tau)$ approaches its asymptote from below and that $C(\tau)$ approaches its limiting value from above.

As an alternative to these analytical treatments, it is not difficult to sum the partition function numerically on a programmable calculator. The summation is greatly speeded up by calculating the Boltzmann factors recursively:

$$B_j \equiv \exp[-j(j+1)\varepsilon_0/\tau] = B_{j-1} \times C_j \quad ,$$

$$C_j \equiv \exp[-2j\varepsilon_0/\tau] = C_{j-1} \times B_1 \quad ,$$

$$B_0 = C_0 = 1 \quad .$$

In this way only one exponential must be evaluated for each τ ; the remaining exponentials in the series follow by simple multiplications, at a large saving in calculation time.

If Z is summed numerically, the energy is most conveniently obtained from the first equality in (3.12), by also summing

$$U = \frac{1}{Z} \sum_s \varepsilon_s \exp(-\varepsilon_s/\tau) \quad .$$

In this way the differentiation of numerical data is avoided. Similarly, the heat capacity can be obtained without differentiation from

$$C = \frac{\partial U}{\partial \tau} = \frac{1}{\tau^2} \left[\frac{1}{Z} \sum_s \varepsilon_s^2 \exp(-\varepsilon_s/\tau) - U^2 \right] \quad .$$

3.7) ZIPPER PROBLEM

(a) A state in which s links are open can be realized in only one way. Thus the partition function is

$$\begin{aligned} Z &= 1 + \exp(-\varepsilon/\tau) + \exp(-2\varepsilon/\tau) + \dots + \exp(-N\varepsilon/\tau) \quad . \\ &= \sum_{s=0}^N x^s = \frac{1-x^{N+1}}{1-x} \quad , \quad \text{where } x = \exp(-\varepsilon/\tau) \quad . \end{aligned} \quad (93)$$

(b) The average number of open links is

$$\langle s \rangle = \frac{1}{Z} \sum_{s=0}^N s x^s = x \frac{d}{dx} \log Z \quad . \quad (S1)$$

If $\varepsilon \gg \tau$, then $x \ll 1$, and we may neglect the term x^{N+1} in (93) to obtain

$$\langle s \rangle = -x \frac{d}{dx} \log(1-x) = \frac{x}{1-x} = 1/[\exp(\varepsilon/\tau) - 1] \quad .$$

This is of the form of the Planck distribution.

Extension. Our assumption that each link has only one open state is an unrealistic assumption, which neglects that the two halves of an open link may have many different orientations relative to each other. It is instructive to generalize the problem by assuming that each open link has G open states with the energy ε . The change has far-reaching consequences. A state of the zipper with s open links is then G^s -fold degenerate, and the partition function now becomes

$$Z = 1 + G \exp(-\varepsilon/\tau) + G^2 \exp(-2\varepsilon/\tau) + \dots$$

$$\dots + G^N \exp(-N\varepsilon/\tau) = \sum_{s=0}^N x^s = \frac{1-x^{N+1}}{1-x} \quad ,$$

where

$$x = G \exp(-\varepsilon/\tau) \quad ,$$

which differs from the earlier form only by the factor $G > 1$ in the definition of x . Because of this factor, values $x > 1$ are now possible. This has drastic consequences if the total number of links is very large, $N \gg 1$. In this case the opening of the zipper approaches the behavior of an abrupt phase transition at the sharp transition temperature

$$\tau_0 = \varepsilon / \log G \quad ,$$

which is the temperature for which $x = 1$. For temperatures very little below τ_0 , only a very small fraction of the links are open, for temperatures very little above τ_0 almost all links are open. The larger N , the narrower the temperature interval over which the opening takes place. We give here only the key points in the derivation of this result.

