(c) How large is the fractional error in the entropy when you ignore this factor?

6. *Integrated deviation.* For the example that gave the result (17), calculate approximately the probability that the fractional deviation from equilibrium δ/N_1 is 10^{-10} or larger. Take $N_1 = N_2 = 10^{22}$. You will find it convenient to use an asymptotic expansion for the complementary error function. When $x \gg 1$,

$$2x\exp(x^2)\int_x^\infty \exp(-t^2)\,dt \approx 1 + \text{small terms.}$$

Chapter 3

Boltzmann Distribution and Helmholtz Free Energy

Units: Thermodynamic results can easily be translated from fundamental units to conventional units. The only quantity that will cause difficulty is the heat capacity, defined below in (17a) as $C(\text{fund.}) \equiv t(\partial a/\partial t)$ in fundamental units and as $C(\text{conv.}) = T(\partial S/\partial T)$ in conventional units. These two quantities are not equal, for $C(\text{conv.}) = k_B C(\text{fund.})$.

The laws of thermodynamics may easily be obtained from the principles of statistical mechanics, of which they are the incomplete expression.

Gibbs

We are able to distinguish in mechanical terms the thermal action of one system on another from that which we call mechanical in the narrower sense . . . so as to specify cases of thermal action and cases of mechanical action.

Gibbs

In this chapter we develop the principles that permit us to calculate the values of the physical properties of a system as a function of the temperature. We assume that the system $\mathcal{S}$ of interest to us is in thermal equilibrium with a very large system $\mathcal{R}$, called the reservoir. The system and the reservoir will have a common temperature τ because they are in thermal contact.

The total system $\mathcal{R} + \mathcal{S}$ is a closed system, insulated from all external influences, as in Figure 3.1. The total energy $U_0 = U_{\mathcal{R}} + U_{\mathcal{S}}$ is constant. In particular, if the system is in a state of energy ε_s, then $U_0 - \varepsilon_s$ is the energy of the reservoir.
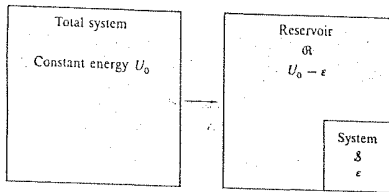

Figure 3.1 Representation of a closed total system decomposed into a reservoir $\mathcal{R}$ in thermal contact with a system $\mathcal{S}$.

BOLTZMANN FACTOR

A central problem of thermal physics is to find the probability that the system $\mathcal{S}$ will be in a specific quantum state s of energy ε_s. This probability is proportional to the Boltzmann factor.

When we specify that $\mathcal{S}$ should be in the state s, the number of accessible states of the total system is reduced to the number of accessible states of the reservoir $\mathcal{R}$, at the appropriate energy. That is, the number $g_{\mathcal{R}+\mathcal{S}}$ of states
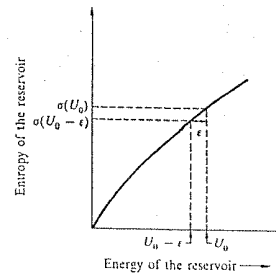
Figure 3.2 The change of entropy when the reservoir transfers energy ε to the system. The fractional effect of the transfer on the reservoir is small when the reservoir is large, because a large reservoir will have a high entropy.

accessible to $\mathcal{R} + \mathcal{S}$ is

$$g_{\mathcal{R}} \times 1 = g_{\mathcal{R}} , \qquad (1)$$

because for our present purposes we have specified the state of $\mathcal{S}$.

If the system energy is ε_s, the reservoir energy is $U_0 - \varepsilon_s$. The number of states accessible to the reservoir in this condition is $g_{\mathcal{R}}(U_0 - \varepsilon_s)$, as in Figure 3.2. The ratio of the probability that the system is in quantum state 1 at energy ε_1 to the probability that the system is in quantum state 2 at energy ε_2 is the ratio of the two multiplicities:

$$\frac{P(\varepsilon_1)}{P(\varepsilon_2)} = \frac{\text{Multiplicity of } \mathcal{R} \text{ at energy } U_0 - \varepsilon_1}{\text{Multiplicity of } \mathcal{R} \text{ at energy } U_0 - \varepsilon_2} = \frac{g_{\mathcal{R}}(U_0 - \varepsilon_1)}{g_{\mathcal{R}}(U_0 - \varepsilon_2)}. \qquad (2)$$

This result is a direct consequence of what we have called the fundamental assumption. The two situations are shown in Figure 3.3. Although questions about the system depend on the constitution of the reservoir, we shall see that the dependence is only on the temperature of the reservoir.

If the reservoirs are very large, the multiplicities are very, very large numbers. We write (2) in terms of the entropy of the reservoir:

$$\frac{P(\varepsilon_1)}{P(\varepsilon_2)} = \frac{\exp[\sigma_{\mathcal{R}}(U_0 - \varepsilon_1)]}{\exp[\sigma_{\mathcal{R}}(U_0 - \varepsilon_2)]} = \exp[\sigma_{\mathcal{R}}(U_0 - \varepsilon_1) - \sigma_{\mathcal{R}}(U_0 - \varepsilon_2)]. \qquad (3)$$
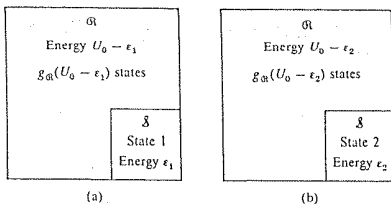
Figure 3.3 The system in (a), (b) is in quantum state 1, 2. The reservoir has $g_{\Re}(U_0 - \varepsilon_1)$, $g_{\Re}(U_0 - \varepsilon_2)$ accessible quantum states, in (a) and (b) respectively.

With

$$\Delta\sigma_{\Re} \equiv \sigma_{\Re}(U_0 - \varepsilon_1) - \sigma_{\Re}(U_0 - \varepsilon_2) , \qquad (4)$$

the probability ratio for the two states 1, 2 of the system is simply

$$\frac{P(\varepsilon_1)}{P(\varepsilon_2)} = \exp(\Delta\sigma_{\Re}). \qquad (5)$$

Let us expand the entropies in (4) in a Taylor series expansion about $\sigma_{\Re}(U_0)$. The Taylor series expansion of $f(x)$ about $f(x_0)$ is

$$f(x_0 + a) = f(x_0) + a\left(\frac{df}{dx}\right)_{x=x_0} + \frac{1}{2!}a^2\left(\frac{d^2f}{dx^2}\right)_{x=x_0} + \cdots . \qquad (6)$$

Thus

$$\sigma \ (U_0 - \varepsilon) = \sigma_{\Re}(U_0) - \varepsilon(\partial\sigma_{\Re}/\partial U)_{V,N} + \cdots$$
$$= \sigma_{\Re}(U_0) - \varepsilon/\tau + \cdots , \qquad (7)$$

where $1/\tau \equiv (\partial\sigma_{\Re}/\partial U)_{V,N}$ gives the temperature. The partial derivative is taken

at energy U_0. The higher order terms in the expansion vanish in the limit of an infinitely large reservoir.*

Therefore $\Delta\sigma_{\Re}$ defined by (4) becomes

$$\Delta\sigma_{\Re} = -(\varepsilon_1 - \varepsilon_2)/\tau. \qquad (8)$$

The final result of (5) and (8) is

$$\boxed{\frac{P(\varepsilon_1)}{P(\varepsilon_2)} = \frac{\exp(-\varepsilon_1/\tau)}{\exp(-\varepsilon_2/\tau)}.} \qquad (9)$$

A term of the form $\exp(-\varepsilon/\tau)$ is known as a **Boltzmann factor**. This result is of vast utility. It gives the ratio of the probability of finding the system in a single quantum state 1 to the probability of finding the system in a single quantum state 2.

Partition Function

It is helpful to consider the function

$$Z(\tau) = \sum_s \exp(-\varepsilon_s/\tau) , \qquad (10)$$

called the **partition function**. The summation is over the Boltzmann factor $\exp(-\varepsilon_s/\tau)$ for all states s of the system. The partition function is the proportionality factor between the probability $P(\varepsilon_s)$ and the Boltzmann factor $\exp(-\varepsilon_s/\tau)$:

$$P(\varepsilon_s) = \frac{\exp(-\varepsilon_s/\tau)}{Z}. \qquad (11)$$

We see that $\sum P(\varepsilon_s) = Z/Z = 1$: the sum of all probabilities is unity.

The result (11) is one of the most useful results of statistical physics. The average energy of the system is $U = \langle\varepsilon\rangle = \sum \varepsilon_s P(\varepsilon_s)$, or

$$U = \frac{\sum_s \varepsilon_s \exp(-\varepsilon_s/\tau)}{Z} = \tau^2(\partial \log Z/\partial\tau). \qquad (12)$$

* We expand $\sigma(U_0 - \varepsilon)$ and not $g(U_0 - \varepsilon)$ because the expansion of the latter quantity immediately gives convergence difficulties.
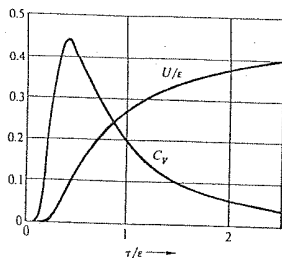
Figure 3.4 Energy and heat capacity of a two state system as functions of the temperature τ. The energy is plotted in units of ε.

The average energy refers to those states of a system that can exchange energy with a reservoir. The notation $\langle \cdots \rangle$ denotes such an average value and is called the thermal average or ensemble average. In (12) the symbol U is used for $\langle \varepsilon \rangle$ in conformity with common practice; U will now refer to the system and not, as earlier, to the system + reservoir.

Example: Energy and heat capacity of a two state system. We treat a system of one particle with two states, one of energy 0 and one of energy ε. The particle is in thermal contact with a reservoir at temperature τ. We want to find the energy and the heat capacity of the system as a function of the temperature τ. The partition function for the two states of the particle is

$$Z = \exp(-0/\tau) + \exp(-\varepsilon/\tau) = 1 + \exp(-\varepsilon/\tau). \tag{13}$$

The average energy is

$$U \equiv \langle \varepsilon \rangle = \frac{\varepsilon \exp(-\varepsilon/\tau)}{Z} = \varepsilon \frac{\exp(-\varepsilon/\tau)}{1 + \exp(-\varepsilon/\tau)}. \tag{14}$$

This function is plotted in Figure 3.4.

If we shift the zero of energy and take the energies of the two states as $-\tfrac{1}{2}\varepsilon$ and $+\tfrac{1}{2}\varepsilon$, instead of as 0 and ε, the results appear differently. We have

$$Z = \exp(\varepsilon/2\tau) + \exp(-\varepsilon/2\tau) = 2\cosh(\varepsilon/2\tau) , \tag{15}$$

and

$$\langle \varepsilon \rangle = \frac{(-\tfrac{1}{2}\varepsilon)\exp(\varepsilon/2\tau) + (\tfrac{1}{2}\varepsilon)\exp(-\varepsilon/2\tau)}{Z} = -\varepsilon \frac{\sinh(\varepsilon/2\tau)}{2\cosh(\varepsilon/2\tau)}$$

$$= -\tfrac{1}{2}\varepsilon \tanh(\varepsilon/2\tau). \tag{16}$$

The heat capacity C_V of a system at constant volume is defined as

$$C_V \equiv \tau(\partial\sigma/\partial\tau)_V , \tag{17a}$$

which by the thermodynamic identity (34a) derived below is equivalent to the alternate definition

$$C_V \equiv (\partial U/\partial\tau)_V. \tag{17b}$$

We hold V constant because the values of the energy are calculated for a system at a specified volume. From (14) and (17b),

$$C_V = \varepsilon \frac{\partial}{\partial\tau} \frac{1}{\exp(\varepsilon/\tau) + 1} = \left(\frac{\varepsilon}{\tau}\right)^2 \frac{\exp(\varepsilon/\tau)}{[\exp(\varepsilon/\tau) + 1]^2}. \tag{18a}$$

The same result follows from (16).

In conventional units C_V is defined as $T(\partial S/\partial T)_V$ or $(\partial U/\partial T)_V$, whence

$$\text{(conventional)} \qquad C_V = k_B\left(\frac{\varepsilon}{k_B T}\right)^2 \frac{\exp(\varepsilon/k_B T)}{[\exp(\varepsilon/k_B T) + 1]^2}. \tag{18b}$$

In fundamental units the heat capacity is dimensionless; in conventional units it has the dimensions of energy per kelvin. The specific heat is defined as the heat capacity per unit mass.

The hump in the plot of heat capacity versus temperature in Figure 3.4 is called a Schottky anomaly. For $\tau \gg \varepsilon$ the heat capacity (18a) becomes

$$C_V \simeq (\varepsilon/2\tau)^2. \tag{19}$$

Notice that $C_V \propto \tau^{-2}$ in this high temperature limit. In the low temperature limit the temperature is small in comparison with the energy level spacing ε. For $\tau \ll \varepsilon$ we have

$$C_V \simeq (\varepsilon/\tau)^2 \exp(-\varepsilon/\tau). \tag{20}$$

The exponential factor $\exp(-\varepsilon/\tau)$ reduces C_V rapidly as τ decreases, because $\exp(-1/x) \to 0$ as $x \to 0$.

