PART II

STATISTICAL MECHANICS

15

STATISTICAL MECHANICS IN THE ENTROPY REPRESENTATION: THE MICROCANONICAL FORMALISM

15-1 PHYSICAL SIGNIFICANCE OF THE ENTROPY FOR CLOSED SYSTEMS

Thermodynamics constitutes a powerful formalism of great generality, erected on a basis of a very few, very simple hypotheses. The central concept introduced through those hypotheses is the entropy. It enters the formulation abstractly as the variational function in a mathematical extremum principle determining equilibrium states. In the resultant formalism, however, the entropy is one of a set of extensive parameters, together with the energy, volume, mole numbers and magnetic moment. As these latter quantities each have clear and fundamental physical interpretations it would be strange indeed if the entropy alone were to be exempt from physical interpretation.

The subject of statistical mechanics provides the physical interpretation of the entropy, and it accordingly provides a heuristic justification for the extremum principle of thermodynamics. For some simple systems, for which we have tractable models, this interpretation also permits explicit calculation of the entropy and thence of the fundamental equation.

We focus first on a closed system of given volume and given number of particles. For definiteness we may think of a fluid, but this is in no way necessary. The parameters U, V, and N are the only constraints on the system. Quantum mechanics tells us that, if the system is macroscopic, there may exist many discrete quantum states consistent with the specified values of U, V, and N. The system may be in any of these permissible states.

Naively we might expect that the system, finding itself in a particular quantum state, would remain forever in that state. Such, in fact, is the lore of elementary quantum mechanics; the "quantum numbers" that specify a particular quantum state are ostensibly "constants of the motion." This naive fiction, relatively harmless to the understanding of atomic systems (to which quantum mechanics is most commonly applied) is flagrantly misleading when applied to macroscopic systems.

The apparent paradox is seated in the assumption of *isolation* of a physical system. *No physical system is, or ever can be, truly isolated.* There exist weak, long-range, random gravitational, electromagnetic and other forces that permeate all physical space. These forces not only couple spatially separated material systems, but the force fields *themselves* constitute physical systems in direct interaction with the system of interest. The very vacuum is now understood to be a complex fluctuating entity in which occur continual elaborate processes of creation and reabsorption of electrons, positrons, neutrinos, and a myriad of other esoteric subatomic entities. All of these events can couple with the system of interest.

For a simple system such as a hydrogen atom in space the very weak interactions to which we have alluded seldom induce transitions between quantum states. This is so because the quantum states of the hydrogen atom are widely spaced in energy, and the weak random fields in space cannot easily transfer such large energy differences to or from the atom. Even so, such interactions occassionally do occur. An excited atom may "spontaneously" emit a photon, decaying to a lower energy state. Quantum field theory reveals that such ostensibly "spontaneous" transitions actually are *induced* by the interactions between the excited atom and the modes of the vacuum. The quantum states of atoms are *not* infinitely long lived, precisely because of their interaction with the random modes of the vacuum.

For a macroscopic system the energy differences between successive quantum states become minute. In a macroscopic assembly of atoms each energy eigenstate of a single atom "splits" into some 10^{23} energy eigenstates of the assembly, so that the average energy difference between successive states is decreased by a factor of $\sim 10^{-23}$. The slightest random field, or the weakest coupling to vacuum fluctuations, is then sufficient to buffet the system chaotically from quantum state to quantum state.

A realistic view of a macroscopic system is one in which the system makes enormously rapid random transitions among its quantum states. A macroscopic measurement senses only an average of the properties of myriads of quantum states.

All "statistical mechanicians" agree with the preceding paragraph, but not all would agree on the *dominant* mechanism for inducing transitions. Various mechanisms compete and others may well dominate in some or even in all systems. No matter—it is sufficient that *any* mechanism exists, and it is only the conclusion of rapid, random transitions that is needed to validate statistical mechanical theory.

Because the transitions are induced by purely random processes, it is reasonable to suppose that *a macroscopic system samples every permissible quantum state with equal probability*—a permissible quantum state being one consistent with the external constraints.

The assumption of equal probability of all permissible microstates is the fundamental postulate of statistical mechanics. Its justification will be examined more deeply in Part III, but for now we adopt it on two bases; its a priori reasonableness, and the success of the theory that flows from it.

Suppose now that some external constraint is removed—such as the opening of a valve permitting the system to expand into a larger volume. From the microphysical point of view the removal of the constraint activates the possibility of many microstates that previously had been precluded. Transitions occur into these newly available states. After some time the system will have lost all distinction between the original and the newly available states, and the system will thenceforth make random transitions that sample the *augmented* set of states with equal probability. *The number of microstates among which the system undergoes transitions, and which thereby share uniform probability of occupation, increases to the maximum permitted by the imposed constraints.*

This statement is strikingly reminiscent of the entropy postulate of thermodynamics, according to which the entropy increases to the maximum permitted by the imposed constraints. It suggests that the entropy can be identified with the number of microstates consistent with the imposed macroscopic constraints.

One difficulty arises: The entropy is additive (extensive), whereas the number of microstates is multiplicative. The number of microstates available to two systems is the *product* of the numbers available to each (the number of "microstates" of two dice is $6 \times 6 = 36$). To interpret the entropy, then, we require an *additive* quantity that measures the number of microstates available to a system. The (unique!) answer is to *identify the entropy with the logarithm of the number of available microstates* (the logarithm of a product being the sum of the logarithms). Thus

$$S = k_B \ln \Omega \tag{15.1}$$

where Ω is the number of microstates consistent with the macroscopic constraints. The constant prefactor merely determines the scale of S; it is chosen to obtain agreement with the Kelvin scale of temperature, defined by $T^{-1} = \partial S/\partial U$. We shall see that this agreement is achieved by taking the constant to be Boltzmann's constant $k_B = R/N_A = 1.3807 \times 10^{-23}\,\mathrm{J/K}$.

