

Each energy level is $(2\ell + 1)$ -fold degenerate. The energy unit ε is equal to $\frac{1}{2}\hbar^2/(\text{moment of inertia})$, or approximately 2×10^{-21} J for the HCl molecule. The characteristic separation between levels is of the order of ε , which corresponds to a temperature $\varepsilon/k_B \approx 15$ K for HCl—larger for lighter molecules and smaller for heavier molecules.

The rotational partition sum per molecule is

$$z_{\text{rot}} = \sum_{\ell=0}^{\infty} (2\ell + 1) e^{-\beta\ell(\ell+1)\varepsilon} \quad (16.29)$$

If $k_B T \gg \varepsilon$ the sum can be replaced by an integral. Then, noting that $2\ell + 1$ is the derivative of $\ell(\ell + 1)$, and writing x for the quantity $\ell(\ell + 1)$,

$$z_{\text{rot}} \approx \int_0^{\infty} e^{-\beta\varepsilon x} dx = \frac{1}{\beta\varepsilon} = \frac{k_B T}{\varepsilon} \quad (16.30)$$

If $k_B T$ is less than or of the order of ε it may be practical to calculate several terms of the series explicitly, to some ℓ' such that $\ell'(\ell' + 1) \gg k_B T$, and to integrate over the remaining range (from ℓ' to infinity); see Problem 16.3-2.

It is left to the reader to show that for $k_B T \gg \varepsilon$ the average energy is $k_B T$.

The case of homonuclear diatomic molecules, such as O_2 or H_2 , is subject to quantum mechanical symmetry conditions into which we shall not enter. Only the even terms in the partition sum, or only the odd terms, are permitted (depending upon detailed characteristics of the atoms). At high temperatures this restriction merely halves the rotational partition sum per molecule.

The nuclear and electronic contributions can be computed in similar fashion, but generally only the lowest energy levels of each contribute. Then z_{nuc} is simply the “degeneracy” (multiplicity) of the lowest energy configuration. Each of these factors simply contributes $\tilde{N}k_B T \ln(\text{multiplicity})$ to the Helmholtz potential.

It is of interest to return to the assumption that the various modes are independent. This assumption is generally a good (but *not* a rigorous) approximation. Thus the vibrations of a diatomic molecule change the instantaneous interatomic distance and thereby change the instantaneous moment of inertia of rotation. It is only because the vibrations generally are very fast relative to the rotations that the rotations sense only the *average* interatomic distance, and thereby become effectively independent of the vibrations.

PROBLEMS

16.3-1. Calculate the average rotational energy per molecule and the rotational heat capacity per molecule for heteronuclear diatomic molecules in the region $k_B T \gg \epsilon$.

16.3-2. Calculate the rotational contribution to the Helmholtz potential per molecule by evaluating the first two terms of equation 16.29 explicitly and by integrating over the remaining terms. For this purpose note that the leading terms in the Euler–McLaurin sum formula are

$$\sum_{j=0}^{\infty} f(j) \approx \int_0^{\infty} f(\theta) d\theta + \frac{1}{2}f(0) - \frac{1}{12}f'(0) + \dots$$

where f' denotes the derivative of $f(\theta)$.

16.3-3. A particular heteronuclear diatomic gas has one vibrational mode, of frequency ω , and its characteristic rotational energy parameter is ϵ (equation 16.28). Assume no intermolecular forces, so that the gas is ideal. Calculate its full fundamental equation in the temperature region in which $T \gg \epsilon/k_B$ but $T \approx \hbar\omega/k_B$.

16-4 PROBABILITIES IN FACTORIZABLE SYSTEMS

We may inquire as to the *physical* significance of the factor z associated with a single element in the partition sum of a factorizable macroscopic system. Following equation 16.17 we referred to z as the “partition sum per element.” And in equation 16.19 we saw that $-k_B T \ln z$ is the additive contribution of that element to the Helmholtz potential. It is easily shown (Problem 16.4-1) that the probability of occupation by the i th element of its j th orbital state, in a factorizable system, is

$$f_j^i = e^{-\beta\epsilon_{ij}}/z_i \quad (16.31)$$

In all these respects the statistical mechanics of the single element is closely analogous to that of a macroscopic system.

The polymer model of Section 15.4 is particularly instructive. Consider a polymer chain with a weight suspended as shown in Fig. 15.4. The magnitude of the weight is equal to the tension \mathcal{F} applied to the chain. The length of the chain is (equation 15.14)

$$L_x = (N_x^+ - N_x^-)a \quad (16.32)$$

and the total energy (of chain plus weight) in a given configuration is

$$E = (N_y^+ + N_y^-)\epsilon - \mathcal{F}L_x = (N_y^+ + N_y^-)\epsilon + (N_x^- - N_x^+)a\mathcal{F} \quad (16.33)$$

The term $-\mathcal{T}L_x$ is the potential energy of the suspended weight (the potential energy being the weight \mathcal{T} multiplied by the height, and the height being taken as zero when $L_x = 0$). According to equation 16.33 we can associate an energy $a\mathcal{T}$ with every monomer unit along $-x$, an energy $-a\mathcal{T}$ with every monomer unit along $+x$, and an energy ϵ with every monomer unit along either $+y$ or $-y$. The partition sum factors and the partition sum per monomer unit is

$$z = e^{-\beta a\mathcal{T}} + e^{+\beta a\mathcal{T}} + e^{-\beta\epsilon} + e^{-\beta\epsilon} \quad (16.34)$$

The Helmholtz potential is given by

$$-\beta F = \tilde{N} \ln z \quad (16.35)$$

Furthermore the probability that a monomer unit is along $-x$ is

$$p_{-x} = e^{-\beta a\mathcal{T}}/z \quad (16.36)$$

and the probability that it is along $+x$ is

$$p_{+x} = e^{+\beta a\mathcal{T}}/z \quad (16.37)$$

Consequently the mean length of the chain is

$$\langle L_x \rangle = \tilde{N}(p_{+x} - p_{-x})a \quad (16.38)$$

$$= 2\tilde{N}a \sinh(\beta a\mathcal{T})/z \quad (16.39)$$

It is left to the reader to calculate the mean energy U from the fundamental equations (16.34 and 16.35) and to show that both the energy and the length agree with the results of Section 15.4.