Definition: Reversible process. A process is reversible if carried out in such a way that the system is always infinitesimally close to the equilibrium condition. For example, if the entropy is a function of the volume, any change of volume must be carried out so slowly that the entropy at any volume V is closely equal to the equilibrium entropy $\sigma(V)$. Thus, the entropy is well defined at every stage of a reversible process, and by reversing the direction of the change the system will be returned to its initial condition. In reversible processes, the condition of the system is well defined at all times, in contrast to irreversible processes, where usually we will not know what is going on during the process. We cannot apply the mathematical methods of thermal physics to systems whose condition is undefined.

A volume change that leaves the system in the same quantum state is an example of an isentropic reversible process. If the system always remains in the same state the entropy change will be zero between any two stages of the process, because the number of states in an ensemble (p. 31) of similar systems does not change. Any process in which the entropy change vanishes is an isentropic reversible process. But reversible processes are not limited to isentropic processes, and we shall have a special interest also in isothermal reversible processes.

PRESSURE

Consider a system in the quantum state s of energy ε_s. We assume ε_s to be a function of the volume of the system. The volume is decreased slowly from V to $V - \Delta V$ by application of an external force. Let the volume change take place sufficiently slowly that the system remains in the same quantum state s throughout the compression. The "same" state may be characterized by its quantum numbers (Figure 3.5) or by the number of zeros in the wavefunction.

The energy of the state s after the reversible volume change is

$$\varepsilon_s(V - \Delta V) = \varepsilon_s(V) - (d\varepsilon_s/dV)\Delta V + \cdots. \tag{21}$$

Consider a pressure p_s applied normal to all faces of a cube. The mechanical work done on the system by the pressure in a contraction (Figure 3.6) of the cube volume from V to $V - \Delta V$ appears as the change of energy of the system:

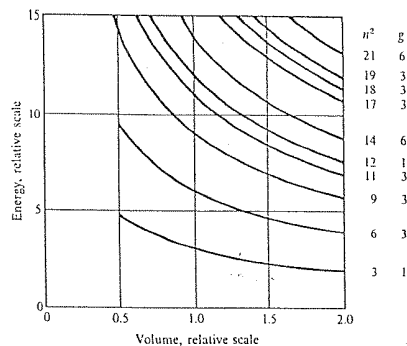$$U(V - \Delta V) - U(V) = \Delta U = -(d\varepsilon_s/dV)\Delta V. \tag{22}$$

Figure 3.5 Dependence of energy on volume, for the energy levels of a free particle confined to a cube. The curves are labeled by $n^2 = n_x^2 + n_y^2 + n_z^2$, as in Figure 1.2. The multiplicities g are also given. The volume change here is isotropic: a cube remains a cube. The energy range $\delta\varepsilon$ of the states represented in an ensemble of systems will increase in a reversible compression, but we know from the discussion in Chapter 2 that the width of the energy range itself is of no practical importance. It is the change in the average energy that is important.
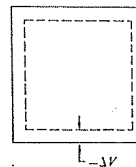

Figure 3.6 Volume change $-\Delta V$ in uniform compression of a cube.

Here U denotes the energy of the system. Let A be the area of one face of the cube; then

$$A(\Delta x + \Delta y + \Delta z) = \Delta V , \tag{23}$$

if all increments ΔV and $\Delta x = \Delta y = \Delta z$ are taken as positive in the compression. The work done in the compression is

$$\Delta U = p_s A(\Delta x + \Delta y + \Delta z) = p_s \Delta V , \tag{24}$$

so that, on comparison with (22),

$$p_s = -d\varepsilon_s/dV \tag{25}$$

is the pressure on a system in the state s.

We average (25) over all states of the ensemble to obtain the average pressure $\langle p \rangle$, usually written as p:

$$\boxed{p = -\left(\frac{\partial U}{\partial V}\right)_\sigma ,} \tag{26}$$

where $U \equiv \langle \varepsilon \rangle$. The entropy σ is held constant in the derivative because the number of states in the ensemble is unchanged in the reversible compression we have described. We have a collection of systems, each in some state, and each remains in this state in the compression.

The result (26) corresponds to our mechanical picture of the pressure on a system that is maintained in some specific state. Appendix D discusses the result more deeply. For applications we shall need also the later result (50) for the pressure on a system maintained at constant temperature.

We look for other expressions for the pressure. The number of states and thus the entropy depend only on U and on V, for a fixed number of particles, so that only the two variables U and V describe the system. The differential of the entropy is

$$d\sigma(U,V) = \left(\frac{\partial \sigma}{\partial U}\right)_V dU + \left(\frac{\partial \sigma}{\partial V}\right)_U dV. \tag{27}$$

This gives the differential change of the entropy for arbitrary independent differential changes dU and dV. Assume now that we select dU and dV interdependently, in such a way that the two terms on the right-hand side of (27)

cancel. The overall entropy change $d\sigma$ will be zero. If we denote these interdependent values of dU and dV by $(\delta U)_\sigma$ and $(\delta V)_\sigma$, the entropy change will be zero:

$$0 = \left(\frac{\partial \sigma}{\partial U}\right)_V (\delta U)_\sigma + \left(\frac{\partial \sigma}{\partial V}\right)_U (\delta V)_\sigma. \tag{28}$$

After division by $(\delta V)_\sigma$,

$$0 = \left(\frac{\partial \sigma}{\partial U}\right)_V \frac{(\delta U)_\sigma}{(\delta V)_\sigma} + \left(\frac{\partial \sigma}{\partial V}\right)_U. \tag{29}$$

But the ratio $(\delta U)_\sigma/(\delta V)_\sigma$ is the partial derivative of U with respect to V at constant σ:

$$(\delta U)_\sigma/(\delta V)_\sigma \equiv (\partial U/\partial V)_\sigma. \tag{30}$$

With this and the definition $1/\tau \equiv (\partial \sigma/\partial U)_V$, Eq. (29) becomes

$$\left(\frac{\partial U}{\partial V}\right)_\sigma = -\tau\left(\frac{\partial \sigma}{\partial V}\right)_U. \tag{31}$$

By (26) the left-hand side of (31) is equal to $-p$, whence

$$\boxed{p = \tau\left(\frac{\partial \sigma}{\partial V}\right)_U.} \tag{32}$$

Thermodynamic Identity

Consider again the differential (27) of the entropy; substitute the new result for the pressure and the definition of τ to obtain

$$d\sigma = \frac{1}{\tau} dU + \frac{p}{\tau} dV , \tag{33}$$

or

$$\boxed{\tau d\sigma = dU + p dV.} \tag{34a}$$

This useful relation will be called the thermodynamic identity. The form with N variable will appear in (5.38). A simple transposition gives

$$dU = \tau d\sigma - p dV, \quad \text{or} \quad dU = T dS - p dV. \tag{34b}$$

If the actual process of change of state of the system is reversible, we can identify $\tau d\sigma$ as the heat added to the system and $-p dV$ as the work done on the system. The increase of energy is caused in part by mechanical work and in part by the transfer of heat. Heat is defined as the transfer of energy between two systems brought into thermal contact (Chapter 8).

HELMHOLTZ FREE ENERGY

The function

$$\boxed{F \equiv U - \tau\sigma} \tag{35}$$

is called the Helmholtz free energy. This function plays the part in thermal physics at constant temperature that the energy U plays in ordinary mechanical processes, which are always understood to be at constant entropy, because no internal changes of state are allowed. The free energy tells us how to balance the conflicting demands of a system for minimum energy and maximum entropy. The Helmholtz free energy will be a minimum for a system $\mathscr{S}$ in thermal contact with a reservoir $\mathcal{R}$, if the volume of the system is constant.

We first show that F is an extremum in equilibrium at constant τ and V. By definition, for infinitesimal reversible transfer from $\mathcal{R}$ to $\mathscr{S}$,

$$dF_{\mathscr{S}} = dU_{\mathscr{S}} - \tau d\sigma_{\mathscr{S}} \tag{36}$$

at constant temperature. But $1/\tau = (\partial\sigma_{\mathscr{S}}/\partial U_{\mathscr{S}})_V$, so that $dU_{\mathscr{S}} = \tau d\sigma$ at constant volume. Therefore (36) becomes

$$dF_{\mathscr{S}} = 0 , \tag{37}$$

which is the condition for F to be an extremum with respect to all variations at constant volume and temperature. We like F because we can calculate it from the energy eigenvalues ε_s of the system (see p. 72).

Comment. We can show that the extremum is a minimum. The total energy is $U = U_{\mathcal{R}} + U_{\mathscr{S}}$. Then the total entropy is

$$\sigma = \sigma_{\mathcal{R}} + \sigma_{\mathscr{S}} = \sigma_{\mathcal{R}}(U - U_{\mathscr{S}}) + \sigma_{\mathscr{S}}(U_{\mathscr{S}})$$
$$\simeq \sigma_{\mathcal{R}}(U) - U_{\mathscr{S}}(\partial\sigma_{\mathcal{R}}/\partial U_{\mathcal{R}})_{V,N} + \sigma_{\mathscr{S}}(U_{\mathscr{S}}). \tag{38}$$

We know that

$$(\partial\sigma_{\mathcal{R}}/\partial U_{\mathcal{R}})_{V,N} \equiv 1/\tau , \tag{39}$$

so that (38) becomes

$$\sigma = \sigma_{\mathcal{R}}(U) - F_{\mathscr{S}}/\tau , \tag{40}$$

where $F_{\mathscr{S}} = U_{\mathscr{S}} - \tau\sigma_{\mathscr{S}}$ is the free energy of the system. Now $\sigma_{\mathcal{R}}(U)$ is constant; and we recall that $\sigma = \sigma_{\mathcal{R}} + \sigma_{\mathscr{S}}$ in equilibrium is a maximum with respect to $U_{\mathscr{S}}$. It follows from (40) that $F_{\mathscr{S}}$ must be a minimum with respect to $U_{\mathscr{S}}$ when the system is in the most probable configuration. The free energy of the system at constant τ, V will increase for any departure from the equilibrium configuration.

Example: Minimum property of the free energy of a paramagnetic system. Consider the model system of Chapter 1, with $N_\uparrow$ spins up and $N_\downarrow$ spins down. Let $N = N_\uparrow + N_\downarrow$; the spin excess is $2s = N_\uparrow - N_\downarrow$. The entropy in the Stirling approximation is found with the help of an approximate form of (1.31):

$$\sigma(s) \simeq -\left(\frac{1}{2}N + s\right)\log\left(\frac{1}{2} + \frac{s}{N}\right) - \left(\frac{1}{2}N - s\right)\log\left(\frac{1}{2} - \frac{s}{N}\right). \tag{41}$$

The energy in a magnetic field B is $-2smB$, where m is the magnetic moment of an elementary magnet. The free energy function (to be called the Landau function in Chapter 10) is $F_L(\tau,s,B) \equiv U(s,B) - \tau\sigma(s)$, or

$$F_L(\tau,s,B) = -2smB + \left(\frac{1}{2}N + s\right)\tau\log\left(\frac{1}{2} + \frac{s}{N}\right) + \left(\frac{1}{2}N - s\right)\tau\log\left(\frac{1}{2} - \frac{s}{N}\right). \tag{42}$$

At the minimum of $F_L(\tau,s,B)$ with respect to s, this function becomes equal to the equilibrium free energy $F(\tau,B)$. That is, $F_L(\tau,\langle s\rangle,B) = F(\tau,B)$, because $\langle s\rangle$ is a function of τ and B. The minimum of F_L with respect to the spin excess occurs when

$$(\partial F_L/\partial s)_{\tau,B} = 0 = -2mB + \tau\log\frac{N + 2s}{N - 2s}. \tag{43}$$

Thus in the magnetic field B the thermal equilibrium value of the spin excess $2s$ is given by

$$\frac{N + \langle 2s \rangle}{N - \langle 2s \rangle} = \exp(2mB/\tau); \qquad \langle 2s \rangle = N\left(\frac{\exp(2mB/\tau) - 1}{\exp(2mB/\tau) + 1}\right), \qquad (44)$$

or, on dividing numerator and denominator by $\exp(mB/\tau)$,

$$\langle 2s \rangle = N \tanh(mB/\tau). \qquad (45)$$

The magnetization M is the magnetic moment per unit volume. If n is the number of spins per unit volume, the magnetization in thermal equilibrium in the magnetic field is

$$M = \langle 2s \rangle m/V = nm \tanh(mB/\tau). \qquad (46)$$

The free energy of the system in equilibrium can be obtained by substituting (45) in (42). It is easier, however, to obtain F directly from the partition function for one magnet:

$$Z = \exp(mB/\tau) + \exp(-mB/\tau) = 2\cosh(mB/\tau). \qquad (47)$$

Now use the relation $F = -\tau \log Z$ as derived below. Multiply by N to obtain the result for N magnets. (The magnetization is derived more simply by the method of Problem 2.)

Differential Relations

The differential of F is

$$dF = dU - \tau d\sigma - \sigma d\tau ,$$

or, with use of the thermodynamic identity (34a),

$$dF = -\sigma d\tau - p dV , \qquad (48)$$

for which

$$\boxed{\left(\frac{\partial F}{\partial \tau}\right)_V = -\sigma; \qquad \left(\frac{\partial F}{\partial V}\right)_\tau = -p.} \qquad (49)$$

These relations are widely used.

