

Supplement to Chapter 7

REVIEW QUESTIONS

- 7.1** Describe a system that is naturally analyzed using the grand canonical ensemble.
- 7.2** For a classical system, write down the probability density for the grand canonical ensemble and explain what it means? In other words, what is the physical interpretation of the function that you have written down?
- 7.3** Describe the model that was used for surface adsorption.
- 7.4** For the surface adsorption model, calculate the grand partition function.
- 7.5** Explain how a relationship can be obtained between the density of particles adsorbed on the surface and the density of particles in the gas.
- 7.6** Describe the possible energy eigenvalues of a many-particle ideal quantum system for the cases of bosons and fermions.
- 7.7** For an ideal quantum system, how are the single-particle energy values ε_k determined?
- 7.8** Derive the grand potential for an ideal many-boson system with a single-particle energy spectrum ε_k .
- 7.9** Do the same for an ideal many-fermion system.
- 7.10** Write formulas for N and E , as discrete sums involving the single-particle energy spectrum, for ideal Bose–Einstein and Fermi–Dirac systems.
- 7.11** For an ideal Fermi gas of spin- $\frac{1}{2}$ particles, derive integral formulas for N and E .
- 7.12** How is the chemical potential related to the affinity?
- 7.13** Prove that $p = \frac{2}{3}E/V$ for an ideal Fermi gas.
- 7.14** Derive a formula for the chemical potential of an ideal Fermi gas at zero temperature.
- 7.15** How is the Fermi energy defined?
- 7.16** Using the low temperature expansion for a Fermi–Dirac integral derived in the Mathematical Appendix, show that the specific heat of an ideal Fermi gas is proportional to T at low temperatures.
- 7.17** Explain why it is true that using the integral formula for N for the ideal Bose gas leads to difficulty and how one solves the problem.
- 7.18** For the ideal Bose gas, derive the formula for the critical density as a function of the temperature.
- 7.19** For the ideal Bose gas, derive the formula for the critical temperature as a function of the density.
- 7.20** Using variables n and $\tau = kT$, show the phase diagram for the ideal Bose gas.
- 7.21** What quantity is discontinuous across the Bose–Einstein transition line?
- 7.22** What is wrong with the ideal Bose gas as a model for any real physical system?
- 7.23** What is the rule that determines whether a particular atom satisfies Bose–Einstein or Fermi–Dirac statistics?
- 7.24** Draw a sketch of the phase diagram for ^4He .
- 7.25** In liquid helium, as $T \rightarrow 0$, what happens to the superfluid density?
- 7.26** In liquid helium, as $T \rightarrow 0$, what happens to the condensate density?
- 7.27** Draw a sketch of the excitation spectrum for liquid helium. Explain the physical meaning of what you have drawn.

- 7.28** Assuming that elementary excitations are the only possible excited states of the system (a false assumption), prove that liquid helium will be a superfluid below a critical velocity and relate that critical velocity to the excitation spectrum.
- 7.29** Why is ground glass (or some equivalent stuff) used in demonstrations of superfluid flow?
- 7.30** Describe quantized vortices in liquid helium. Are they the same as rotons?
- 7.31** For the quasiparticles in liquid helium, and for the photon gas, why is the affinity equal to zero?
- 7.32** Derive the phonon contribution to the specific heat of liquid helium at very low temperature.
- 7.33** Derive the energy density of radiation within a cavity at temperature T .
- 7.34** Derive Wien's displacement law for the location of the maximum in the frequency distribution function.

EXERCISES

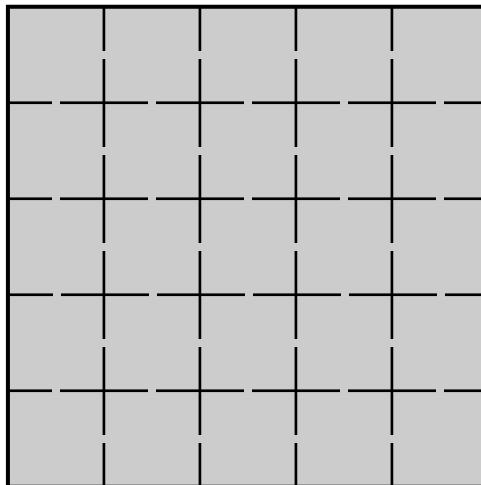


Fig. S7.1 A system composed of a large number of weakly interacting identical subsystems.

Exercise 7.1 Consider a system composed of a large number M of identical boxes (Fig. S7.1). Each box has a pinhole that connects it with each of its nearest neighbors. The particles may have interactions, but we will neglect the interactions between particles that are in different boxes. The eigenstates of a set of N particles in one of the boxes are $\psi_1^N, \psi_2^N, \dots$, with energies E_1^N, E_2^N, \dots . Given that the complete closed system has N_T particles and a fixed energy E_T , use the method of the most probable distribution (from Chapter 2) to calculate the probability that a given system is in quantum state ψ_k^N . Show that it agrees with the grand canonical ensemble.

Solution In order to make the analysis clearer, it is useful to assume that, once each minute, the pinholes simultaneously open for only 1 second and then remain closed for the other 59 seconds. We only describe the system while the pinholes are closed and each box is therefore a completely isolated subsystem. We number

the boxes from 1 to M . A microstate is defined by giving the quantum state of the set of particles in each box. The macrostate is defined by saying how many boxes are in state ψ_k^N for every value of N and k . Let ν_k^N be the number of subsystems in state ψ_k^N . Certainly, the set of nonnegative integers ν_k^N must satisfy the three constraints

$$\sum_N \sum_k \nu_k^N = M \quad (\text{the number of boxes}) \quad (\text{S7.1})$$

$$\sum_N \sum_k N \nu_k^N = N_T \quad (\text{the number of particles}) \quad (\text{S7.2})$$

$$\sum_N \sum_k E_k^N \nu_k^N = E_T \quad (\text{the total energy}) \quad (\text{S7.3})$$

The number of microstates that correspond to a given macrostate (defined by a particular set of ν_k^N 's) is

$$K = \frac{M!}{\prod_N \prod_k \nu_k^N!} \quad (\text{S7.4})$$

Using Stirling's approximation and Lagrange's method, we maximize the function

$$F = \log M! - \sum_{N,k} \nu_k^N (\log \nu_k^N - 1) - \gamma \sum_{N,k} \nu_k^N - \alpha \sum_{N,K} N \nu_k^N - \beta \sum_{N,k} E_k^N \nu_k^N \quad (\text{S7.5})$$

Setting $\partial F / \partial \nu_k^N = 0$ gives

$$-\log \nu_k^N - \gamma - \alpha N - \beta E_k^N = 0 \quad (\text{S7.6})$$

or

$$\nu_k^N = C e^{-\alpha N - \beta E_k^N} \quad (\text{S7.7})$$

The fraction of systems in state ψ_k^N is equal to the probability that a randomly chosen system will be in that state. It is

$$P_{Nk} = \frac{\nu_k^N}{\sum \nu_k^N} = \Lambda^{-1} e^{-\alpha N - \beta E_k^N} \quad (\text{S7.8})$$

where

$$\Lambda = \sum_{N,k} e^{-\alpha N - \beta E_k^N} \quad (\text{S7.9})$$

This result obviously agrees with the grand canonical ensemble prediction. We have simply used $M-1$ identical boxes as our reservoir for any given box.

Exercise 7.2 Derive the equations of state of a monatomic ideal gas, using classical mechanics and the grand canonical ensemble.