It is not difficult to show that the expression (S1) for $\langle s \rangle$ can be written as

$$\langle s \rangle \cong (N+1) \left[\frac{1}{1-\exp(-y)} - \frac{1}{y} \right] \quad (S2)$$

where

$$y = -(N+1) \times \varepsilon \times \Delta(1/\tau) \cong +(N+1)(\log G)^2 (\Delta\tau/\tau_0) \quad (S3)$$

and where in the $1/y$ -term in (S2) we assumed $|y| \ll N+1$. If N is very large, this does not exclude values $|y| \gg 1$. If $|y| \gg 1$ the square bracket in (S2) is easily seen to have the limits

$$[\dots] \cong \begin{cases} 1/|y| & \text{for } -y \gg 1 \\ 1 - 1/y & \text{for } +y \gg 1 \end{cases} .$$

For example, for $y = \bar{\tau} 100$, we have $\langle s \rangle / (N+1) \cong 0.01$ and 0.99 , corresponding to 1% or 99% open links. But if N is much larger than $|y|$, these values of y correspond to a very small temperature deviation from τ_0 . Suppose $N+1 = 1000$ and $\log G = 10$. Then, from (S3), $y = \bar{\tau} 100$ corresponds to $\Delta\tau/\tau_0 = \bar{\tau} 10^{-5}$, a very narrow transition interval indeed.

3.8) QUANTUM CONCENTRATION

According to (59) the energies of the states of the system are $\varepsilon = \varepsilon_1 \times (n_x^2 + n_y^2 + n_z^2)$, where $\varepsilon_1 = \hbar^2 \pi^2 / 2ML^2$, and where n_x , n_y and n_z are independent positive integers. Each distinguishable triplet (n_x, n_y, n_z) represents one orbital. In the ground orbital $n_x = n_y = n_z = 1$, $\varepsilon = 3\varepsilon_1$. We have $3\varepsilon_1 = \tau$ when $1/L^2 = 2M\tau/3\pi^2\hbar^2$, hence

$$n = 1/L^3 = (4/3\pi)^{3/2} \times (M\tau/2\pi\hbar^2)^{3/2} = 0.28n_Q .$$

3.9) PARTITION FUNCTION FOR TWO SYSTEMS

Every state s_1 of system 1, with energy ε_{s_1} , can be combined with every state s_2 of system 2, with energy ε_{s_2} , to form the different states s of the combined system, with energy $\varepsilon_s = \varepsilon_{s_1} + \varepsilon_{s_2}$:

$$\begin{aligned}
Z(1+2) &= \sum_{\mathbf{s}} \exp[-\varepsilon_{\mathbf{s}}/\tau] = \sum_{s_1} \sum_{s_2} \exp[-(\varepsilon_{s_1} + \varepsilon_{s_2})/\tau] \\
&= \left[\sum_{s_1} \exp(-\varepsilon_{s_1}/\tau) \right] \left[\sum_{s_2} \exp(-\varepsilon_{s_2}/\tau) \right] \quad . \\
&= Z(1)Z(2) \quad . \qquad (94)
\end{aligned}$$

3.10) ELASTICITY OF POLYMERS

(a) The problem is formally almost the same as the model spin system of chapter 1. Suppose that the molecular structure of each link is not invariant under inversion (example: ABC \neq CBA). We may then associate a vector with each link, pointing either to the left or to the right, analogously to the spin vector pointing up or down. If N_{\rightarrow} and N_{\leftarrow} are the numbers of links with vectors pointing to the left and to the right, we may define a "length excess" $2s$ analogously to the spin excess of (1.11): $2s = N_{\rightarrow} - N_{\leftarrow}$. The number of states with a given length excess is the same as $g(N,s)$ in (1.15):

$$g(N,s) = N! / [(\frac{1}{2}N+s)! (\frac{1}{2}N-s)!] \quad , \quad N = N_{\rightarrow} + N_{\leftarrow} \quad . \quad (S1)$$

The value of $g(N,s)$ does not change when the sign of s changes. The number of states with a given magnitude of s is obtained by adding $g(N,s) + g(N,-s)$, which yields (97).

