

Chapter 4

The Canonical Ensemble

4.1 QUANTUM ENSEMBLES

A statistical ensemble for a dynamical system is a collection of system points in the system phase space. Each system point represents a full system in a particular dynamical state. Therefore, a statistical ensemble may be pictured as a vast collection of exact replicas of a particular system. If the system under study is a bottle of beer, then the ensemble can be thought of as a huge warehouse filled with individual, noninteracting, bottles of beer. It cannot be pictured as a very large barrel of beer, which would be a single, different system. Each system in the ensemble has exactly the same Hamiltonian function, but, in general, different systems in the ensemble are in different dynamical states. Since the systems all have the same Hamiltonian function, it makes sense to represent the dynamical states of all the systems by points in a single phase space. Thus, the state of the complete ensemble is represented by a “dust cloud” in the phase space, containing a vast number of discrete points. The danger inherent in using this picture of an ensemble is that it is very easy to confuse it with the similar picture of a gas containing a vast number of point particles. This is unfortunate because the two things behave in quite different ways. The motion of a single gas particle is affected by the positions and velocities of its neighbors, because the gas particles interact. In contrast, each point in the ensemble representation is a system point for an isolated system that moves through the phase space according to Hamilton’s equations with no regard for the states of the other isolated systems in the ensemble. For the uniform ensemble the dust cloud is of uniform density inside the energy surface and of zero density outside it. For the microcanonical ensemble the system points of the ensemble are confined to the energy surface itself.

A quantum system is defined by a Hermitian Hamiltonian operator rather than a Hamiltonian function. The possible energy states of the system are the solutions of Schrödinger’s equation

$$H\psi_n(\mathbf{r}_1, \dots, \mathbf{r}_N) = E_n\psi_n(\mathbf{r}_1, \dots, \mathbf{r}_N) \quad (4.1)$$

A statistical ensemble for a quantum system will be pictured as a vast collection of replicas of the system. Each will have the same Hamiltonian operator, but, in general, different members of the ensemble will be in different quantum states. The quantum states are assumed to be energy eigenstates with energies within some particular energy interval. This is not the only reasonable way to choose the set of allowed microstates. A more general way is to allow any microstate that is a normalized linear combination of the energy eigenstates within the above-mentioned energy interval. That would include states that were not themselves exact energy eigenstates. In the problems, the reader will be asked to show that this more general procedure actually leads to exactly the same results as the assumption made here.

4.2 THE UNIFORM QUANTUM ENSEMBLE

For the uniform quantum ensemble the probability of finding a system, chosen at random from the ensemble, in eigenstate ψ_n is assumed to be

$$P_n = \theta(E - E_n)/\Omega(E) \quad (4.2)$$

This means that all states of energy less than E are equally likely but all states of energy greater than E have zero probability. The normalization constant Ω is equal to the number of quantum states of energy less than E .

$$\Omega(E) = \sum_{n=1}^{\infty} \theta(E - E_n) = \left\{ \begin{array}{l} \text{number of} \\ \text{eigenstates} \\ \text{with } E_n < E \end{array} \right\} \quad (4.3)$$

For a system of N particles in a volume V , Ω is a function of N and V also. In the Mathematical Appendix it is shown that, as $\hbar \rightarrow 0$

$$\Omega(N, E, V) \rightarrow \frac{1}{h^K N!} \int \theta(E - H(x, p)) d^K x d^K p \quad (4.4)$$

where $H(x, p)$ is the classical Hamiltonian function corresponding to the operator H . This identifies the thermodynamic entropy function as, essentially, the logarithm of the number of quantum states of the system with energy less than E .

$$S(N, E, V) = k \log \Omega(N, E, V) \quad (4.5)$$

It has been mentioned before that the value of the constant k depends on our unit of temperature. In relating thermodynamics to statistical mechanics, it is often convenient to use what will be called a rational system of units, in which the entropy is exactly equal to $\log \Omega$. The temperature is then measured in joules (that is, $\tau = kT$ is called the temperature). The entropy in rational units will be written as S° . The relationship between S° and S is very simple.

$$S^\circ = \log \Omega \quad (4.6)$$

and therefore,

$$S^\circ = S/k \quad (4.7)$$

In rational units,

$$\frac{\partial S^\circ}{\partial E} = \frac{1}{\tau} \quad \text{and} \quad \frac{\partial S^\circ}{\partial V} = \frac{p}{\tau} \quad (4.8)$$

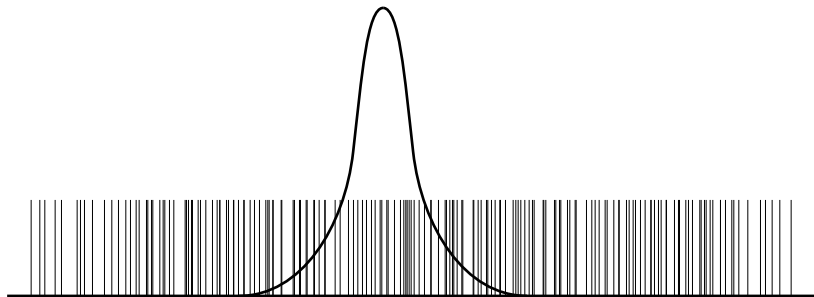


Fig. 4.1 If the “spread” in δ_ϵ is much larger than the average spacing between energy levels, then the function $P_n(E) = C\delta_\epsilon(E - E_n)$ is a smooth function of E .

4.3 THE MICROCANONICAL QUANTUM ENSEMBLE

In defining the microcanonical quantum ensemble a small technical problem arises. It would be natural simply to replace $\theta(E - E_n)$ in Eq. (4.2) by $\delta(E - E_n)$. However, because the energy spectrum of a bound system is discrete, the probability function $P_n = \text{const.} \times \delta(E - E_n)$ would be a very irregular function of

E . In fact, unless E were equal to one of the energy eigenvalues, all terms P_n would be zero and thus the probability could not be normalized. In reality, although the energy eigenvalues are discrete, the spacing between adjacent eigenvalues, for a macroscopic system, is extremely small. In Problem 4.2 the reader is asked to show that the energy spacing between neighboring levels in one mole of gas is of the order $\Delta E \sim e^{-N_A}$. If we replace the Dirac delta function by a function $\delta_\epsilon(E - E_n)$, which has a “spread” ϵ that is much larger than the energy spacing but much smaller than the uncertainty in any realistic energy measurement, then, for any value of E , the probability becomes a smooth function of n (Fig. 4.1). Thus the quantum microcanonical probability will be defined as

$$P_n = \delta_\epsilon(E - E_n)/\Omega'(E) \quad (4.9)$$

where $\Omega' = d\Omega/dE$ is the density of eigenstates as a function of energy. That is, $\Omega'dE$ is the number of energy eigenstates with eigenvalues in the range dE .

Differentiating Eq. (4.6), in the form $\Omega = e^{S^\circ}$, and using the thermodynamic relation $\partial S^\circ/\partial E = 1/\tau$, gives $\Omega' = e^{S^\circ}/\tau$. Taking the logarithm of this relation, we get

$$\log \Omega' = S^\circ - \log \tau \quad (4.10)$$

To estimate the relative sizes of the two terms, we note that, for one mole of helium at 0°C and atmospheric pressure S° (the entropy in rational units) is a pure number equal to $15 N_A$ (see Problem 4.3). In general, for any macroscopic system, the entropy function has the general form $S^\circ(N, E, V) = N s^\circ(\epsilon, v)$, where s° is the entropy per particle, ϵ is the energy per particle, and v is the volume per particle. The second term in Eq. (4.10) is not proportional to N , and, therefore, for a large system it is completely negligible in comparison to the first. Thus, an equally valid formula for the entropy is

$$\begin{aligned} S^\circ(N, E, V) &= \log \Omega'(N, E, V) \\ &= \log \left[\sum_n \delta_\epsilon(E - E_n) \right] \end{aligned} \quad (4.11)$$

In quantum mechanical systems, observables are represented by Hermitian operators. It is clear from our interpretation of a quantum ensemble, that the expectation value of an observable A is given by

$$\langle A \rangle = \sum_n P_n (\psi_n | A | \psi_n) \quad (4.12)$$

where the sum extends over all energy eigenstates of the system and P_n is the probability of eigenstate ψ_n .

4.4 VIBRATIONAL SPECIFIC HEATS OF SOLIDS

As an example of the use of the quantum microcanonical ensemble, we will analyze the contribution to the heat capacity of a crystalline solid that is due to its quantized lattice vibrations. Such quantized lattice vibrations are called *phonons*, and thus the calculation will yield the phonon contribution to the specific heat of the solid.

We will first do the calculation using an approximation introduced by Albert Einstein. We consider a crystal composed of N atoms arranged in a cubic lattice. If all the atoms but one are held at their equilibrium positions and that atom is displaced slightly in the x direction, it will execute simple harmonic motion, with some angular frequency ω , parallel to the x axis. It could also oscillate parallel to the y or z axes. Thus, the single atom is equivalent to a set of three independent harmonic oscillators of equal frequencies. In the Einstein model, the complete crystal is assumed to be equivalent to a system of $K = 3N$ independent harmonic oscillators, all of angular frequency ω . Thus, to calculate the vibrational energy of the crystal, we must first determine the energy spectrum of a system composed of K identical harmonic oscillators. We number the oscillators with an index k , running from 1 to K . The k th oscillator has energy levels

$$E_{n_k} = \hbar\omega(n_k + \frac{1}{2}) \quad (4.13)$$

where $n_k = 0, 1, \dots$. The *system* has one energy eigenstate for each set of quantum numbers n_1, n_2, \dots, n_K .

$$E(n_1, n_2, \dots, n_K) = E_o + \hbar\omega(n_1 + \dots + n_K) \quad (4.14)$$

where $E_o = K\hbar\omega/2$. E_o may be dropped if we measure all energies relative to the ground-state energy. The energy eigenvalues of the system have a uniform spacing $\hbar\omega$, but, for large K , they are highly degenerate. The quantity $\Omega'(E)$ is the density of eigenstates, not the density of eigenvalues. We can calculate $\Omega'(E)$ at the energy $E = \hbar\omega M$ by taking the number of eigenstates in the energy interval from $E - \hbar\omega/2$ to $E + \hbar\omega/2$ and dividing by $\hbar\omega$. Therefore

$$\begin{aligned} \Omega'(\hbar\omega M) &= \frac{1}{\hbar\omega} \left\{ \begin{array}{l} \text{the number of ways of choosing } K \\ \text{integers } n_1, n_2, \dots, n_K \text{ adding up to } M \end{array} \right\} \\ &\equiv \frac{W(K, M)}{\hbar\omega} \end{aligned} \quad (4.15)$$