Solution The Hamiltonian function for an N -particle monatomic ideal gas is

$$H_N = \sum_{n=1}^N p_n^2 / 2m \quad (\text{S7.10})$$

To derive equations of state, one first calculates the grand partition function, defined as

$$\begin{aligned} \Lambda(\alpha, \beta, V) &= \sum_{N=0}^{\infty} \frac{e^{-\alpha N}}{N! h^{3N}} \int_V d^{3N} r \int d^{3N} p e^{-\beta H_N} \\ &= \sum_{N=0}^{\infty} \frac{e^{-\alpha N}}{N! h^{3N}} V^N (2\pi m / \beta)^{3N/2} \end{aligned} \quad (\text{S7.11})$$

But

$$(2\pi m / \beta)^{1/2} / h = \frac{\sqrt{2\pi m k T}}{h} = 1 / \lambda(\beta) \quad (\text{S7.12})$$

where λ is the thermal de Broglie wavelength. Also $e^{-\alpha N} = (e^{-\alpha})^N$. Thus

$$\Lambda = \sum_{N=0}^{\infty} \frac{1}{N!} \left(\frac{e^{-\alpha V}}{\lambda^3} \right)^N = \exp(e^{-\alpha V}/\lambda^3) \quad (\text{S7.13})$$

The grand potential is the logarithm of Λ .

$$\psi(\alpha, \beta, V) = e^{-\alpha V}/\lambda^3(\beta) \quad (\text{S7.14})$$

N , E , and βp are given by the derivatives of ψ .

$$N = -\frac{\partial \psi}{\partial \alpha} = e^{-\alpha V}/\lambda^3 \quad (\text{S7.15})$$

$$E = -\frac{\partial \psi}{\partial \beta} = \frac{3}{2\beta} e^{-\alpha V}/\lambda^3 \quad (\text{S7.16})$$

and

$$\beta p = \frac{\partial \psi}{\partial V} = e^{-\alpha}/\lambda^3 \quad (\text{S7.17})$$

Dividing the second and third equations by the first, one obtains the desired equations of state.

$$\frac{E}{N} = \frac{3}{2} kT \quad \text{and} \quad \frac{p}{NkT} = \frac{1}{V} \quad (\text{S7.18})$$

Exercise 7.3 The inside surface of a 1 cm^3 box is covered with adsorption sites. Each site has an area of 4 \AA^2 and a binding energy of 200 K (the energy of a particle at the site is -200 K). The box contains argon gas. At 300 K the box is evacuated to a pressure of 10^{-7} atmospheres. It is completely sealed and the temperature is then reduced to 8 K. Without adsorption the pressure would drop to $(8/300) \times 10^{-7} = 2.67 \times 10^{-9}$ atmospheres. Taking adsorption into account, determine the actual pressure at 8 K.

Solution Each of the six faces has an area of $1 \text{ cm}^2 = 10^{16} \text{ \AA}^2$. Thus the total number of adsorption sites is

$$N_s = 1.5 \times 10^{16} \quad (\text{S7.19})$$

The mass of an argon atom is $39.95 u = 6.64 \times 10^{-26} \text{ kg}$. Therefore, the constant γ , appearing in Eq. (7.29), is

$$\gamma = k^{5/2} (2\pi m)^{3/2} / h^3 = 6.55 \times 10^5 \quad (\text{S7.20})$$

The pressure at 300 K, in SI units, is $1.01 \times 10^{-2} \text{ N/m}^2$. According to Eq. (7.30), the number of adsorbed particles at 300 K is

$$N_a = \frac{N_s p}{p + \gamma T^{5/2} e^{-T_o/T}} = 290 \quad (\text{S7.21})$$

which is completely negligible. Thus the number of particles in the system is

$$N = \frac{pV}{kT} = 2.44 \times 10^{12} \quad (\text{S7.22})$$

At 8 K we know that $p \leq NkT/V = 2.70 \times 10^{-4} \text{ N/m}^2$. But

$$\gamma T^{5/2} e^{-T_o/T} = 1.65 \times 10^{-3} \quad (\text{S7.23})$$

which indicates that the two terms in the denominator of Eq. (7.36) are of comparable size, so neither can be neglected. Using the fact that

$$N_a = N - \frac{pV}{kT} \quad (\text{S7.24})$$

one obtains the following quadratic equation for p .

$$N - (V/kT)p = \frac{N_s p}{p + \gamma T^{5/2} e^{-T_o/T}} \quad (\text{S7.25})$$

Putting in the known values of all constants and solving the quadratic equation, one finds a unique positive root.

$$p = 2.67 \times 10^{-7} \text{ N/m}^2 = 2.64 \times 10^{-12} \text{ atm} \quad (\text{S7.26})$$

The disappearance of the gas onto the walls, which had no effect at 300 K, reduces the pressure at 8 K by a factor of 1000.

Exercise 7.4 Consider an ideal gas composed of monatomic molecules of mass m and diatomic molecules of mass $2m$ and moment of inertia I . The molecules may undergo the chemical reaction $2A \leftrightarrow B$. A diatomic molecule has a ground-state energy of $E_g = -\varepsilon$ in comparison with two separated atoms. (a) Considering the monatomic and diatomic molecules as distinct species, calculate the grand potential $\psi(\alpha_1, \alpha_2, \beta, V)$ using classical mechanics and taking into account the rotational but not the vibrational degrees of freedom of the diatomic molecules. (b) Impose the condition for chemical reaction equilibrium, $2\alpha_1 = \alpha_2$, and obtain an equation for the pressure as a function of the temperature and the total density of atoms. (c) For Cl_2 , $\varepsilon = 4.0 \times 10^{-19} \text{ J} = 29,000 \text{ K}$, and $\hbar^2/2I = 4.95 \times 10^{-24} \text{ J} = 0.25 \text{ K}$. Use these values to plot the pressure as a function of T for a density of $n(\text{STP})$.

Solution (a) The Hamiltonian for the system with K monatomic and L diatomic molecules is

$$\begin{aligned} H &= \sum_{k=1}^K \frac{p_k^2}{2m} - \varepsilon L + \sum_{\ell=1}^L \left(\frac{P_\ell^2}{4m} + \frac{P_{\phi\ell}^2 + P_{\theta\ell}^2 / \sin^2 \theta_\ell}{2I} \right) \\ &= H_1 - \varepsilon L + H_2 \end{aligned} \quad (\text{S7.27})$$

The grand partition function is obtained by summing independently over all values of K and L .

$$\begin{aligned} \Lambda &= \sum_{K=0}^{\infty} \sum_{L=0}^{\infty} \left(\frac{e^{-\alpha_1 K}}{K! h^{3K}} \int d^{3K} x d^{3K} p e^{-\beta H_1} \right) \\ &\quad \times \left(\frac{e^{-\alpha_2 L + \beta \varepsilon L}}{L! h^{5L}} \int d^{5L} x d^{5L} P e^{-\beta H_2} \right) \\ &= \sum_K \left(\frac{e^{-\alpha_1 K}}{K! h^{3K}} \int d^{3K} x d^{3K} p e^{-\beta H_1} \right) \\ &\quad \times \sum_L \left(\frac{e^{-(\alpha_2 - \beta \varepsilon)L}}{L! h^{5L}} \int d^{5L} x d^{5L} P e^{-\beta H_2} \right) \end{aligned} \quad (\text{S7.28})$$

The sum over K is identical to the partition function that was calculated in the last exercise.

$$\sum_K \left(\frac{e^{-\alpha_1 K}}{K! h^{3K}} \int d^{3K} x d^{3K} p e^{-\beta H_1} \right) = \exp(e^{-\alpha_1} V / \lambda_1^3) \quad (\text{S7.29})$$

where $\lambda_1 = h / \sqrt{2\pi m k T}$. The integral in the second term is the L th power of a five-dimensional integral of the form

$$\begin{aligned} I_5 &= \frac{1}{h^5} \int_V d^3 x \int d^3 P e^{-\beta P^2 / 4m} \int d\theta d\phi \\ &\quad \times \int dP_\theta dP_\phi \exp[-\beta(P_\theta^2 + P_\phi^2 / \sin^2 \theta) / 2I] \end{aligned} \quad (\text{S7.30})$$