With the definition 15.1 *the basis of statistical mechanics is established.*

Just as the thermodynamic postulates were elaborated through the formalism of Legendre transformations, so this single additional postulate will be rendered more powerful by an analogous structure of mathematical formalism. Nevertheless this single postulate is dramatic in its brevity, simplicity, and completeness. The statistical mechanical formalism that derives directly from it is one in which we "simply" calculate the logarithm of the number of states available to the system, thereby obtaining S as a function of the constraints U, V, and N. That is, it is statistical mechanics in the entropy representation, or, in the parlance of the field, it is statistical mechanics in the *microcanonical formalism*.

In the following sections of this chapter we treat a number of systems by this microcanonical formalism as examples of its logical completeness.

As in thermodynamics, the entropy representation is not always the most convenient representation. For statistical mechanical calculations it is frequently so inconvenient that it is analytically intractable. The Legendre transformed representations are usually far preferable, and we shall turn to them in the next chapter. Nevertheless the microcanonical formulation establishes the clear and basic logical foundation of statistical mechanics.

PROBLEMS

15.1-1. A system is composed of two harmonic oscillators each of natural frequency ω_0 and each having permissible energies $(n+\frac{1}{2})\hbar\omega_0$, where n is any non-negative integer. The total energy of the system is $E' = n'\hbar\omega_0$, where n' is a positive integer. How many microstates are available to the system? What is the entropy of the system?

A second system is also composed of two harmonic oscillators, each of natural frequency $2\omega_0$. The total energy of this system is $E'' = n''\hbar\omega_0$, where n'' is an even integer. How many microstates are available to this system? What is the entropy of this system?

What is the entropy of the system composed of the two preceding subsystems (separated and enclosed by a totally restrictive wall)? Express the entropy as a function of E' and E''.

Answer:

$$S_{\text{tot}} = k_B \ln\left(\frac{E'E''}{2\hbar^2\omega_0^2}\right)$$

15.1-2. A system is composed of two harmonic oscillators of natural frequencies ω_0 and $2\omega_0$, respectively. If the system has total energy $E = (n+\frac{1}{2})\hbar\omega_0$, where n is an odd integer, what is the entropy of the system?

If a composite system is composed of two non-interacting subsystems of the type just described, having energies E_1 and E_2, what is the entropy of the composite system?

15-2 THE EINSTEIN MODEL OF A CRYSTALLINE SOLID

With a identification of the meaning of the entropy we proceed to calculate the fundamental equation of macroscopic systems. We first apply the method to Einstein's simplified model of a nonmetallic crystalline solid.

It is well to pause immediately and to comment on so early an introduction of a specific model system. In the eleven chapters of this book devoted to thermodynamic theory there were few references to specific model systems, and those occasional references were kept carefully distinct from the logical flow of the general theory. In statistical mechanics we almost immediately introduce a model system, and this will be followed by a considerable number of others. The difference is partially a matter of convention. To some extent it reflects the simplicity of the general formalism of statistical mechanics, which merely adds the logical interpretation of the entropy to the formalism of thermodynamics; the interest therefore shifts to applications of that formalism, which underlies the various material sciences (such as solid state physics, the theory of liquids, polymer physics, and the like). But, most important, it reflects the fact that counting the number of states available to physical systems requires computational skills and experience that can be developed only by explicit application to concrete problems.

To account for the thermal properties of crystals, Albert Einstein, in 1907, introduced a highly idealized model focusing only on the vibrational modes of the crystal. Electronic excitations, nuclear modes, and various other types of excitations were ignored. Nevertheless, for temperatures that are neither very close to absolute zero nor very high, the model is at least qualitatively successful.

Einstein's model consists of the assumption that each of the $\tilde{N}$ atoms in the crystal can be considered to be bound to its equilibrium position by a harmonic force. Each atom is free to vibrate around its equilibrium position in any of the three coordinate directions, with a natural frequency ω_0.

More realistically (recall Section 1.2) the atoms of crystals are harmonically bound to their neighboring atoms rather than to fixed points. Accordingly the vibrational modes are strongly coupled, giving rise to $3\tilde{N}$ collective normal modes. The frequencies are distributed from zero (for very long wave length modes) to some maximum frequency (for the modes of minimum permissible wave length, comparable to the interatomic distance). There are far more high frequency modes than low frequency modes, with the consequence that the frequencies tend to cluster mainly in a narrow range of frequencies, to which the Einstein frequency ω_0 is a rough approximation.

In the Einstein model, then, a crystal of $\tilde{N}$ atoms is replaced by $3\tilde{N}$ harmonic oscillators, all with the same natural frequency ω_0.

For the present purposes it is convenient to choose the zero of energy so that the energy of a harmonic oscillator of natural frequency ω_0 can take only the discrete values $n\hbar\omega_0$, with $n = 0, 1, 2, 3, \ldots$. Here $\hbar = h/2\pi = 1.055 \times 10^{-34}$ J-s., h being Planck's constant.

In the language of quantum mechanics, each oscillator can be "occupied by an integral number of energy quanta," each of energy $\hbar\omega_0$.

The number of possible states of the system, and hence the entropy, can now be computed easily. If the energy of the system is U it can be considered as constituting $U/\hbar\omega_0$ quanta. These quanta are to be distributed among $3\tilde{N}$ vibrational modes. The number of ways of distributing the $U/\hbar\omega_0$ quanta among the $3\tilde{N}$ modes is the number of states Ω available to the system.