The problem of computing $W(K, M)$ can be solved with the following trick. We interpret the integers as Bose–Einstein occupation numbers for K quantum states. Then $W(K, M)$ is the quantity given in Eq. (2.57). That is, $W(K, M) = (K + M - 1)! / (K - 1)!M!$ and

$$\Omega'(\hbar\omega M) = \frac{(K + M - 1)!}{\hbar\omega(K - 1)!M!} \quad (4.16)$$

Using Stirling's approximation, writing $E = \hbar\omega M$, and dropping terms that are negligible in comparison with K or M , which are assumed to be very large numbers, one obtains (see Problem 4.6)

$$S^o(E) = \log \Omega'(E) = \left(K + \frac{E}{\hbar\omega}\right) \log \left(K + \frac{E}{\hbar\omega}\right) - K \log K - \left(\frac{E}{\hbar\omega}\right) \log \left(\frac{E}{\hbar\omega}\right) \quad (4.17)$$

The thermodynamic identity $\partial S^o(E)/\partial E = 1/kT$ gives

$$\frac{1}{\hbar\omega} \left[\log \left(K + \frac{E}{\hbar\omega}\right) - \log \left(\frac{E}{\hbar\omega}\right) \right] = \frac{1}{kT} \quad (4.18)$$

which can be solved for E as a function of T .

$$\frac{E(T)}{K} = \frac{\hbar\omega}{e^{\hbar\omega/kT} - 1} \quad (4.19)$$

There are K identical oscillators; therefore $E(T)/K$ can be interpreted as the average energy per oscillator at temperature T .

The *specific heat* of a system is defined as the amount of energy required to raise the temperature of the system by one unit. Therefore, the vibrational specific heat of the crystal C_v , in the Einstein approximation, is given by

$$C_v = \frac{\partial E}{\partial T} = Kk(\hbar\omega/kT)^2 \frac{e^{\hbar\omega/kT}}{(e^{\hbar\omega/kT} - 1)^2} \quad (4.20)$$

At high temperatures (that is, for $kT \gg \hbar\omega$), $(e^{\hbar\omega/kT} - 1)^{-2} \approx (kT/\hbar\omega)^2$ and

$$C_v(T) \approx Kk \quad (4.21)$$

This result, that the specific heat of a solid is equal to Boltzmann's constant times the number of normal modes, was known as the *Dulong–Petit law*. It is the result one gets by using classical mechanics, rather than quantum mechanics, in the calculation. It was exactly the deviations from the Dulong–Petit law that occur at lower temperatures that Einstein was trying to explain. If $kT \ll \hbar\omega$, then $(e^{\hbar\omega/kT} - 1)^{-2} \approx e^{-2\hbar\omega/kT}$ and

$$C_v(T) \approx Kk(\hbar\omega/kT)^2 e^{-\hbar\omega/kT} \quad (4.22)$$

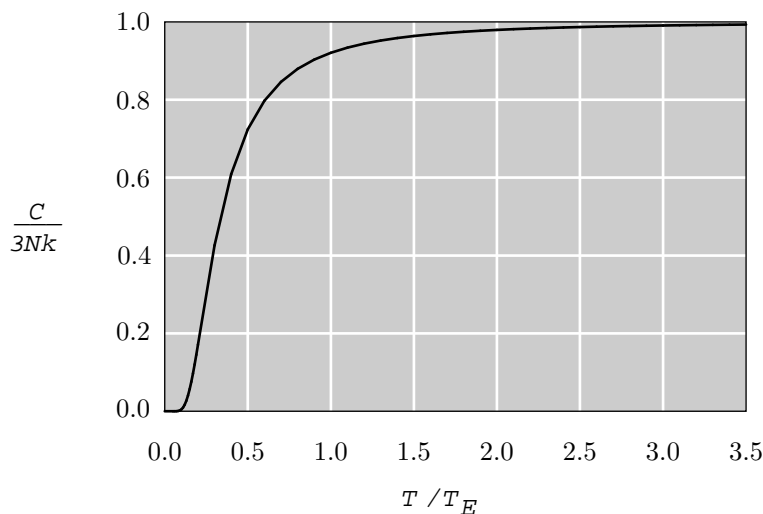


Fig. 4.2 The Einstein specific heat function. The plot shows the ratio of the Einstein prediction for the vibrational specific heat of a crystal to the Dulong—Petit, or classical prediction. The *Einstein temperature* is defined by the relation $kT_E = \hbar\omega$.

As T goes to zero the factor $(\hbar\omega/kT)^2$ goes to infinity but the exponential factor goes to zero much more rapidly and therefore dominates. (The best way to see this is to look at what happens to $\log C_v$ as $T \rightarrow 0$.) $C_v(T)$ goes to zero, as T goes to zero, essentially exponentially. The Einstein result for the vibrational specific heat is plotted in Fig. 4.2. The explanation for the vanishing of the specific heat at low T , as a consequence of quantum mechanics, was a great triumph of the Einstein theory. However, the detailed quantitative result disagreed with experimental measurements, which clearly indicated that $C_v(T) \rightarrow \text{const.} \times T^3$ as $T \rightarrow 0$. A more quantitatively accurate theory was first given by Peter Debye.

4.5 THE FREQUENCY DISTRIBUTION FUNCTION

In the Mathematical Appendix it is proved that, for small vibrations, the Hamiltonian function of a crystal of N atoms is exactly the same as the Hamiltonian function of a system of $K = 3N$ harmonic oscillators with different angular frequencies $\omega_1, \omega_2, \dots, \omega_K$. Each angular frequency ω_k is associated with a possible normal-mode motion of the crystal lattice. A normal mode is a solution of the classical equations of motion in which all of the coordinates oscillate with the same frequency. That is, $x_i(t) = A_i \sin(\omega t + \phi_i)$, where the amplitude and phase of the oscillation are generally different for different coordinates, but the angular frequency is the same. (This sounds a bit confusing—when the particles are vibrating with any particular normal mode motion they all move with the same angular frequency but that common frequency will be different for different normal modes.) Using Eq. (4.19), for the average thermal energy of an oscillator of angular frequency ω , at temperature T , we can write the thermal energy of the crystal as a sum over all the normal modes of the crystal lattice.

$$E(T) = \sum_{k=1}^K \frac{\hbar\omega_k}{e^{\hbar\omega_k/kT} - 1} \quad (4.23)$$

We now define a function, called the *frequency distribution function* $D(\omega)$, by saying that $D(\omega) d\omega$ is equal to the number of normal modes with angular frequencies in the range $d\omega$ (see Fig. 4.3). With this definition, $D(\omega)$ satisfies the normalization condition

$$\int_0^\infty D(\omega) d\omega = K = 3N \quad (4.24)$$

In terms of the frequency distribution function, Eq. (4.23) can be written

$$E(T) = \int_0^\infty \frac{\hbar\omega}{e^{\hbar\omega/kT} - 1} D(\omega) d\omega \quad (4.25)$$

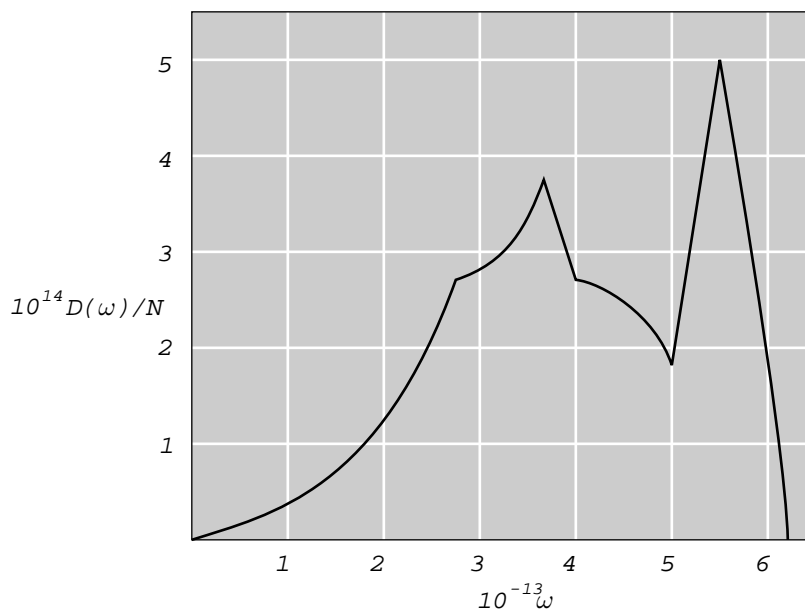


Fig. 4.3 The density of vibrational normal modes for aluminum. As can be seen in this typical example, $D(\omega)$ is usually a quite irregular function of ω that is only crudely approximated by the Debye theory given in Section 4.6.

At high temperature $e^{\hbar\omega/kT} \approx 1 + \hbar\omega/kT$ and

$$E(T) \approx \int_0^\infty kTD(\omega) d\omega = 3NkT \quad (4.26)$$

which shows that the thermal energy at high temperatures is independent of the details of the frequency distribution function and is given by the Dulong–Petit law.