This integral can be found in Eqs. (4.63) and (4.64).

$$I_5 = \frac{2IV}{\beta \hbar \lambda_2^3} \quad (\text{S7.31})$$

The sum over L in Eq. (S7.28) can now be computed easily.

$$\sum_{L=0}^{\infty} \frac{1}{L!} \left(e^{-\alpha_2 + \beta\epsilon} \frac{2IV}{\beta\hbar^2\lambda_2^3} \right)^L = \exp\left(e^{-\alpha_2 + \beta\epsilon} \frac{2IV}{\beta\hbar^2\lambda_2^3} \right) \quad (\text{S7.32})$$

The grand potential, $\psi = \log \Lambda$, is

$$\psi(\alpha_1, \alpha_2, \beta, V) = \frac{e^{-\alpha_1} V}{\lambda_1^3(\beta)} + \frac{2e^{-\alpha_2 + \beta\epsilon} IV}{\beta\hbar^2\lambda_2^3(\beta)} \quad (\text{S7.33})$$

(b) Imposing the condition for chemical reaction equilibrium, $\alpha_2 = 2\alpha_1$, and dropping the subscript on α_1 , we obtain a grand potential with the single affinity variable α , which represents the affinity for A atoms.

$$\psi(\alpha, \beta, V) = e^{-\alpha} \frac{V}{\lambda_1^3} + e^{-2\alpha + \beta\epsilon} \frac{2IV}{\beta\hbar^2\lambda_2^3} \quad (\text{S7.34})$$

The particle density is given in terms of ψ by the standard thermodynamic identity

$$n = -V^{-1} \frac{\partial \psi}{\partial \alpha} = \frac{e^{-\alpha}}{\lambda^3} + \frac{4\sqrt{2}I}{\hbar^2\beta} \frac{e^{-2\alpha + \beta\epsilon}}{\lambda^3} \quad (\text{S7.35})$$

where we have used the fact that $\lambda_2 = \lambda_1/\sqrt{2}$ and have dropped the subscript on λ_1 . In order to analyze the relationship between pressure and density, it is convenient to introduce a new variable, called the *activity*, that will play an important role when we study the nonideal gas in the next chapter. The activity is defined by

$$\zeta = \frac{e^{-\alpha}}{\lambda^3(\beta)} \quad (\text{S7.36})$$

If we define a rotational temperature, $T_R = \hbar^2/2kI$, we can write n in terms of ζ and T as

$$n = \zeta + 2\sqrt{2}\lambda^3(T/T_R)e^{\epsilon/kT}\zeta^2 \equiv \zeta + 2C(T)\zeta^2 \quad (\text{S7.37})$$

The pressure can be expressed in terms of ζ and T by using the fact that $p/kT = \psi/V$.

$$p/kT = \zeta + \sqrt{2}\lambda^3(T/T_R)e^{\epsilon/kT}\zeta^2 = \zeta + C(T)\zeta^2 \quad (\text{S7.38})$$

The pressure equation of state is obtained by solving for ζ as a function of n and then using that function in the second equation. Equation (S7.38) is a quadratic equation that can be easily solved to give (note that ζ must be positive)

$$\zeta = \frac{(1 + 8Cn)^{1/2} - 1}{4C} \quad (\text{S7.39})$$

Noting that $p/kT = n - C\zeta^2$, we get

$$\frac{p}{kT} = n - \frac{[(1 + 8Cn)^{1/2} - 1]^2}{16C} \quad (\text{S7.40})$$

For small n we can obtain the correction to the simple monatomic ideal gas law, $p = nkT$, by expanding the square root to first order in n . The result is

$$\frac{p}{kT} \approx n - C(T)n^2 \quad (\text{S7.41})$$

The pressure is reduced, in comparison with a monatomic gas, because the number of gas particles diminishes as atoms combine to form diatomic molecules. (c) For Cl_2 the binding energy and rotational temperature have been given. Using these values to calculate $C(T)$ and setting n equal to $n(\text{STP})$ in Eq. (S7.32), we can plot $p(T)$ at constant n . At low T we expect $p \approx \frac{1}{2}nkT$ because most of the atoms will be bound into

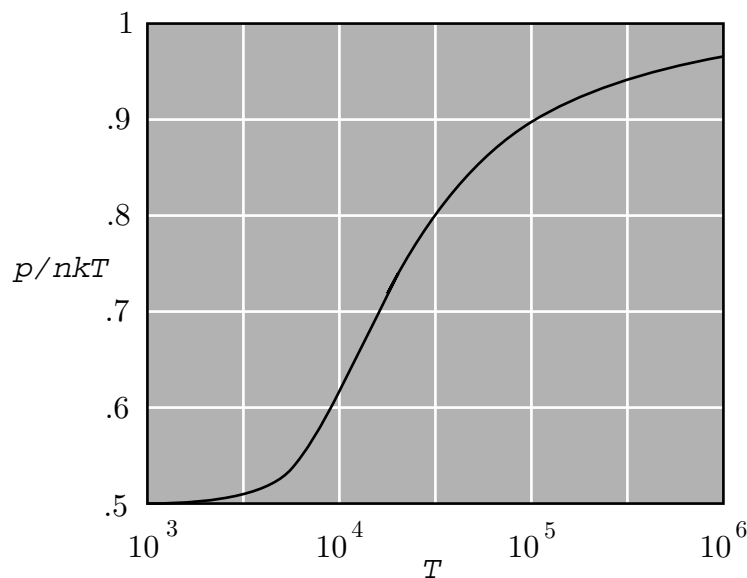


Fig. S7.2 The function p/nkT , where n is the density of atoms. At low temperature, the atoms form themselves into diatomic molecules and so $p = nkT/2$.

diatomic molecules. At high T we expect $p \approx nkT$. This is nicely illustrated in Fig. S7.2, where p/nkT is plotted on a logarithmic T scale.

Exercise 7.5 N_o molecules of hemoglobin are transported between the atmosphere, where the partial pressure of oxygen is 0.2 atm, to a region where the temperature is the same but the partial pressure of oxygen is 0.02 atm. Each molecule of hemoglobin has four sites that can hold an oxygen molecule. Assuming that Eq. (7.24) is applicable to the attachment of oxygen to hemoglobin (which is only a very rough approximation) and that the sites are 75% filled in the oxygen-rich atmosphere, calculate how many molecules of oxygen are released when the hemoglobin is transported to the oxygen-poor region.

Solution Let the partial pressure of oxygen in the oxygen-rich atmosphere be p_H and that in the oxygen-poor atmosphere be p_L . Then, by Eq. (7.24), in the oxygen-rich atmosphere

$$f_a = 0.75 = \frac{p_H}{p_H + g/z_a} \quad (\text{S7.42})$$

This can be solved for the unknown quantity g/z_a .

$$g/z_a = p_H/3 \quad (\text{S7.43})$$

According to the statement of the problem, $p_L = 0.1 p_H$. Thus, at p_L , the fraction of occupied sites is

$$f_a = \frac{0.1 p_H}{0.1 p_H + p_H/3} = \frac{3}{13} = 0.23 \quad (\text{S7.44})$$

The number of oxygen molecules released is

$$4N_o(0.75 - 0.23) = 2.08N_o \quad (\text{S7.45})$$

Exercise 7.6 In reality, the oxygen molecules attached to the four binding sites of a hemoglobin molecule have significant attractive interactions that were ignored in the last exercise. In order to determine qualitatively the effect of adsorbate interactions, consider the following extreme case. We assume that each hemoglobin molecule has two double binding sites. At any double site a single oxygen molecule will not stick

but a pair of oxygen molecules will attach with an energy $\varepsilon = -kT_o$. (a) Derive the equivalent of Eq. (7.24) for this system. (b) For this system, repeat the last exercise.