The problem is isomorphic to the calculation of the number of ways of placing $U/\hbar\omega_0$ identical (indistinguishable) marbles in $3\tilde{N}$ numbered (distinguishable) boxes.

FIGURE 15.1
Illustrating the combinatorial problem of distributing $U/\hbar\omega_0$ indistinguishable objects ("marbles") in $3\tilde{N}$ distinguishable "boxes."

The combinatorial problem can be visualized as follows. Suppose we have $U/\hbar\omega_0$ marbles and $3\tilde{N} - 1$ match sticks. We lay these out in a linear array, in any order. One such array is shown in Fig. 15.1. The interpretation of this array is that three quanta (marbles) are assigned to the first mode, two quanta to the second, none to the third, and so forth, and two quanta are assigned to the last mode (the $3\tilde{N}$-th). Thus the number of ways of distributing the $U/\hbar\omega_0$ quanta among the $3\tilde{N}$ modes is the number of permutations of $(3\tilde{N} - 1 + U/\hbar\omega_0)$ objects, of which $U/\hbar\omega_0$ are identical (marbles or quanta), and $3\tilde{N} - 1$ are identical (match sticks). That is

$$\Omega = \frac{(3\tilde{N} - 1 + U/\hbar\omega_0)!}{(3\tilde{N} - 1)!(U/\hbar\omega_0)!} \simeq \frac{(3\tilde{N} + U/\hbar\omega_0)!}{(3\tilde{N})!(U/\hbar\omega_0)!} \tag{15.2}$$

This completes the calculation, for the entropy is simply the logarithm of this quantity (multiplied by k_B). To simplify the result we employ the Stirling approximation for the logarithm of the factorial of a large number

$$\ln(M!) \simeq M \ln M - M + \cdots \qquad (\text{if } M \gg 1) \tag{15.3}$$

whence the molar entropy is

$$s = 3R\ln\left(1 + \frac{u}{u_0}\right) + 3R\frac{u}{u_0}\ln\left(1 + \frac{u_0}{u}\right) \tag{15.4}$$

where

$$u_0 \equiv 3N_A\hbar\omega_0 \tag{15.5}$$

This is the fundamental equation of the system.

It will be left to the problems to show that the fundamental equation implies reasonable thermal behavior. The molar heat capacity is zero at zero temperature, rises rapidly with increasing temperature, and approaches a constant value ($3R$) at high temperature, in qualitative agreement with experiment. The rate of increase of the heat capacity is not quantitatively correct because of the naiveté of the model of the vibrational modes. This will be improved subsequently in the "Debye model" (Section 16.7), in which the vibrational modes are treated more realistically.

The heat capacity of the Einstein model is plotted in Fig. 15.2. The molar heat capacity c_v is zero at $T = 0$, and it asymptotes to $3R$ at high temperature. The rise in c_v occurs in the region $k_BT \simeq \frac{1}{3}\hbar\omega_0$ (in particular $c_v/3R = \frac{1}{2}$ and the point of maximum slope both occur near $k_BT/\hbar\omega_0 \simeq \frac{1}{3}$). At low temperature c_v rises exponentially, whereas experimentally the heat capacity rises approximately as T^3.

The mechanical implications of the model—the pressure–volume relationship and compressibility—are completely unreasonable. The entropy, according to equation 15.5, is independent of the volume, whence the pressure $T\partial S/\partial V$ is identically zero! Such a nonphysical result is, of course, a reflection of the naive omission of volume dependent effects from the model.

Certain consequences of the model give important general insights. Consider the thermal equation of state

$$\frac{1}{T} = \frac{\partial S}{\partial U} = \frac{k_B}{\hbar\omega_0}\ln\left(1 + \frac{3N}{U}N_A\hbar\omega_0\right) \tag{15.6}$$

Now, noting that there are $3NN_A$ oscillators in the system

$$\text{mean energy per oscillator} = \frac{U}{3NN_A} = \frac{\hbar\omega_0}{e^{\hbar\omega_0/k_BT} - 1} \tag{15.7}$$

The quantity $\hbar\omega_0/k_B$ is called the "Einstein temperature" of the crystal, and it generally is of the same order of magnitude as the melting