At very low temperature, the function $(e^{\hbar\omega/kT} - 1)^{-1}$ goes rapidly to zero with increasing ω . Therefore, at very low T , only the lowest-frequency normal modes contribute to the vibrational thermal energy of the crystal. But the low-frequency modes are long-wavelength vibrational waves. That is, they are simply sound waves. In a gas, sound waves are always longitudinally polarized waves. The vibratory motion of the particles is parallel to the direction of travel of the wave. The same is not true for sound waves in a solid. In a solid, two types of sound waves are possible: longitudinal waves and transverse waves. For a given direction of travel and wavelength (that is, for a given wave vector \mathbf{k}), there is one longitudinal sound wave and two perpendicularly polarized transverse sound waves. Both types of sound waves satisfy the relation $\lambda = v/\nu$, where v is the sound speed, but the value of v is different for the two types. For any type of wave motion, the relationship between the wave vector and the angular frequency is called the *dispersion relation* for the wave. For both types of sound waves the dispersion relation can be written in the form $\omega(k) = vk$, where $k = 2\pi/\lambda$. Using this, one can show (see Problem 4.9) that $D(\omega)$ is of the form

$$D(\omega) = \frac{V}{2\pi^2} \left(\frac{1}{v_L^3} + \frac{2}{v_T^3} \right) \omega^2 \equiv VA\omega^2 \quad (4.27)$$

where v_L and v_T are the longitudinal and transverse sound speeds and V is the volume of the crystal. Of course, this form is valid only for small values of ω . However, for small T , it is only small values of ω that contribute to the integral in Eq. (4.25). Therefore, at sufficiently low temperatures, we expect that the

vibrational energy of a crystal is given by

$$\begin{aligned}
 E(T) &= VA \int_0^\infty \frac{\hbar\omega^3 d\omega}{e^{\hbar\omega/kT} - 1} \\
 &= VA \frac{(kT)^4}{\hbar^3} \int_0^\infty \frac{x^3 dx}{e^x - 1} \\
 &= VA \frac{(kT)^4}{\hbar^3} \frac{\pi^4}{15}
 \end{aligned} \tag{4.28}$$

where the integral has been evaluated using the Table of Integrals in the Mathematical Appendix. The vibrational specific heat, defined by $C_v = dE(T)/dT$, is thus expected to be proportional to T^3 at low temperatures. As mentioned before, this expectation is borne out by experiment. One class of crystals that do not satisfy this $C_v \approx T^3$ law at low temperatures is strongly anisotropic crystals, such as graphite. For those crystals the sound velocity is strongly directional, and therefore they do not satisfy the simple dispersion relation used previously.

4.6 THE DEBYE APPROXIMATION

An approximation, introduced by Peter Debye, is to use the frequency distribution function $D(\omega) = VA\omega^2$ for all ω up to a value ω_D , which is chosen to give a total of $3N$ normal modes. Above ω_D , $D(\omega)$ is assumed to vanish.

$$D(\omega) = \begin{cases} VA\omega^2, & \omega < \omega_D \\ 0, & \omega > \omega_D \end{cases} \tag{4.29}$$

This form will yield the correct behavior of C_v at low T , because it is correct for long wavelengths. It will also give the correct behavior at high T , because the high- T behavior is independent of the form of $D(\omega)$ except for its total normalization. In using the Debye approximation, it is best to treat the constant A as an adjustable parameter, chosen so as to obtain the best overall fit to the specific heat curve at intermediate temperatures. A is related to ω_D by the normalization condition

$$VA \int_0^{\omega_D} \omega^2 d\omega = 3N \tag{4.30}$$

which gives $VA = 9N/\omega_D^3$. In the Debye approximation

$$\frac{E}{N} = \frac{9\hbar}{\omega_D^3} \int_0^{\omega_D} \frac{\omega^3 d\omega}{e^{\hbar\omega/kT} - 1} \tag{4.31}$$

or

$$\frac{E}{N\hbar\omega_D} = 9\lambda^{-4} \int_0^\lambda \frac{x^3 dx}{e^x - 1} \tag{4.32}$$

where $\lambda = T_D/T$ and the *Debye temperature* T_D is defined by

$$kT_D = \hbar\omega_D$$

The integral cannot be evaluated in closed form, but expansions of it in a power series in λ and numerical tables of the integral can be found in standard handbooks.*

The vibrational specific heat is defined by $C_v = \partial E/\partial T$. At low temperatures it approaches the limit [see Eq. (4.28) and Fig. 4.4]

$$\frac{C_v}{Nk} \approx \frac{12\pi^4}{5} \left(\frac{T}{T_D}\right)^3 \tag{4.33}$$

* For example, *Handbook of Mathematical Functions*, M. Abramowitz and I.A. Stegun, National Bureau of Standards, p. 998. Also see Exercise 4.11.

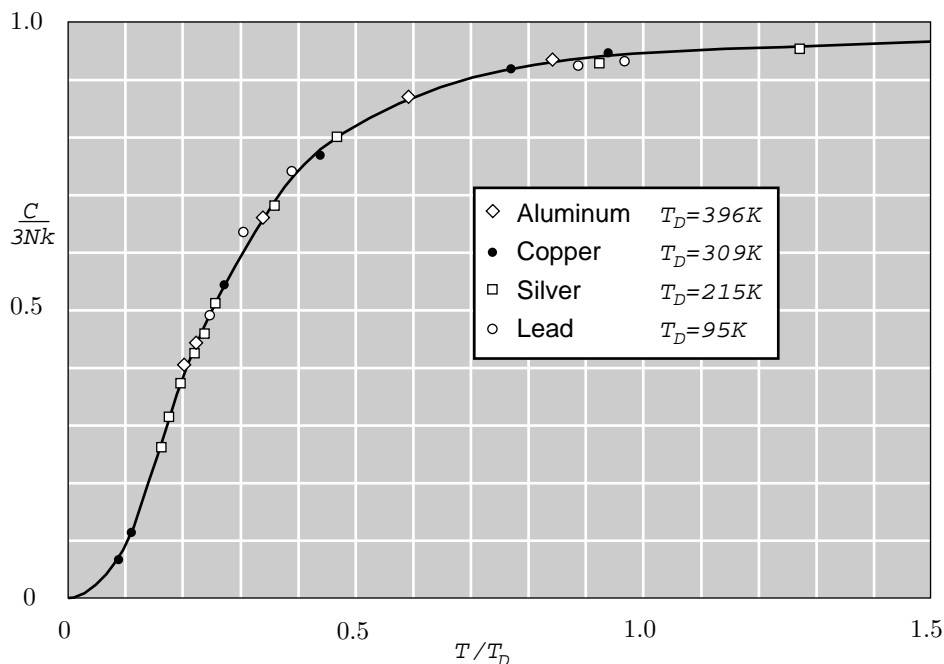


Fig. 4.4 A comparison of the Debye prediction (curve) with the experimental values of the vibrational specific heat for four metals. The data are plotted as a function of T/T_D . Values of T_D are chosen for each substance so as to give the best fit to the experimental data. (Data from G. Wannier, *Statistical Mechanics*, Dover Publ.)

4.7 THE CANONICAL ENSEMBLE

Both the uniform ensemble and the microcanonical ensemble describe isolated systems of known energy. By “isolated” we mean that the system does not exchange energy with any external system. However, most experiments are carried out on systems that are not isolated. For example, when the equilibrium states of a chemical reaction are under study, the reaction vessel is maintained at constant temperature by being kept in contact with a large thermal reservoir, such as a water bath, that can absorb any energy evolved in the reaction. The statistical ensemble that describes a system of known temperature, rather than one of known energy, is the canonical ensemble. The canonical ensemble probability function can be derived by considering a system composed of two weakly interacting parts. The first part is a relatively small but still macroscopic system that will be called the *sample*, while the second part is a very large system, called the *reservoir*. The total system is assumed to be isolated and to have a total energy E . We will describe the total system by a microcanonical ensemble and ask the question: “What is the probability of finding the sample in an eigenstate of energy E_n ”?

When we say that the two subsystems interact weakly, we mean that the energy eigenvalues of the combined system can be approximated by the sum $E_n + E_N$, where E_n is any energy eigenvalue of the sample and E_N is any energy eigenvalue of the reservoir. In the intermediate stages of the calculation, it is most efficient to lump all multiplicative factors that are independent of E_n into a single normalization constant that can be easily evaluated at the end.

If the total system has an energy E , then the probability of finding the sample in its n th eigenstate and the reservoir in its N th eigenstate is $\text{const} \times \delta(E - E_n - E_N)$. If we sum this over all the eigenstates of the reservoir, we obtain the probability of finding the sample in its n th eigenstate, independent of the state of the reservoir.

$$P_n = \text{const.} \times \sum_N \delta(E - E_n - E_N) \quad (4.34)$$

But, by Eq. (4.11), the entropy function of the reservoir alone, at an energy $E - E_n$, would be given by

$$e^{S_R^0(E-E_n)} = \sum_N \delta(E - E_n - E_N) \quad (4.35)$$

The assumption that the sample is small relative to the reservoir allows S_R^o to be expanded to first order in a power series in E_n . Using the fact that $\partial S^o/\partial E = 1/kT$, we obtain

$$S_R^o(E - E_n) = S_R^o(E) - \beta E_n \quad (4.36)$$

where $\beta = 1/kT$ and T is the temperature of the reservoir at energy E . This allows the sum in Eq. (4.34) to be evaluated in the form

$$P_n = \text{const.} \times \sum_N \delta(E - E_n - E_N) = \text{const.} \times e^{-\beta E_n} \quad (4.37)$$

The final normalization constant is calculated by demanding that the sum over all n of P_n be unity.

$$(\text{const.})^{-1} = \sum_n e^{-\beta E_n} \equiv Z(\beta) \quad (4.38)$$

$Z(\beta)$ is called the *partition function* of the sample. It will, in general, depend on other parameters, such as the volume and number of particles in the sample, that determine the sample energy spectrum. In terms of the partition function, the probability that the system will be found in its n th energy eigenstate is

$$P_n = \frac{e^{-\beta E_n}}{Z} \quad (4.39)$$

It will now be shown that, just as the logarithm of the normalization constant for the uniform and micro-canonical ensembles give the entropy function of the system, $\log Z(N, \beta, V)$ is equal to another important thermodynamic function.

4.8 THE CANONICAL POTENTIAL

Using the fact that the number of eigenstates in the energy interval dE is given by $\Omega'(E)dE = e^{S^o(E)}dE$, $Z(N, \beta, V)$ can be written as

$$Z(N, \beta, V) = \int e^{S^o(N, E, V) - \beta E} dE \quad (4.40)$$

Changing the variable of integration to $\varepsilon = E/N$, the energy per particle, and recalling that $S^o(N, E, V) = Ns^o(\varepsilon, v)$, where s^o is the entropy per particle and $v = V/N$, one obtains

$$Z(N, \beta, V) = N \int_0^\infty e^{N(s^o - \beta\varepsilon)} d\varepsilon \quad (4.41)$$

In the Mathematical Appendix, it is shown that, for any function $f(x)$ that has a single maximum at \bar{x} , as N goes to infinity,

$$\int e^{Nf(x)} dx \rightarrow \left(\frac{2\pi}{N|f''(\bar{x})|} \right)^{1/2} e^{Nf(\bar{x})} \quad (4.42)$$

This gives, for $Z(N, \beta, V)$,

$$Z(N, \beta, V) = \left(\frac{2\pi N}{|\partial^2 s^o / \partial \varepsilon^2|_{\bar{\varepsilon}}} \right)^{1/2} e^{N[s^o(\bar{\varepsilon}, v) - \beta \bar{\varepsilon}]} \quad (4.43)$$

where $\bar{\varepsilon}$ is given by $(\partial s^o(\varepsilon, v)/\partial \varepsilon)_{\bar{\varepsilon}} = \beta$. This is equivalent to the condition that

$$\left. \frac{\partial S^o(N, E, V)}{\partial E} \right|_{\bar{E}} = \beta = \frac{1}{\tau} \quad (4.44)$$

But this is exactly the thermodynamic relation between the energy and the temperature. This shows that, for a given reservoir temperature, the only sample energy that contributes significantly to the partition

function integral is the expected thermodynamic energy for that temperature. Taking the logarithm of Z and dropping terms that are negligible in comparison with N , we get

$$\log Z(N, \beta, V) = S^o(N, \bar{E}, V) - \beta \bar{E} \equiv \phi(N, \beta, V) \quad (4.45)$$

where \bar{E} is a function of N , β , and V defined by Eq. (4.44). In the future we will write simply $E(N, \beta, V)$ for $\bar{E}(N, \beta, V)$.