Solution (a) The grand potential for the system is $2N_o$ times the grand potential for one double site. The grand partition function for a double site is (the possible values of N are 0 and 2)

$$\Lambda = 1 + e^{-2\alpha + T_o/T} \quad (\text{S7.46})$$

Thus

$$\psi = 2N_o \log(1 + e^{-2\alpha + T_o/T}) \quad (\text{S7.47})$$

The number of attached oxygen molecules is

$$N = -\frac{\partial\psi}{\partial\alpha} = 4N_o/(e^{2\alpha - T_o/T} + 1) \quad (\text{S7.48})$$

Letting $f_a = N/4N_o$, we can solve this equation for $e^{2\alpha - T_o/T}$.

$$e^{2\alpha - T_o/T} = \frac{1 - f_a}{f_a} \quad (\text{S7.49})$$

which gives, for α ,

$$2\alpha - T_o/T = \log\left(\frac{1 - f_a}{f_a}\right) \quad (\text{S7.50})$$

We assume that the hemoglobin is in equilibrium with an ideal gas, for which the affinity can be written in terms of the pressure and temperature as

$$\alpha = \log(g/p) \quad (\text{S7.51})$$

Eliminating α between Eqs. (S7.50) and (S7.51) gives a relation between p and f_a .

$$2\log(g/p) - T_o/T = \log[(1 - f_a)/f_a] \quad (\text{S7.52})$$

or

$$\frac{g^2}{p^2} e^{-T_o/T} = \frac{1 - f_a}{f_a} \quad (\text{S7.53})$$

Solving this for f_a gives

$$f_a = \frac{p^2}{p^2 + g^2 e^{-T_o/T}} \quad (\text{S7.54})$$

This formula is similar in structure to Eq. (7.24), but p has been replaced by p^2 . (b) In the oxygen-rich atmosphere, $f_a = 0.75$. Therefore

$$0.75 = \frac{p_H^2}{p_H^2 + g^2 e^{-T_o/T}} \quad (\text{S7.55})$$

which determines the value of $g^2 e^{-T_o/T}$.

$$g^2 e^{-T_o/T} = p_H^2/3 \quad (\text{S7.56})$$

In the oxygen-poor environment, $p_L = 0.1 p_H$, and

$$f_a = \frac{0.01 p_H^2}{0.01 p_H^2 + p_H^2/3} = \frac{3}{103} \approx 0.03 \quad (\text{S7.57})$$

The number of oxygen molecules released is

$$4N_o(0.75 - 0.03) = 2.88 N_o \quad (\text{S7.58})$$

which is almost a 50% improvement in efficiency in comparison to the system without oxygen–oxygen interactions. Just such an interaction effect adds to the efficiency of the hemoglobin in our blood.

Exercise 7.7 A surface with K adsorption sites is in equilibrium with a mixed ideal gas containing molecules of types A and B . Each site can take either a single A molecule, with energy $\varepsilon_A = -kT_A$, or a single B molecule, with energy $\varepsilon_B = -kT_B$. The partial pressures of the two gases are p_A and p_B . f_A and f_B are the fractions of sites that are occupied by the two types of particles. (a) Derive equations for f_A and f_B in terms of p_A and p_B . (b) Assume that both gases are monatomic and that $T_A = T_B$. Determine the relation between p_A and p_B that will give equal numbers of adsorbed A and B atoms.

Solution (a) The partition function for a single site is

$$\Lambda_1 = 1 + e^{-\alpha_A + T_A/T} + e^{-\alpha_B + T_B/T} \quad (\text{S7.59})$$

and the grand potential per site is

$$\psi_1 = \log(1 + e^{-\alpha_A + T_A/T} + e^{-\alpha_B + T_B/T}) \quad (\text{S7.60})$$

The probability that the site is occupied by an A molecule is f_A , which is the same as the average number of A molecules at the site. Thus

$$f_A = -\frac{\partial \psi_1}{\partial \alpha_A} = \frac{e^{-\alpha_A + T_A/T}}{\Lambda_1} \quad (\text{S7.61})$$

Also

$$f_B = -\frac{\partial \psi_1}{\partial \alpha_B} = \frac{e^{-\alpha_B + T_B/T}}{\Lambda_1} \quad (\text{S7.62})$$

The equation, $\alpha = \log(g/p)$, for the affinity of an ideal gas, implies that

$$e^{-\alpha_A} = p_A/g_A \quad \text{and} \quad e^{-\alpha_B} = p_B/g_B \quad (\text{S7.63})$$

Using this in Eqs. (S7.61) and (S7.62) gives the desired equilibrium relations.

$$f_A = \frac{p_A e^{T_A/T} / g_A}{1 + p_A e^{T_A/T} / g_A + p_B e^{T_B/T} / g_B} \quad (\text{S7.64})$$

and

$$f_B = \frac{p_B e^{T_B/T} / g_B}{1 + p_A e^{T_A/T} / g_A + p_B e^{T_B/T} / g_B} \quad (\text{S7.65})$$

(b) If $f_A = f_B$ and $T_A = T_B$, then

$$\frac{p_A}{p_B} = \frac{g_A}{g_B} \quad (\text{S7.66})$$

For a monatomic gas

$$g = (kT)^{5/2} (2\pi m)^{3/2} / h^3 \quad (\text{S7.67})$$

Therefore, the condition for equal occupation of the adsorption sites is that

$$\frac{p_A}{p_B} = \frac{m_A^{3/2}}{m_B^{3/2}} \quad (\text{S7.68})$$

Exercise 7.8 Let f_n be the average occupation number of the n th single-particle quantum state in an ideal Fermi Dirac system. Consider the expression (called the *variational entropy*)

$$S_{\text{var}} = -\sum_n [f_n \log f_n + (1 - f_n) \log(1 - f_n)] \quad (\text{S7.69})$$

(a) Show that, if S_{var} is maximized under the conditions that

$$\sum_n f_n = N \quad \text{and} \quad \sum_n f_n E_n = E \quad (\text{S7.70})$$

then the resulting distribution is the Fermi–Dirac distribution. (b) Show that, at the maximum, S_{var} is equal to the equilibrium entropy of the Fermi–Dirac system.