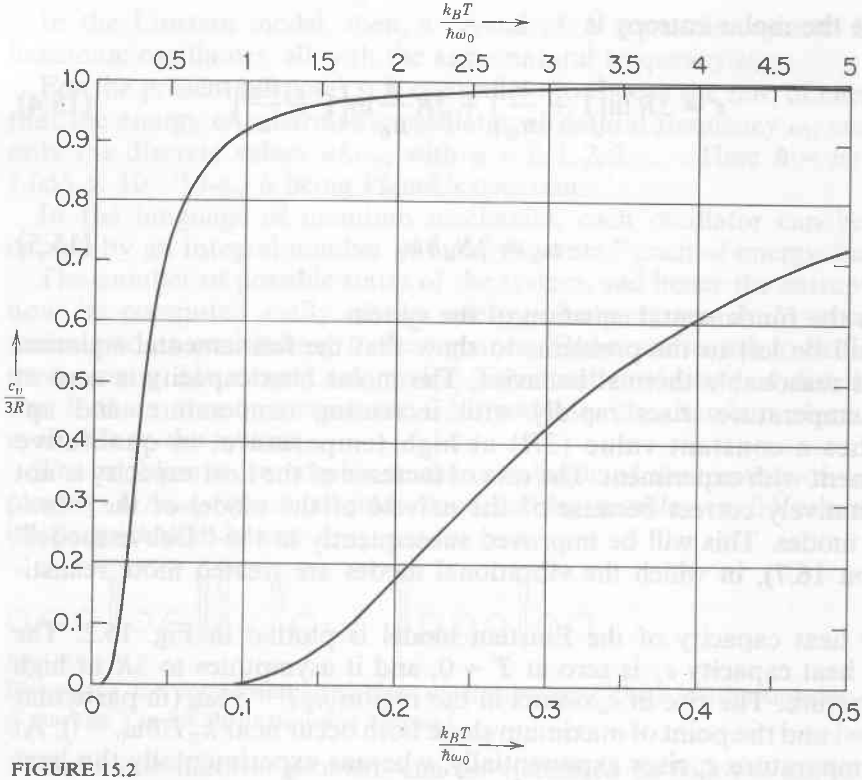

FIGURE 15.2
Heat capacity of the Einstein model, or of a single harmonic oscillator. The upper curve refers to the upper scale of $k_BT/\hbar\omega_0$, and the lower curve to the lower (expanded) scale. The ordinate can be interpreted as the heat capacity of one harmonic oscillator in units of k_B, or as the molar heat capacity in units of $3R$.

temperature of the solid. Thus below the melting temperature, the mean energy of an oscillator is less than, or of the order of, $\hbar\omega_0$. Alternatively stated, the solid melts before the Einstein oscillators attain quantum numbers appreciably greater than unity.

PROBLEMS

15.2-1. Calculate the molar heat capacity of the Einstein model by equation 15.7. Show that the molar heat capacity approaches $3R$ at high temperatures. Show that the temperature dependence of the molar heat capacity is exponential near zero temperature, and calculate the leading exponential term.

15.2-2. Obtain an equation for the mean quantum number $\bar{n}$ of an Einstein oscillator as a function of the temperature. Calculate $\bar{n}$ for $k_BT/\hbar\omega_0 = 0, 1, 2, 3, 4, 10, 50, 100$ (ignore the physical reality of melting of the crystal!).

15.2-3. Assume that the Einstein frequency ω_0 for a particular crystal depends upon the molar volume:

$$\omega_0 = \omega_0^0 - A\ln\left(\frac{v}{v_0}\right)$$

a) Calculate the isothermal compressibility of this crystal.

b) Calculate the heat transfer if a crystal (of one mole) is compressed at constant temperature from v_i to v_f.

15-3 THE TWO-STATE SYSTEM

Another model that illustrates the principles of statistical mechanics in a simple and transparent fashion is the "two-state model." In this model each "atom" can be either in its "ground state" (with energy zero) or in its "excited state" (with energy ε).

To avoid conflict with certain general theorems about energy spectra we assume that each atom has additional states, but all of such high energy as to exceed the total energy of the system under consideration. Such states are then inaccessible to the system and need not be considered further in the calculation.

If U is the energy of the system then U/ε atoms are in the excited state and $(\tilde{N} - U/\varepsilon)$ atoms are in the ground state. The number of ways of choosing U/ε atoms from the total number $\tilde{N}$ is

$$\Omega = \frac{\tilde{N}!}{(U/\varepsilon)!(\tilde{N} - U/\varepsilon)!} \tag{15.8}$$

The entropy is therefore

$$S = k_B \ln\Omega = k_B \ln(\tilde{N}!) - k_B \ln\left(\frac{U}{\varepsilon}!\right) - k_B \ln\left[\left(\tilde{N} - \frac{U}{\varepsilon}\right)!\right] \tag{15.9}$$

or, invoking Stirling's approximation (equation 15.3)

$$S = \left(\frac{U}{\varepsilon} - \tilde{N}\right) k_B \ln\left(1 - \frac{U}{\tilde{N}\varepsilon}\right) - \frac{U}{\varepsilon} k_B \ln\frac{U}{\tilde{N}\varepsilon} \tag{15.10}$$

Again, because of the artificiality of the model, the fundamental equation is independent of the volume. The thermal equation of state is easily calculated to be

$$\frac{1}{T} = \frac{k_B}{\varepsilon}\ln\left(\frac{\tilde{N}\varepsilon}{U} - 1\right) \tag{15.11}$$

Recalling that the calculation is subject to the condition $U < \tilde{N}\varepsilon$, we observe that the temperature is a properly positive number. Solving for the energy

$$U = \frac{\tilde{N}\varepsilon}{1 + e^{\varepsilon/k_BT}} \tag{15.12}$$

The energy approaches $\tilde{N}\varepsilon/2$ as the temperature approaches infinity in this model (although we must recall that additional states of high energy would alter the high temperature properties). At infinite temperature half the atoms are excited and half are in their ground state.

The molar heat capacity is

$$c = \frac{du}{dT} = N_A \frac{\varepsilon^2}{k_BT^2} \frac{e^{\varepsilon/k_BT}}{(1 + e^{\varepsilon/2k_BT})^2} = N_A \frac{\varepsilon^2}{k_BT^2} (e^{\varepsilon/2k_BT} + e^{-\varepsilon/2k_BT})^{-2} \tag{15.13}$$

A graph of this temperature dependence is shown in Fig 15.3. The molar heat capacity is zero both at very low temperatures and at very high

FIGURE 15.3
Heat capacity of the two-state model; the "Schottky hump."

temperatures, peaking in the region of $k_B T = .42\varepsilon$. This behavior is known as a "Schottky hump." Such a maximum, when observed in empirical data, is taken as an indication of a pair of low lying energy states, with all other energy states lying at considerably higher energies. This is an example of the way in which thermal properties can reveal information about the atomic structure of materials.

PROBLEMS

15.3-1. In the two-state model system of this section suppose the excited state energy ε of an "atom" depends on its average distance from its neighboring atoms so that

$$\varepsilon = \frac{a}{\tilde{v}^{\gamma}}, \qquad \tilde{v} \equiv \frac{V}{\tilde{N}}$$

where a and γ are positive constants. This assumption, applied to a somewhat more sophisticated model of a solid, was introduced by Gruneisen, and γ is the "Gruneisen parameter." Calculate the pressure P as a function of $\tilde{v}$ and T.