PROBLEMS

16.4-1. The probability that the i th element is in its j th orbital state is the sum of the probabilities of all microstates of the system in which the i th element is in its j th orbital state. Use this fact to show that for a "factorizable system" the probability of the i th element being in its j th orbital state is as given in equation 16.31.

16.4-2. Demonstrate the equivalence of the fundamental equations found in this section and in Section 15.4.

16-5 STATISTICAL MECHANICS OF SMALL SYSTEMS: ENSEMBLES

The preceding sections have demonstrated a far reaching similarity between the statistical mechanics of a macroscopic system and that of an individual “element” of a factorizable system. The partition sum per element has the same structure as the full partition sum, and it is subject to the same probability interpretation. The logarithm of the partition sum of an element is an additive contribution to the total Helmholtz potential. Does this imply that we can simply apply the statistical mechanics to each element? We can indeed, *when the elements satisfy the factorizability criteria* of Section 16.2.

A further conclusion can be drawn from the preceding observations. *We can apply the canonical formalism to small (nonmacroscopic) systems in diathermal contact with a thermal reservoir.*

Suppose that we are given such a small system. We can imagine it to be replicated many times over, with each replica put into diathermal contact with the reservoir and hence (indirectly) with all other replicas. The “ensemble” of replicas then constitutes a thermodynamic system to which statistical mechanics and thermodynamics apply. Nevertheless no property of the individual element is influenced by its replicas, from which it is “shielded” by the intermediate thermal reservoir. Application of statistical mechanics to the individual element is isomorphic to its application to the full ensemble.

Statistical mechanics is fully valid when applied to a single element in diathermal contact with a thermal reservoir. In contrast, thermodynamics, with its emphasis on extensivity of potentials, applies only to an ensemble of elements, or to macroscopic systems.

Example

An atom has energy levels of energies, $0, \epsilon_1, \epsilon_2, \epsilon_3, \dots$ with degeneracies of $1, 2, 2, 1, \dots$. The atom is in equilibrium with electromagnetic radiation which acts as a thermal reservoir at temperature T . The temperature is such that $e^{-\beta\epsilon_j}$ is negligible (with respect to unity) for all energies ϵ_j with $j \geq 4$. Calculate the mean energy and the mean square deviation of the energy from its average value.

Solution

The partition sum is

$$z = 1 + 2e^{-\beta\epsilon_1} + 2e^{-\beta\epsilon_2} + e^{-\beta\epsilon_3}$$

The mean energy is

$$\langle \epsilon \rangle = (2\epsilon_1 e^{-\beta\epsilon_1} + 2\epsilon_2 e^{-\beta\epsilon_2} + \epsilon_3 e^{-\beta\epsilon_3}) / z$$

and the mean squared energy is

$$\langle \epsilon^2 \rangle = (2\epsilon_1^2 e^{-\beta\epsilon_1} + 2\epsilon_2^2 e^{-\beta\epsilon_2} + \epsilon_3^2 e^{-\beta\epsilon_3}) / z$$

The mean square deviation is $\langle \epsilon^2 \rangle - \langle \epsilon \rangle^2$. For such a small system the mean square deviation may be very large. Only for macroscopic systems are the fluctuations negligible relative to average or observed values.

It should be noted that an energy level with a two-fold degeneracy implies *two states* that have the same energy. The partition sum is over states, not over "levels."

PROBLEMS

16.5-1. The energies of the orbital states of a given molecule are such that $\epsilon_0 = 0$, $\epsilon_1/k_B = 200$ K, $\epsilon_2/k_B = 300$ K, $\epsilon_3/k_B = 400$ K and all other orbital states have very high energy. Calculate the dispersion $\sigma \equiv \sqrt{\langle \epsilon^2 \rangle - \langle \epsilon \rangle^2}$ of the energy if the molecule is in equilibrium at $T = 300$ K. What is the probability of occupation of each orbital state?

16.5-2. A hydrogen atom in equilibrium with a radiation field at temperature T can be in its ground orbital level (the "1-s" level, which is two-fold spin degenerate), or it can be in its first excited energy level (eight-fold degenerate). Neglect the probability of higher energy states. What is the probability that the atom will be in an "orbital p -state"?

16.5-3. A small system has two normal modes of vibration, with natural frequencies ω_1 and $\omega_2 = 2\omega_1$. What is the probability that, at temperature T , the system has an energy less than $5\omega_1/2$? The zero of energy is taken as its value at $T = 0$.

$$(1+x)(1+x^2)(1+x+2x^2) \quad \text{where } x \equiv \exp(-\beta\hbar\omega_1) \quad \text{Answer:}$$

16.5-4. DNA, the genetic molecule deoxyribonucleic acid, exists as a twisted pair of polymer molecules, each with \tilde{N} monomer units. The two polymer molecules are cross-linked by \tilde{N} "base pairs." It requires energy ϵ to unlink each base pair, and a base pair can be unlinked only if it has a neighboring base pair that is already unlinked (or if it is at the end of the molecule). Find the probability that n pairs are unlinked at temperature T if

a) one end of the molecule is prevented from unlinking, so that the molecule "unwinds" from one end only.

b) the molecule can unwind from both ends.

Reference: C. Kittel, *Amer. J. Phys.* **37**, 917 (1969).

16.5-5. Calculate the probability that a harmonic oscillator of natural frequency ω_0 is in a state of odd quantum number ($n = 1, 3, 5, \dots$) at temperature T . To what values do you expect this probability to reduce in the limits of zero and infinite temperature? Show that your result conforms to these limiting values. Find the dominant behavior of the probability P_{odd} near $T = 0$ and in the high temperature region.

16.5-6. A small system has two energy levels, of energies 0 and ϵ , and of degeneracies g_0 and g_1 . Find the entropy of this system at temperature T . Calculate the energy and the heat capacity of the system at temperature T . What is the dominant behavior of the heat capacity at very low and at very high temperature? Sketch the heat capacity. How would this sketch be affected by an increase in the ratio g_1/g_0 ? Explain this effect qualitatively.