Solution (a) Using Lagrange’s method, we maximize the quantity

$$F = - \sum [f_n \log f_n + (1 - f_n) \log(1 - f_n)] - \alpha \sum f_n - \beta \sum f_n E_n \quad (\text{S7.71})$$

without restrictions. $\partial F / \partial f_n = 0$ gives the relation

$$-\log f_n + \log(1 - f_n) - \alpha - \beta E_n = 0 \quad (\text{S7.72})$$

or

$$\log\left(\frac{1 - f_n}{f_n}\right) = \alpha + \beta E_n \quad (\text{S7.73})$$

Exponentiating both sides, this can easily be solved for f_n .

$$f_n = \frac{1}{e^{\alpha + \beta E_n} + 1} \quad (\text{S7.74})$$

which is exactly the usual Fermi–Dirac distribution function. (b) In order to identify S^o with S_{var} , we note that, according to Eq. (7.39),

$$\psi = S_{\text{FD}}^o - \alpha N - \beta E = \sum_n \log(1 + e^{-\alpha - \beta E_n}) \quad (\text{S7.75})$$

But $N = \sum f_n$ and $E = \sum f_n E_n$. Therefore,

$$S_{\text{FD}}^o = \sum_n [\log(1 + e^{-\alpha - \beta E_n}) + (\alpha + \beta E_n) f_n] \quad (\text{S7.76})$$

Using the equilibrium relation $f_n = (e^{\alpha + \beta E_n} + 1)^{-1}$, we can derive the following identities, that will allow us to express S_{FD}^o entirely in terms of f_n .

$$e^{-\alpha - \beta E_n} = \frac{f_n}{1 - f_n} \quad (\text{S7.77})$$

and

$$\alpha + \beta E_n = \log\left(\frac{1 - f_n}{f_n}\right) \quad (\text{S7.78})$$

Thus

$$\begin{aligned} S_{\text{FD}}^o &= \sum_n \left[\log\left(1 + \frac{f_n}{1 - f_n}\right) + f_n \log\left(\frac{1 - f_n}{f_n}\right) \right] \\ &= \sum_n [-\log(1 - f_n) + f_n \log(1 - f_n) - f_n \log f_n] \\ &= - \sum_n [f_n \log f_n + (1 - f_n) \log(1 - f_n)] \end{aligned} \quad (\text{S7.79})$$

which agrees with S_{var} .

Exercise 7.9 Repeat the last exercise for a boson system, using the following variational entropy function.

$$S_{\text{var}} = - \sum_n [f_n \log f_n - (1 + f_n) \log(1 + f_n)] \quad (\text{S7.80})$$

Solution (a) The quantity to be maximized is

$$F = - \sum_n [f_n \log f_n - (1 + f_n) \log(1 + f_n)] - \alpha \sum_n f_n - \beta \sum_n f_n E_n \quad (\text{S7.81})$$

Setting $\partial F/\partial f_n = 0$ gives

$$-\log f_n + \log(1 + f_n) - \alpha - \beta E_n = 0 \quad (\text{S7.82})$$

or

$$\log\left(\frac{1 + f_n}{f_n}\right) = \alpha + \beta E_n \quad (\text{S7.83})$$

which implies that

$$f_n = \frac{1}{e^{\alpha + \beta E_n} - 1} \quad (\text{S7.84})$$

(b) Equation (7.37) gives the following expression for the entropy of an ideal Bose–Einstein system.

$$S_{\text{BE}}^o = - \sum_n \log(1 - e^{-\alpha - \beta E_n}) + \sum_n (\alpha + \beta E_n) f_n \quad (\text{S7.85})$$

and Eq. (7.44) yields the relation

$$e^{-\alpha - \beta E_n} = f_n / (1 + f_n)$$

These relations allow us to express S_{BE}^o entirely in terms of f_n .

$$\begin{aligned} S_{\text{BE}}^o &= - \sum_n \left[\log\left(1 - \frac{f_n}{1 + f_n}\right) - f_n \log\left(\frac{1 + f_n}{f_n}\right) \right] \\ &= - \sum_n [f_n \log f_n - (1 + f_n) \log(1 + f_n)] \end{aligned} \quad (\text{S7.86})$$

Exercise 7.10 If almost all single-particle quantum states have average occupation numbers much less than one, then both Fermi–Dirac and Bose–Einstein statistics can be approximated by Boltzmann statistics. Show that, in that case, it is convenient to work with a canonical ensemble and that the canonical potential is given by

$$\phi(N, \beta) = N [\log(Z_1/N) + 1] \quad (\text{S7.87})$$

where the single-particle partition function, Z_1 , is given by the following sum over single-particle quantum states.

$$Z_1(\beta) = \sum_k e^{-\beta \varepsilon_k} \quad (\text{S7.88})$$

Solution If $e^{-\alpha - \beta \varepsilon_k} \ll 1$, then $\log(1 + \zeta e^{-\alpha - \beta \varepsilon_k}) \approx \zeta e^{-\alpha - \beta \varepsilon_k}$, where $\zeta = \pm 1$, depending upon the type of statistics satisfied by the particles, and

$$\begin{aligned} \psi(\alpha, \beta) &= \zeta \sum_k \log(1 + \zeta e^{-\alpha - \beta \varepsilon_k}) \\ &\approx \sum_k e^{-\alpha - \beta \varepsilon_k} \\ &= e^{-\alpha} Z_1(\beta) \end{aligned} \quad (\text{S7.89})$$

Since

$$N = - \frac{\partial \psi}{\partial \alpha} = e^{-\alpha} Z_1 \quad (\text{S7.90})$$

it is easy to solve for α as a function of N and β . (This cannot be done outside the Boltzmann approximation.)

$$\alpha = - \log(N/Z_1) \quad (\text{S7.91})$$

The canonical potential is constructed by expressing $\psi + \alpha N$ as a function of N and β .

$$\begin{aligned} \phi &= e^{-\alpha} Z_1(\beta) + \alpha N \\ &= N + N \log(Z_1/N) \\ &= N [\log(Z_1/N) + 1] \end{aligned} \quad (\text{S7.92})$$

Exercise 7.11 The density of states function, $D(\varepsilon)$, is defined by saying that the number of single-particle quantum states with energy in the interval $d\varepsilon$ is equal to $D(\varepsilon) d\varepsilon$. Calculate the density of states function for: (a) a three-dimensional gas of spin-0 particles satisfying periodic boundary conditions in a cube of volume L^3 , and (b) the same system satisfying hard-wall boundary conditions [$\psi(x, y, z) = 0$ on the walls].

Solution (a) For periodic boundary conditions in three dimensions, the allowed wave vectors form a three-dimensional cubic lattice in k space with a density $(2\pi/L)^3$. For a zero-spin particle there is only one eigenstate for each wave vector. The number of states with energy less than $\varepsilon = \hbar^2 k^2/2m$ is

$$\begin{aligned} N(\varepsilon) &= (4\pi k^3/3)/(2\pi/L)^3 \\ &= \frac{L^3 k^3}{6\pi^2} \\ &= \frac{(2m)^{3/2} L^3}{6\pi^2 \hbar^3} \varepsilon^{3/2} \end{aligned} \quad (\text{S7.93})$$

The density of states function is the derivative of $N(\varepsilon)$.

$$D(\varepsilon) = N'(\varepsilon) = \frac{(2m)^{3/2} L^3}{4\pi^2 \hbar^2} \varepsilon^{1/2} \quad (\text{S7.94})$$

(b) The eigenfunctions of the Schrödinger equation

$$-\frac{\hbar^2}{2m} \left(\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} \right) = \varepsilon \psi \quad (\text{S7.95})$$

that satisfy the boundary conditions

$$\begin{aligned} 0 &= \psi(0, y, z) = \psi(x, 0, z) = \psi(x, y, 0) \\ &= \psi(L, y, z) = \psi(x, L, z) = \psi(x, y, L) \end{aligned} \quad (\text{S7.96})$$

are of the form

$$\psi(x, y, z) = (2/L)^{3/2} \sin(n_1 \pi x/L) \sin(n_2 \pi y/L) \sin(n_3 \pi z/L) \quad (\text{S7.97})$$

where n_1, n_2 , and n_3 have the values $1, 2, 3, \dots$. The corresponding energy eigenvalue is

$$\varepsilon_{n_1 n_2 n_3} = \frac{\hbar^2 \pi^2}{2mL^2} (n_1^2 + n_2^2 + n_3^2) \quad (\text{S7.98})$$

Plotting the values of n_1, n_2 , and n_3 in a three-dimensional n space, we see that there is one point for each unit cube in the positive octant. The condition that $\varepsilon_{n_1 n_2 n_3} < \varepsilon$ is the same as the condition that $n_1^2 + n_2^2 + n_3^2 < R^2$, where $R^2 = 2m\varepsilon/\pi^2 \hbar^2$. The number of eigenstates that satisfy that condition is equal to 1/8 of the volume of a sphere of radius R .

$$\begin{aligned} N(\varepsilon) &= (1/8)(4\pi R^3/3) \\ &= \frac{\pi}{6} \left(\frac{2mL^2 \varepsilon}{\hbar^2 \pi^2} \right)^{3/2} \\ &= \frac{(2m)^{3/2} L^3}{6\pi^2 \hbar^3} \varepsilon^{3/2} \end{aligned} \quad (\text{S7.99})$$

Since this is identical to Eq. (S7.93), the density of states function is unaffected by the change in the boundary conditions.