Answer:

$$P = \frac{\gamma a}{\tilde{v}^{\gamma+1}}\left(e^{a/k_B T \tilde{v}^{\gamma}} + 1\right)^{-1}$$

15-4 A POLYMER MODEL—THE RUBBER BAND REVISITED

There exists another model of appealing simplicity that is euphemistically referred to as a "polymer model." Its connection with a real polymer is tenuous, but that connection is perhaps close enough to serve the pedagogical purpose of providing some sense of physical reality while again illustrating the basic algorithm of statistical mechanics. And in particular the model provides an insight to the behavior of a "rubber band," as discussed on purely phenomenological grounds in Section 3.7. As we saw in that section the extensive parameter of interest, which replaces the volume, is the *length*; the corresponding intensive parameter, analogous to the pressure, is the *tension*. We are interested in the equation of state relating tension to length and temperature.

The "rubber band" can be visualized as a bundle of long chain polymers. Each polymer chain is considered to be composed of $\tilde{N}$ monomer units each of length a, and we focus our attention on one particular polymer chain in the bundle. One end of the polymer chain is fixed at a point that is taken as the origin of coordinates. The other end of the chain is subject to an externally applied tension $\mathscr{T}$, parallel to the positive x-axis (Fig. 15.4).

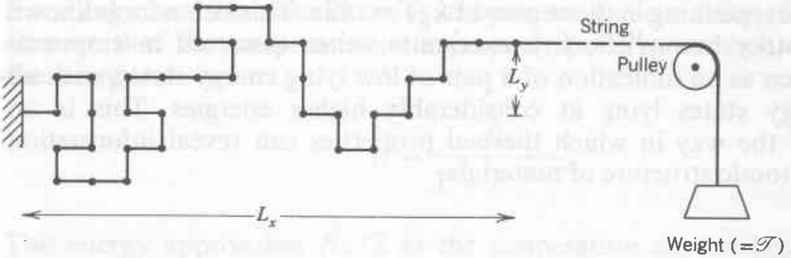

FIGURE 15.4
“Polymer” model. The string should be much longer than shown, so that the end of th polymer is free to move in the y-direction, and the applied tension $\mathscr{T}$ is directed along th x-direction.

In the polymer model each monomer unit of the chain is permitted to lie either parallel or antiparallel to the x-axis, and zero energy is associated with these two orientations. Each monomer unit has the additiona possibility of lying *perpendicular* to the x-axis, in the $+y$ or $-y$ directions *only*. Such a “perpendicular” monomer unit presumably suffer interference with other polymer chains in the bundle; we represent thi interference by assigning a positive energy ε to such a perpendicula monomer.

A somewhat more reasonable model of the polymer might permit the perpendicular monomers to lie along the $\pm z$ directions as well as alon the $\pm y$ directions, and, more importantly, would account for the interference of a chain doubling back on itself. Such models complicate th analysis without adding to the pedagogic clarity or qualitative content of the result.

We calculate the entropy S of one polymer chain as a function of the energy $U \equiv U'\varepsilon$, of the coordinates L_x and L_y of the end of the polyme chain, and of the number $\tilde{N}$ of monomer units in the chain.

Let N_x^+ and N_x^- be the numbers of monomers along the $+x$ and $-x$ directions respectively, and similarly for N_y^+ and N_y^-. Then

$$N_x^+ + N_x^- + N_y^+ + N_y^- = \tilde{N}$$

$$N_x^+ - N_x^- = \frac{L_x}{a} \equiv L'_x$$

$$N_y^+ - N_y^- = \frac{L_y}{a} \equiv L'_y$$

$$N_y^+ + N_y^- = \frac{U}{\varepsilon} \equiv U' \qquad (15.14)$$

from which we find

$$N_x^+ = \tfrac{1}{2}\left(\tilde{N} - U' + L'_x\right)$$

$$N_x^- = \tfrac{1}{2}\left(\tilde{N} - U' - L'_x\right)$$

$$N_y^+ = \tfrac{1}{2}\left(U' + L'_y\right)$$

$$N_y^- = \tfrac{1}{2}\left(U' - L'_y\right) \tag{15.15}$$

The number of configurations of the polymer consistent with given coordinates L_x and L_y of its terminus, and with given energy U, is

$$\Omega\left(U, L_x, L_y, \tilde{N}\right) = \frac{\tilde{N}!}{N_x^+!N_x^-!N_y^+!N_y^-!} \tag{15.16}$$

The entropy is, then, using the Stirling approximation (equation 15.3)

$$S = k_B \ln \Omega = \tilde{N} k_B \ln \tilde{N} - N_x^+ k_B \ln N_x^+ - N_x^- k_B \ln N_x^-$$
$$- N_y^+ k_B \ln N_y^+ - N_y^- k_B \ln N_y^- \tag{15.17}$$

or

$$S = \tilde{N} k_B \ln \tilde{N} - \tfrac{1}{2}\left(\tilde{N} - U' + L'_x\right) k_B \ln\left[\tfrac{1}{2}\left(\tilde{N} - U' + L'_x\right)\right]$$
$$- \tfrac{1}{2}\left(\tilde{N} - U' - L'_x\right) k_B \ln\left[\tfrac{1}{2}\left(\tilde{N} - U' - L'_x\right)\right]$$
$$- \tfrac{1}{2}\left(U' + L'_y\right) k_B \ln\left[\tfrac{1}{2}\left(U' + L'_y\right)\right]$$
$$- \tfrac{1}{2}\left(U' - L'_y\right) k_B \ln\left[\tfrac{1}{2}\left(U' - L'_y\right)\right] \tag{15.18}$$