(b) By inserting (1.36) into (S1), and by setting $s^2 = \ell^2/4\rho^2$:

$$\begin{aligned}
g(N,s) + g(N,-s) &= 2g(N,0) \exp(-2s^2/N) \quad , \\
\sigma(\ell) &= \log[g(N,s) + g(N,-s)] = \log[2g(N,0)] - 2s^2/N \\
&= \log[g(N,0)] - \ell^2/2N\rho^2 \quad . \qquad (98)
\end{aligned}$$

$$\begin{aligned}
(c) \quad (\partial\sigma/\partial\ell)_N &= - \ell/N\rho^2 \quad , \\
f &= - \tau(\partial\sigma/\partial\ell)_N = + \ell\tau/N\rho^2 \quad . \qquad (99)
\end{aligned}$$

Discussion. The problem contains two subtle points that may lead to questions from some students even though they do not influence the final result (99). They were inten-

tionally omitted from the problem statement, but lend themselves to a classroom discussion.

If the individual links do not have a built-in directionality, states with positive and negative s are indistinguishable and should not be counted separately. The factor 2 in (97) should then be omitted, but only if the chain is free to move in space. To exert an external mechanical force, the two ends must be held. This re-establishes a directionality along the chain even if the individual links are invariant under inversion. But in this case the states with positive values of s and those with negative values are not accessible from each other while the length of the chain is kept fixed. Hence only half the states counted in (97) matter for the entropy of the tied-down chain. This reduces the entropy by $\log 2$, but it has no effect on the force calculation, because such a constant difference does not change the derivative of the entropy.

Comment: Temperature Effects in a Rubber Band. According to (98), the configurational entropy of a polymer chain decreases as the chain is stretched. But if the polymer is kept thermally isolated, the total entropy in a reversible process must remain constant. The decrease in configurational entropy must then be compensated by an increase of the entropy of the purely thermal degrees of freedom, that is, by an increase in temperature of the polymer. Conversely, if a previously stretched polymer is released, its temperature decreases. The effect is easily demonstrated on rubber bands, and it lends itself to a demonstration experiment. Every student is given a fairly thick rubber band and is asked to hold its two ends firmly with two hands in such a way that the central portion of the band touches the student's forehead, a region of the body quite sensitive to temperature changes. If the band is suddenly stretched to about twice its length, the tem-

perature of the band increases perceptibly. The band is held stretched for a while, to permit temperature equilibrium with the "temperature sensor" to be achieved. On removing the tension, the band will then cool perceptibly. While neither the heating nor the cooling effect are very strong by themselves, the difference between the two is very perceptible, provided the rubber band is one with sufficient heat capacity. We owe this little experiment to Prof. W.G. May of the University of Colorado. -- The instructor should make absolutely sure that the rubber band is sufficiently strong, is held firmly enough, and is not overstretched, to avoid any possibility of eye injury.

3.11) ONE-DIMENSIONAL GAS

In one dimension, the orbital energies are, from (58) and (59), $\varepsilon_n = \varepsilon_1 n^2$, where $\varepsilon_1 = (\hbar^2/2M)(\pi/L)^2$ and n is a positive integer. The single-particle partition function is

$$\begin{aligned} Z_1 &= \sum_n \exp(-\varepsilon_1 n^2/\tau) \cong \int_0^\infty \exp(-\varepsilon_1 n^2/\tau) dn \\ &= (\pi\tau/4\varepsilon_1)^{1/2} = n_{Q1}L, \end{aligned}$$

where

$$n_{Q1} = (M\tau/2\pi\hbar^2)^{1/2} = (n_Q)^{1/3}$$

is the one-dimensional quantum concentration analogous to the three-dimensional quantum concentration n_Q defined in (62) and (63).

$$\begin{aligned} \text{For } N \text{ particles: } Z_N &= Z_1^N/N!, \\ F &= -\tau \log Z_N = \tau \log N! - \tau N \log Z_1 \\ &\cong \tau(N \log N - N) - \tau N \log(n_{Q1}L) \\ &= \tau N[\log(n/n_{Q1}) - 1], \end{aligned}$$

where $n = N/L$. With the help of $\partial \log n_{Q1} / \partial \tau = 1/2\tau$:

$$\sigma = -(\partial F / \partial \tau)_n = N[\log(n/n_Q) - 3/2],$$

which should be compared with (76).