$\phi(N, \beta, V)$ is called the *canonical potential*. It plays the same role for a system at known temperature, as is played by the entropy function for a system of known energy. What those roles are will be fully developed in the chapter on thermodynamics. The thermodynamic relations, $\partial S^o/\partial E = \beta$ and $\partial S^o/\partial V = \beta p$, may be used to derive equivalent relations giving the energy and pressure in terms of the canonical potential.

$$\frac{\partial \phi}{\partial \beta} = \left(\frac{\partial S^o}{\partial E} - \beta \right) \frac{\partial E}{\partial \beta} - E = -E(N, \beta, V) \quad (4.46)$$

and

$$\frac{\partial \phi}{\partial V} = \frac{\partial S^o}{\partial V} + \left(\frac{\partial S^o}{\partial E} - \beta \right) \frac{\partial E}{\partial V} = \beta p \quad (4.47)$$

4.9 ENERGY FLUCTUATIONS IN THE CANONICAL ENSEMBLE

The canonical ensemble describes a system in contact with a reservoir. For such a system, the energy is not exactly fixed—the system can exchange energy with the reservoir. We will now evaluate the magnitude of the energy fluctuations. In the canonical ensemble, the expectation values of the energy and of the square of the energy are given by

$$\langle E \rangle = \frac{\sum E_n e^{-\beta E_n}}{\sum e^{-\beta E_n}} = \frac{-\partial Z / \partial \beta}{Z} \quad (4.48)$$

and

$$\langle E^2 \rangle = \frac{\sum E_n^2 e^{-\beta E_n}}{\sum e^{-\beta E_n}} = \frac{\partial^2 Z / \partial \beta^2}{Z} \quad (4.49)$$

This gives the following simple formula for the square of the energy fluctuation.

$$\begin{aligned} (\Delta E)^2 &= \langle E^2 \rangle - \langle E \rangle^2 \\ &= \frac{\partial^2 Z / \partial \beta^2}{Z} - \frac{(\partial Z / \partial \beta)^2}{Z^2} \\ &= \frac{\partial}{\partial \beta} \left(\frac{\partial Z / \partial \beta}{Z} \right) \\ &= \frac{\partial}{\partial \beta} \left(\frac{\partial \log Z}{\partial \beta} \right) \\ &= \frac{\partial^2 \phi}{\partial \beta^2} \\ &= -\frac{\partial E}{\partial \beta} \\ &= \tau^2 \frac{\partial E}{\partial \tau} \\ &= \tau^2 C \end{aligned} \quad (4.50)$$

where $C = \partial E / \partial \tau$ is the specific heat of the system, a quantity that is proportional to the size of the system. Written in terms of the specific heat per particle, $c = C/N$, and the energy per particle, $\varepsilon = E/N$, the ratio of the energy fluctuation to the energy is

$$\frac{\Delta E}{E} = \frac{\tau c}{\varepsilon \sqrt{N}} \quad (4.51)$$

Clearly, the $1/\sqrt{N}$ dependence of the energy fluctuation is another manifestation of the law of large numbers. Thus, for a system of one mole, $\Delta E/E$ is of the order of 10^{-12} , and is therefore completely negligible. Because the energy fluctuation in the canonical ensemble is negligible for a macroscopic system, the predictions of the physical properties of such a system, made using the canonical ensemble, are identical with those made using the microcanonical ensemble, which has zero energy fluctuation. Although the canonical ensemble was introduced to describe a system in contact with a reservoir, it can perfectly well be used to describe an isolated system. The choice of which ensemble to use is purely one of convenience for a particular calculation; in fact, they give identical results.

4.10 THE CLASSICAL CANONICAL ENSEMBLE

An analysis, equivalent to that which led to Eq. (4.39) for the probability function of a quantum canonical ensemble (see Problem 4.18), would show that a classical system, in interaction with a reservoir at temperature T , has a probability $P(x, p)$ of being found in the dynamical state (x, p) given by

$$P(x, p) = I^{-1} e^{-\beta H(x, p)} \quad (4.52)$$

The classical normalization integral I can be related to the partition function Z by using the identity

$$I = \int e^{-\beta H} d^K x d^K p = \int_0^\infty dE \int \delta(E - H) e^{-\beta E} d^K x d^K p \quad (4.53)$$

and using Eq. 3.84, which gives the integral $\int \delta(E - H) d^K x d^K p$ in terms of S^o . One obtains

$$I = h^K N! \int_0^\infty e^{S^o - \beta E} dE \quad (4.54)$$

Equation (4.40) then gives, for a classical system,

$$Z(N, \beta, V) = \frac{I}{h^K N!} = \frac{1}{h^K N!} \int e^{-\beta H} d^K x d^K p \quad (4.55)$$

Written in terms of Z , rather than I , the canonical probability density function is

$$P(x, p) = e^{-\beta H(x, p)} / h^K N! Z \quad (4.56)$$

4.11 MOLECULAR GASES

The canonical ensemble is a convenient tool for studying the contributions of internal degrees of freedom, such as rotation and vibration, to the thermal properties of an ideal gas. It will be assumed that the rotational motion can be adequately described by classical mechanics. In Problem 4.19, the correct quantum mechanical treatment is described, and the range of validity of the classical treatment is determined. In order to have a definite focus, we will consider a specific system, namely, a gas of diatomic molecules with only rotational degrees of freedom. Such a molecule can be pictured as two point masses, m_A and m_B , at fixed distances, a and b , from their center of mass. By the definition of a center of mass it is necessary that $m_A a = m_B b$.

Diatomic molecules come in two classes, *homonuclear* molecules, in which the nuclei of the two atoms are identical, and *heteronuclear* molecules, in which they differ in some way. For a homonuclear molecule, the quantum mechanical wave function must be either symmetric or antisymmetric under exchange of the two nuclei. It must be symmetric if the number of fermions (neutrons and protons) in each nucleus is even, and it must be antisymmetric if that number is odd. Such symmetry requirements add a certain amount of extra complication to the analysis that we will avoid by restricting ourselves to heteronuclear molecules. (However, see Problem 4.20.) That a molecule is heteronuclear does not require that its atoms be of different chemical species. It is enough that they be different isotopes of the same element. It is even sufficient, if

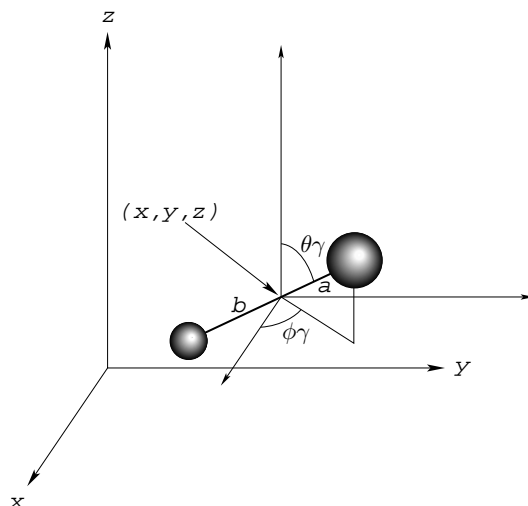


Fig. 4.5 The five coordinates that define the configuration of a diatomic molecule with a fixed internuclear distance. x , y , and z are the coordinates of the center of mass, while θ and ϕ are spherical angles that give the orientation of the axis in a local coordinate system.

they are the same isotope, that the value of the z component of their nuclear spin be different. That is, if the two nuclei differ in any characteristic at all, then the analysis to be given is applicable.

The configuration of the molecule is described by five coordinates (x, y, z, θ, ϕ) (Fig. 4.5), where the first three give the location of the center of mass and the last two are spherical angles defining the direction of the line from B to A . For each of the five coordinates there is a corresponding canonical momentum. Thus the phase space of a single molecule is ten-dimensional, and the phase space of the N -particle system has $2K$ dimensions with $K = 5N$.

Our first task is to determine the Hamiltonian function for the rotational motion. It is easy to see that the rotational kinetic energy T_R is given by

$$T_R = \frac{1}{2}(m_A a^2 + m_B b^2)(\dot{\theta}^2 + \sin^2 \theta \dot{\phi}^2) \equiv \frac{1}{2}I(\dot{\theta}^2 + \sin^2 \theta \dot{\phi}^2) \quad (4.57)$$

where I is the moment of inertia of the molecule. The canonical angular momenta are

$$p_\theta = \frac{\partial T_R}{\partial \dot{\theta}} = I\dot{\theta} \quad \text{and} \quad p_\phi = \frac{\partial T_R}{\partial \dot{\phi}} = I \sin^2 \theta \dot{\phi} \quad (4.58)$$

Writing the rotational kinetic energy in terms of canonical coordinates and momenta gives

$$T_R = \frac{1}{2I} \left(p_\theta^2 + \frac{p_\phi^2}{\sin^2 \theta} \right) \quad (4.59)$$

The Hamiltonian function for a single molecule is therefore

$$H = \frac{1}{2m}(p_x^2 + p_y^2 + p_z^2) + \frac{1}{2I} \left(p_\theta^2 + \frac{p_\phi^2}{\sin^2 \theta} \right) \quad (4.60)$$

In general, if a single molecule has a $2k$ -dimensional phase space with a Hamiltonian $H(x, p)$, then the partition function for the N -particle system is, by Eq. (4.55),

$$Z = \frac{1}{N!} \left(\frac{1}{h^k} \int e^{-\beta H(x,p)} d^k x d^k p \right)^N \equiv \frac{z^N}{N!} \quad (4.61)$$

where z is the partition function for a single molecule. The canonical potential is given by

$$\phi = N \log z - \log N! \quad (4.62)$$

For a diatomic molecule, the integration over the center of mass coordinates and momenta gives

$$\frac{1}{h^3} \int_V d^3x \int e^{-\beta p^2/2m} d^3p = \frac{V}{\lambda^3} \quad (4.63)$$

where $\lambda = \sqrt{\beta \hbar^2 / 2\pi m}$ is the thermal de Broglie wavelength of the molecule. The integration over the internal coordinates and momenta gives what we will call the rotational partition function.