The free energy F in the result $p = -(\partial F/\partial V)_\tau$ acts as the effective energy for an *isothermal* change of volume; contrast this result with (26). The result

may be written as

$$p = -\left(\frac{\partial U}{\partial V}\right)_\tau + \tau\left(\frac{\partial \sigma}{\partial V}\right)_\tau , \qquad (50)$$

by use of $F \equiv U - \tau\sigma$. The two terms on the right-hand side of (50) represent what we may call the energy pressure and the entropy pressure. The energy pressure $-(\partial U/\partial V)_\tau$ is dominant in most solids and the entropy pressure $\tau(\partial\sigma/\partial V)_\tau$ is dominant in gases and in elastic polymers such as rubber (Problem 10). The entropy contribution is testimony of the importance of the entropy: the naive feeling from simple mechanics that $-dU/dV$ must tell everything about the pressure is seriously incomplete for a process at constant temperature, because the entropy can change in response to the volume change even if the energy is independent of volume, as for an ideal gas at constant temperature.

Maxwell relation. We can now derive one of a group of useful thermodynamic relations called Maxwell relations. Form the cross-derivatives $\partial^2 F/\partial V \partial\tau$ and $\partial^2 F/\partial\tau \partial V$, which must be equal to each other. It follows from (49) that

$$(\partial\sigma/\partial V)_\tau = (\partial p/\partial\tau)_V , \qquad (51)$$

a relation that is not at all obvious. Other Maxwell relations will be derived later at appropriate points, by similar arguments. The methodology of obtaining thermodynamic relations is discussed by R. Gilmore, J. Chem. Phys. 75, 5964 (1981).

Calculation of F from Z

Because $F \equiv U - \tau\sigma$ and $\sigma = -(\partial F/\partial\tau)_V$, we have the differential equation

$$F = U + \tau(\partial F/\partial\tau)_V, \qquad \text{or} \qquad -\tau^2\partial(F/\tau)/\partial\tau = U. \qquad (52)$$

We show that this equation is satisfied by

$$F/\tau = -\log Z , \qquad (53)$$

where Z is the partition function. On substitution,

$$\partial(F/\tau)/\partial\tau = -\partial\log Z/\partial\tau = -U/\tau^2 \qquad (54)$$

by (12). This proves that

$$\boxed{F = -\tau \log Z}\tag{55}$$

satisfies the required differential equation (52).

It would appear possible for F/τ to contain an additive constant α such that $F = -\tau \log Z + \alpha\tau$. However, the entropy must reduce to $\log g_0$ when the temperature is so low that only the g_0 coincident states at the lowest energy ε_0 are occupied. In that limit $\log Z \to \log g_0 - \varepsilon_0/\tau$, so that $\sigma = -\partial F/\partial\tau \to \partial(\tau \log Z)/\partial\tau = \log g_0$ only if $\alpha = 0$.

We may write the result as

$$Z = \exp(-F/\tau);\tag{56}$$

and the Boltzmann factor (11) for the occupancy probability of a quantum state s becomes

$$P(\varepsilon_s) = \frac{\exp(-\varepsilon_s/\tau)}{Z} = \exp[(F - \varepsilon_s)/\tau].\tag{57}$$

IDEAL GAS: A FIRST LOOK

One atom in a box. We calculate the partition function Z_1 of one atom of mass M free to move in a cubical box of volume $V = L^3$. The orbitals of the free particle wave equation $-(h^2/2M)\nabla^2\psi = \varepsilon\psi$ are

$$\psi(x,y,z) = A \sin(n_x\pi x/L)\sin(n_y\pi y/L)\sin(n_z\pi z/L) ,\tag{58}$$

where n_x, n_y, n_z are any positive integers, as in Chapter 1. Negative integers do not give independent orbitals, and a zero does not give a solution. The energy values are

$$\varepsilon_n = \frac{h^2}{2M}\left(\frac{\pi}{L}\right)^2 (n_x^2 + n_y^2 + n_z^2).\tag{59}$$

We neglect the spin and all other structure of the atom, so that a state of the system is entirely specified by the values of n_x, n_y, n_z.

The partition function is the sum over the states (59):

$$Z_1 = \sum_{n_x}\sum_{n_y}\sum_{n_z} \exp[-h^2\pi^2(n_x^2 + n_y^2 + n_z^2)/2ML^2\tau].\tag{60}$$

Provided the spacing of adjacent energy values is small in comparison with τ, we may replace the summations by integrations:

$$Z_1 = \int_0^\infty dn_x \int_0^\infty dn_y \int_0^\infty dn_z \exp[-\alpha^2(n_x^2 + n_y^2 + n_z^2)].\tag{61}$$

The notation $\alpha^2 \equiv h^2\pi^2/2ML^2\tau$ is introduced for convenience. The exponential may be written as the product of three factors

$$\exp(-\alpha^2 n_x^2)\exp(-\alpha^2 n_y^2)\exp(-\alpha^2 n_z^2) ,$$

so that

$$Z_1 = \left(\int_0^\infty dn_x \exp(-\alpha^2 n_x^2)\right)^3 = (1/\alpha)^3\left(\int_0^\infty dx \exp(-x^2)\right)^3 = \pi^{3/2}/8\alpha^3 ,$$

whence

$$Z_1 = \frac{V}{(2\pi h^2/M\tau)^{3/2}} = n_Q V = n_Q/n ,\tag{62}$$

in terms of the concentration $n = 1/V$.

Here

$$\boxed{n_Q \equiv (M\tau/2\pi h^2)^{3/2}}\tag{63}$$

is called the **quantum concentration**. It is the concentration associated with one atom in a cube of side equal to the thermal average de Broglie wavelength, which is a length roughly equal to $h/M\langle v\rangle \sim h/(M\tau)^{1/2}$. Here $\langle v\rangle$ is a thermal average velocity. This concentration will keep turning up in the thermal physics of gases, in semiconductor theory, and in the theory of chemical reactions.

For helium at atmospheric pressure at room temperature, $n \approx 2.5 \times 10^{19}\,\mathrm{cm^{-3}}$ and $n_Q \approx 0.8 \times 10^{25}\,\mathrm{cm^{-3}}$. Thus, $n/n_Q \approx 3 \times 10^{-6}$, which is very

small compared to unity, so that helium is very dilute under normal conditions. Whenever $n/n_Q \ll 1$ we say that the gas is in the classical regime. An ideal gas is defined as a gas of noninteracting atoms in the classical regime.

The thermal average energy of the atom in the box is, as in (12),

$$U = \frac{\sum_n \varepsilon_n \exp(-\varepsilon_n/\tau)}{Z_1} = \tau^2(\partial \log Z_1/\partial\tau) , \tag{64}$$

because $Z_1^{-1}\exp(-\varepsilon_n/\tau)$ is the probability the system is in the state n. From (62),

$$\log Z_1 = -\tfrac{3}{2}\log(1/\tau) + \text{terms independent of } \tau ,$$

so that for an ideal gas of one atom

$$\boxed{U = \tfrac{3}{2}\tau.} \tag{65}$$

If $\tau = k_B T$, where k_B is the Boltzmann constant, then $U = \tfrac{3}{2}k_B T$, the well-known result for the energy per atom of an ideal gas.

The thermal average occupancy of a free particle orbital satisfies the inequality

$$Z_1^{-1}\exp(-\varepsilon_n/\tau) < Z_1^{-1} = n/n_Q ,$$

which sets an upper limit of 4×10^{-6} for the occupancy of an orbital by a helium atom at standard concentration and temperature. For the classical regime to apply, this occupancy must be $\ll 1$. We note that ε_n as defined by (59) is always positive for a free atom.

Example: N atoms in a box. There follows now a tricky argument that we will use temporarily until we develop in Chapter 6 a powerful method to deal with the problem of many noninteracting identical atoms in a box. We first treat an ideal gas of N atoms in a box, all atoms of different species or different isotopes. This is a simple extension of the one atom result. We then discuss the major correction factor that arises when all atoms are identical, of the same isotope of the same species.
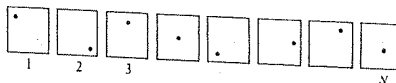
Figure 3.7 An N particle system of free particles with one particle in each of N boxes. The energy is N times that for one particle in one box.

Figure 3.8 Atoms of different species in a single box.

If we have one atom in each of N distinct boxes (Figure 3.7), the partition function is the product of the separate one atom partition functions:

$$Z_{N \text{ boxes}} = Z_1(1) Z_1(2) \cdots Z_1(N) , \tag{66}$$

because the product on the right-hand side includes every independent state of the N boxes, such as the state of energy

$$\varepsilon_\alpha(1) + \varepsilon_\beta(2) + \cdots \varepsilon_\zeta(N) , \tag{67}$$

where $\alpha, \beta, \ldots, \zeta$ denote the orbital indices of atoms in the successive boxes. The result (66) also gives the partition function of N noninteracting atoms all of different species in a single box (Figure 3.8):

$$Z_\alpha(\bullet) Z_\mu(\square) Z_j(\ast) \cdots Z_\zeta(\triangle) ,$$

this being the same problem because the energy eigenvalues are the same as for (67). If the masses of all these different atoms happened to be the same, the total partition function would be Z_1^N, where Z_1 is given by (62).

When we consider the more common problem of N identical particles in one box, we have to correct Z_1^N because it overcounts the distinct states of the N identical particle system. Particles of a single species are not distinguishable: electrons do not carry registration numbers. For two labeled particles $\bullet$ and $\ast$ in a single box, the state $\varepsilon_\alpha(\bullet) + \varepsilon_\beta(\ast)$ and the state $\varepsilon_\alpha(\ast) + \varepsilon_\beta(\bullet)$ are distinct states, and both combinations must be counted in the partition function. But for two identical particles the state of energy $\varepsilon_\alpha + \varepsilon_\beta$ is the identical state as $\varepsilon_\beta + \varepsilon_\alpha$, and only one entry is to be made in the state sum in the partition function.

If the orbital indices are all different, each entry will occur $N!$ times in $Z_1{}^N$, whereas the entry should occur only once if the particles are identical. Thus, $Z_1{}^N$ overcounts the states by a factor of $N!$, and the correct partition function for N identical particles is

$$Z_N = \frac{1}{N!} Z_1{}^N = \frac{1}{N!} (n_Q V)^N \tag{68}$$

in the classical regime. Here $n_Q = (M\tau/2\pi\hbar^2)^{3/2}$ from (63).

There is a step in the argument where we assume that all N occupied orbitals are always different orbitals. It is no simple matter to evaluate directly the error introduced by this approximation, but later we will confirm by another method the validity of (68) in the classical regime $n \ll n_Q$. The $N!$ factor changes the result for the entropy of the ideal gas. The entropy is an experimentally measurable quantity, and it has been confirmed that the $N!$ factor is correct in this low concentration limit.

Energy. The energy of the ideal gas follows from the N particle partition function by use of (12):

$$U = \tau^2(\partial \log Z_N/\partial\tau) = \tfrac{3}{2}N\tau , \tag{69}$$

consistent with (65) for one particle. The free energy is

$$F = -\tau \log Z_N = -\tau \log Z_1{}^N + \tau \log N!. \tag{70}$$

With the earlier result $Z_1 = n_Q V = (M\tau/2\pi\hbar^2)^{3/2}V$ and the Stirling approximation $\log N! \simeq N \log N - N$, we have

$$F = -\tau N \log[(M\tau/2\pi\hbar^2)^{3/2}V] + \tau N \log N - \tau N. \tag{71}$$

From the free energy we can calculate the entropy and the pressure of the ideal gas of N atoms. The pressure follows from (49):

$$p = -(\partial F/\partial V)_\tau = N\tau/V , \tag{72}$$

or

$$pV = N\tau , \tag{73}$$

which is called the ideal gas law. In conventional units,

$$pV = Nk_B T. \tag{74}$$

The entropy follows from (49):

$$\sigma = -(\partial F/\partial\tau)_V = N \log[(M\tau/2\pi\hbar^2)^{3/2}V] + \tfrac{3}{2}N - N\log N + N , \tag{75}$$

or

$$\sigma = N[\log(n_Q/n) + \tfrac{5}{2}] , \tag{76}$$

with the concentration $n \equiv N/V$. This result is known as the Sackur-Tetrode equation for the entropy of a monatomic ideal gas. It agrees with experiment. The result involves $\hbar$ through the term n_Q, so even for the classical ideal gas the entropy involves a quantum concept. We shall derive these results again in Chapter 6 by a direct method that does not explicitly involve the $N!$ or identical particle argument. The energy (69) also follows from $U = F + \tau\sigma$; with use of (71) and (76) we have $U = \tfrac{3}{2}N\tau$.

Example: Equipartition of energy. The energy $U = \tfrac{3}{2}N\tau$ from (69) is ascribed to a contribution $\tfrac{1}{2}\tau$ from each "degree of freedom" of each particle, where the number of degrees of freedom is the number of dimensions of the space in which the atoms move: 3 in this example. In the classical form of statistical mechanics, the partition function contains the kinetic energy of the particles in an integral over the momentum components p_x, p_y, p_z. For one free particle

$$Z_1 \propto \iiint \exp[-(p_x{}^2 + p_y{}^2 + p_z{}^2)/2M\tau]dp_x\,dp_y\,dp_z , \tag{77}$$

a result similar to (61). The limits of integration are $\pm\infty$ for each component. The thermal average energy may be calculated by use of (12) and is equal to $\tfrac{3}{2}\tau$.