SUPPLEMENTARY MATERIAL TO CHAPTER 3

NUMERICAL EXPRESSIONS FOR THE QUANTUM CONCENTRATION

The quantum concentration of n_Q of Eq. (63) occurs so frequently in numerical calculations that it is worthwhile to list the following numerical expressions:

$$\begin{aligned} n_Q &= 2.41466 \times 10^{15} \text{ cm}^{-3} \times [(M/m_e) \times (T/1K)]^{3/2} \\ &= 1.25469 \times 10^{19} \text{ cm}^{-3} \times [(M/m_e) \times (T/300K)]^{3/2} \\ &= 1.87930 \times 10^{20} \text{ cm}^{-3} \times [(M/1\text{amu}) \times (T/1K)]^{3/2} \\ &= 9.76513 \times 10^{23} \text{ cm}^{-3} \times [(M/1\text{amu}) \times (T/300K)]^{3/2} . \end{aligned}$$

SUMS AS INTEGRALS: THE EULER-McLAURIN SUMMING FORMULA

The uncritical replacement of partition function sums by integrals can lead to errors that, while seemingly negligible relative to the partition function itself, may be quite noticeable in the temperature dependence of quantities that are obtained from the derivatives of the partition function, especially heat capacities. Problem 3.6 gave an example. In such cases the replacement of a sum by an integral must be done more carefully, as follows. Let $f(x)$ be an analytic function such that $f(j) = f_j$, with $f(x)$ itself and all its derivatives vanishing as $x \rightarrow \infty$. The Euler-McLaurin summing formula then states that

$$\sum_{j=0}^{\infty} f_j = \int_0^{\infty} f(x) dx + \sum_{n=0}^{\infty} A_n f^{(n)}(0) , \quad (1)$$

where $f^{(n)}(0)$ is the n -th derivative of $f(x)$ at $x = 0$, and where the first six coefficients A_n have the values

$$\begin{aligned} A_0 &= + 1/2 , & A_1 &= - 1/12 , & A_2 &= 0 , \\ A_3 &= + 1/720 , & A_4 &= 0 , & A_5 &= - 1/30,240 . \end{aligned}$$

All even-numbered coefficients with $n > 0$ vanish.

To derive (1) we expand $f(x)$ in the interval $j \leq x < j+1$ into a Taylor Series:

$$f(x) = \sum_{m=0}^{\infty} \frac{1}{m!} f^{(m)}(j)(x-j)^m .$$

We integrate from j to $j+1$ and sum over all $j \geq 0$:

$$\int_0^{\infty} f(x) dx = \sum_{j=0}^{\infty} f_j + \sum_{m=1}^{\infty} \frac{1}{(m+1)!} \sum_{j=0}^{\infty} f^{(m)}(j) . \quad (2)$$

Similarly, for the derivatives of $f(x)$,

$$\int_0^{\infty} f^{(n+1)}(x) dx = - f^{(n)}(0) = \sum_{m=n+1}^{\infty} \frac{1}{(m-n)!} \sum_{j=0}^{\infty} f^{(m)}(j) .$$

We multiply each of these equations by an as yet unspecified coefficient A_n and sum over all n :

$$\begin{aligned} - \sum_{n=0}^{\infty} A_n f^{(n)}(0) &= \sum_{n=0}^{\infty} \sum_{m=n+1}^{\infty} \frac{A_n}{(m-n)!} \sum_{j=0}^{\infty} f^{(m)}(j) \\ &= \sum_{m=1}^{\infty} \left[\sum_{n=0}^{m-1} \frac{A_n}{(m-n)!} \sum_{j=0}^{\infty} f^{(m)}(j) \right] . \end{aligned} \quad (3)$$

In the last line we have interchanged the two sums according to

$$\sum_{n=0}^{\infty} \sum_{m=n+1}^{\infty} = \sum_{m=1}^{\infty} \sum_{n=0}^{m-1} .$$

We now choose the A_n such that

$$\sum_{n=0}^{m-1} \frac{A_n}{(m-n)!} = \frac{1}{(m+1)!} \quad \text{for all } m \geq 1 . \quad (4)$$

In this case the right-hand side of (3) equals the double sum in (2). If we subtract (3) from (2), the two double sums cancel, and the result is the Euler-McLaurin summing formula (1).