$$\begin{aligned} z(\text{rot}) &= \frac{1}{h^2} \int_0^{2\pi} d\phi \int_0^\pi d\theta \int_{-\infty}^{\infty} e^{-\beta p_\theta^2/2I} dp_\theta \int_{-\infty}^{\infty} e^{-\beta p_\phi^2/2I \sin^2 \theta} dp_\phi \\ &= \frac{2I}{\beta \hbar^2} \end{aligned} \quad (4.64)$$

When this is all put together, and Stirling's approximation is used for $N!$, one gets

$$\begin{aligned} \phi(N, \beta, V) &= N \left(\log(V/N) + \frac{3}{2} \log(2\pi m / \beta \hbar^2) + \log(2I / \beta \hbar^2) + 1 \right) \\ &= N \left(\log(V/N) - \frac{5}{2} \log \beta + \log(2I(m/2\pi)^{3/2} k^{5/2} / \hbar^5) + 1 \right) \end{aligned} \quad (4.65)$$

The pressure and energy equations of state are given by the thermodynamic relations

$$\frac{p}{kT} = \frac{\partial \phi}{\partial V} = \frac{N}{V} \quad (4.66)$$

or

$$pV = NkT \quad (4.67)$$

and

$$E = -\frac{\partial \phi}{\partial \beta} = \frac{5}{2} NkT \quad (4.68)$$

The internal degrees of freedom have no effect on the pressure equation for an ideal gas. This is natural, since the pressure is due to the momentum transferred to the wall by the rebounding particles and only center of mass momentum is involved in that transfer. The two rotational degrees of freedom each add a term $kT/2$ to the thermal energy per particle. This is an example of a general theorem, called the equipartition theorem, that will be given later in this chapter.

4.12 DIPOLAR MOLECULES IN AN ELECTRIC FIELD

If atom A is not identical to atom B , then the molecule will almost surely have a net electric dipole moment because electrons will be drawn somewhat from one atom to the other. We will assume that the molecule has a dipole moment μ pointing in the direction of atom A and that the gas is placed in a uniform electric field, $\mathbf{E} = \mathcal{E}\hat{z}$. There will then be a potential energy that will depend on the orientation of the molecule.

$$V = -\mu \mathcal{E} \cos \theta \quad (4.69)$$

With this modification, the Hamiltonian function for a single molecule is

$$H = \frac{1}{2m}(p_x^2 + p_y^2 + p_z^2) + \frac{1}{2I} \left(p_\theta^2 + \frac{p_\phi^2}{\sin^2 \theta} \right) - \mu \mathcal{E} \cos \theta \quad (4.70)$$

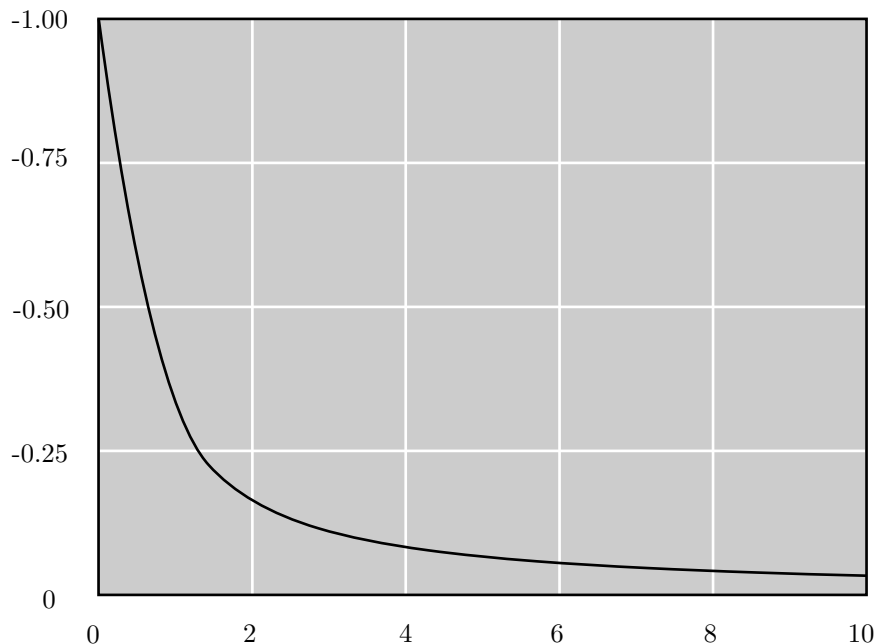


Fig. 4.6 A graph of the function $(E/N - \frac{5}{2}kT)/\mu\mathcal{E}$ in terms of the variable $x = kT/\mu\mathcal{E}$ for a dipolar gas in an electric field. This gives the part of the energy due to the interaction of the dipoles with the external field (divided by $\mu\mathcal{E}$). Note that the values on the vertical axis are negative.

A recalculation of the rotational partition function (see Problem 4.23) gives

$$\phi(N, \beta, V) = N \left(\log(V/N) - \frac{5}{2} \log \beta + \log \left(\frac{\sinh(\beta\mu\mathcal{E})}{\beta\mu\mathcal{E}} \right) + \text{const.} \right) \quad (4.71)$$

The pressure equation of state is unaffected by the change in the internal Hamiltonian. However, the energy equation of state now becomes

$$E = -\frac{\partial \phi}{\partial \beta} = \frac{5}{2}NkT + N[kT - \mu\mathcal{E} \coth(\mu\mathcal{E}/kT)] \quad (4.72)$$

The function $E(T) - \frac{5}{2}NkT$, which is the dipolar contribution to the thermal energy, is plotted in Fig. 4.6.

For low temperature or large electric field strength (that is, for $kT \ll \mu\mathcal{E}$), the axes of the molecules only undergo small fluctuations about the z direction. In that case the two internal degrees of freedom act like a two-dimensional harmonic oscillator with an energy of $-\mu\mathcal{E}$ at the zero point and contribute an amount $-\mu\mathcal{E} + 2kT$ to the energy per particle (see Problem 4.24).

Using the first two terms of the expansion, $\coth x = 1/x + x/3 - x^3/45 + \dots$, valid for small x , we find that the potential energy contribution to the thermal energy goes to zero as $1/T$ for large T . That is, for $kT \gg \mu\mathcal{E}$,

$$kT - \mu\mathcal{E} \coth(\mu\mathcal{E}/kT) \approx -\frac{\mu^2 \mathcal{E}^2}{3kT} \quad (4.73)$$

4.13 THE DIELECTRIC CONSTANT OF A GAS

The dielectric constant of a substance is defined by $\kappa = 1 + \chi_e$, where χ_e is the electric susceptibility and $\epsilon_0 \chi_e$ is the ratio of the polarization of the medium to the electric field strength. The polarization of a molecular gas is simply the density of molecules times their average dipole moment. There are two contributions to the average dipole moment. One contribution, called the orientational dipole moment, is due to the lining up of the preexisting electric dipoles in the electric field. This is what will be calculated

here. The other contribution, called the induced dipole moment, is due to a change in the internal state of the molecule in response to the electric field (the electrons and nuclei shift their positions relative to one another). Calculating the induced dipole moment is a problem in pure quantum mechanics and therefore it will be ignored in this book, although, even in polar molecules, it may be larger than the orientational dipole moment.

Clearly, the average dipole moment will be in the z direction, since that is the direction of the electric field. The average dipole moment is therefore

$$\bar{\mu}_z = \frac{1}{N} \left\langle \sum_i^N \mu \cos \theta_i \right\rangle \quad (4.74)$$

$\bar{\mu}_z$ will be evaluated by first deriving a thermodynamic relation that is valid in a much wider context. In particular, the derivation will not assume that the system is composed of noninteracting particles. We will only assume that the Hamiltonian function, in the presence of an electric field, is of the form

$$H = H_o - \sum_{i=1}^N \mu \mathcal{E} \cos \theta_i \quad (4.75)$$

where H_o is the system Hamiltonian when $\mathcal{E} = 0$. If the system is described by K momentum variables and K coordinates, some of which are the angles $\theta_1, \dots, \theta_N$, then the canonical potential is

$$\phi = \log \left[\int \exp \left(-\beta H_o + \beta \mathcal{E} \sum \mu \cos \theta_i \right) d^K x d^K p \right] \quad (4.76)$$

The derivative of ϕ , with respect to the electric field strength \mathcal{E} is

$$\frac{\partial \phi}{\partial \mathcal{E}} = \beta \frac{\int (\sum \mu \cos \theta_j) \exp \left[-\beta H_o + \beta \mathcal{E} \sum \mu \cos \theta_i \right] d^K x d^K p}{\int \exp \left[-\beta H_o + \beta \mathcal{E} \sum \mu \cos \theta_i \right] d^K x d^K p} \quad (4.77)$$

Comparing this with Eq. (4.74), we see that

$$N \bar{\mu}_z = kT \frac{\partial \phi}{\partial \mathcal{E}} \quad (4.78)$$

Equation (4.71), for ϕ , then gives the average dipole moment as

$$\bar{\mu}_z = \mu \coth(\beta \mu \mathcal{E}) - \frac{1}{\beta \mathcal{E}} \quad (4.79)$$

To calculate the dielectric constant we need only the term that is linear in \mathcal{E} . We may therefore use the expansion of $\coth x$, valid for small x , to get

$$\bar{\mu}_z \approx \frac{\mu^2}{3kT} \mathcal{E} \quad (4.80)$$

The electric susceptibility is obtained by multiplying by the particle density n and dividing by the field strength.

$$\epsilon_o \chi_e = \frac{\mu^2 n}{3kT} \quad (4.81)$$

As was stated before, this calculation ignores the contribution of the induced dipole moment to the polarization of the gas. Therefore, a single measurement of the dielectric constant of the gas could not be used, in combination with Eq. (4.81), to determine the permanent dipole moment of the molecule (Fig. 4.7). However, the induced dipole moment is independent of temperature, while the orientational dipole moment