16.5-7. Two simple harmonic oscillators, each of natural frequency ω , are coupled in such a way that there is no interaction between them if the oscillators have different quantum numbers, whereas their combined energy is $(2n + 1)\hbar\omega + \Delta$ if the oscillators have the same quantum number n . The system is in thermal equilibrium at temperature T . Find the probability that the two oscillators have identical quantum numbers. Find and interpret the zero-temperature limit of your result, for all values of Δ .

16-6 DENSITY OF STATES AND DENSITY OF ORBITAL STATES

We return to large systems, and we shall shortly demonstrate several applications of the canonical formalism to crystals and to electromagnetic radiation. These applications, and a wide class of other applications, call on the concept of a "density of states function." Because this concept lies outside statistical mechanics proper, and because we shall find it so pervasively useful, it is convenient to discuss it briefly in advance.

In the canonical formalism we repeatedly are called upon to compute sums of the form

$$\text{"sum"} = \sum_j (\dots) e^{-\beta E_j} \quad (16.40)$$

The sum is over all states j of the system, and E_j is the energy of the j th state. If the quantity in the parenthesis is unity, the "sum" is the partition sum Z . If the parenthetical quantity is the energy then the "sum" divided by Z is the average energy U (equation 16.12). And similar situations hold for other dynamical variables.

For macroscopic systems the energies E_j are generally (but not always) closely spaced, in the sense that $\beta(E_{j+1} - E_j) \ll 1$. Under these circumstances the sum can be replaced by an integral

$$\text{"sum"} = \int_{E_{\min}}^{\infty} (\dots) e^{-\beta E} D(E) dE \quad (16.41)$$

where E_{\min} is the energy of the ground state of the system (the minimum possible energy) and $D(E)$ is the "density of states" function defined by

$$\text{number of states in interval } dE = D(E) dE \quad (16.42)$$

In many systems the energy eigenstates are combinations of orbital (single-element) states, the partition sum factors, and analogues of equations 16.41 and 16.42 can be applied to single elements. The quantity analogous to $D(E)$ is then a "density of orbital states"; we shall designate it also by $D(E)$.

Further, the orbital states are very commonly normal modes that are wavelike in character. This is true of the vibrational modes of a crystal and of the electromagnetic modes of a cavity containing electromagnetic radiation. From the viewpoint of quantum mechanics it is even the case for the translational modes of a gas, the waves being the quantum mechanical wave functions of the molecules. The density of orbital states function is then subject to certain general considerations, which we briefly review.

Consider a system in a cubic "box" of linear dimension L (the results are independent of this arbitrary but convenient choice of shape). A standing wave parallel to an edge must have a wavelength λ such that an integral number of half wavelengths "fit" in the length L . That is, the wave vector $k \equiv 2\pi/\lambda$ must be of the form $n\pi/L$. For a wave of general orientation, in three dimensions, we have similar restrictions on each of the three components of \mathbf{k}

$$\mathbf{k} = \left(\frac{\pi}{L}\right)(n_1, n_2, n_3) = \left(\frac{\pi}{V^{1/3}}\right)(n_1, n_2, n_3) \quad (16.43)$$

$$n_1, n_2, n_3 = \text{integers}$$

We consider only isotropic media, for which the frequency is a function only of the amplitude k of \mathbf{k}

$$\omega = \omega(k), \text{ or inversely, } k = k(\omega) \quad (16.44)$$

Then the number of orbital states with frequency less than ω is the number of sets of positive integers for which

$$(n_1^2 + n_2^2 + n_3^2)^{1/2} \leq V^{1/3} \frac{k(\omega)}{\pi} \quad (16.45)$$

We can think of $(n_1^2 + n_2^2 + n_3^2)^{1/2}$ as the radius in an abstract space in which n_1 , n_2 , and n_3 are integral distances along the three coordinate axes. The number of such integral lattice points with radii less than $V^{1/3}k(\omega)/\pi$ is the volume inside this radius. Only one octant of this spherical volume is physically acceptable, because n_1 , n_2 , and n_3 in equation 16.43 must be positive. Thus the number of orbital states with

frequency less than ω is

$$\text{number of orbital states with frequency } \leq \omega = \left(\frac{1}{8}\right)\left(\frac{4\pi}{3}\right)\left[V^{1/3}\frac{k(\omega)}{\pi}\right]^3 \quad (16.46)$$

Differentiating we find the number of orbital states $D'(\omega)d\omega$ in the interval $d\omega$

$$D'(\omega)d\omega = \frac{V}{6\pi^2} \frac{dk^3(\omega)}{d\omega} d\omega = \frac{V}{2\pi^2} k^2(\omega) \frac{dk(\omega)}{d\omega} d\omega \quad (16.47)$$

The quantity $D'(\omega)d\omega$ then is analogous to $D(E)dE$ in the “sum” (equation 16.41); see Problem 16.6-1.

This is the general result we require. Because various models of interest correspond to various functional relations $\omega(k)$, we shall be able to convert sums to integrals simply by evaluating the “density of orbital states” function $D'(\omega)$ by equation 16.41. So prepared, we proceed to several applications of the canonical formalism.

PROBLEMS

16.6-1. Show that the number of orbital states in the energy interval $d\varepsilon = \hbar d\omega$ is $D(\varepsilon) = D'(\omega)/\hbar$, where $D'(\omega)d\omega$ is the number of orbital states in the frequency interval $d\omega$.

16.6-2. For the particles of a gas $\varepsilon = p^2/2m = (\hbar^2/2m)k^2$, or $\omega = \varepsilon/\hbar = \hbar k^2/2m$. Find the density of orbital states function $D'(\omega)$.

$$\text{Answer: } D'(\omega) = \frac{V}{2\pi^2} k^2 \left/ \left(\frac{\hbar k}{m} \right) \right. = \frac{m^{3/2} V}{2^{1/2} \pi^2 \hbar^{3/2}} \omega^{1/2}$$

16.6-3. For excitations obeying the spectral relation $\omega = Ak^n$, $n > 0$, find the density of orbital states function $D'(\omega)$.

16-7 THE DEBYE MODEL OF NONMETALLIC CRYSTALS

At the conclusion of Section 16.2 we reviewed the Einstein model of a crystalline solid, and we observed that the canonical formalism makes more sophisticated models practical. The “Debye model” is moderately more sophisticated and enormously more successful.