With the statistical mechanical phase of the calculation completed, the thermodynamic formalism comes into play. The y-component of the tension $\mathcal{T}_y$ is conjugate to the extensive coordinate L_y (see Problem 15.4-1). Setting $\mathcal{T}_y = 0$ gives

$$-\frac{\mathcal{T}_y}{T} = \frac{\partial S}{\partial L_y} = \frac{k_B}{2a} \ln \frac{U' - L'_y}{U' + L'_y} = 0 \tag{15.19}$$

from which we conclude (as expected) that

$$L_y = L'_y = 0 \tag{15.20}$$

Similarly

$$-\frac{\mathscr{T}_x}{T} = \frac{\partial S}{\partial L_x} = \frac{k_B}{2a}\ln\frac{\tilde{N} - U' - L'_x}{\tilde{N} - U' + L'_x} \tag{15.21}$$

and

$$\frac{1}{T} = \frac{\partial S}{\partial U} = \frac{k_B}{2\varepsilon}\ln\left(\tilde{N} + L'_x - U'\right) + \frac{k_B}{2\varepsilon}\ln\left(\tilde{N} - L'_x - U'\right) - \frac{k_B}{\varepsilon}\ln U' \tag{15.22}$$

or

$$e^{2\varepsilon/k_B T} = \frac{(\tilde{N} - U')^2 - L_x'^2}{U'^2} \tag{15.23}$$

This is the "thermal equation of state." The "mechanical equation of state" (15.21) can be written in an analogous exponential form

$$e^{-2\mathscr{T}_x a/k_B T} = \frac{\tilde{N} - U' - L'_x}{\tilde{N} - U' + L'_x} \tag{15.24}$$

The two preceding equations are the equations of state in the entropy representation, and accordingly they involve the energy U'. That is not generally convenient. We proceed, then, to eliminate U' between the two equations. With some algebra we find (see Problem 15.4-2) that

$$\frac{L'_x}{\tilde{N}} = \frac{\sinh(\mathscr{T}_x a/k_B T)}{\cosh(\mathscr{T}_x a/k_B T) + e^{-\varepsilon/k_B T}} \tag{15.25}$$

For small $\mathscr{T}_x a$ (relative to $k_B T$) the equation can be expanded to first order

$$L_x = \frac{\mathscr{T}_x \tilde{N} a^2}{k_B T}\,\frac{1}{1 + e^{-\varepsilon/k_B T}} + \cdots \tag{15.26}$$

The modulus of elasticity of the rubber band (the analogue of the compressibility $-1/V(\partial V/\partial P)_T$) is, for small $\mathscr{T}_x$

$$\frac{1}{\tilde{N}}\left(\frac{\partial L_x}{\partial \mathscr{T}_x}\right)_T = \frac{a^2}{k_B T}\left(1 + e^{-\varepsilon/k_B T}\right)^{-1} \tag{15.27}$$

The fact that this elastic modulus *decreases* with increasing temperature (or that the "stiffness" increases) is in dramatic contrast to the behavior of a spring or of a stretched wire. The behavior of the polymer is sometimes compared to the behavior of a snake; if we grasp a snake by the head and tail and attempt to stretch it straight the resistance is attributable to the writhing activity of the snake. The snake, in its writhing, assumes all possible configurations, and more configurations are accessible if the two ends are not greatly distant from each other. At low temperatures the rubber band is like a torpid snake. At high temperatures the number of configurations available, and the rate of transitions among them, is greater, resulting in a greater contractive tension. It is the *entropy* of the snake and of the rubber band that is responsible for the tendency of the ends to draw together!

The behavior described is qualitatively similar to that of the simple phenomenological model of Section 3.7. But compared to a truly realistic model of a rubber band, both models are extremely naive.

PROBLEMS

15.4-1. Is the sign correct in equation 15.19? Explain.

15.4-2. Eliminate U/ε between equations 15.23 and 15.24 and show that the formal solution is equation 15.25 with a ± sign before the second term in the denominator. Consider the qualitative dependence of $L_x/\tilde{N}a$ on ε, and show that physical reasoning rejects the negative sign in the denominator, thus validating equation 15.25.

15.4-3. A rubber band consisting of n polymer chains is stretched from zero length to its full extension ($L = \tilde{N}a$) at constant temperature T. Does the energy of the system increase or decrease? Calculate the work done on the system and the heat transfer to the system.

15.4-4. Calculate the heat capacity at constant length for a "rubber band" consisting of n polymer chains. Express the answer in terms of T and L_x.

15.4-5. Calculate the "coefficient of longitudinal thermal expansion" defined by

$$\kappa_T' \equiv \frac{1}{L_x}\left(\frac{\partial L_x}{\partial T}\right)_{\mathcal{T}_x}$$

Express κ_T' as a function of T and sketch the qualitative behavior. Compare this with the behavior of a metallic wire and discuss the result.

15-5 COUNTING TECHNIQUES AND THEIR CIRCUMVENTION; HIGH DIMENSIONALITY

To repeat, the basic algorithm of statistical mechanics consists of counting the number of states consistent with the constraints imposed; the entropy is then the product of Boltzmann's constant and the logarithm of the permissible number of states.