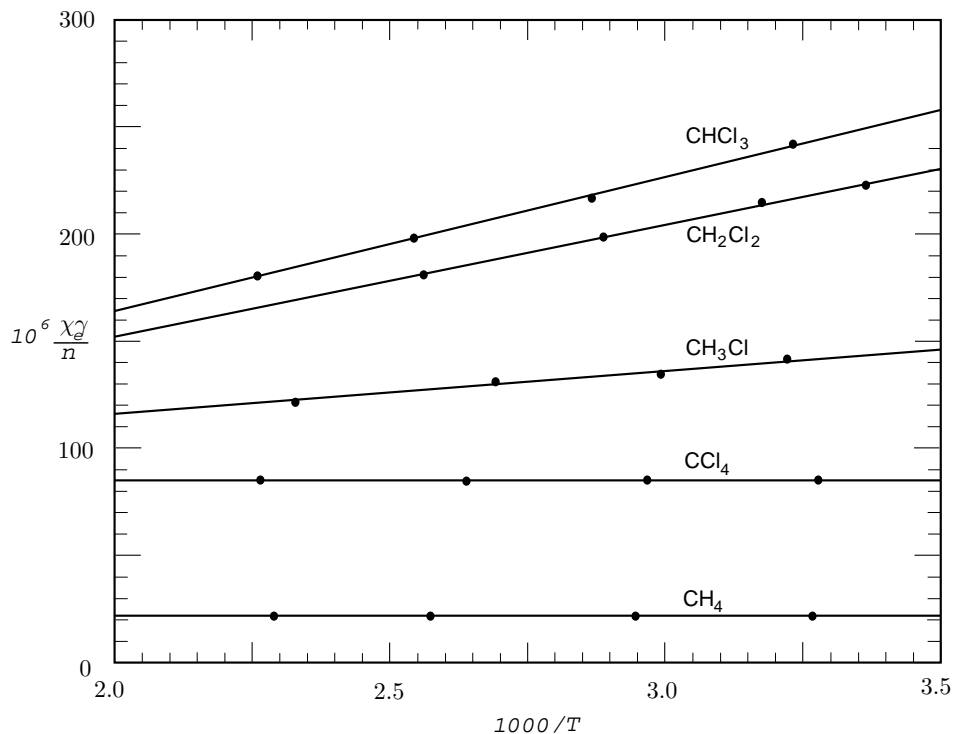


Fig. 4.7 The electric susceptibility of various chlorinated methanes. n is in moles/m³ and T in K.

has the characteristic $1/T$ behavior shown in Eq. (4.81). Thus, a measurement of χ_e at a number of different temperatures does allow a separation of the two effects and, therefore, a determination of the molecular dipole moment μ . Before the introduction of microwave spectroscopy, this was the standard technique for determining molecular dipole moments. (See Problems 4.21 and 4.22.)

4.14 THE VIBRATIONAL ENERGY OF A GAS

The eigenvalues of the square of the angular momentum of a quantized rotating diatomic molecule are $\hbar^2\ell(\ell + 1)$, where $\ell = 0, 1, \dots$. The corresponding energy eigenvalues are $E_\ell = \hbar^2\ell(\ell + 1)/2I$. Therefore, quantum mechanical effects will become noticeable when kT is of the order of $\hbar^2/2I$. For diatomic molecules like O₂, Cl₂, or KCl the quantity $\hbar^2/2kI$ is about one Kelvin; a temperature at which the substance does not exist as a gas. It is only for the isotopes of hydrogen that quantum mechanical effects are significant in the rotational thermal energy.

In contrast, the “stretching mode” of most diatomics demands a quantum mechanical treatment. For this vibrational mode, the significant temperature would be $T = \hbar\omega/k$, where ω is the vibrational angular frequency. For typical diatomic molecules, such as the three mentioned, $\hbar\omega/k$ is a few thousand Kelvin, far above room temperature. In fact, at temperatures near room temperature, the stretching vibrational motion is completely unexcited. For those temperatures, the approximation of taking the interatomic distance as fixed is an accurate one.

The potential associated with the interaction between the atoms in a diatomic molecule is of the general form shown in Fig. 4.8. Near the equilibrium distance the potential function may be approximated as a quadratic, leading to the energy spectrum of a one-dimensional harmonic oscillator. The contribution of the vibrational modes of all N diatomic molecules is just the thermal energy of N identical harmonic oscillators, given in Eq. (4.19).

$$E_{\text{vib}}(T) = \frac{N\hbar\omega}{e^{\hbar\omega/kT} - 1} \quad (4.82)$$

This should be added to the translational and rotational energies given in Eq. 4.60

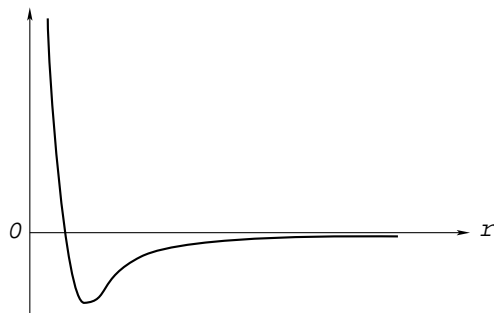


Fig. 4.8 A typical interatomic potential energy function.

4.15 THE SCHOTTKY SPECIFIC HEAT

As another example of the use of the canonical ensemble, we will consider a solid composed of N atoms (or molecules) and assume that each atom may be in one of two possible quantum states with energies 0 and ε . We want to calculate the specific heat per particle, $C = \partial(E/N)/\partial T$, as a function of temperature.

The atoms in a solid, being localized in space, may be treated as distinguishable particles.* If, in addition to being distinguishable, the particles do not interact, then the energy eigenvalues of the system are of the form

$$E = E_{\alpha_1} + \cdots + E_{\alpha_N} \quad (4.83)$$

where the index α_i numbers the quantum states of the i th particle. The partition function then becomes the N th power of a partition function for a single atom.

$$Z = \sum_{\{\alpha\}} \exp[-\beta(E_{\alpha_1} + \cdots + E_{\alpha_N})] = \left(\sum_{\alpha} e^{-\beta E_{\alpha}} \right)^N \equiv (Z_{\text{at}})^N \quad (4.84)$$

The canonical potential of the system is then N times the canonical potential of a single atom.

$$\phi = N \log Z_{\text{at}} \quad (4.85)$$

The partition function of a two-level atom has only two terms.

$$Z_{\text{at}} = 1 + e^{-\beta\varepsilon} \quad (4.86)$$

Thus

$$\phi(\beta) = N \log(1 + e^{-\beta\varepsilon}) \quad (4.87)$$

The thermal energy as a function of T is

$$E(T) = -\frac{\partial\phi}{\partial\beta} = N\varepsilon \frac{e^{-\beta\varepsilon}}{1 + e^{-\beta\varepsilon}} = \frac{N\varepsilon}{e^{\varepsilon/kT} + 1} \quad (4.88)$$

The specific heat per particle is

$$C = \frac{\varepsilon^2 e^{\varepsilon/kT}}{kT^2 (e^{\varepsilon/kT} + 1)^2} \quad (4.89)$$

* Solid helium, in which there is a significant amplitude for particle exchange, is the only exception to this rule.

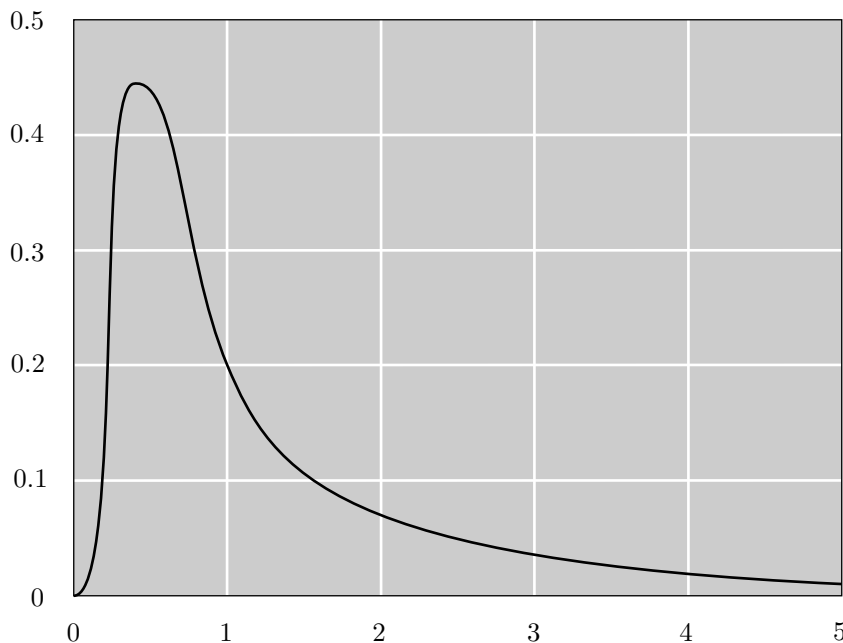


Fig. 4.9 The Schottky specific heat anomaly. C/k is plotted as a function of $x = kT/\varepsilon$.

A graph of $C(T)$ shows that the specific heat has a single large maximum at a temperature $T \approx 0.42 \varepsilon/k$. This characteristic pattern is known as a Schottky anomaly (see Fig. 4.9).

4.16 SEPARABLE SYSTEMS

The system considered, composed of N noninteracting identical atoms, is a special case of a system whose energy spectrum is of the form of a sum of terms, each of which depends on an independent set of quantum numbers. For example, consider a system with energy levels

$$E = E_a + E_b + E_c \quad (4.90)$$

where a , b , and c are independent sets of quantum numbers. That the quantum numbers are “independent” means, for instance, that the allowed values of c do not depend on the values of a or b . This condition of independence is not satisfied by the quantum numbers (n, l, m) that index the hydrogenic wave functions. A system whose energy eigenvalues satisfy Eq. (4.90), with independent quantum numbers, has a partition function of the form

$$\begin{aligned} Z &= \sum_{a,b,c} e^{-\beta(E_a + E_b + E_c)} \\ &= \left(\sum_a e^{-\beta E_a} \right) \left(\sum_b e^{-\beta E_b} \right) \left(\sum_c e^{-\beta E_c} \right) \\ &= Z_A Z_B Z_C \end{aligned} \quad (4.91)$$

and a canonical potential

$$\phi = \phi_A + \phi_B + \phi_C \quad (4.92)$$

A separable system may be composed of two or more physically separate systems that are in weak thermal contact, or it may simply be a single system with different weakly interacting degrees of freedom, such as the collection of translational, rotational, and vibrational degrees of freedom for a diatomic molecule.