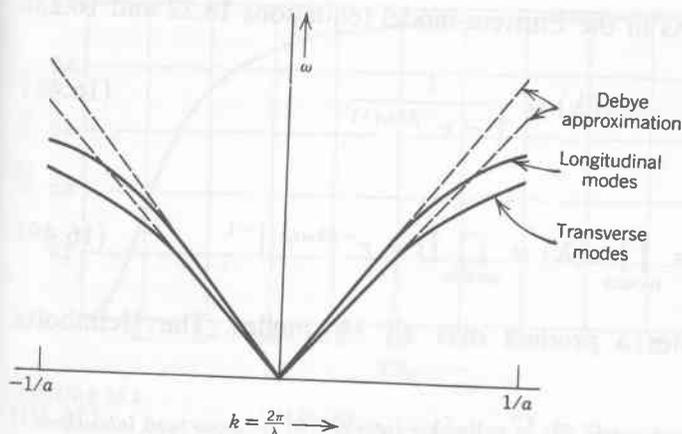


FIGURE 16.1

Dispersion relation for vibrational modes, schematic. The shortest wave length is of the order of the interatomic distance. There are \tilde{N} longitudinal modes and $2\tilde{N}$ transverse modes. The Debye approximation replaces the physical dispersion relation with the linear extrapolation of the long wave length region, or $\omega = v_L k$ and $\omega = v_t k$ for longitudinal and transverse modes respectively.

Again consider \tilde{N} atoms on a lattice, each atom being bound to its neighbors by harmonic forces ("springs"). The vibrational modes consist of \tilde{N} longitudinal and $2\tilde{N}$ transverse normal modes, each of which has a sinusoidal or "wavelike" structure. The shortest wave lengths are of the order of twice the interatomic distance. The very long wave length longitudinal modes are not sensitive to the crystal structure and they are identical to sound waves in a continuous medium. The dispersion curves of ω versus k ($= 2\pi/\lambda$) are accordingly linear in the long wave length limit, as shown in Fig. 16.1. For shorter wave lengths the dispersion curves "flatten out," with a specific structure that reflects the details of the crystal structure. P. Debye¹, following the lead of Einstein, bypassed the mechanical complications and attempted only to capture the general features in a simple, tractable approximation. The Debye model assumes that the modes all lie on linear "dispersion curves" (Fig. 16.1), as they would in a continuous medium. The slope of the longitudinal dispersion curve is v_L , the velocity of sound in the medium. The slope of the transverse dispersion curve is v_t .

The thermodynamic implications of the model are obtained by calculating the partition sum. The energy is additive over the modes, so that the partition sum factorizes. For each mode the possible energies are $n\hbar\omega(\lambda)$ with $n = 1, 2, 3, \dots$, where $\omega(\lambda) = 2\pi\nu(\lambda)$ is given by the dotted linear

¹P. Debye, *Ann. Phys.* 39, 789 (1912).

curves in Fig. 16.1. As in the Einstein model (equations 16.22 and 16.23)

$$z(\lambda) = \frac{1}{1 - e^{-\beta\hbar\omega(\lambda)}} \quad (16.48)$$

and

$$Z = \prod_{\text{modes}} z(\lambda) = \prod_{\text{modes}} [1 - e^{-\beta\hbar\omega(\lambda)}]^{-1} \quad (16.49)$$

where \prod_{modes} denotes a product over all $3\tilde{N}$ modes. The Helmholtz potential is

$$F = k_B T \sum_{\text{modes}} \ln(1 - e^{-\beta\hbar\omega(\lambda)}) \quad (16.50)$$

It is left to the reader to show that the molar heat capacity is

$$c_v = \beta^2 \hbar^2 k_B \sum_{\text{modes}} \frac{\omega^2 e^{\beta\hbar\omega}}{(e^{\beta\hbar\omega} - 1)^2} \quad (16.51)$$

The summation over the modes is best carried out by replacing the sum by an integral

$$c_v = \frac{\hbar^2}{k_B T^2} \int_0^{\omega_{\max}} \frac{\omega^2 e^{\beta\hbar\omega}}{(e^{\beta\hbar\omega} - 1)^2} D'(\omega) d\omega \quad (16.52)$$

where $D'(\omega) d\omega$ is the number of modes in the interval $d\omega$. To evaluate $D'(\omega)$ we turn to equation 16.47. For the longitudinal modes the functional relation $k(\omega)$ is (Fig. 16.1)

$$k = \omega/v_L \quad (16.53)$$

and similarly for the two polarizations of transverse modes. It follows, from equation 16.47, that

$$D'(\omega) = \frac{v}{2\pi^2} \left(\frac{1}{v_L^3} + \frac{2}{v_t^3} \right) \omega^2 \quad (16.54)$$

The maximum frequency² ω_{\max} is determined by the condition that the

²In the literature ω_{\max} is often specified in terms of the "Debye temperature," defined by $\hbar\omega_{\max}/k_B$ and conventionally designated by θ_D .

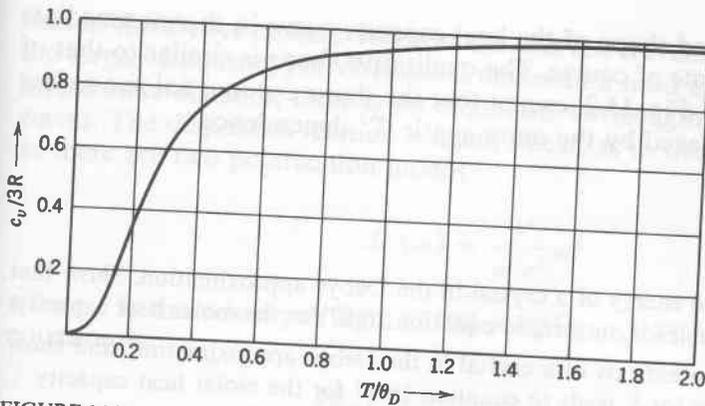


FIGURE 16.2

Vibrational heat capacity of a crystal according to the Debye approximation.

total number of modes be $3N_A$

$$\int_0^{\omega_{\max}} D'(\omega) d\omega = 3N_A \quad (16.55)$$

from which it follows that

$$\omega_{\max}^3 = \frac{18N_A\pi^2}{v} \left(\frac{1}{v_L^3} + \frac{2}{v_T^3} \right)^{-1} \quad (16.56)$$

Inserting $D'(\omega)$ in the integral 16.52 and changing the integration variable from ω to $u (= \beta\hbar\omega)$

$$c_v = \frac{9N_A k_B}{u_m^3} \int_0^{u_m} \frac{u^4 e^u}{(e^u - 1)^2} du \quad (16.57)$$

The molar heat capacity, computed from this equation, is shown schematically in Fig. 16.2.