The result is generalized in the classical theory. Whenever the hamiltonian of the system is homogeneous of degree 2 in a canonical momentum component, the classical limit of the thermal average kinetic energy associated with that momentum will be $\tfrac{1}{2}\tau$. Further, if the hamiltonian is homogeneous of degree 2 in a position coordinate component, the thermal average potential energy associated with that coordinate will also be $\tfrac{1}{2}\tau$. The result thus
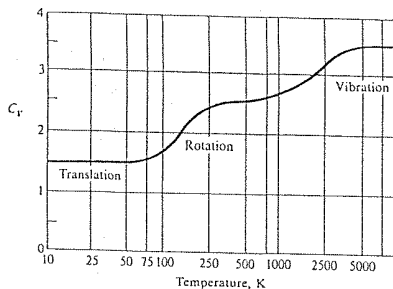
Figure 3.9   Heat capacity at constant volume of one molecule of H_2 in the gas phase. The vertical scale is in fundamental units; to obtain a value in conventional units, multiply by k_B. The contribution from the three translational degrees of freedom is $\frac{3}{2}$; the contribution at high temperatures from the two rotational degrees of freedom is 1; and the contribution from the potential and kinetic energy of the vibrational motion in the high temperature limit is 1. The classical limits are attained when $\tau \gg$ relevant energy level separations.

applies to the harmonic oscillator in the classical limit. The quantum results for the harmonic oscillator and for the diatomic rotator are derived in Problems 3 and 6, respectively. At high temperatures the classical limits are attained, as in Figure 3.9.

Example: Entropy of mixing.   In Chapter 1 we calculated the number of possible arrangements of A and B in a solid made up of $N - t$ atoms A and t atoms B. We found in (1.20) for the number of arrangements:

$$g(N,t) = \frac{N!}{(N - t)!\, t!}.$$ (78)

The entropy associated with these arrangements is

$$\sigma(N,t) = \log g(N,t) = \log N! - \log(N - t)! - \log t!,$$ (79)

and is plotted in Figure 3.10 for $N = 20$. This contribution to the total entropy of an alloy
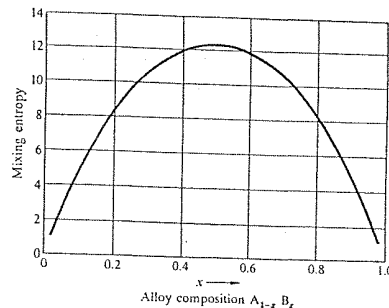
Figure 3.10   Mixing entropy of a random binary alloy as a function of the proportions of the constituent atoms A and B. The curve plotted was calculated for a total of 20 atoms. We see that this entropy is a maximum when A and B are present in equal proportions ($x = 0.5$), and the entropy is zero for pure A or pure B.

system is called the entropy of mixing. The result (79) may be put in a more convenient form by use of the Stirling approximation:

$$\sigma(N,t) \simeq N \log N - N - (N - t)\log(N - t) + N - t - t \log t + t$$
$$= N \log N - (N - t)\log(N - t) - t \log t$$
$$= -(N - t)\log(1 - t/N) - t \log(t/N),$$

or, with $x \equiv t/N$,

$$\sigma(x) = -N[(1 - x)\log(1 - x) + x \log x].$$ (80)

This result gives the entropy of mixing of an alloy $A_{1-x}B_x$ treated as a random (homogeneous) solid solution. The problem is developed in detail in Chapter 11.

We ask: Is the homogeneous solid solution the equilibrium condition of a mixture of A and B atoms, or is the equilibrium a two-phase system, such as a mixture of crystallites of pure A and crystallites of pure B? The complete answer is the basis of much of the science of metallurgy: the answer will depend on the temperature and on the interatomic interaction energies U_{AA}, U_{BB}, and U_{AB}. In the special case that the interaction energies between

AA, BB, and AB neighbor pairs are all equal, the homogeneous solid solution will have a lower free energy than the corresponding mixture of crystallites of the pure elements. The free energy of the solid solution $A_{1-x}B_x$ is

$$F = F_0 - \tau\sigma(x) = F_0 + N\tau[(1-x)\log(1-x) + x\log x] , \quad (81)$$

which we must compare with

$$F = (1-x)F_0 + xF_0 = F_0 \quad (82)$$

for the mixture of A and B crystals in the proportion $(1-x)$ to x. The entropy of mixing is always positive—all entropies are positive—so that the solid solution has the lower free energy in this special case.

There is a tendency for at least a very small proportion of any element B to dissolve in any other element A, even if a strong repulsive energy exists between a B atom and the surrounding A atoms. Let this repulsive energy be denoted by U, a positive quantity. If a very small proportion $x \ll 1$ of B atoms is present, the total repulsive energy is xNU, where xN is the number of B atoms. The mixing entropy (80) is approximately

$$\sigma = -xN\log x \quad (83)$$

in this limit, so that the free energy is

$$F(x) = N(xU + \tau x\log x) , \quad (84)$$

which has a minimum when

$$\partial F/\partial x = N(U + \tau\log x + \tau) = 0 , \quad (85)$$

or

$$x = \exp(-1)\exp(-U/\tau). \quad (86)$$

This shows there is a natural impurity content in all crystals.

SUMMARY

1. The factor

$$P(\varepsilon_s) = \exp(-\varepsilon_s/\tau)/Z$$

is the probability of finding a system in a state s of energy ε_s, when the system

is in thermal contact with a large reservoir at temperature τ. The number of particles in the system is assumed constant.

2. The partition function is

$$Z \equiv \sum_s \exp(-\varepsilon_s/\tau).$$

3. The pressure is given by

$$p = -(\partial U/\partial V)_\sigma = \tau(\partial\sigma/\partial V)_U.$$

4. The Helmholtz free energy is defined as $F \equiv U - \tau\sigma$. It is a minimum in equilibrium for a system held at constant τ, V.

5. $\sigma = -(\partial F/\partial\tau)_V;$ $p = -(\partial F/\partial V)_\tau.$

6. $F = -\tau\log Z$. This result is very useful in calculations of F and of quantities such as p and σ derived from F.

7. For an ideal monatomic gas of N atoms of spin zero,

$$Z_N = (n_Q V)^N/N! ,$$

if $n = N/V \ll n_Q$. The quantum concentration $n_Q \equiv (M\tau/2\pi h^2)^{3/2}$. Further,

$$pV = N\tau; \quad \sigma = N[\log(n_Q/n) + \tfrac{5}{2}]; \quad C_V = \tfrac{3}{2}N.$$

8. A process is reversible if the system remains infinitesimally close to the equilibrium state at all times during the process.

PROBLEMS

1. *Free energy of a two state system.* (a) Find an expression for the free energy as a function of τ of a system with two states, one at energy 0 and one at energy ε. (b) From the free energy, find expressions for the energy and entropy of the system. The entropy is plotted in Figure 3.11.

2. *Magnetic susceptibility.* (a) Use the partition function to find an exact expression for the magnetization M and the susceptibility $\chi \equiv dM/dB$ as a function of temperature and magnetic field for the model system of magnetic moments in a magnetic field. The result for the magnetization is $M = nm\tanh(mB/\tau)$, as derived in (46) by another method. Here n is the particle
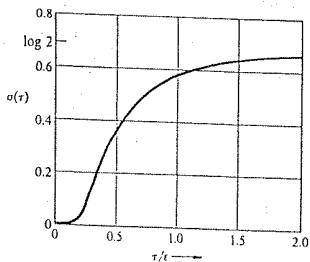
Figure 3.11 Entropy of a two-state system as a function of τ/ε. Notice that $\sigma(\tau) \to \log 2$ as $\tau \to \infty$.

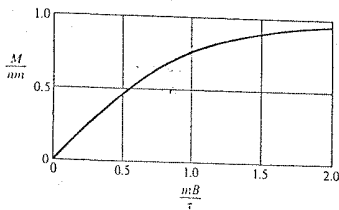

Figure 3.12 Plot of the total magnetic moment as a function of mB/τ. Notice that at low mB/τ the moment is a linear function of mB/τ, but at high mB/τ the moment tends to saturate.

concentration. The result is plotted in Figure 3.12. (b) Find the free energy and express the result as a function only of τ and the parameter $x \equiv M/nm$. (c) Show that the susceptibility is $\chi = nm^2/\tau$ in the limit $mB \ll \tau$.

3. *Free energy of a harmonic oscillator.* A one-dimensional harmonic oscillator has an infinite series of equally spaced energy states, with $\varepsilon_s = s\hbar\omega$, where
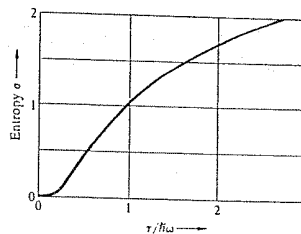
Figure 3.13 Entropy versus temperature for harmonic oscillator of frequency ω.

s is a positive integer or zero, and ω is the classical frequency of the oscillator. We have chosen the zero of energy at the state $s = 0$. (a) Show that for a harmonic oscillator the free energy is

$$F = \tau \log[1 - \exp(-\hbar\omega/\tau)]. \tag{87}$$

Note that at high temperatures such that $\tau \gg \hbar\omega$ we may expand the argument of the logarithm to obtain $F \simeq \tau \log(\hbar\omega/\tau)$. (b) From (87) show that the entropy is

$$\sigma = \frac{\hbar\omega/\tau}{\exp(\hbar\omega/\tau) - 1} - \log[1 - \exp(-\hbar\omega/\tau)]. \tag{88}$$

The entropy is shown in Figure 3.13 and the heat capacity in Figure 3.14.

4. *Energy fluctuations.* Consider a system of fixed volume in thermal contact with a reservoir. Show that the mean square fluctuation in the energy of the system is

$$\langle (\varepsilon - \langle \varepsilon \rangle)^2 \rangle = \tau^2 (\partial U/\partial \tau)_V. \tag{89}$$

Here U is the conventional symbol for $\langle \varepsilon \rangle$. *Hint*: Use the partition function Z to relate $\partial U/\partial \tau$ to the mean square fluctuation. Also, multiply out the term $(\cdots)^2$. *Note*: The temperature τ of a system is a quantity that by definition does

Figure 3.14 Heat capacity versus temperature for harmonic oscillator of frequency ω. The horizontal scale is in units of $\tau/\hbar\omega$, which is identical with T/θ_E, where θ_E is called the Einstein temperature. In the high temperature limit $C_V \to k_B$, or 1 in fundamental units. This value is known as the classical value. At low temperatures C_V decreases exponentially.
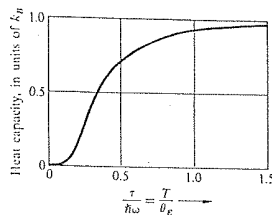
not fluctuate in value when the system is in thermal contact with a reservoir. Any other attitude would be inconsistent with our definition of the temperature of a system. The energy of such a system may fluctuate, but the temperature does not. Some workers do not adhere to a rigorous definition of temperature. Thus Landau and Lifshitz give the result

$$\langle(\Delta\tau)^2\rangle = \tau^2/C_V \,, \tag{90}$$

but this should be viewed as just another form of (89) with $\Delta\tau$ set equal to $\Delta U/C_V$. We know from (89) that $\Delta U = C_V\,\Delta\tau$, whence (90) becomes $\langle(\Delta U)^2\rangle = \tau^2 C_V$, which is our result (89).

5. *Overhauser effect.* Suppose that by a suitable external mechanical or electrical arrangement one can add $\alpha\varepsilon$ to the energy of the heat reservoir whenever the reservoir passes to the system the quantum of energy ε. The net increase of energy of the reservoir is $(\alpha - 1)\varepsilon$. Here α is some numerical factor, positive or negative. Show that the effective Boltzmann factor for this abnormal system is given by

$$P(\varepsilon) \propto \exp[-(1 - \alpha)\varepsilon/\tau]. \tag{91}$$

This reasoning gives the statistical basis of the Overhauser effect whereby the nuclear polarization in a magnetic field can be enhanced above the thermal equilibrium polarization. Such a condition requires the active supply of energy to the system from an external source. The system is not in equilibrium, but is said to be in a steady state. Cf. A. W. Overhauser, Phys. Rev. 92, 411 (1953).

6. *Rotation of diatomic molecules.* In our first look at the ideal gas we considered only the translational energy of the particles. But molecules can rotate,

with kinetic energy. The rotational motion is quantized; and the energy levels of a diatomic molecule are of the form

$$\varepsilon(j) = j(j + 1)\varepsilon_0 \tag{92}$$

where j is any positive integer including zero: $j = 0, 1, 2, \ldots$. The multiplicity of each rotational level is $g(j) = 2j + 1$. (a) Find the partition function $Z_R(\tau)$ for the rotational states of one molecule. Remember that Z is a sum over all states, not over all levels—this makes a difference. (b) Evaluate $Z_R(\tau)$ approximately for $\tau \gg \varepsilon_0$, by converting the sum to an integral. (c) Do the same for $\tau \ll \varepsilon_0$, by truncating the sum after the second term. (d) Give expressions for the energy U and the heat capacity C, as functions of τ, in both limits. Observe that the rotational contribution to the heat capacity of a diatomic molecule approaches 1 (or, in conventional units, k_B) when $\tau \gg \varepsilon_0$. (e) Sketch the behavior of $U(\tau)$ and $C(\tau)$, showing the limiting behaviors for $\tau \to \infty$ and $\tau \to 0$.