4.17 THE EQUIPARTITION THEOREM

The equipartition theorem is a general formula for calculating the contribution to the thermal energy of terms that appear quadratically in the Hamiltonian function of a classical system. Let q be one of the

coordinates in phase space (either an x_i or a p_i) and let Q be the set of $(2K-1)$ other coordinates. Suppose that the Hamiltonian function is of the form

$$H = A(Q)q^2 + H'(Q) \quad (4.93)$$

and that q has the range $-\infty < q < \infty$. Certainly, this is the form of the translational kinetic energy terms, where q is any component of the momentum of any particle and $A = 1/2m$. But it is also the form of the rotational kinetic energy terms for a diatomic molecule, where q is either p_θ or p_ϕ . In the canonical ensemble

$$E = \langle Aq^2 \rangle + \langle H' \rangle \quad (4.94)$$

and

$$\langle Aq^2 \rangle = \frac{\int Aq^2 e^{-\beta(Aq^2+H')} dq dQ}{\int e^{-\beta(Aq^2+H')} dq dQ} \quad (4.95)$$

Taking the q integral first, we get

$$\int Aq^2 e^{-\beta(Aq^2+H')} dq dQ = \frac{\sqrt{\pi}}{2\beta^{3/2}} \int A^{-1/2} e^{-\beta H'} dQ \quad (4.96)$$

and

$$\int e^{-\beta(Aq^2+H')} dq dQ = \frac{\sqrt{\pi}}{2\beta^{1/2}} \int A^{-1/2} e^{-\beta H'} dQ \quad (4.97)$$

which shows that

$$\langle Aq^2 \rangle = \frac{1}{2\beta} = \frac{1}{2}kT \quad (4.98)$$

Thus, each purely quadratic term in a classical Hamiltonian function contributes an amount $kT/2$ to the thermal energy.

This makes the task of calculating the thermal energy of a classical system of K one-dimensional harmonic oscillators completely trivial. Both the momentum variables and the coordinate variables appear quadratically in the Hamiltonian with the result that

$$\frac{E(T)}{K} = kT \quad (4.99)$$

Comparing this with the equivalent equation for quantum mechanical harmonic oscillators [Eq. (4.19)], we see that the high-temperature limit of the quantum mechanical result is equivalent to the classical limit.

PROBLEMS

4.1 A more general form of the uniform quantum ensemble could be constructed as follows. Let $|E_1\rangle, \dots, |E_K\rangle$ be the set of all energy eigenstates with eigenvalues less than some given energy E . Instead of assuming that each member of the ensemble is in a definite energy eigenstate, we simply assume that each member of the ensemble has a wave function that is a linear combination of the first K eigenstates.

$$|\psi\rangle = \sum_k^K c_k |E_k\rangle = \sum_k^K (a_k + ib_k) |E_k\rangle$$

where c_k is a complex number and a_k and b_k are real. This is equivalent to assuming that there is zero probability of finding the system with energy larger than E . Assume that the probability distribution for the expansion coefficients is constant, except for the normalization condition $\langle\psi|\psi\rangle = \sum_k (a_k^2 + b_k^2) = 1$. Show that the ensemble average $\langle A \rangle$ of any operator, taken with this “more general” ensemble agrees exactly with $\langle A \rangle$ taken with the ordinary uniform ensemble. (Warning: this is a very hard problem.)

4.2 $\Omega(E)$ is the number of eigenstates with energy less than E . Therefore, $d\Omega/dE$ is the number of eigenstates per unit energy interval (the *eigenstate density*) and $(d\Omega/dE)^{-1}$ is the average spacing between energy eigenvalues (counting degenerate eigenvalues as having zero spacing). Evaluate the average spacing, using the classical approximation [Eq. (4.4)], for one mole of neon at STP, neglecting interparticle interactions.

4.3 Show that, for one mole of helium at 0°C and atmospheric pressure, using the classical approximation, $S^\circ = 15 N_A$. For the same system, evaluate $\log \tau$ and compare the two terms in Eq. (4.10).

4.4 The normal modes of a violin string with a fundamental angular frequency ω_o may be considered as a set of noninteracting harmonic oscillators. (a) Express the average vibrational energy of the system at temperature T , measured from the ground state, as an infinite series. Remember that there are two normal modes for each allowed wavelength. (b) For $kT \gg \hbar\omega_o$, the infinite sum may be approximated by an integral that can be found in the Table of Integrals. Calculate the thermal energy of the system in that limit. (c) For $kT \ll \hbar\omega_o$, the sum may be evaluated by using the fact that $\exp(n\hbar\omega_o/kT) \gg 1$ for any positive integer n . Calculate the thermal energy of the system in that limit.

4.5 A quantum system is composed of K distinguishable subsystems. The k th subsystem has an energy spectrum $E_{n_k} = \varepsilon n_k^2$, where $n_k = 0, 1, 2, \dots$. Calculate $\Omega(E)$ for the system, when $E \gg \varepsilon$.

4.6 Derive Eq. (4.17) from Eq. (4.16).

4.7 Shown in Fig. 4.10 is a simple model of a one-dimensional crystal. The springs all have spring constant k and, at equilibrium, the particles are all separated by length ℓ . Let x_n be the deviation from equilibrium of the n th particle. (a) Show that the equation of motion of the n th particle is $m\ddot{x}_n = k(x_{n+1} + x_{n-1} - 2x_n)$, where $n = 1, \dots, N$ and x_o and x_{N+1} are defined to be zero. (b) Show that there are N solutions of the equations of motion of the form

$$x_n(t) = A \cos(\omega_K t) \sin\left(\pi \frac{K}{N+1} n\right)$$

where $K = 1, \dots, N$ and, putting those solutions into the equations of motion, determine the normal mode angular frequencies ω_K . (c) Treating the system quantum mechanically, write the thermal energy per particle at temperature T as a sum over the variable K . Rewrite it as an integral, using the integration variable $k = \pi K/(N+1)$ which, for large N , has the range $0 < k < \pi$. The *thermal energy* is the energy at temperature T relative to the ground state energy. (d) Expand the integral obtained in (c) as a power series in \hbar , retaining only the first two nonvanishing terms. Verify that the first term gives the classical, Dulong-Petit value, which for a one-dimensional system is $E(T) = NkT$. (e) Take $\omega_o = \sqrt{k/m} = 10^{13}$ rad/sec (a reasonable value for real crystals) and $T = 300\text{K}$. Determine the ratio of the second (quantum) term in the expansion to the first (classical) term. Is it negligible?

4.8 Equation (4.33) gives the specific heat for a crystal at low temperature, according to the Debye theory. Use this, along with the facts that $S^\circ = 0$ at $T = 0$ and $dS^\circ/dE = 1/kT$, to calculate $S^\circ(T)$ when $T \ll T_D$.

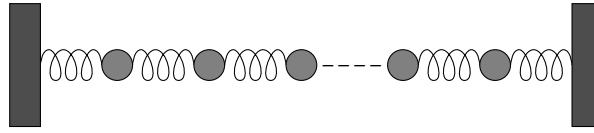


Fig. 4.10

4.9 Consider an elastic material in the form of a cube of side L . If $\mathbf{u}(\mathbf{r}, t)$ is the displacement from equilibrium of the material at location \mathbf{r} at time t , then, for sound waves, $\mathbf{u}(\mathbf{r}, t)$ satisfies the wave equation $\nabla^2 \mathbf{u} - v^{-2} \partial^2 \mathbf{u} / \partial t^2 = 0$. If we impose the condition that the material at the surface does not move, then $\mathbf{u}(x, y, z, t)$ satisfies *zero boundary conditions*,

$$\mathbf{u}(0, y, z, t) = \mathbf{u}(x, 0, z, t) = \mathbf{u}(x, y, 0, t) = 0$$

and

$$\mathbf{u}(L, y, z, t) = \mathbf{u}(x, L, z, t) = \mathbf{u}(x, y, L, t) = 0$$

The solutions of the wave equation, for vibrational waves, with zero boundary conditions at the surface, are $\mathbf{A} \sin(k_x x) \sin(k_y y) \sin(k_z z)$, where \mathbf{A} is any vector and $k_i = \pi K_i / L$ ($i = x, y, z$) with $K_i = 1, 2, 3, \dots$. Thus the possible values of the wave vector form a cubic lattice in k space with lattice spacing π/L . However, the possible wave vectors are limited to the positive octant (the region in k space with all components positive). (a) Show that the number of solutions with $|\mathbf{k}| < K$ is $K^3 L^3 / 6\pi^2$. (b) If \mathbf{A} is parallel to \mathbf{k} then the normal mode is said to be longitudinal. If the two vectors are perpendicular then it is said to be transverse. There are one longitudinal and two transverse modes for each wave vector. From the result of (a), using the dispersion relations $\omega = v_L k$ and $v_T k$ for longitudinal and transverse sound waves, derive Eq. (4.27) for the frequency distribution function.

4.10 In the Debye approximation, one demands that the total number of normal modes be equal to the number of coordinates, namely $3N$. A slightly better approximation would be to treat the longitudinal and transverse sound waves separately by demanding that there be N longitudinal vibrations (of velocity v_L) and $2N$ transverse vibrations (of velocity v_T). Using such an approximation, redo the Debye theory to the point of deriving a modified form of Eq. (4.32).

4.11 Show that the probability distribution in the energy, for a classical system, in contact with a reservoir at temperature T , is given by $P(E) = Z(\beta)^{-1} \exp[S^o(E) - \beta E]$.

4.12 A classical system has a Hamiltonian function of the form $H(x, p) = H_o(x, p) + \alpha h(x, p)$. The value of the canonical partition function is then a function of the parameter α . Show that $\langle h \rangle$, the canonical average of the observable $h(x, p)$, is given by

$$\langle h \rangle = -kT \frac{\partial \phi}{\partial \alpha}$$

4.13 Show that the formula in Problem 4.12 also holds for a quantum mechanical system, where H_o and h are Hermitian operators. (Warning: This problem requires a knowledge of first-order quantum mechanical perturbation theory.)

4.14 Calculate the partition function $Z(\beta)$ for a system of K noninteracting, quantum harmonic oscillators of angular frequency ω , and use your result to calculate the specific heat of such a system.