At high temperature ($k_B T \gg \hbar\omega_{\max}$) the behavior of c_v is best explored by examining equation 16.51. In this limit $u^2 e^u / (e^u - 1)^2 \rightarrow 1$. Hence each mode contributes k_B to the molar heat capacity (a result of much more general validity, as we shall see subsequently). The molar heat capacity in the high temperature limit is $3N_A k_B$, or $3R$.

At low temperature, where $\beta\hbar\omega_m \equiv u_m \gg 1$, the upper limit in the integral in equation 16.57 can be replaced by infinity; the integral is then simply a constant, and the temperature dependence of c_v arises from the u_m^3 in the denominator. Hence $c_v \sim T^3$ in the low temperature region, a result in excellent agreement with observed heat capacities of nonmetallic

crystals. The detailed shape of the heat capacity curve in the intermediate region is less accurate of course. The qualitative shape is similar to that of the Einstein model, Fig. 15.2, except that the sharp exponential rise at low temperature is replaced by the more gentle T^3 dependence.

PROBLEMS

16.7-1. Calculate the energy of a crystal in the Debye approximation. Show that the expression for U leads, in turn, to equation 16.57 for the molar heat capacity.

16.7-2. Calculate the entropy of a crystal in the Debye approximation, and show that your expression for S leads to equation 16.57 for the molar heat capacity.

16.7-3. The frequency $\omega(\lambda)$ of the vibrational mode of wave length λ is altered if the crystal is mechanically compressed. To describe this effect Gruneisen introduced the "Gruneisen parameter"

$$\gamma \equiv - \frac{V}{\omega(\lambda)} \frac{d\omega(\lambda)}{dV}$$

Taking γ as a constant (independent of λ, V, T, \dots) calculate the mechanical equation of state $P(T, V, N)$ for a Debye–Gruneisen crystal.

Show that for a Debye–Gruneisen crystal

$$v\alpha = \gamma\kappa_T c_v$$

16-8 ELECTROMAGNETIC RADIATION

The derivation of the fundamental equation (3.57) of electromagnetic radiation is also remarkably simple in the canonical formalism. Assume the radiation to be contained within a closed vessel, which we may think of as a cubical cavity with perfectly conducting walls. Then the energy resides in the resonant electromagnetic modes of the cavity. As in the Einstein and Debye models, the possible energies of a mode of frequency ω are $n\hbar\omega$, with $n = 0, 1, 2, \dots$. Equations 16.48 and 16.49 are again valid, and

$$F = k_B T \sum_{\text{modes}} \ln(1 - e^{-\beta\hbar\omega(\lambda)}) \quad (16.58)$$

The sum can be calculated by replacing the sum by an integral (the modes are densely distributed in energy)

$$F = k_B T \int_0^\infty \ln(1 - e^{-\beta\hbar\omega}) D'(\omega) d\omega \quad (16.59)$$

The sole new feature here is that there is no maximum frequency (such as

that in the Debye model). Whereas the shortest wavelength (and therefore the largest frequency) of vibrational modes in a solid is determined by the interatomic distance, there is no minimum wavelength of electromagnetic waves. The dispersion relation is again linear, as in the Debye model, and as there are two polarization modes

$$D'(\omega) = \frac{V}{\pi^2 c^3} \omega^2 \quad (16.60)$$

where c is the velocity of light (2.998×10^8 m/s). Then the fundamental equation is

$$F = \frac{Vk_B T}{\pi^2 c^3} \int_0^\infty \omega^2 \ln(1 - e^{-\beta \hbar \omega}) d\omega \quad (16.61)$$

To calculate the energy we use the convenient identity (recall equation 16.13)

$$U = F + TS = F - T \frac{\partial F}{\partial T} = \frac{\partial(\beta F)}{\partial \beta} \quad (16.62)$$

from which

$$U = \frac{V\hbar}{\pi^2 c^3} \int_0^\infty \frac{e^{-\beta \hbar \omega}}{1 - e^{-\beta \hbar \omega}} \omega^3 d\omega \quad (16.63)$$

The integral $\int_0^\infty x^3 (e^x - 1)^{-1} dx$ is $3!\zeta(4) = \pi^4/15$, where ζ is the Riemann zeta function³, whence

$$U = \frac{\pi^2 k_B^4}{15 \hbar^3 c^3} VT^4 \quad (16.64)$$

This is the "Stefan-Boltzmann Law," as introduced in equation 3.52. By a simple statistical mechanical calculation we have evaluated the constant b of equation 3.52 in terms of fundamental constants.

PROBLEMS

16.8-1. Show that including the "zero-point energies" of the electromagnetic modes (i.e., $E_n = (n + 1/2)\hbar\omega$) leads to an infinite energy density U/V ! This infinite energy density is presumably constant and unchangeable and hence physically unobservable.

³cf. M. Abramowitz and I. A. Stegun, *Handbook of Mathematical Functions*, National Bureau of Standards Applied Mathematics Series, No. 55, 1964. [See equation 23.2.7.]