7. *Zipper problem.* A zipper has N links; each link has a state in which it is closed with energy 0 and a state in which it is open with energy ε. We require, however, that the zipper can only unzip from the left end, and that the link number s can only open if all links to the left $(1, 2, \ldots, s - 1)$ are already open. (a) Show that the partition function can be summed in the form

$$Z = \frac{1 - \exp[-(N + 1)\varepsilon/\tau]}{1 - \exp(-\varepsilon/\tau)}. \tag{93}$$

(b) In the limit $\varepsilon \gg \tau$, find the average number of open links. The model is a very simplified model of the unwinding of two-stranded DNA molecules—see C. Kittel, Amer. J. Physics 37, 917 (1969).

8. *Quantum concentration.* Consider one particle confined to a cube of side L; the concentration in effect is $n = 1/L^3$. Find the kinetic energy of the particle when in the ground orbital. There will be a value of the concentration for which this zero-point quantum kinetic energy is equal to the temperature τ. (At this concentration the occupancy of the lowest orbital is of the order of unity; the lowest orbital always has a higher occupancy than any other orbital.) Show that the concentration n_0 thus defined is equal to the quantum concentration n_Q defined by (63), within a factor of the order of unity.

9. *Partition function for two systems.* Show that the partition function $Z(1 + 2)$ of two independent systems 1 and 2 in thermal contact at a common temperature τ is equal to the product of the partition functions of the separate systems:

$$Z(1 + 2) = Z(1)Z(2). \tag{94}$$

10. Elasticity of polymers. The thermodynamic identity for a one-dimensional system is

$$\tau d\sigma = dU - f dl \tag{95}$$

when f is the external force exerted on the line and dl is the extension of the line. By analogy with (32) we form the derivative to find

$$-\frac{f}{\tau} = \left(\frac{\partial \sigma}{\partial l}\right)_U. \tag{96}$$

The direction of the force is opposite to the conventional direction of the pressure.

We consider a polymeric chain of N links each of length ρ, with each link equally likely to be directed to the right and to the left. (a) Show that the number of arrangements that give a head-to-tail length of $l = 2|s|\rho$ is

$$g(N,-s) + g(N,s) = \frac{2N!}{(\frac{1}{2}N + s)! \, (\frac{1}{2}N - s)!}. \tag{97}$$

(b) For $|s| \ll N$ show that

$$\sigma(l) = \log[2g(N,0)] - l^2/2N\rho^2. \tag{98}$$

(c) Show that the force at extension l is

$$f = l\tau/N\rho^2. \tag{99}$$

The force is proportional to the temperature. The force arises because the polymer wants to curl up: the entropy is higher in a random coil than in an uncoiled configuration. Warming a rubber band makes it contract; warming a steel wire makes it expand. The theory of rubber elasticity is discussed by H. M. James and E. Guth, Journal of Chemical Physics 11, 455 (1943); Journal of Polymer Science 4, 153 (1949); see also L. R. G. Treloar, *Physics of rubber elasticity*, Oxford, 1958.

11. One-dimensional gas. Consider an ideal gas of N particles, each of mass M, confined to a one-dimensional line of length L. Find the entropy at temperature τ. The particles have spin zero.

Thermal Radiation and Planck Distribution

[We consider] the distribution of the energy U among N oscillators of frequency v. If U is viewed as divisible without limit, then an infinite number of distributions are possible. We consider however—and this is the essential point of the whole calculation—U as made up of an entirely determined number of finite equal parts, and we make use of the natural constant $h = 6.55 \times 10^{-27}$ erg-sec. This constant when multiplied by the common frequency v of the oscillators gives the element of energy ε in ergs ....

M. Planck

PLANCK DISTRIBUTION FUNCTION

The Planck distribution describes the spectrum of the electromagnetic radiation in thermal equilibrium within a cavity. Approximately, it describes the emission spectrum of the Sun or of metal heated by a welding torch. The Planck distribution was the first application of quantum thermal physics. Thermal electromagnetic radiation is often called black body radiation. The Planck distribution also describes the thermal energy spectrum of lattice vibrations in an elastic solid.

The word "mode" characterizes a particular oscillation amplitude pattern in the cavity or in the solid. We shall always refer to $\omega = 2\pi f$ as the frequency of the radiation. The characteristic feature of the radiation problem is that a mode of oscillation of frequency ω may be excited only in units of the quantum of energy $\hbar\omega$. The energy ε_s of the state with s quanta in the mode is

$$\varepsilon_s = s\hbar\omega ,\tag{1}$$

where s is zero or any positive integer (Figure 4.1). We omit the zero point energy $\frac{1}{2}\hbar\omega$.

These energies are the same as the energies of a quantum harmonic oscillator of frequency ω, but there is a difference between the concepts. A harmonic
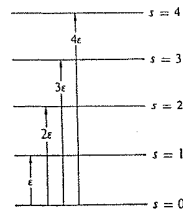

Figure 4.1   States of an oscillator that represents a mode of frequency ω of an electromagnetic field. When the oscillator is in the orbital of energy $s\hbar\omega$, the state is equivalent to s photons in the mode.
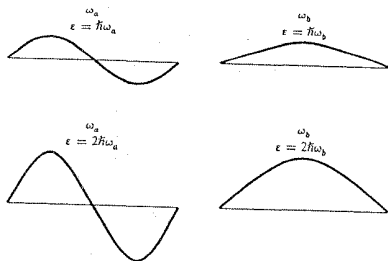
Figure 4.2   Representation in one dimension of two electromagnetic modes a and b, of frequency ω_a and ω_b. The amplitude of the electromagnetic field is suggested in the figures for one photon and two photon occupancy of each mode.

oscillator is a localized oscillator, whereas the electric and magnetic energy of an electromagnetic cavity mode is distributed throughout the interior of the cavity (Figure 4.2). For both problems the energy eigenvalues are integral multiples of $\hbar\omega$, and this is the reason for the similarity in the thermal physics of the two problems. The language used to describe an excitation is different: s for the oscillator is called the quantum number, and s for the quantized electromagnetic mode is called the number of photons in the mode.

We first calculate the thermal average of the number of photons in a mode, when these photons are in thermal equilibrium with a reservoir at a temperature τ. The partition function (3.10) is the sum over the states (1):

$$Z = \sum_{s=0}^{\infty} \exp(-s\hbar\omega/\tau). \tag{2}$$

This sum is of the form $\sum x^s$, with $x \equiv \exp(-\hbar\omega/\tau)$. Because x is smaller than 1, the infinite series may be summed and has the value $1/(1-x)$, whence

$$Z = \frac{1}{1 - \exp(-\hbar\omega/\tau)}. \tag{3}$$

The probability that the system is in the state s of energy $s\hbar\omega$ is given by the Boltzmann factor:

$$P(s) = \frac{\exp(-s\hbar\omega/\tau)}{Z}. \tag{4}$$

The thermal average value of s is

$$\langle s \rangle = \sum_{s=0}^{\infty} sP(s) = Z^{-1}\sum s\exp(-s\hbar\omega/\tau). \tag{5}$$

With $y \equiv \hbar\omega/\tau$, the summation on the right-hand side has the form:

$$\sum s\exp(-sy) = -\frac{d}{dy}\sum \exp(-sy)$$
$$= -\frac{d}{dy}\left(\frac{1}{1 - \exp(-y)}\right) = \frac{\exp(-y)}{[1 - \exp(-y)]^2}.$$

From (3) and (5) we find

$$\langle s \rangle = \frac{\exp(-y)}{1 - \exp(-y)},$$

or

$$\boxed{\langle s \rangle = \frac{1}{\exp(\hbar\omega/\tau) - 1}.} \tag{6}$$

This is the Planck distribution function for the thermal average number of photons (Figure 4.3) in a single mode of frequency ω. Equally, it is the average number of phonons in the mode. The result applies to any kind of wave field with energy in the form of (1).

PLANCK LAW AND STEFAN-BOLTZMANN LAW

The thermal average energy in the mode is

$$\langle \varepsilon \rangle = \langle s \rangle \hbar\omega = \frac{\hbar\omega}{\exp(\hbar\omega/\tau) - 1}. \tag{7}$$

Figure 4.3 Planck distribution as a function of the reduced temperature $\tau/\hbar\omega$. Here $\langle s(\omega)\rangle$ is the thermal average of the number of photons in the mode of frequency ω. A plot of $\langle s(\omega)\rangle + \frac{1}{2}$ is also given, where $\frac{1}{2}$ is the effective zero point occupancy of the mode; the dashed line is the classical asymptote. Note that we write

$$\langle s\rangle + \frac{1}{2} = \frac{1}{2}\coth(\hbar\omega/2\tau).$$
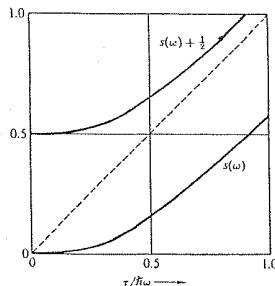
The high temperature limit $\tau \gg \hbar\omega$ is often called the classical limit. Here $\exp(\hbar\omega/\tau)$ may be approximated as $1 + \hbar\omega/\tau + \cdots$, whence the classical average energy is

$$\langle\varepsilon\rangle \simeq \tau. \tag{8}$$

There is an infinite number of electromagnetic modes within any cavity. Each mode n has its own frequency ω_n. For radiation confined within a perfectly conducting cavity in the form of a cube of edge L, there is a set of modes of the form

$$E_x = E_{x0}\sin\omega t\cos(n_x\pi x/L)\sin(n_y\pi y/L)\sin(n_z\pi z/L) , \tag{9a}$$

$$E_y = E_{y0}\sin\omega t\sin(n_x\pi x/L)\cos(n_y\pi y/L)\sin(n_z\pi z/L) , \tag{9b}$$

$$E_z = E_{z0}\sin\omega t\sin(n_x\pi x/L)\sin(n_y\pi y/L)\cos(n_z\pi z/L). \tag{9c}$$

Here E_x, E_y and E_z are the three electric field components, and E_{x0}, E_{y0} and E_{z0} are the corresponding amplitudes. The three components are not independent, because the field must be divergence-free:

$$\text{div }\mathbf{E} = \frac{\partial E_x}{\partial x} + \frac{\partial E_y}{\partial y} + \frac{\partial E_z}{\partial z} = 0. \tag{10}$$

When we insert (9) into (10) and drop all common factors, we find the condition

$$E_{x0}n_x + E_{y0}n_y + E_{z0}n_z = \mathbf{E_0 \cdot n} = 0. \tag{11}$$

This states that the field vectors must be perpendicular to the vector $\mathbf{n}$ with the components n_x, n_y and n_z, so that the electromagnetic field in the cavity is a transversely polarized field. The polarization direction is defined as the direction of $\mathbf{E_0}$.

For a given triplet n_x, n_y, n_z we can choose two mutually perpendicular polarization directions, so that there are two distinct modes for each triplet n_x, n_y, n_z.

On substitution of (9) in the wave equation

$$c^2\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)E_z = \frac{\partial^2 E_z}{\partial t^2} , \tag{12}$$

with c the velocity of light, we find

$$c^2\pi^2(n_x^2 + n_y^2 + n_z^2) = \omega^2 L^2. \tag{13}$$

This determines the frequency ω of the mode in terms of the triplet of integers n_x, n_y, n_z. If we define

$$n \equiv (n_x^2 + n_y^2 + n_z^2)^{1/2} , \tag{14}$$

then the frequencies are of the form

$$\omega_n = n\pi c/L. \tag{15}$$

The total energy of the photons in the cavity is, from (7),

$$U = \sum_n\langle\varepsilon_n\rangle = \sum_n\frac{\hbar\omega_n}{\exp(\hbar\omega_n/\tau) - 1}. \tag{16}$$

The sum is over the triplet of integers n_x, n_y, n_z. Positive integers alone will describe all independent modes of the form (9). We replace the sum over n_x, n_y, n_z by an integral over the volume element $dn_x\,dn_y\,dn_z$ in the space of the mode indices. That is, we set

$$\sum_n(\cdots) = \frac{1}{8}\int_0^\infty 4\pi n^2\,dn(\cdots) , \tag{17}$$

where the factor $\frac{1}{8} = (\frac{1}{2})^3$ arises because only the positive octant of the space is involved. We now multiply the sum or integral by a factor of 2 because there are two independent polarizations of the electromagnetic field (two independent sets of cavity modes). Thus

$$U = \pi \int_0^\infty dn\, n^2 \frac{\hbar\omega_n}{\exp(\hbar\omega_n/\tau) - 1}$$

$$= (\pi^2 \hbar c/L) \int_0^\infty dn\, n^3 \frac{1}{\exp(\hbar c n\pi/L\tau) - 1}, \qquad (18)$$

with (15) for ω_n. Standard practice is to transform the definite integral to one over a dimensionless variable. We set $x \equiv \pi\hbar c n/L\tau$, and (18) becomes

$$U = (\pi^2 \hbar c/L)(\tau L/\pi\hbar c)^4 \int_0^\infty dx\, \frac{x^3}{\exp x - 1}. \qquad (19)$$

The definite integral has the value $\pi^4/15$; it is found in good standard tables such as Dwight (cited in the general references). The energy per unit volume is

$$\boxed{\frac{U}{V} = \frac{\pi^2}{15\hbar^3 c^3} \tau^4,} \qquad (20)$$

with the volume $V = L^3$. The result that the radiant energy density is proportional to the fourth power of the temperature is known as the Stefan-Boltzmann law of radiation.