The relation (4) may be written in the form

$$A_{m-1} = \frac{1}{(m+1)!} - \sum_{n=0}^{m-2} \frac{A_n}{(m-n)!} \text{ for all } m \geq 1 .$$

This is a recursion relation that permits the calculation of each A_n from the preceding values. These are the values given earlier. In the mathematical literature the coefficients are usually expressed in terms of the so-called Bernoulli numbers, a relationship not of interest to us.

ANISOTROPIC VOLUME CHANGES:

THE IRRELEVANCE OF THE SHAPE OF A VOLUME

At several places in Chapter 3 -- pp. 65/66 and 72/73 -- as well as in later Chapters, we make the simplifying assumption that the system has the shape of a cube of volume $V = L^3$ and that any volume changes are isotropic, so that a cube remains a cube. None of this matters. We show this here without relying on intuition for the particularly simple case of free particles confined to a parallelepiped with the dimensions L_x , L_y , and L_z , with the volume $V = L_x L_y L_z$. A more general proof is found in C. Kittel, Quantum Theory of Solids, Wiley, New York, 1963, pp. 339-341.

For a parallelepiped the orbitals of the free particle wave equation are

$$\psi(x,y,z) = A \sin(n_x \pi x / L_x) \sin(n_y \pi y / L_y) \sin(n_z \pi z / L_z) ,$$

instead of (58), and the corresponding energies are

$$\varepsilon_n = \frac{\hbar^2 \pi^2}{2M} \left[\left(\frac{n_x}{L_x} \right)^2 + \left(\frac{n_y}{L_y} \right)^2 + \left(\frac{n_z}{L_z} \right)^2 \right] ,$$

instead of (59). If the remainder of the argument on pp. 72/73 is carried out for the parallelepiped one finds, instead of (61),

$$z_1 = \int_0^\infty dn_x \int_0^\infty dn_y \int_0^\infty dn_z \exp[-(\alpha_x^2 n_x^2 + \alpha_y^2 n_y^2 + \alpha_z^2 n_z^2)] ,$$

where $\alpha_x^2 = \hbar^2 \pi^2 / (2ML_x^2 \tau)$, etc. Executing the integrals as on p. 73 leads to

$$z_1 = \pi^{3/2} / (8\alpha_x \alpha_y \alpha_z) = \frac{L_x L_y L_z}{(2\pi \hbar^2 / M \tau)^{3/2}} .$$

But $L_x L_y L_z$ is of course V , hence the final result is the same as in (62), depending only on the magnitude of the volume but not its shape.

But if this is true for the partition function, it must be true for all properties derivable from it, including -- from (55) -- the Helmholtz free energy and therefore -- from (49) -- the entropy. In particular, if the pressure p is the volume derivative of the energy at constant entropy for an isotropic volume change, the same must be true for an anisotropic volume change: An anisotropic volume change may be viewed as an isotropic volume change followed by a change in shape at constant volume. Our discussion shows that the change of shape does not have any effect.

In terms of the discussion of Appendix D, the following comments are in order. Consider the ensemble of states whose energy falls into the energy interval $(\varepsilon, \varepsilon + d\varepsilon)$, with

$d\varepsilon \ll \tau$. During a change of shape some of the states initially in that ensemble leave the ensemble, while other states move into the ensemble. But the total number of states in the ensemble remains the same, which is the only thing that matters, because the entropy is the logarithm of that number.