16.8-2. Show that the energy per unit volume of electromagnetic radiation in the frequency range $d\omega$ is given by the “Planck Radiation Law”

$$\frac{U_\omega}{V} d\omega = \frac{\hbar\omega^3}{\pi^2 c^3} (e^{\beta\hbar\omega} - 1)^{-1} d\omega$$

and that at high temperature ($k_B T \gg \hbar\omega$) this reduces to the “Rayleigh–Jeans Law”

$$\frac{U_\omega}{V} d\omega \approx \frac{\omega^2}{\pi^2 c^3} k_B T d\omega$$

16.8-3. Evaluating the number of photons per unit volume in the frequency range $d\omega$, as

$$(N_\omega/V) d\omega = (U_\omega/V) d\omega / \hbar\omega$$

where U_ω is given in problem 16.8-2, calculate the total number of photons per unit volume. Show that the average energy per photon (U/N) is approximately $2.2k_B T$. Note that the integral encountered can be written in terms of the Riemann zeta function, as in the preceding footnote.

16.8-4. Since radiation within a cavity propagates isotropically with velocity c , the flux of energy impinging on unit area of the wall (or passing in one direction through an imaginary unit surface within the cavity) is given by the “Stefan–Boltzmann Law”:

$$\text{Energy flux per unit area} = \frac{1}{4} c(U/V) = \frac{1}{4} cbT^4 \equiv \sigma_B T^4$$

The factor of $c/4$ arises as $\frac{1}{2}(c/2)$; the factor of $\frac{1}{2}$ selecting only the radiation crossing the imaginary area from “right” to “left” (or vice versa), and the factor of $c/2$ representing the average component of the velocity normal to the area element. The constant $\sigma_B (= cb/4)$ is known as the “Stefan–Boltzmann constant.” As an exercise in elementary kinetic theory, derive the Stefan–Boltzmann law (explicitly demonstrating the averages described).

16-9 THE CLASSICAL DENSITY OF STATES

The basic algorithm for the calculation of a fundamental equation in the canonical formalism requires only that we know the energy of each of the discrete states of the system. Or, if the energy eigenvalues are reasonably densely distributed, it is sufficient to know the density of orbital states. In either case discreteness (and therefore countability) of the states is assumed. This fact raises two questions. First, how can we apply statistical mechanics to classical systems? Second, how did Willard Gibbs invent statistical mechanics in the nineteenth century, long before the birth of quantum mechanics and the concept of discrete states?

As a clue we return to the central equation of the formalism—the equation for the partition sum, which, for a wavelike mode, is (equation 16.47)

$$z = e^{-\beta\bar{F}} = \int e^{-\beta\epsilon} D'(\omega) d\omega = \int e^{-\beta\epsilon} \frac{V}{2\pi^2} k^2(\omega) dk(\omega) \quad (16.65)$$

We seek to write this equation in a form compatible with classical mechanics, for which purpose we identify $\hbar\mathbf{k}$ with the (generalized) momentum

$$\hbar\mathbf{k} = \mathbf{p} \quad (16.66)$$

whence

$$z = \frac{1}{2\pi^2\hbar^3} \int e^{-\beta\epsilon} V p^2 dp \quad (16.67)$$

To treat the coordinates and momenta on an equal footing the volume can be written as an integral over the spatial coordinates. Furthermore, the role of the energy E in classical mechanics is played by the Hamiltonian function $\mathcal{H}(x, y, z, p_x, p_y, p_z)$. And finally we shift from $4\pi p^2 dp$ to $dp_x dp_y dp_z$ as the “volume element in the momentum subspace,” whence the partition function becomes

$$z = \frac{1}{h^3} \int e^{-\beta\mathcal{H}} dx dy dz dp_x dp_y dp_z \quad (16.68)$$

Except for the appearance of the classically inexplicable prefactor ($1/h^3$), this representation of the partition sum (per mode) is fully classical. It was in this form that statistical mechanics was devised by Josiah Willard Gibbs in a series of papers in the *Journal of the Connecticut Academy* between 1875 and 1878. Gibbs’ postulate of equation 16.68 (with the introduction of the quantity h , for which there was no a priori classical justification) must stand as one of the most inspired insights in the history of physics. To Gibbs, the numerical value of h was simply to be determined by comparison with empirical thermophysical data.

The expression 16.68 is written as if for a single particle, with three position coordinates and three momentum coordinates. This is purely symbolic. The x , y , and z can be any “generalized coordinates” (q_1, q_2, \dots), and the momenta p_x , p_y , and p_z are then the “conjugate momenta.” The number of coordinates and momenta is dictated by the structure of the system, and more generally we can write

$$Z = \int e^{-\beta\mathcal{H}} \prod_j \left(\frac{dq_j}{h^{1/2}} \frac{dp_j}{h^{1/2}} \right) \quad (16.69)$$

This is the basic equation of the statistical mechanics of classical systems.

Finally we take note of a simple heuristic interpretation of the “classical density of orbital states” function. *In the classical phase space* (coordinate–momentum space) *each hypercube of “linear dimension”* $h^{\frac{1}{2}}$ *corresponds to one quantum mechanical state.* It is as if the orbital states are “squeezed as closely together” in phase space as is permitted by the Heisenberg uncertainty principle $\Delta q_j \Delta p_j \geq h$.

Whatever the interpretation, and quite independently of the plausibility arguments of this section, classical statistical mechanics is defined by equation 6.68 or 6.69.

16-10 THE CLASSICAL IDEAL GAS

The monatomic classical ideal gas provides a direct and simple application of the classical density of states and of the classical algorithm (16.69) for the calculation of the partition function.

The model of the gas is a collection of \tilde{N} ($= NN_A$) point mass “atoms” in a container of volume V , maintained at a temperature T by diathermal contact with a thermal reservoir. The energy of the gas is the sum of the energies of the individual atoms. Interactions between molecules are disbarred (unless such interactions make no contribution to the energy—as, for instance, the instantaneous collisions of hard mass points).

The energy is the sum of one-particle “kinetic energies,” and the partition sum factors. We undertake to calculate z_{transl} , the one-particle translational partition sum, and from the classical formulation (16.69) we find directly that

$$\begin{aligned} z_{\text{transl}} &= \frac{1}{h^3} \iiint dx dy dz \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} dp_x dp_y dp_z e^{-\beta(p_x^2 + p_y^2 + p_z^2)/2m} \\ &= \frac{V}{h^3} [2\pi m k_B T]^{3/2} \end{aligned} \quad (16.70)$$

It is of interest to note that we could have obtained this result by treating the particle *quantum mechanically*, by summing over its discrete states, and by approximating the summation by an integral. This exercise is left to the reader (Problem 16.10-4).