For many applications of this theory we decompose (20) into the spectral density of the radiation. The spectral density is defined as the energy per unit volume per unit frequency range, and is denoted as u_ω. We can find u_ω from (18) rewritten in terms of ω:

$$U/V = \int d\omega\, u_\omega = \frac{\hbar}{\pi^2 c^3} \int d\omega\, \frac{\omega^3}{\exp(\hbar\omega/\tau) - 1}, \qquad (21)$$

so that the spectral density is

$$\boxed{u_\omega = \frac{\hbar}{\pi^2 c^3} \frac{\omega^3}{\exp(\hbar\omega/\tau) - 1}.} \qquad (22)$$
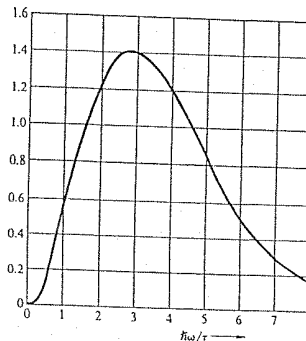
Figure 4.4   Plot of $x^3/(e^x - 1)$ with $x \equiv \hbar\omega/\tau$. This function is involved in the Planck radiation law for the spectral density u_ω. The temperature of a black body may be found from the frequency ω_{max} at which the radiant energy density is a maximum, per unit frequency range. This frequency is directly proportional to the temperature.

This result is the Planck radiation law; it gives the frequency distribution of thermal radiation (Figure 4.4). Quantum theory began here.

The entropy of the thermal photons can be found from the relation (3.34a) at constant volume: $d\sigma = dU/\tau$, whence from (20),

$$d\sigma = \frac{4\pi^2 V}{15\hbar^3 c^3} \tau^2\, d\tau.$$

Thus the entropy is

$$\sigma(\tau) = (4\pi^2 V/45)(\tau/\hbar c)^3. \qquad (23)$$

The constant of integration is zero, from (3.55) and the relation between F and σ.

A process carried out at constant photon entropy will have $V\tau^3$ = constant.

The measurement of high temperatures depends on the flux of radiant energy from a small hole in the wall of a cavity maintained at the temperature of interest. Such a hole is said to radiate as a black body—which means that the radiation emission is characteristic of a thermal equilibrium distribution. The energy flux density J_U is defined as the rate of energy emission per unit area. The flux density is of the order of the energy contained in a column of unit area and length equal to the velocity of light times the unit of time. Thus,

$$J_U = [cU(\tau)/V] \times \text{(geometrical factor)}. \tag{24}$$

The geometrical factor is equal to $\frac{1}{4}$; the derivation is the subject of Problem 15. The final result for the radiant energy flux is

$$J_U = \frac{cU(\tau)}{4V} = \frac{\pi^2\tau^4}{60h^3c^2}, \tag{25}$$

by use of (20) for the energy density U/V. The result is often written as

$$J_U = \sigma_B T^4; \tag{26}$$

the Stefan-Boltzmann constant

$$\sigma_B \equiv \pi^2 k_B^4/60h^3c^2 \tag{26a}$$

has the value 5.670×10^{-8} W m^{-2} K^{-4} or 5.670×10^{-5} erg cm^{-2} s^{-1} K^{-4}. (Here σ_B is not the entropy.) A body that radiates at this rate is said to radiate as a black body. A small hole in a cavity whose walls are in thermal equilibrium at temperature T will radiate as a black body at the rate given in (26). The rate is independent of the physical constitution of the walls of the cavity and depends only on the temperature.

Emission and Absorption: Kirchhoff Law

The ability of a surface to emit radiation is proportional to the ability of the surface to absorb radiation. We demonstrate this relation, first for a black body or black surface and, second, for a surface with arbitrary properties. An object is defined to be black in a given frequency range if all electromagnetic radiation incident upon it in that range is absorbed. By this definition a hole in a cavity is black if the hole is small enough that radiation incident through the hole will

reflect enough times from the cavity walls to be absorbed in the cavity with negligible loss back through the hole.

The radiant energy flux density J_U from a black surface at temperature τ is equal to the radiant energy flux density J_U emitted from a small hole in a cavity at the same temperature. To prove this, let us close the hole with the black surface, hereafter called the object. In thermal equilibrium the thermal average energy flux from the black object to the interior of the cavity must be equal, but opposite, to the thermal average energy flux from the cavity to the black object.

We prove the following: If a non-black object at temperature τ absorbs a fraction a of the radiation incident upon it, the radiation flux emitted by the object will be a times the radiation flux emitted by a black body at the same temperature. Let a denote the absorptivity and e the emissivity, where the emissivity is defined so that the radiation flux emitted by the object is e times the flux emitted by a black body at the same temperature. The object must emit at the same rate as it absorbs if equilibrium is to be maintained. It follows that $a = e$. This is the Kirchhoff law. For the special case of a perfect reflector, a is zero, whence e is zero. A perfect reflector does not radiate.

The arguments can be generalized to apply to the radiation at any frequency, as between ω and $\omega + d\omega$. We insert a filter between the object and the hole in the black body. Let the filter reflect perfectly outside this frequency range, and let it transmit perfectly within this range. The flux equality arguments now apply to the transmitted spectral band, so that $a(\omega) = e(\omega)$ for any surface in thermal equilibrium.

Estimation of Surface Temperature

One way to estimate the surface temperature of a hot body such as a star is from the frequency at which the maximum emission of radiant energy takes place (see Figure 4.4). What this frequency is depends on whether we look at the energy flux per unit frequency range or per unit wavelength range. For u_ω, the energy density per unit frequency range, the maximum is given from the Planck law, Eq. (22), as

$$\frac{d}{dx}\left(\frac{x^3}{\exp x - 1}\right) = 0,$$

or

$$3 - 3\exp(-x) = x.$$

This equation may be solved numerically. The root is

$$\hbar\omega_{max}/k_B T = x_{max} \simeq 2.82 \,, \qquad (27)$$

as in Figure 4.4.

Example: Cosmic black body background radiation. A major recent discovery is that the universe accessible to us is filled with radiation approximately like that of a black body at 2.9 K. The existence of this radiation (Figure 4.5) is important evidence for big bang cosmological models which assume that the universe is expanding and cooling with time. This radiation is left over from an early epoch when the universe was composed primarily of electrons and protons at a temperature of about 4000 K. The plasma of electrons and protons interacted strongly with electromagnetic radiation at all important frequencies, so that the matter and the black body radiation were in thermal equilibrium. By the time the universe had cooled to 3000 K, the matter was primarily in the form of atomic hydrogen. This interacts with black body radiation only at the frequencies of the hydrogen spectral lines. Most of the black body radiation energy thus was effectively decoupled from the matter. Thereafter the radiation evolved with time in a very simple way: the photon gas was cooled by expansion at constant entropy to a temperature of 2.9 K. The photon gas will remain at constant entropy if the frequency of each mode is lowered during the expansion of the universe with the number of photons in each mode kept constant. We show in (58) below that the entropy is constant if the number of photons in each mode is constant—the occupancies determine the entropy.

After the decoupling the evolution of matter into heavier atoms (which are organized into galaxies, stars, and dust clouds) was more complicated than before decoupling. Electromagnetic radiation, such as starlight, radiated by the matter since the decoupling is superimposed on the cosmic black body radiation.

ELECTRICAL NOISE

As an important example of the Planck law in one dimension, we consider the spontaneous thermal fluctuations in voltage across a resistor. These fluctuations, which are called noise, were discovered by J. B. Johnson and explained by H. Nyquist.* The characteristic property of Johnson noise is that the mean-square noise voltage is proportional to the value of the resistance R, as shown by Figure 4.6. We shall see that $\langle V^2 \rangle$ is also directly proportional to the tem-

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* H. Nyquist, Phys. Rev. 32, 110 (1928); a deeper discussion is given by C. Kittel, *Elementary statis-tical physics*, Wiley, 1958, Sections 27-30.
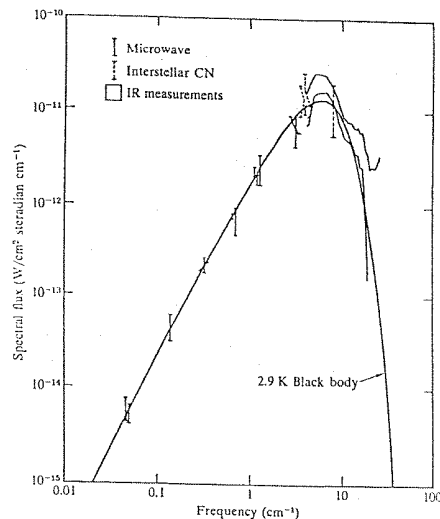
Figure 4.5 Experimental measurements of the spectrum of the cosmic black body radiation. Observations of the flux were made with microwave heterodyne receivers at frequencies below the peak, were deduced from optical measurements of the spectrum of interstellar CN molecules near the peak, and were measured with a balloon-borne infrared spectrometer at frequencies above the peak. Courtesy of P. L. Richards.

perature τ and the bandwidth Δf of the circuit. (This section presumes a knowl-edge of electromagnetic wave propagation at the intermediate level.)

The Nyquist theorem gives a quantitative expression for the thermal noise voltage generated by a resistor in thermal equilibrium. The theorem is therefore needed in any estimate of the limiting signal-to-noise ratio of an experimental
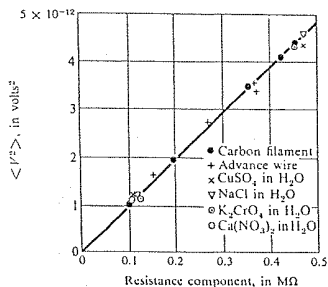
Figure 4.6   Voltage squared versus resistance for various kinds of conductors, including electrolytes. After J. B. Johnson.

apparatus. In the original form the Nyquist theorem states that the mean square voltage across a resistor of resistance R in thermal equilibrium at temperature τ is given by

$$\langle V^2 \rangle = 4R\tau \, \Delta f \,, \tag{28}$$

where Δf is the frequency* bandwidth within which the voltage fluctuations are measured; all frequency components outside the given range are ignored. We show below that the thermal noise power per unit frequency range delivered by a resistor to a matched load is τ; the factor 4 enters where it does because in the circuit of Figure 4.7, the power delivered to an arbitrary resistive load R' is

$$\langle I^2 \rangle R' = \frac{\langle V^2 \rangle R'}{(R + R')^2} \,, \tag{29}$$

which at match $(R' = R)$ is $\langle V^2 \rangle / 4R$.

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* In this section the word frequency refers to cycles per unit time, and not to radians per unit time.
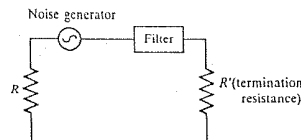
Figure 4.7   Equivalent circuit for a resistance R with a generator of thermal noise that delivers power to a load R'. The current

$$I = \frac{V}{R + R'} \,,$$

so that the mean power dissipated in the load is

$$\mathscr{P} = \langle I^2 \rangle R' = \frac{\langle V^2 \rangle R'}{(R' + R)^2} \,,$$

which is a maximum with respect to R' when $R' = R$. In this condition the load is said to be matched to the power supply. At match, $\mathscr{P} = \langle V^2 \rangle / 4R$. The filter enables us to limit the frequency bandwidth under consideration; that is, the bandwidth to which the mean square voltage fluctuation applies.

Consider as in Figure 4.8 a lossless transmission line of length L and characteristic impedance $Z_c = R$ terminated at each end by a resistance R. Thus the line is matched at each end, in the sense that all energy traveling down the line will be absorbed without reflection in the appropriate resistance. The entire circuit is maintained at temperature τ.

A transmission line is essentially an electromagnetic system in one dimension. We follow the argument given above for the distribution of photons in thermal equilibrium, but now in a space of one dimension instead of three dimensions. The transmission line has two photon modes (one propagating in each direction) of frequency $2\pi f_n = 2n\pi/L$ from (15), so that there are two modes in the frequency range

$$\delta f = c'/L, \tag{30}$$

where c' is the propagation velocity on the line. Each mode has energy

$$\frac{\hbar\omega}{\exp(\hbar\omega/\tau) - 1} \tag{31}$$

in equilibrium, according to the Planck distribution. We are usually concerned with circuits in the classical limit $\hbar\omega \ll \tau$ so that the thermal energy per mode is τ. If follows that the energy on the line in the frequency range Δf is

$$2\tau L\,\Delta f/c. \qquad (32)$$

The rate at which energy comes off the line in one direction is

$$\tau\,\Delta f. \qquad (33)$$

The power coming off the line at one end is all absorbed in the terminal impedance R at that end; there are no reflections when the terminal impedance is matched to the line. In thermal equilibrium the load must emit energy to the line at the same rate, or else its temperature would rise. Thus the power input to the load is

$$\mathcal{G} = \tau\langle I^2 \rangle R = \tau\,\Delta f, \qquad (34)$$

but $V = 2RI$, so that (28) is obtained. The result has been used in low temperature thermometry, in temperature regions (Figure 4.9) where it is more convenient to measure $\langle V^2 \rangle$ than τ. Johnson noise is the noise across a resistor when no dc current is flowing. Additional noise (not discussed here) appears when a dc current flows.