Unfortunately counting problems tend to require difficult and sophisticated techniques of combinatorial mathematics (if they can be done at all!) In fact only a few highly artificial, idealized models permit explicit solution of the counting problem, even with the full armamentarium of combinatorial theory. If statistical mechanics is to be a useful and practical science it is necessary that the difficulties of the counting problem somehow be circumvented. One method of simplifying the counting problem is developed in this section. It is based on certain rather startling properties of systems of "high dimensionality"—a concept to be defined shortly. The method is admittedly more important for the insights it provides to the behavior of complex systems than for the aid it provides in practical calculations. More general and powerful methods of circumventing the counting problem are based on a transfer from thermodynamics to statistical mechanics of the technique of Legendre transformations. That transfer will be developed in the following chapters.

For now we turn our attention to the simplifying effects of *high dimensionality*, a concept that can best be introduced in terms of an explicit model. We choose the simplest model with which we are already familiar—the Einstein model.

Recall that the Einstein solid is a collection of $\tilde{N}$ atoms, each of which is to be associated with three harmonic oscillators (corresponding to the oscillations of the atom along the x, y, and z axes). A quantum state of the system is specified by the $3\tilde{N}$ quantum numbers $n_1, n_2, n_3, \ldots, n_{3\tilde{N}}$, and the energy of the system is

$$U(n_1, n_2, \ldots, n_{3\tilde{N}}) = \sum_{j=1}^{3\tilde{N}} n_j \hbar\omega_0 \tag{15.28}$$

Each such state can be represented by a "point," with coordinates $n_1, n_2, n_3, \ldots, n_{3\tilde{N}}$, in a $3\tilde{N}$-dimensional "state space." Only points with positive integral coordinates are permissible, corresponding to the discreteness or "quantization" of states in quantum mechanics. It is to be stressed that a single point represents the quantum state of the *entire crystal*.

The locus of states with a given energy U is a "diagonal" hyperplane with intercepts $U/\hbar\omega_0$ on each of the $3\tilde{N}$ coordinate axes (Fig. 15.5). All states lying "inside" the plane (i.e., closer to the origin) have energies less than U, and all states lying outside the plane, further from the origin, have energies greater than U.

The first critical observation which is called to our attention by Fig. 15.5 is that an arbitrary "diagonal plane," corresponding to an arbitrary energy U, will generally pass through *none* of the discrete coordinate points in the space! That is, an arbitrarily selected number U generally

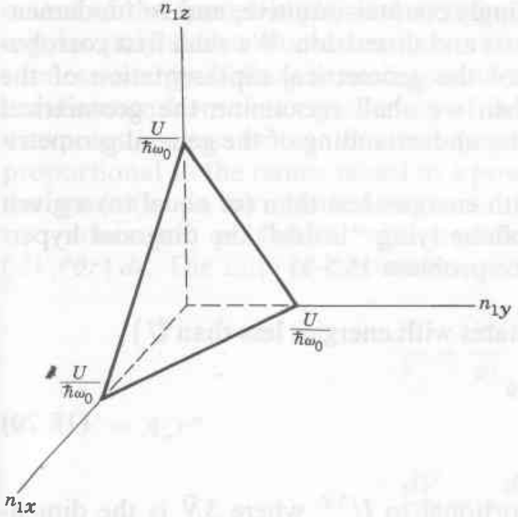

FIGURE 15.5
Quantum state space for the Einstein solid. The three-dimensional state space shown is for an Einstein solid composed of a single atom. Each additional atom would increase the dimensionality of the space by three. The hyperplane U has intercepts $U/\hbar\omega_0$ on all axes. There is one state for each unit of hypervolume, and (neglecting surface corrections) the number of states with energy less than U is equal to the volume inside the diagonal hyperplane U.

cannot be represented in the form of equation 15.28, such a decomposition being possible only if $U/\hbar\omega_0$ is an integer.

More generally, if we inquire as to the number of quantum states of a system with an *arbitrarily chosen and mathematically precise* energy, we almost always find zero. But such a question is unphysical. As we have stressed previously the random interactions of every system with its environment make the energy slightly imprecise. Furthermore we never know (and cannot measure) the energy of any system with absolute precision.

The entropy is not the logarithm of the number of quantum states that lie on the diagonal hyperplane U of Fig. 15.5, *but rather it is the logarithm of the number of quantum states that lie in the close vicinity of the diagonal hyperplane.*

This consideration leads us to study the number of states between two hyperplanes: U and $U - \Delta$. The energy separation Δ is determined by the imprecision of the energy of the macroscopic system. That imprecision may be thought of as a consequence either of environmental interactions or of imprecision in the preparation (measurement) of the system.

The remarkable consequence of high dimensionality is that *the volume between the two planes* ($U - \Delta$ and U), *and hence the entropy, is essentially independent of the separation* Δ *of the planes*!

This result is (at first) so startlingly counter-intuitive, and so fundamental, that it warrants careful analysis and discussion. We shall first corroborate the assertion on the basis of the geometrical representation of the states of the Einstein solid. Then we shall reexamine the geometrical representation to obtain a heuristic understanding of the general geometrical basis of the effect.

The number of states $\tilde{\Omega}(U)$ with energies less than (or equal to) a given value U is equal to the hypervolume lying "inside" the diagonal hyperplane U. This hypervolume is (see problem 15.5-1)

$$\tilde{\Omega}(U) = (\text{number of states with energies less than } U)$$

$$= \frac{1}{(3\tilde{N})!}\left(\frac{U}{\hbar\omega_0}\right)^{3\tilde{N}} \tag{15.29}$$

The fact that this result is proportional to $U^{3\tilde{N}}$, where $3\tilde{N}$ is the dimensionality of the "state space," is the critical feature of this result. The precise form of the coefficient in equation 15.29 will prove to be of only secondary importance.