4.15 In Fig. 4.11 is shown the “surface” or upper boundary of a two-dimensional square crystal. In this *solid-on-solid* model, we assume that there are no overhangs (filled lattice sites that lie above empty ones). The configuration of the surface can then be defined by N integer height variables y_1, y_2, \dots, y_N . (In the figure, $y_1 = 0$ and $y_2 = -1$.) The surface energy is assumed to be proportional to the length of the surface. If we assign zero energy to the straight surface, then $E = \varepsilon \sum_{n=1}^N |y_n - y_{n-1}|$, where $y_o = 0$. The canonical partition function for the system is

$$Z(N, \beta) = \sum_{y_1} \cdots \sum_{y_N} \exp\left(-\beta \varepsilon \sum |y_n - y_{n-1}|\right)$$

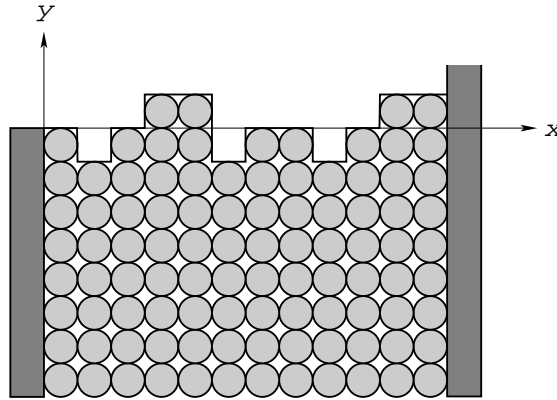


Fig. 4.11

(a) By a transformation of variables, $u_n = y_n - y_{n-1}$, evaluate $Z(N, \beta)$. (b) Determine the probability distribution for the “step height” u_n . It should be independent of n . (c) Using the central limit theorem, determine the probability distribution for the coordinate of the last step, y_N .

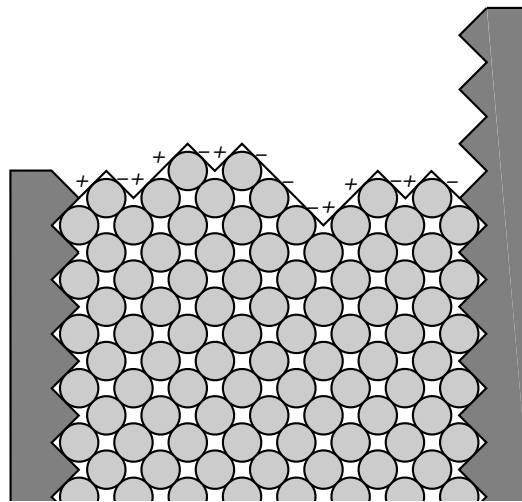


Fig. 4.12

4.16 Another model of the surface of a two-dimensional crystal is shown in Fig. 4.12. A configuration of the surface can be described by a sequence of N variables $\sigma_1, \dots, \sigma_N$ that take the values $\sigma = \pm 1$ according to the scheme shown in the figure. The y coordinate of the right-hand end (in appropriate units) is $y = \sum \sigma_n$. If there is an interaction between the crystal particles and the right-hand wall, then it is reasonable to assume that the energy is given by $E = \varepsilon y$, where $\varepsilon < 0$ for an attractive interaction and $\varepsilon > 0$ for a repulsive one. (a) Calculate the canonical potential, ϕ , as a function of N , β , and ε . (b) Show that $\langle y \rangle = \partial \phi / \partial \varepsilon$ and calculate $\langle y \rangle$ as a function of N , β , and ε .

4.17 The Riemann zeta function is defined as the sum of the infinite series

$$\zeta(K) = \sum_{n=1}^{\infty} n^{-K}$$

Using the identities $e^x - 1 = e^x(1 - e^{-x})$ and $(1 - x)^{-1} = \sum x^n$ derive the formula, given in the Table of Integrals, for $\int x^n dx / (e^x - 1)$.

4.18 Consider an isolated classical system composed of a large reservoir and a small but macroscopic sample. The Hamiltonian for the total system is $H_T(x, p, X, P) = H(x, p) + H_R(X, P)$. Using a microcanonical ensemble to describe the system, derive Eq. (4.52) for the probability distribution of the sample.

4.19 The rotational partition function of a diatomic molecule calculated by classical mechanics is $z(\text{rot}) = 2I/\beta\hbar^2$. Calculated quantum mechanically, $z(\text{rot})$ is given by the following sum over rotational states

$$z(\text{rot}) = \sum_{\ell} g_{\ell} \exp(-\beta\epsilon_{\ell})$$

where $g_{\ell} = (2\ell + 1)$ is the degeneracy of the rotational state of angular momentum $\sqrt{\ell(\ell + 1)}\hbar$ and $\epsilon_{\ell} = \ell(\ell + 1)\hbar^2/2I$. (a) Show that, if the quantum mechanical sum is approximated by an integral over a continuous ℓ variable, the classical value is obtained. This procedure would be valid for small values of $\beta\hbar^2/2I$ ($kT \gg \hbar^2/2I$). (b) Evaluate the sum numerically for $\beta\hbar^2/2I = 1, 0.5,$ and 0.1 and compare your result with the classical approximation.

4.20 For a homonuclear diatomic molecule, the rotational wave function must be even or odd under interchange of the nuclei; that is, $\psi(\mathbf{R}_A, \mathbf{R}_B) = \pm\psi(\mathbf{R}_B, \mathbf{R}_A)$. If nucleus A (which is identical with nucleus B) is composed of an even number of fermions (protons and neutrons), then the nucleus is a Bose–Einstein particle and the $+$ sign holds; in the other case, the nucleus is a Fermi–Dirac particle and the $-$ sign holds. For the case of a BE homonuclear diatomic molecule, because of the symmetry of the wave function, the angular momentum quantum number ℓ must be even. Therefore, the sum in Problem 4.19 is over $\ell = 0, 2, 4, \dots$ (Actually, for homonuclear molecules, even the nuclear spin gets into the game. Exchanging the coordinates of the nuclei means also exchanging the nuclear spins. This adds another complication. The reader can now see why we avoided this case. For this problem, assume that the nucleus has a spin of zero, in which case the nuclei can be treated like point particles.) Do Problem 4.19(a) for the case of a BE homonuclear diatomic molecule and show that, when $kT \gg \hbar^2/2I$, $z(\text{rot}) \approx I/\beta\hbar^2$, which is exactly half the result for heteronuclear molecules.

4.21 Using the experimental data shown in Fig. 4.7, determine the permanent dipole moments of methane (CH_4) and methyl chloride (CH_3Cl). Note that the density in the figure is given in moles/ m^3 .

4.22 Using the experimental data shown in Fig. 4.13, determine the permanent dipole moments of ammonia (NH_3) and sulfur dioxide (SO_2).

4.23 Using the Hamiltonian given in Eq. (4.70), calculate $z(\text{rot})$ for a dipolar molecule in an electric field.

4.24 Expand the energy for a dipolar gas in an electric field, given in Eq. (4.72), to first order in T to obtain a low-temperature approximation for the specific heat per particle.

4.25 A long polymer under tension τ is made up of N monomers that can each be in a compact or an elongated state. Thus the polymer has 2^N possible states. Assume that the length of the polymer is $L = N_c\ell_c + N_e\ell_e$, where $\ell_e > \ell_c$ and N_c and N_e are the numbers of compact and elongated monomers, respectively. Take the energy as $E = \tau(N\ell_e - L)$ and calculate the average length as a function of T and τ .

4.26 A weight W hangs on a chain of N links, each of length ℓ and negligible weight (see Fig. 4.14). Each link can rotate freely from $-\pi$ to π , but only in the plane of the paper. The energy of the system is given in terms of its configuration by $E = -W\ell \sum_{n=1}^N \cos\theta_n$. Ignore any kinetic energy and calculate the canonical potential of the system by integrating $e^{-\beta E}$ over all the possible configurations. You will need the integral, $\int_{-\pi}^{\pi} e^{z \cos\theta} d\theta = 2\pi I_0(z)$, where $I_0(z)$ is a modified Bessel function. Using the asymptotic form of the Bessel function $I_0(z) \sim e^z/\sqrt{2\pi z}$ valid for $z \gg 1$, determine the average energy of the system when $kT \ll W\ell$ and show that it agrees with the prediction of the equipartition theorem.

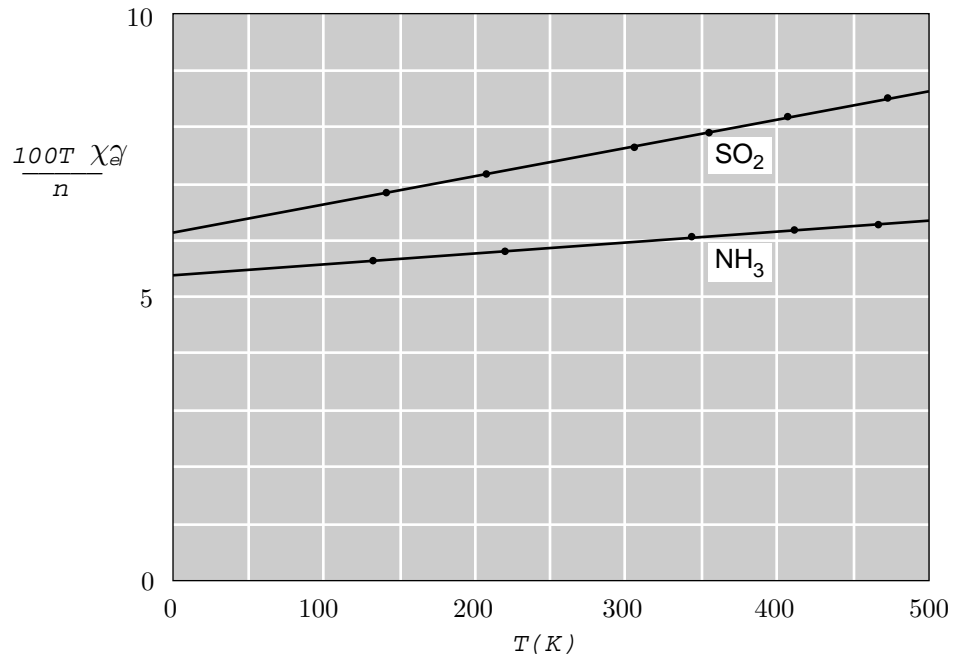


Fig. 4.13 Values of $100T\chi_e/n$, where n is the particle density in moles/ m^3 for NH_3 and SO_2 .

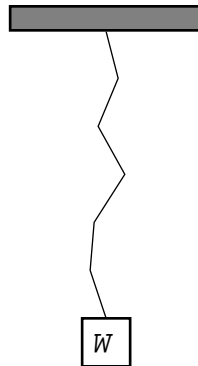


Fig. 4.14