Figure 4.8 Transmission line of length L with matched terminations, as conceived for the derivation of the Nyquist theorem. The characteristic impedance Z_c of the transmission line has the value R. According to the fundamental theorem of transmission lines, the terminal resistors are matched to the line when their resistance has the same value R.

approximation to the actual distribution. The sonic spectrum of a lattice must,

So I decided to calculate the spectral distribution of the possible free vibrations for a continuous solid and to consider this distribution as a good enough

PHONONS IN SOLIDS: DEBYE THEORY

The energy of an elastic wave in a solid is quantized just as the energy of an electromagnetic wave in a cavity is quantized. The quantum of energy of an elastic wave is called a phonon. The thermal average number of phonons in an elastic wave of frequency ω is given by the Planck distribution function, just as for photons:

$$\langle s(\omega) \rangle = \frac{1}{\exp(\hbar\omega/\tau) - 1}. \qquad (35)$$

We assume that the frequency of an elastic wave is independent of the amplitude of the elastic strain. We want to find the energy and heat capacity of the elastic waves in solids. Several of the results obtained for photons may be carried over to phonons. The results are simple if we assume that the velocities of all elastic waves are equal—independent of frequency, direction of propagation, and direction of polarization. This assumption is not very accurate, but it helps

of course, deviate from this as soon as the wavelength becomes comparable to the distances of the atoms. . . . The only thing which had to be done was to adjust to the fact that every solid of finite dimensions contains a finite number of atoms and therefore has a finite number of free vibrations. . . . At low enough temperatures, and in perfect analogy to the radiation law of Stefan-Boltzmann . . . , the vibrational energy content of a solid will be proportional to T^4.
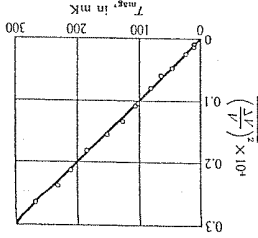
P. Debye

Figure 4.9 Mean square noise voltage fluctuations observed experimentally from a $3\,\mu\Omega$ resistor in the mixing chamber of a dilution refrigerator as a function of magnetic temperature indicated by a CMN powder thermometer. After R. R. Giffard, R. A. Webb, and J. C. Wheatley, J. Low Temp Physics 6, 533 (1972).

account for the general trend of the observed results in many solids, with a minimum of computation.

There are two important features of the experimental results: the heat capacity of a nonmetallic solid varies as τ^3 at low temperatures, and at high temperatures the heat capacity is independent of the temperature. In metals there is an extra contribution from the conduction electrons, treated in Chapter 7.

Number of Phonon Modes

There is no limit to the number of possible electromagnetic modes in a cavity, but the number of elastic modes in a finite solid is bounded. If the solid consists of N atoms, each with three degrees of freedom, the total number of modes is $3N$. An elastic wave has three possible polarizations, two transverse and one longitudinal, in contrast to the two possible polarizations of an electromagnetic wave. In a transverse elastic wave the displacement of the atoms is perpendicular to the propagation direction of the wave; in a longitudinal wave the displacement is parallel to the propagation direction. The sum of a quantity over all modes may be written as, including the factor 3,

$$\sum_n (\cdots) = \frac{3}{8} \int 4\pi n^2 \, dn(\cdots) \, , \tag{36}$$

by extension of (17). Here n is defined in terms of the triplet of integers n_x, n_y, n_z, exactly as for photons. We want to find $n_{\max}$ such that the total number of elastic modes is equal to $3N$:

$$\frac{3}{8} \int_0^{n_{\max}} 4\pi n^2 \, dn = 3N. \tag{37}$$

In the photon problem there was no corresponding limitation on the total number of modes. It is customary to write n_D, after Debye, for $n_{\max}$. Then (37) becomes

$$\frac{1}{2}\pi n_D^3 = 3N; \qquad n_D = (6N/\pi)^{1/3}. \tag{38}$$

The thermal energy of the phonons is, from (16),

$$U = \sum \langle \varepsilon_n \rangle = \sum \langle s_n \rangle \hbar \omega_n = \sum \frac{\hbar \omega_n}{\exp(\hbar \omega_n/\tau) - 1} \, , \tag{39}$$

or, by (36) and (38),

$$U = \frac{3\pi}{2} \int_0^{n_D} dn \, n^2 \, \frac{\hbar \omega_n}{\exp(\hbar \omega_n/\tau) - 1}. \tag{40}$$

By analogy with the evaluation of (19), with the velocity of sound v written in place of the velocity of light c,

$$U = (3\pi^2 \hbar v/2L)(\tau L/\pi \hbar v)^4 \int_0^{x_D} dx \, \frac{x^3}{\exp x - 1} \, , \tag{41}$$

where $x \equiv \pi \hbar v n/L\tau$. For L^3 we write the volume V. Here, with (38), the upper limit of integration is

$$x_D = \pi \hbar v n_D/L\tau = \hbar v (6\pi^2 N/V)^{1/3}/\tau \, , \tag{42}$$

usually written as

$$x_D = \theta/T = k_B \theta/\tau \, , \tag{43}$$

where θ is called the Debye temperature:

$$\theta = (\hbar v/k_B)(6\pi^2 N/V)^{1/3}. \tag{44}$$

The result (41) for the energy is of special interest at low temperatures such that $T \ll \theta$. Here the limit x_D on the integral is much larger than unity, and x_D may be replaced by infinity. We note from Figure 4.4 that there is little contribution to the integrand out beyond $x = 10$. For the definite integral we have

$$\int_0^\infty dx \, \frac{x^3}{\exp x - 1} = \frac{\pi^4}{15} \, , \tag{45}$$

as earlier. Thus the energy in the low temperature limit is

$$U(T) \simeq \frac{3\pi^4 N \tau^4}{5(k_B \theta)^3} \simeq \frac{3\pi^4 N k_B T^4}{5\theta^3} \, , \tag{46}$$

proportional to T^4. The heat capacity is, for $\tau \ll k_B \theta$ or $T \ll \theta$,

$$C_V = \left(\frac{\partial U}{\partial \tau}\right)_V = \frac{12\pi^4 N}{5} \left(\frac{\tau}{k_B \theta}\right)^3. \tag{47a}$$
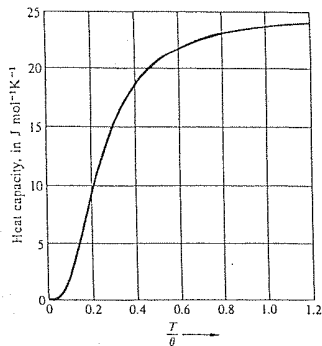
Figure 4.10   Low temperature heat capacity of solid argon, plotted against T^3 to show the excellent agreement with the Debye T^3 law. The value of θ from these data is 92 K. Courtesy of L. Finegold and N. E. Phillips.

In conventional units,

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = \frac{12\pi^4 N k_B}{5}\left(\frac{T}{\theta}\right)^3. \tag{47b}$$

This result is known as the Debye T^3 law.* Experimental results for argon are plotted in Figure 4.10. Representative experimental values of the Debye temperature are given in Table 4.1. The calculated variation of C_V versus T/θ is plotted in Figure 4.11. The high temperature limit $T \gg \theta$ is the subject of Problem 11. Several related thermodynamic functions for a Debye solid are given in Table 4.2 and are plotted in Figure 4.12.

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* P. Debye, Annalen der Physik 39, 789 (1912); M. Born and T. v. Kármán, Physikalische Zeitschrift 13, 297 (1912); 14, 65 (1913).

Table 4.1   Debye temperature θ_0 in K

Li 344	Be 1440												B	C 2230	N	O	F	Ne 75
Na 158	Mg 400												Al 428	Si 645	P	S	Cl	Ar 92
K 91	Ca 230	Sc 360	Ti 420	V 380	Cr 630	Mn 410	Fe 470	Co 445	Ni 450	Cu 343	Zn 327	Ga 320	Ge 374	As 282	Se 90	Br	Kr 72
Rb 56	Sr 147	Y 280	Zr 291	Nb 275	Mo 450	Tc	Ru 600	Rh 480	Pd 274	Ag 225	Cd 209	In 108	Sn w 200	Sb 211	Te 153	I	Xe 64
Cs 38	Ba 110	Laβ 142	Hf 252	Ta 240	W 400	Re 430	Os 500	Ir 420	Pt 240	Au 165	Hg 71.9	Tl 78.5	Pb 105	Bi 119	Po	At	Rn
Fr	Ra	Ac															

Ce	Pr	Nd	Pm	Sm	Eu	Gd 200	Tb	Dy 210	Ho	Er	Tm	Yb 120	Lu 210
Th 163	Pa	U 207	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

NOTE: The subscript zero on the θ denotes the low temperature limit of the experimental values.

Figure 4.11 Heat capacity C_V of a solid, according to the Debye approximation. The vertical scale is in J mol^{-1} K^{-1}. The horizontal scale is the temperature normalized to the Debye temperature θ. The region of the T^3 law is below 0.10. The asymptotic value at high values of T/θ is 24.943 J mol^{-1} K^{-1}.

Table 4.2 Values of C_V, S, U, and F on the Debye theory, in units J mol^{-1} K^{-1}

| θ/T	C_V	$S = k_B \sigma$	$U_\tau\theta$	F/θ
0	24.943	∞	∞	
0.1	24.93	90.70	240.2	-666.8
0.2	24.89	73.43	115.6	-251
0.3	24.83	63.34	74.2	-137
0.4	24.75	56.21	53.5	-87
0.5	24.63	50.70	41.16	-60.3
0.6	24.50	46.22	32.9	-44.1
0.7	24.34	42.46	27.1	-33.5
0.8	24.16	39.22	22.8	-26.2
0.9	23.96	36.38	19.5	-20.9
1.0	23.74	33.87	16.82	-17.05
1.5	22.35	24.49	9.1	-7.23
2	20.59	18.30	5.5	-3.64
3	16.53	10.71	2.36	-1.21
4	12.55	6.51	1.13	-0.49
5	9.20	4.08	0.58	-0.23
6	6.23	2.64	0.323	-0.118
7	4.76	1.77	0.187	-0.066
8	3.45	1.22	0.114	-0.039
9	2.53	0.874	0.073	-0.025
10	1.891	0.643	0.048	-0.016
15	0.576	0.192	0.0096	-0.0032
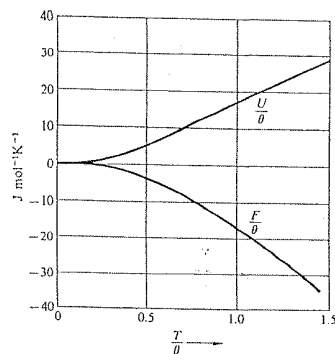
Figure 4.12 Energy U and free energy $F \equiv U - \tau\sigma$ of a solid, according to the Debye theory. The Debye temperature of the solid is θ.

SUMMARY

1. The Planck distribution function is

$$\langle s \rangle = \frac{1}{\exp(\hbar\omega/\tau) - 1},$$

for the thermal average number of photons in a cavity mode of frequency ω.

2. The Stefan-Boltzmann law is

$$\frac{U}{V} = \frac{\pi^2}{15\hbar^3 c^3}\tau^4,$$

for the radiant energy density in a cavity at temperature τ.

3. The Planck radiation law is

$$u_\omega = \frac{\hbar}{\pi^2 c^3} \frac{\omega^3}{\exp(\hbar\omega/\tau) - 1} ,$$

for the radiation energy per unit volume per unit range of frequency.

4. The flux density of radiant energy is $J_U = \sigma_B T^4$, where σ_B is the Stefan-Boltzmann constant $\pi^2 k_B^4/60\hbar^3 c^2$.

5. The Debye low temperature limit of the heat capacity of a dielectric solid is, in conventional units,

$$C_V = \frac{12\pi^4 N k_B}{5} \left(\frac{T}{\theta}\right)^3 ,$$

where the Debye temperature

$$\theta \equiv (\hbar v/k_B)(6\pi^2 N/V)^{1/3}.$$

PROBLEMS

1. Number of thermal photons. Show that the number of photons $\sum \langle s_n \rangle$ in equilibrium at temperature τ in a cavity of volume V is

$$N = 2.404\pi^{-2} V(\tau/\hbar c)^3. \tag{48}$$

From (23) the entropy is $\sigma = (4\pi^4 V/45)(\tau/\hbar c)^3$, whence $\sigma/N \simeq 3.602$. It is believed that the total number of photons in the universe is 10^8 larger than the total number of nucleons (protons, neutrons). Because both entropies are of the order of the respective number of particles (see Eq. 3.76), the photons provide the dominant contribution to the entropy of the universe, although the particles dominate the total energy. We believe that the entropy of the photons is essentially constant, so that the entropy of the universe is approximately constant with time.