Having now calculated z we might expect to evaluate Z as $z^{\tilde{N}}$, and thereby to calculate the Helmholtz potential F . If we do so we find a Helmholtz potential that is not extensive! We could have anticipated this impending catastrophe, for the one-particle partition function z is extensive (equation 16.70) whereas we expect it to be intensive ($F = -\tilde{N}k_B T \ln z$). The problem lies not in an error of calculation, but in a fundamental principle. *To identify Z as $z^{\tilde{N}}$ is to assume the particles to be*

distinguishable, as if each bears an identifying label or number (like a set of billiard balls). Quantum mechanics, unlike classical mechanics, gives a profound meaning to the concept of indistinguishability. Indistinguishability does *not* imply merely that the particles are “identical”—it requires that the identical particles behave under interchange in ways that have no classical analogue. Identical particles must obey either Fermi–Dirac or Bose–Einstein “permutational parity”; concepts with statistical mechanical consequences which we shall study in greater detail in Chapter 17. Now, however, we seek only a classical solution. We do so by recognizing that $z^{\tilde{N}}$ is the partition sum of a set of *distinguishable* particles. We therefore attempt to correct this partition sum by division by $\tilde{N}!$. The rationale is that all $\tilde{N}!$ permutations of the “labels” among the \tilde{N} distinguishable particles should be counted as a single state for indistinguishable particles. Thus we finally arrive at the partition sum for a classical monatomic ideal gas

$$Z = (1/\tilde{N}!) z_{\text{transl}}^{\tilde{N}} \quad (16.71)$$

with z_{transl} as calculated in equation 16.70.

The Helmholtz potential is

$$F = -k_B T \ln Z = -\tilde{N} k_B T \ln \left[\frac{V}{\tilde{N}} \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} \right] - \tilde{N} k_B T \quad (16.72)$$

where we have utilized the Stirling approximation ($\ln \tilde{N}! \approx \tilde{N} \ln \tilde{N} - \tilde{N}$) which holds for large \tilde{N} .

To compare this equation with the fundamental equation introduced in Chapter 3 we make a Legendre transform to entropy representation, finding

$$S = \tilde{N} k_B \left[\frac{5}{2} - \frac{3}{2} \ln(3\pi\hbar^2/m) \right] + \tilde{N} k_B \ln(U^{3/2} V / \tilde{N}^{5/2}) \quad (16.73)$$

This is precisely the form of the monatomic ideal gas equation with which we have become familiar. The constant s_0 , undetermined in the thermodynamic context, has now been evaluated in terms of fundamental constants.

Reflection on the problem of counting states reveals that division by $\tilde{N}!$ is a rather crude classical attempt to account for indistinguishability. The error can be appreciated by considering a model system of two identical particles, each of which can exist in either of two orbital states (Fig. 16.3). Classically we find four states for the distinguishable particles, and we then divide by $2!$ to “correct” for indistinguishability. If the particles are fermions only one particle is permitted in a single one-particle state, so that there is only *one* permissible state of the system. For bosons, in

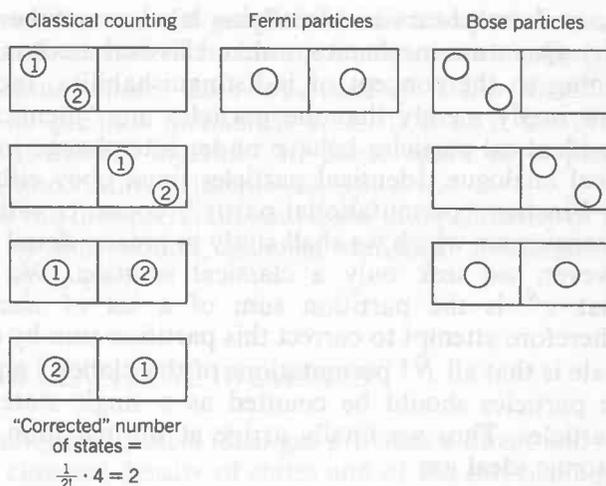


FIGURE 16.3 States of a two-particle system according to classical, Fermi and Bose counting.

contrast, any number of particles are permitted in a one-particle state; consequently there are *three* permissible states of the system (Fig. 16.3). "Corrected classical counting" is incorrect for either type of real particle!

At sufficiently high temperature the particles of a gas are distributed over many orbital states, from very low to very high energies. The probability of two particles being in the same orbital state becomes very small at high temperature. The error of classical counting then becomes insignificant, as that error is associated with the occurrence of more than one particle in a one-particle state. *All gases approach ideal gas behavior at sufficiently high temperature.*

Consider now a mixture of two monatomic ideal gases. The partition sum is factorizable and, as in equation 16.71

$$Z = Z_1 Z_2 = \frac{1}{\tilde{N}_1!} z_1^{\tilde{N}_1} \frac{1}{\tilde{N}_2!} z_2^{\tilde{N}_2} \quad (16.74)$$

The Helmholtz potential is the sum of the Helmholtz potentials for the two gases. The volume appearing in the Helmholtz potential of *each* gas is the common volume occupied by *both*. The temperature is, of course, the common temperature. The fundamental equation so obtained is equivalent to that introduced in Section 3.4 (equation 3.40), but again we have evaluated the constants that were arbitrary in the thermodynamic context.

PROBLEMS

16.10-1. Show that the calculation of $Z = z^{\tilde{N}}$, with z given by equation 16.70, is correct for an ensemble of individual atoms each in a (different) volume V . Show

that the fundamental equation obtained from $Z = z^{\tilde{N}}$ is properly extensive when so interpreted.

16.10-2. Show that the fundamental equation of a “multicomponent simple ideal gas,” which follows from equation 16.74, is identical to that of equation 3.40.

16.10-3. The factors $(1/\tilde{N}_1!)(1/\tilde{N}_2!)$ in equation 16.74 give an additive contribution to the Helmholtz potential that does not depend in any way on the forms of z_1 and z_2 . Show that these factors lead to a “mixing” term in the entropy (*not* in the Helmholtz potential!) of the form

$$\tilde{s}_{\text{mixing}} = (-x_1 \ln x_1 - x_2 \ln x_2)k_B$$

This mixing term appears in fluids as well as in ideal gases. It accounts for the fact that the mixing of two fluids is an irreversible process (recall Example 2 of Section 4.5).