Exercise 7.12 For a system of fermions with a density of states function $D(\varepsilon)$, determine the dependence of the chemical potential on temperature for fixed N and $kT \ll \varepsilon_F$.

Solution The average occupation of a quantum state of energy ε is $\{\exp[(\varepsilon - \mu)/kT] + 1\}^{-1}$. The number of such quantum states within the energy interval $d\varepsilon$ is $D(\varepsilon)d\varepsilon$. Thus N is given in terms of the density of states function by

$$N = \int_0^\infty \frac{D(\varepsilon) d\varepsilon}{e^{(\varepsilon - \mu)/kT} + 1} \quad (\text{S7.100})$$

For $kT \ll \varepsilon_F$ the integral can be evaluated to order T^2 by using Eq. (7.55).

$$N = \int_0^\mu D(\varepsilon) d\varepsilon + \frac{\pi^2 k^2 T^2}{6} D'(\mu) \quad (\text{S7.101})$$

At $T = 0$, $\mu = \varepsilon_F$. Therefore, at low temperature, one can write μ as $\varepsilon_F + \delta\mu$ and expand Eq. (S7.101) to first order in $\delta\mu$.

$$N = \int_0^{\varepsilon_F} D(\varepsilon) d\varepsilon + D(\varepsilon_F) \delta\mu + \frac{\pi^2 k^2 T^2}{6} [D'(\varepsilon_F) + D''(\varepsilon_F) \delta\mu] \quad (\text{S7.102})$$

Using the fact that ε_F is defined by the relation

$$N = \int_0^{\varepsilon_F} D(\varepsilon) d\varepsilon \quad (\text{S7.103})$$

and dropping the term proportional to $T^2 \delta\mu$, which is of higher order than T^2 , one obtains the following formula for the chemical potential shift.

$$\delta\mu = -\frac{\pi^2 k^2 T^2}{6} \frac{D'(\varepsilon_F)}{D(\varepsilon_F)} \quad (\text{S7.104})$$

Therefore

$$\mu(T) = \varepsilon_F - \frac{\pi^2 k^2 T^2}{6} \frac{D'(\varepsilon_F)}{D(\varepsilon_F)} \quad (\text{S7.105})$$

Exercise 7.13 Write the specific heat of a system of fermions as a one-dimensional integral involving the density of states function and show that at low temperature it is only the density of states at the Fermi energy, and not its derivative, that is important in determining C_V .

Solution The average occupation of a quantum state of energy ε is $\{\exp[(\varepsilon - \mu)/kT] + 1\}^{-1}$. The number of such quantum states within the energy interval $d\varepsilon$ is $D(\varepsilon)d\varepsilon$. Thus the total energy of a fermion system at temperature T is

$$E = \int_0^\infty \frac{\varepsilon D(\varepsilon) d\varepsilon}{e^{(\varepsilon - \mu)/kT} + 1} \quad (\text{S7.106})$$

Using the first two terms in the low-temperature expansion for a general Fermi–Dirac integral, given by Eq. (7.55), we can write E as

$$E = \int_0^\mu \varepsilon D(\varepsilon) d\varepsilon + \frac{\pi^2 k^2 T^2}{6} [D(\mu) + \mu D'(\mu)] \quad (\text{S7.107})$$

In calculating $\partial E/\partial T$, to obtain the specific heat, we must remember that, at fixed N , the chemical potential μ is a function of T , given by Eq. (S7.105). Thus

$$C_V = \frac{\partial E}{\partial T} = \varepsilon_F D(\varepsilon_F) \frac{d\mu}{dT} + \frac{\pi^2 k^2 T}{3} [D(\varepsilon_F) + \varepsilon_F D'(\varepsilon_F)] \quad (\text{S7.108})$$

where we have ignored terms that are proportional to $T^2 \mu'(T)$, because they are of order T^3 . Using the fact that, according to Eq. (S7.105),

$$\frac{d\mu}{dT} = -(\pi^2 k^2 T/3) [D'(\varepsilon_F)/D(\varepsilon_F)]$$

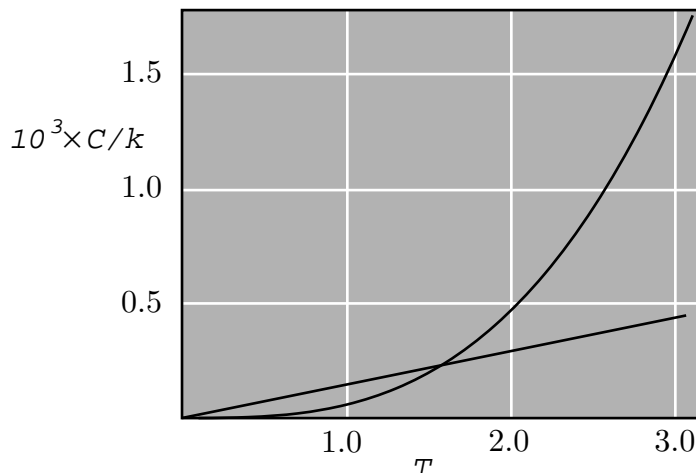


Fig. S7.3 The vibrational and electronic contributions to the specific heat of sodium at low temperatures.

we see that the term involving $D'(\varepsilon_F)$ cancels in the formula for C_V , leaving

$$C_V = \frac{\pi^2 k^2 T}{3} D(\varepsilon_F) \quad (\text{S7.109})$$

Exercise 7.14 At low temperature, the electronic specific heat of a metal is a linear function of temperature while the vibrational specific heat goes as T^3 . For any metal, we can define a crossover temperature T_{cr} as the temperature at which $C_{\text{el}} = C_{\text{vib}}$. Far below T_{cr} the vibrational specific heat can be neglected. Far above T_{cr} the electronic specific heat is negligible. For sodium, plot C_{el} , C_{vib} , and C_{tot} in the range $0 < T < 2T_{\text{cr}}$.

Solution We assume, correctly, that T_{cr} lies well below ε_F/k and T_D . Thus we can use the low-temperature approximations for both C_{el} and C_{vib} . Then the two contributions to the specific heat per atom are

$$C_{\text{el}} = \frac{\pi k^2 T}{2\varepsilon_F} \quad (\text{S7.110})$$

and

$$C_{\text{vib}} = \frac{12\pi^4 k}{5} \frac{T^3}{T_D^3} \quad (\text{S7.111})$$

Setting C_{el} equal to C_{vib} , we obtain, for the crossover temperature,

$$T_{\text{cr}}^2 = \frac{5kT_D^3}{24\pi^3\varepsilon_F} \quad (\text{S7.112})$$

For sodium, $\varepsilon_F/k = 10,000$ K and $T_D = 158$ K, which gives $T_{\text{cr}} = 1.63$ K. C_{el}/k and C_{vib}/k , over the range, $0 < T < 3.2$ K, are shown in Fig. S7.3.