2. Surface temperature of the Sun. The value of the total radiant energy flux density at the Earth from the Sun normal to the incident rays is called the solar constant of the Earth. The observed value integrated over all emission wavelengths and referred to the mean Earth-Sun distance is:

$$\text{solar constant} = 0.136 \text{ J s}^{-1} \text{cm}^{-2}. \tag{49}$$

(a) Show that the total rate of energy generation of the Sun is 4×10^{26} J s^{-1}. (b) From this result and the Stefan-Boltzmann constant $\sigma_B = 5.67 \times 10^{-12}$ J s^{-1} cm^{-2} K^{-4}, show that the effective temperature of the surface of the Sun treated as a black body is $T \cong 6000$ K. Take the distance of the Earth from the Sun as 1.5×10^{13} cm and the radius of the Sun as 7×10^{10} cm.

3. Average temperature of the interior of the Sun. (a) Estimate by a dimensional argument or otherwise the order of magnitude of the gravitational self-energy of the Sun, with $M_\odot = 2 \times 10^{33}$ g and $R_\odot = 7 \times 10^{10}$ cm. The gravitational constant G is 6.6×10^{-8} dyne cm^2 g^{-2}. The self-energy will be negative referred to atoms at rest at infinite separation. (b) Assume that the total thermal kinetic energy of the atoms in the Sun is equal to $-\frac{1}{2}$ times the gravitational energy. This is the result of the virial theorem of mechanics. Estimate the average temperature of the Sun. Take the number of particles as 1×10^{57}. This estimate gives somewhat too low a temperature, because the density of the Sun is far from uniform. "The range in central temperature for different stars, excluding only those composed of degenerate matter for which the law of perfect gases does not hold (white dwarfs) and those which have excessively small average densities (giants and supergiants), is between 1.5 and 3.0×10^7 degrees." (O. Struve, B. Lynds, and H. Pillans, *Elementary astronomy*, Oxford, 1959.)

4. Age of the Sun. Suppose 4×10^{26} J s^{-1} is the total rate at which the Sun radiates energy at the present time. (a) Find the total energy of the Sun available for radiation, on the rough assumptions that the energy source is the conversion of hydrogen (atomic weight 1.0078) to helium (atomic weight 4.0026) and that the reaction stops when 10 percent of the original hydrogen has been converted to helium. Use the Einstein relation $E = (\Delta M)c^2$. (b) Use (a) to estimate the life expectancy of the Sun. It is believed that the age of the universe is about 10×10^9 years. (A good discussion is given in the books by Peebles and by Weinberg, cited in the general references.)

5. Surface temperature of the Earth. Calculate the temperature of the surface of the Earth on the assumption that as a black body in thermal equilibrium it reradiates as much thermal radiation as it receives from the Sun. Assume also that the surface of the Earth is at a constant temperature over the day-night cycle. Use $T_\odot = 5800$ K; $R_\odot = 7 \times 10^{10}$ cm; and the Earth-Sun distance of 1.5×10^{13} cm.

6. Pressure of thermal radiation. Show for a photon gas that:

(a)
$$p = -(\partial U/\partial V)_\sigma = -\sum_j s_j \hbar (d\omega_j/dV) , \tag{50}$$

where s_j is the number of photons in the mode j;

(b) $$d\omega_j/dV = -\omega_j/3V;$$ (51)

(c) $$p = U/3V.$$ (52)

Thus the radiation pressure is equal to $\frac{1}{3} \times$ (energy density).

(d) Compare the pressure of thermal radiation with the kinetic pressure of a gas of H atoms at a concentration of 1 mole cm^{-3} characteristic of the Sun. At what temperature (roughly) are the two pressures equal? The average temperature of the Sun is believed to be near 2×10^7 K. The concentration is highly nonuniform and rises to near 100 mole cm^{-3} at the center, where the kinetic pressure is considerably higher than the radiation pressure.

7. *Free energy of a photon gas.* (a) Show that the partition function of a photon gas is given by

$$Z = \prod_n [1 - \exp(-\hbar\omega_n/\tau)]^{-1},$$ (53)

where the product is over the modes n. (b) The Helmholtz free energy is found directly from (53) as

$$F = \tau \sum_n \log[1 - \exp(-\hbar\omega_n/\tau)].$$ (54)

Transform the sum to an integral; integrate by parts to find

$$F = -\pi^2 V \tau^4/45\hbar^3 c^3.$$ (55)

8. *Heat shields.* A black (nonreflective) plane at temperature T_u is parallel to a black plane at temperature T_l. The net energy flux density in vacuum between the two planes is $J_U = \sigma_B(T_u^4 - T_l^4)$, where σ_B is the Stefan-Boltzmann constant used in (26). A third black plane is inserted between the other two and is allowed to come to a steady state temperature T_m. Find T_m in terms of T_u and T_l, and show that the net energy flux density is cut in half because of the presence of this plane. This is the principle of the heat shield and is widely used to reduce radiant heat transfer. *Comment*: The result for N independent heat shields floating in temperature between the planes T_u and T_l is that the net energy flux density is $J_U = \sigma_B(T_u^4 - T_l^4)/(N + 1)$.

9. *Photon gas in one dimension.* Consider a transmission line of length L on which electromagnetic waves satisfy the one-dimensional wave equation $v^2 \partial^2 E/\partial x^2 = \partial^2 E/\partial t^2$, where E is an electric field component. Find the heat capacity of the photons on the line, when in thermal equilibrium at temperature

τ. The enumeration of modes proceeds in the usual way for one dimension: take the solutions as standing waves with zero amplitude at each end of the line.

10. *Heat capacity of intergalactic space.* Intergalactic space is believed to be occupied by hydrogen atoms in a concentration ≈ 1 atom m^{-3}. The space is also occupied by thermal radiation at 2.9 K, from the Primitive Fireball. Show that the ratio of the heat capacity of matter to that of radiation is $\sim 10^{-9}$.

11. *Heat capacity of solids in high temperature limit.* Show that in the limit $T \gg \theta$ the heat capacity of a solid goes towards the limit $C_V \to 3Nk_B$, in conventional units. To obtain higher accuracy when T is only moderately larger than θ, the heat capacity can be expanded as a power series in $1/T$, of the form

$$C_V = 3Nk_B \times \left[1 - \sum_n \bar{a}_n/T^n\right].$$ (56)

Determine the first nonvanishing term in the sum. Check your result by inserting $T = \theta$ and comparing with Table 4.2.

12. *Heat capacity of photons and phonons.* Consider a dielectric solid with a Debye temperature equal to 100 K and with 10^{22} atoms cm^{-3}. Estimate the temperature at which the photon contribution to the heat capacity would be equal to the phonon contribution evaluated at 1 K.

13. *Energy fluctuations in a solid at low temperatures.* Consider a solid of N atoms in the temperature region in which the Debye T^3 law is valid. The solid is in thermal contact with a heat reservoir. Use the results on energy fluctuations from Chapter 3 to show that the root mean square fractional energy fluctuation $\mathscr{F}$ is given by

$$\mathscr{F}^2 = \langle(\varepsilon - \langle\varepsilon\rangle)^2\rangle/\langle\varepsilon\rangle^2 \approx \frac{0.07}{N}\left(\frac{\theta}{T}\right)^3.$$ (57)

Suppose that $T = 10^{-2}$ K; $\theta = 200$ K; and $N \approx 10^{15}$ for a particle 0.01 cm on a side; then $\mathscr{F} \approx 0.02$. At 10^{-5} K the fractional fluctuation in energy is of the order of unity for a dielectric particle of volume 1 cm^3.

14. *Heat capacity of liquid ^{4}He at low temperatures.* The velocity of longitudinal sound waves in liquid ^{4}He at temperatures below 0.6 K is 2.383×10^4 cm s^{-1}. There are no transverse sound waves in the liquid. The density is 0.145 g cm^{-3}. (a) Calculate the Debye temperature. (b) Calculate the heat capacity per gram on the Debye theory and compare with the experimental value $C_V = 0.0204 \times T^3$, in J g^{-1} K^{-1}. The T^3 dependence of the experimental

value suggests that phonons are the most important excitations in liquid ^{4}He below 0.6 K. Note that the experimental value has been expressed per gram of liquid. The experiments are due to J. Wiebes, C. G. Niels-Hakkenberg, and H. C. Kramers, Physica 32, 625 (1957).

15. *Angular distribution of radiant energy flux.* (a) Show that the spectral density of the radiant energy flux that arrives in the solid angle $d\Omega$ is $cu_\omega \cos\theta \cdot d\Omega/4\pi$, where θ is the angle the normal to the unit area makes with the incident ray, and u_ω is the energy density per unit frequency range. (b) Show that the sum of this quantity over all incident rays is $\frac{1}{4}cu_\omega$.

16. *Image of a radiant object.* Let a lens image the hole in a cavity of area A_H on a black object of area A_0. Use an equilibrium argument to relate the product $A_H\Omega_H$ to $A_0\Omega_0$ where Ω_H and Ω_0 are the solid angles subtended by the lens as viewed from the hole and from the object. This general property of focusing systems is easily derived from geometrical optics. It is also true when diffraction is important. Make the approximation that all rays are nearly parallel (all axial angles small).

17. *Entropy and occupancy.* We argued in this chapter that the entropy of the cosmic black body radiation has not changed with time because the number of photons in each mode has not changed with time, although the frequency of each mode has decreased as the wavelength has increased with the expansion of the universe. Establish the implied connection between entropy and occupancy of the modes, by showing that for one mode of frequency ω the entropy is a function of the photon occupancy $\langle s \rangle$ only:

$$\sigma = \langle s+1 \rangle \log\langle s+1 \rangle - \langle s \rangle \log\langle s \rangle. \tag{58}$$

It is convenient to start from the partition function.

18. *Isentropic expansion of photon gas.* Consider the gas of photons of the thermal equilibrium radiation in a cube of volume V at temperature τ. Let the cavity volume increase; the radiation pressure performs work during the expansion, and the temperature of the radiation will drop. From the result for the entropy we know that $\tau V^{1/3}$ is constant in such an expansion. (a) Assume that the temperature of the cosmic black-body radiation was decoupled from the temperature of the matter when both were at 3000 K. What was the radius of the universe at that time, compared to now? If the radius has increased linearly with time, at what fraction of the present age of the universe did the decoupling take place? (b) Show that the work done by the photons during the expansion is

$$W = (\pi^2/15h^3c^3)V_i\tau_i^3(\tau_i - \tau_f).$$

The subscripts i and f refer to the initial and final states.

19. *Reflective heat shield and Kirchhoff's law.* Consider a plane sheet of material of absorptivity a, emissivity e, and reflectivity $r = 1 - a$. Let the sheet be suspended between and parallel with two black sheets maintained at temperatures τ_u and τ_l. Show that the net flux density of thermal radiation between the black sheets is $(1 - r)$ times the flux density when the intermediate sheet is also black as in Problem 8, which means with $a = e = 1; r = 0$. Liquid helium dewars are often insulated by many, perhaps 100, layers of an aluminized Mylar film called Superinsulation.

SUPPLEMENT: GREENHOUSE EFFECT

The Greenhouse Effect describes the warming of the surface of the Earth caused by the interposition of an infrared absorbent layer of water, as vapor and in clouds, and of carbon dioxide in the atmosphere between the Sun and the Earth. The water may contribute as much 90 percent of the warming effect.

Absent such a layer, the temperature of the surface of the Earth is determined primarily by the requirement of energy balance between the flux of solar radiation incident on the Earth and the flux of reradiation from the Earth; the reradiation flux is proportional to the fourth power of the temperature of the Earth, as in (4.26). This energy balance is the subject of Problem 4.5 and leads to the result $T_E = (R_S/2D_{SE})^{1/2}T_S$, where T_E is the temperature of the Earth and T_S is that of the Sun; here R_S is the radius of the Sun and D_{SE} is the Sun-Earth distance.

The result of that problem is $T_E = 280$ K, assuming $T_S = 5800$ K. The Sun is much hotter than the Earth, but the geometry (the small solid angle subtended by the Sun) reduces the solar flux density incident at the Earth by a factor of roughly $(1/20)^4$.

We assume as an example that the atmosphere is a perfect greenhouse, defined as an absorbent layer that transmits all of the visible radiation that falls on it from the Sun, but absorbs and re-emits all the radiation (which lies in the infrared), from the surface of the Earth. We may idealize the problem by neglecting the absorption by the layer of the infrared portion of the incident solar radiation, because the solar spectrum lies almost entirely at higher frequencies, as evident from Figure 4.4. The layer will emit energy flux I_L up and I_L down; the upward flux will balance the solar flux I_S, so that $I_L = I_S$. The net downward flux will be the sum of the solar flux I_S and the flux I_L down from the layer. The latter increases the net thermal flux incident at the surface of the Earth. Thus

$$I_{E_g} = I_S + I_L = 2I_S \tag{59}$$

where I_{E_g} is the thermal flux from the Earth in the presence of the perfect

greenhouse effect. Because the thermal flux varies as T^4, the new temperature of the surface of the Earth is

$$T_{E_g} = 2^{1/4} T_E \approx (1.19) \ 280 \ \text{K} \approx 333 \ \text{K}, \tag{60}$$

so that the greenhouse warming of the Earth is 333 K − 280 K ≈ 53 K for this extreme example.*

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* For detailed discussions see *Climate change* and *Climate change 1992*, Cambridge U.P., 1990 and 1992: J. T. Houghton et al, editors.

Chapter 5

Chemical Potential and Gibbs Distribution