16.10-4. Consider a particle of mass m in a cubic container of volume V . Show that the separation of successive energy levels is given approximately by $\Delta E \approx \pi^2 \hbar^2 / 2mV^{2/3}$, and roughly evaluate ΔE for helium atoms in a container of volume one m^3 . Show that, for any temperature higher than $\approx 10^{-8}$ K, the quantum mechanical partition sum can be approximated well by an integral. Show that this “approximation” leads to equation 16.70.

16.10-5. A single particle is contained in a vessel of volume $2V$ which is divided into two equal sub-volumes by a partition with a small hole in it. The particle carries an electric charge, and the hole in the partition is the site of a localized electric field; the net effect is that the particle has a potential energy of zero on one side of the partition, and of ϵ_e on the other side. What is the probability that the particle will be found in the zero-potential half of the vessel, if the system is maintained in equilibrium at temperature T ? How would this result be affected by internal modes of the particles? How would the result be affected if the dispersion relation of the particles were such that the energy was proportional to the momentum, rather than to its square? If the container were to contain one mole of an ideal gas (non-interacting particles despite the electric charge on each!) what would be the pressure in each sub-volume?

16-11 HIGH TEMPERATURE PROPERTIES— THE EQUIPARTITION THEOREM

The evaluation of z_{transl} in equation 16.70, in which z_{transl} was found to be proportional to $T^{3/2}$, is but a special case of a general theorem of wide applicability. Consider some normal mode of a system—the mode may be translational, vibrational, rotational, or perhaps of some other more abstract nature. Let a generalized coordinate associated with the mode be q and let the associated (or “conjugate”) momentum be p . Suppose the

energy (Hamiltonian) to be of the form

$$E = Aq^2 + Bp^2 \quad (16.75)$$

Then the classical prescription for calculating the partition function will contain a factor of the form

$$z \sim \iint \frac{dq dp}{h} e^{-\beta(Aq^2 + Bp^2)} \quad (16.76)$$

or, as in equation 16.70, if $A \neq 0$ and $B \neq 0$

$$z \sim \left(\frac{\pi k_B T}{hA} \right)^{1/2} \left(\frac{\pi k_B T}{hB} \right)^{1/2} \quad (16.77)$$

If either A or B is equal to zero the corresponding integral is a (bounded) constant determined by the limits on the associated integral. The integration over x in equation 16.70 is an example of such a case, and the corresponding integral is $V^{1/3}$.

The significant result in 16.77 is that, *at sufficiently high temperature* (so that the classical density of states is applicable) *every quadratic term in the energy contributes a factor of $T^{1/2}$ to the partition function.*

Equivalently, at sufficiently high temperature every quadratic term in the energy contributes a term $(\frac{1}{2}\tilde{N} \ln T)$ to $-\beta F$ or a term $(-\frac{1}{2}\tilde{N}k_B T \ln T)$ to the Helmholtz potential F , or a term $\frac{1}{2}\tilde{N}k_B T(1 + \ln T)$ to the entropy.

Or finally, the result in its most immediately significant form is: *At sufficiently high temperature every quadratic term in the energy contributes a term $\frac{1}{2}\tilde{N}k_B$ to the heat capacity.* This is the "equipartition theorem" of classical statistical mechanics.

A gas of point mass particles has three quadratic terms in the energy: $(p_x^2 + p_y^2 + p_z^2)/2m$. The heat capacity at constant volume of such a gas, at high temperature, is $\frac{3}{2}\tilde{N}k_B$, or $\frac{3}{2}R$ per mole.

Application of the equipartition theorem to a gas of polyatomic molecules is best illustrated by several examples. Consider first a heteronuclear diatomic molecule. It has three translational modes; each such mode has a quadratic kinetic energy but no potential energy; these three modes contribute $\frac{3}{2}k_B$ to the high temperature molar heat capacity. In addition the molecule has one vibrational mode; this mode has both kinetic and potential energy (both quadratic) and the mode therefore contributes $\frac{2}{2}k_B$. Finally the molecule has two rotational modes (i.e., it requires two angles to specify its orientation). These rotational modes have quadratic kinetic energy but no potential energy terms; they contribute $\frac{2}{2}k_B$. Thus the heat capacity per molecule is $\frac{7}{2}k_B$ at high temperature (or $\frac{7}{2}R$ per mole).

In general the total number of modes must be three times the number of atoms in the molecule. This is true because the mode amplitudes are a substitute set of coordinates that can replace the set of cartesian coordinates of each atom in the molecule. The number of the latter clearly is triple the number of atoms.

Consider a heteronuclear triatomic molecule. There are nine modes. Of these, three are translational modes; each contributes $\frac{1}{2}k_B$ to the heat capacity. There are three rotational modes, corresponding to the three angles required to orient a general object in space. Each rotational mode has only a kinetic energy term, and each contributes $\frac{1}{2}k_B$ to the heat capacity. By subtraction there remain three vibrational modes, each with kinetic and potential energy, and each contributing $\frac{2}{2}k_B$. Thus the high temperature heat capacity is $6k_B$ per molecule.

If the triatomic molecule is linear there is one less rotational mode and therefore one additional vibrational mode. The high temperature heat capacity is increased to $\frac{13}{2}k_B$. Note that the *shape* of the molecule can be discerned by measurement of the heat capacity of the gas!

In all of the preceding discussion we have neglected contributions that may arise from the internal structure of the atoms. These contributions generally have much higher energy and they contribute only at enormously high temperature.

If the molecules are *homonuclear* (indistinguishable atoms), rather than heteronuclear, additional quantum mechanical symmetry requirements again complicate the counting of states. Nevertheless, the analogous form of the equipartition theorem emerges at high temperature. The classical partition function simply contains a factor of $(\frac{1}{2})^N$ to account for the indistinguishability of the two atoms within each of the \tilde{N} molecules, and it contains a factor of $1/\tilde{N}!$ to account for the indistinguishability of the \tilde{N} molecules.