Exercise 7.15 A nonuniform ideal gas of spin- $\frac{1}{2}$ fermions is in an external potential field $U(z)$ that depends only on the z coordinate. Assuming that the gas is restricted to the region $z > 0$, that the density of fermions at $z = 0$ is n_0 , and that the density varies slowly enough that the equations for a uniform Fermi–Dirac gas can be used locally, derive an equation for the density function $n(z)$ that minimizes the total energy at $T = 0$.

Solution At $T = 0$ the Fermi energy of an ideal Fermi gas is related to the particle density by

$$n = \frac{4}{3}\gamma\varepsilon_F^{3/2} \quad (\text{S7.113})$$

where $\gamma = 2\pi(2m/\hbar^2)^{3/2}$. Because the density varies with height, the Fermi energy will be a function of z also. At height z , all the momentum states up to an energy $\varepsilon_F(z)$ will be filled and all others empty. This fact, that the momentum distribution of the particles is different at different locations in a nonuniform Fermi gas, contrasts with the situation in a classical gas, where the spatial density may vary from place to place but the momentum distribution is the same everywhere. Therefore, the problem boils down to that of finding the function $\varepsilon_F(z)$ that yields the lowest possible energy with a fixed number of particles. If $\varepsilon_F(z)$ is the desired optimal function, then it should be impossible to decrease the total energy by moving a particle from one height z_1 to another height z_2 . If we wanted to lower the energy by moving a particle from z_1 to z_2 , then we would take the most energetic particle at z_1 , which would have a kinetic energy $\varepsilon_F(z_1)$ and a potential energy $U(z_1)$, and put it into the lowest-energy empty state at z_2 , which would have a kinetic energy $\varepsilon_F(z_2)$ and a potential energy $U(z_2)$. For the minimum energy distribution, those two states should have the same energy. Thus

$$\varepsilon_F(z_1) + U(z_1) = \varepsilon_F(z_2) + U(z_2) \quad (\text{S7.114})$$

for any z_1 and z_2 . If we assume that $U(0) = 0$, then Eq. (S7.114) implies that

$$\varepsilon_F(z) + U(z) = \varepsilon_F(0) \quad (\text{S7.115})$$

Using Eq. (S7.113) to relate $\varepsilon_F(z)$ to the density at z , we get the following equation for the density profile.

$$n(z) = \frac{4}{3}\gamma[\varepsilon_F(0) - U(z)]^{3/2} \quad (\text{S7.116})$$

Note that, at any point where $U(z) > \varepsilon_F(0)$, the density is not given by Eq. (S7.116), which would yield a complex number for $n(z)$, but instead is given by the restriction that $n(z) \geq 0$, which implies that $n(z) = 0$ when $U(z) > \varepsilon_F(0)$.

Exercise 7.16 It is reasonable to treat the collection of electrons in a large atom as a nonuniform Fermi gas at zero temperature. The Fermi energy is then a function of the radial coordinate $\varepsilon_F(r)$. By combining Eq. (S7.116) with Poisson's equation for the electrostatic potential function, namely,

$$\nabla^2\phi = -\frac{\rho}{\epsilon_0} = \frac{e}{\epsilon_0}n(r) \quad (\text{S7.117})$$

one obtains a differential equation for the electrostatic potential within any large atom. The equation so obtained is the *Thomas–Fermi equation*.

Solution For a neutral atom, $\phi = 0$ at $r = \infty$. Equation (S7.116) should therefore be modified to relate the density at location r to the density at $r = \infty$, which is zero. Using the fact that $U(r) = -e\phi(r)$, the equation becomes

$$n(r) = \frac{4}{3}\gamma e^{3/2}[\phi(r)]^{3/2} \quad (\text{S7.118})$$

But $n(r) = (\epsilon_0/e)\nabla^2\phi(r)$. When these two equations are combined, and the value of γ is recalled, one gets the Thomas–Fermi differential equation for $\phi(r)$.

$$\nabla^2\phi(r) = \sigma\phi^{3/2}(r) \quad (\text{S7.119})$$

with

$$\sigma = \frac{(2m)^{3/2}e^{5/2}}{3\pi^2\epsilon_0\hbar^2} \quad (\text{S7.120})$$

Exercise 7.17 The Thomas–Fermi equation does not contain the essential parameter Z , the atomic number of the atom. Certainly $\phi(r)$ cannot be the same for every atom. Determine where the atomic number Z should come into the Thomas–Fermi theory.

Solution The atomic number Z tells one the amount of charge that resides in the nucleus at $r = 0$. As r goes to zero the electrostatic potential should approach a Coulomb potential due to a charge $Q = Ze$. That is, as $r \rightarrow 0$,

$$E_r(r) = -\frac{d\phi(r)}{dr} \rightarrow \frac{Ze}{4\pi\epsilon_0} \frac{1}{r^2} \quad (\text{S7.121})$$

or

$$r^2\phi'(r) \rightarrow -\frac{Ze}{4\pi\epsilon_0} \quad (\text{S7.122})$$

The atomic number appears only as a boundary condition at $r = 0$. The boundary condition at $r = \infty$ has already been used in the derivation of the equation. It is that $\phi(r) \rightarrow 0$ as $r \rightarrow \infty$.

Exercise 7.18 (a) Show that, by making a transformation of the form

$$\phi(r) = \frac{Ze}{4\pi\epsilon_0 r} u(r/a) \quad (\text{S7.123})$$

one can eliminate all physical constants in both the Thomas–Fermi equation and the boundary condition at $r = 0$. Notice that the prefactor, $Ze/4\pi\epsilon_0 r$, is just the simple Coulomb potential of a point charge Ze . (b) Determine the size of the necessary scaling parameter a .

Solution We first consider the boundary condition. From Eq. (S7.123), we see that

$$r^2\phi'(r) = -\frac{Ze}{4\pi\epsilon_0} u(r/a) + r \frac{Ze}{4\pi\epsilon_0 a} u'(r/a) \quad (\text{S7.124})$$

The boundary condition $r^2\phi'(r) \rightarrow -Ze/4\pi\epsilon_0$ will obviously be satisfied if $u(0) = 1$ and $u'(0)$ is any finite number.

In order to transform the Thomas–Fermi equation, we introduce the variable $x = r/a$. Then

$$\frac{d}{dr} = \frac{1}{a} \frac{d}{dx} \quad (\text{S7.125})$$

and

$$\nabla^2\phi(r) = \frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{d\phi}{dr} \right) = \frac{1}{a^2 x^2} \frac{d}{dx} \left(x^2 \frac{d\phi}{dx} \right) \quad (\text{S7.126})$$

In terms of x , Eq. (S7.123) is

$$\phi = \frac{Ze}{4\pi\epsilon_0 a} \frac{u(x)}{x} \quad (\text{S7.127})$$

Then

$$\frac{d}{dx} \left(x^2 \frac{d\phi}{dx} \right) = \frac{Ze}{4\pi\epsilon_0 a} x u''(x) \quad (\text{S7.128})$$

and the Thomas–Fermi equation becomes

$$\frac{Ze}{4\pi\epsilon_0 a^3} \frac{u''(x)}{x} = \sigma \left(\frac{Ze}{4\pi\epsilon_0 a} \right)^{3/2} \frac{u^{3/2}(x)}{x^{3/2}} \quad (\text{S7.129})$$

The ugly constants on both sides cancel if $ze/4\pi\epsilon_0 a^3 = \sigma(Ze/4\pi\epsilon_0 a)^{3/2}$, which gives the required value of a .

$$a = \frac{1}{2} \left(\frac{3\pi}{4} \right)^{2/3} \frac{a_o}{Z^{1/3}} \quad (\text{S7.130})$$

where the Bohr radius $a_o = 4\pi\epsilon_0 \hbar^2 / me^2$. With these substitutions, $u(x)$ satisfies the equation

$$\sqrt{x} u''(x) = u^{3/2}(x) \quad (\text{S7.131})$$

and the boundary conditions

$$u(0) = 1 \quad \text{and} \quad u(\infty) = 0 \quad (\text{S7.132})$$

Exercise 7.19 For an electron whose energy is much larger than $m_e c^2$, the relation between energy and momentum can be approximated by the extreme relativistic relation

$$\varepsilon = cp \quad (\text{S7.133})$$

This approximation can be used for an electron gas in two situations: (a) if the electron density is so high that $\varepsilon_F \gg m_e c^2$, or (b) if the temperature is so high that $kT \gg m_e c^2$, regardless of the electron density.