By subtraction we find the number of states with energies between $U-\Delta$ and U to be

$$\tilde{\Omega}(U) - \tilde{\Omega}(U-\Delta) = \frac{1}{(3\tilde{N})!}\left(\frac{U}{\hbar\omega_0}\right)^{3\tilde{N}} - \frac{1}{(3\tilde{N})!}\left(\frac{U-\Delta}{\hbar\omega_0}\right)^{3\tilde{N}}$$

or

$$\tilde{\Omega}(U) - \tilde{\Omega}(U-\Delta) = \tilde{\Omega}(U)\left[1-\left(1-\frac{\Delta}{U}\right)^{3\tilde{N}}\right] \tag{15.30}$$

But $(1-\Delta/U)$ is less than unity; raising this quantity to an exponent $3\tilde{N} \simeq 10^{23}$ results in a totally negligible quantity (see Problem 15.5-2), so that

$$\Omega(U) = \tilde{\Omega}(U) - \tilde{\Omega}(U-\Delta) \simeq \tilde{\Omega}(U) \tag{15.31}$$

That is, the number $\Omega(U)$ of states with energies between $U-\Delta$ and U is essentially equal to the total number $\tilde{\Omega}(U)$ of states with energies less than U—and this result is essentially independent of Δ!

Thus having corroborated the assertion for our particular model, let us reexamine the geometry to discern the more general geometrical roots of this strange, but enormously useful, result.

The physical volume in Fig. 15.5 can be looked at as one eighth of a regular octahedron (but only the portion of the octahedron in the physical octant of the space has physical meaning). With higher dimensionality the regular polyhedron would become more nearly "spherical." The dimensionless energy $U/\hbar\omega_0$ is analogous to the "radius" of the figure, being the distance from the origin to any of the corners of the polyhedron. This viewpoint makes evident the fact (equation 15.29) that the volume is proportional to the radius raised to a power equal to the dimensionality of the space (r^2 in two dimensions, r^3 in three, etc.). The volume between two concentric polyhedra, with a difference in radii of dr, is $dV = (\partial V/\partial r)\,dr$. The ratio of the volume of this "shell" to the total volume is

$$\frac{dV}{V} = \frac{\partial V}{\partial r}\frac{dr}{V} \tag{15.32}$$

or, if $V = A_n r^n$

$$\frac{dV}{V} = n\frac{dr}{r} \tag{15.33}$$

If we take $n = 10^{23}$ we find $dV/V \simeq 0.1$ only if $dr/r \simeq 10^{-24}$. For dr/r greater than $\sim 10^{-24}$ the equation fails, telling us that the use of differentials is no longer valid. The failure of the differential analysis is evidence that dV/V already becomes on the order of unity for values of dr/r as small as $dr/r \simeq 10^{-23}$.

In an imaginary world of high dimensionality there would be an automatic and perpetual potato famine, for the skin of a potato would occupy essentially its entire volume!

In the real world in which three-dimensional statistical mechanicians calculate entropies as volumes in many-dimensional state spaces, the properties of high dimensionality are a blessing. We need not calculate the number of states "in the vicinity of the system energy U"—it is quite as satisfactory, and frequently easier, to calculate the number of states with energies less than or equal to the energy of the physical system.

Returning to the Einstein solid, we can calculate the fundamental equation using the result 15.29 for $\tilde{\Omega}(U)$, the number of states with energies less than U; the entropy is $S = k_B \ln \tilde{\Omega}(U)$, and it is easily corroborated that this gives the same result as was obtained in equation 15.4.

The two methods that we have used to solve the Einstein model of a solid should be clearly distinguished. In Section 15.2 we assumed that $U/\hbar\omega_0$ was an integer, and we counted the number of ways of distributing quanta among the modes. This was a combinatorial problem, albeit a simple and tractable one because of the extreme simplicity of the model. The second method, in this section, involved no combinatorial calculation whatsoever. Instead we defined a volume in an abstract "state space" and the entropy was related to the total volume *inside* the bounding surface defined by the energy U. The combinatorial approach is not easily transferable to more complicated systems—the method of hypervolumes is general and is usually more tractable. However the last method is not applicable at very low temperature where only a few states are occupied, and where the occupied volume in state space shrinks toward zero.

PROBLEMS

15.5-1. To establish equation 15.29 let Ω_n be the hypervolume subtended by the diagonal hyperplane in n dimensions. Draw appropriate figures for $n = 1$, 2, and 3 and show that if L is the intercept on each of the coordinate axes

$$\Omega_1 = L$$

$$\Omega_2 = \Omega_1 \int_0^L \left(1 - \frac{x}{L}\right) dx = \frac{L^2}{2!}$$

$$\Omega_3 = \Omega_2 \int_0^L \left(1 - \frac{x}{L}\right)^2 dx = \frac{L^3}{3!}$$

and by mathematical induction

$$\Omega_n = \Omega_{n-1} \int_0^L \left(1 - \frac{x}{L}\right)^{n-1} dx = \frac{L^n}{n!}$$

15.5-2. Recalling that

$$\lim_{x \to 0} (1 + x)^{1/x} = e \qquad (\equiv 2.718\ldots)$$

show that

$$\left(1 - \frac{\Delta}{U}\right) \simeq e^{-\Delta/U} \quad \text{for } \frac{\Delta}{U} \ll 1$$

With this approximation discuss the accuracy of equation 15.31 for a range of reasonable values of Δ/U (ranging perhaps from 10^{-3} to 10^{-10}).

With what precision Δ/U would the energy have to be known in order that corrections to equation 15.31 might become significant? Assume a system with $\tilde{N} \simeq 10^{23}$.

15.5-3. Calculate the fraction of the hypervolume between the radii $0.9r$ and r for hyperspheres in 1, 2, 3, 4, and 5 dimensions. Similarly for 10, 30, and 50 dimensions.