For a highly relativistic electron gas, derive the density of states function $D(\varepsilon)$ and the relationship between the Fermi energy ε_F and the electron density.

Solution Consider an electron in a periodic cube of side L . The relativistic single-particle states are still plane waves with wave vectors

$$\mathbf{k} = \left(\frac{2\pi}{L} K_x, \frac{2\pi}{L} K_y, \frac{2\pi}{L} K_z \right) \quad (\text{S7.134})$$

where K_x , K_y , and K_z are integers and $\mathbf{p} = \hbar\mathbf{k}$. Therefore, the allowed momentum states will form a cubic lattice in momentum space with lattice spacing h/L , as shown in Fig. 2.5. For large ε , the number of eigenstates with energy less than ε , taking account of the two possible spin values and the fact that $V = L^3$, is

$$\begin{aligned} N(\varepsilon) &= 2 \frac{4}{3} \pi \left(\frac{\varepsilon}{c} \right)^3 / (h/L)^3 \\ &= \frac{8\pi V}{3(ch)^3} \varepsilon^3 \end{aligned} \quad (\text{S7.135})$$

The density of states function is

$$D(\varepsilon) = N'(\varepsilon) = \frac{8\pi V}{(ch)^3} \varepsilon^2 \quad (\text{S7.136})$$

The Fermi energy is determined by the condition that the total number of single-particle states below ε_F is equal to the number of electrons in the gas.

$$N(\varepsilon_F) = \frac{8\pi V}{3(ch)^3} \varepsilon_F^3 = N \quad (\text{S7.137})$$

or, in terms of the electron density $n = N/V$,

$$\varepsilon_F = (3/8\pi)^{1/3} chn^{1/3} \quad (\text{S7.138})$$

Exercise 7.20 At what temperature is $m_e c^2 = kT$?

Solution

$$T = \frac{m_e c^2}{k} = 5.93 \times 10^9 \text{ K} \quad (\text{S7.139})$$

Such astronomical temperatures occur only in astronomy, in particular, during supernovas and other such explosive events.

Exercise 7.21 At what density is $\varepsilon_F = m_e c^2$?

Solution In answering this question, one can use neither the nonrelativistic formula, which is valid only if $\varepsilon_F \ll m_e c^2$, nor the extreme relativistic formula, valid when $\varepsilon_F \gg m_e c^2$. Since the momentum spectrum is unchanged in going from the nonrelativistic to the relativistic case, it is best to define a Fermi momentum p_F that separates the filled from the unfilled momentum states. If n is the electron density, then

$$n = 2 \frac{4\pi}{3} p_F^3 / h^3 \quad (\text{S7.140})$$

The relativistic relation between energy and momentum is

$$E = c\sqrt{p^2 + m_e^2 c^2} \quad (\text{S7.141})$$

However, the energy given in this formula includes the rest mass energy, $m_e c^2$. The ε_F referred to in the question is the kinetic energy, $E - m_e c^2$. Thus, for a particle at the Fermi surface,

$$\varepsilon_F = c\sqrt{p_F^2 + m_e^2 c^2} - m_e c^2 \quad (\text{S7.142})$$

Setting $\varepsilon_F = m_e c^2$ gives

$$p_F = \sqrt{3} m_e c \quad (\text{S7.143})$$

and, using Eq. (S7.140), one can determine the required electron density.

$$n = 8\pi\sqrt{3} \left(\frac{m_e c}{h}\right)^3 = 3.04 \times 10^{36} \text{ m}^{-3} \quad (\text{S7.144})$$

Electron densities of this magnitude actually occur within white dwarf stars.

Exercise 7.22 Consider an ideal gas that is a mixture of spin- $\frac{1}{2}$ fermions, which we will call A particles, and spin-0 bosons, called B particles. The A particles have mass m , and the B particles have mass $M > 2m$. Assume that a particle transformation reaction



is possible and that $M - 2m \ll m$. Determine the ratio of A particles to B particles as a function of the conserved particles density, $n_o = (2N_A + N_B)/V$, at very low temperature.

Solution Ordinarily, nothing depends on what we take as the zero of our energy scale. However, when chemical reactions are possible (and we can treat this elementary particle reaction as a generalized chemical reaction), then it becomes important to measure the energies of both particles relative to the *same* zero-energy state. If we assume that a stationary A particle has zero energy, then a B particle of momentum \mathbf{p} has an energy

$$E = \varepsilon_o + p^2/2M \quad (\text{S7.146})$$

where $\varepsilon_o = (M - 2m)c^2$. This is what is needed in order for the reaction $B \rightarrow 2A$ to conserve energy. But this shift of the B particle energy scale has some effects on the formulas that were developed in the sections on the ideal Bose gas. For example, if we let ε denote the kinetic energy (that is, $\varepsilon = p^2/2M$), then the density of single-particle quantum states is $V\gamma\varepsilon^{1/2}$, and Eq. (7.65) for the particle density as a function of α becomes

$$n = \gamma \int_o^\infty \frac{\varepsilon^{1/2} d\varepsilon}{e^{\alpha + \beta(\varepsilon_o + \varepsilon)} - 1} \quad (\text{S7.147})$$

The minimum value of the affinity is no longer $\alpha = 0$, but is given by $\alpha + \beta\varepsilon_o = 0$. That is,

$$\alpha = -\beta\varepsilon_o \quad (\text{S7.148})$$

Equation (7.70) for the number of condensate particles in a phase II state is

$$N_{\mathbf{p}=0} = \frac{1}{e^{\alpha + \beta\varepsilon_o} - 1} \quad (\text{S7.149})$$

At very low temperature it is safe to assume that the Bose gas is in a phase II state, which implies that its affinity is approximately $-\beta\varepsilon_o$.

$$\alpha_B \approx -\beta\varepsilon_o \quad (\text{S7.150})$$

At very low temperature the chemical potential of the A particle gas is equal to its Fermi energy, and therefore its affinity is

$$\alpha_A = -\beta\varepsilon_F \quad (\text{S7.151})$$

The reaction equilibrium equation is

$$2\alpha_A = \alpha_B \quad (\text{S7.152})$$

which implies that

$$\varepsilon_F = \frac{1}{2}\varepsilon_o \quad (\text{S7.153})$$

The condition $M - 2m \ll m$ allows us to use nonrelativistic formulas relating the Fermi energy to the density of A particles. That is,

$$n_A = \frac{4}{3}\gamma\varepsilon_F^{3/2} = \frac{8\pi m^{3/2}}{3h^3}\varepsilon_o^{3/2} \quad (\text{S7.154})$$

As the temperature approaches zero, all other particles go into the zero-momentum boson state. Thus the density of B particles is given by the conservation equation

$$n_A + 2n_B = n_o \quad (\text{S7.155})$$

That is

$$n_B = \frac{1}{2} \left(n_o - \frac{8\pi m^{3/2}}{3h^3} \varepsilon_o^{3/2} \right) \quad (\text{S7.156})$$

If this equation gives a negative value for n_B , then actually $n_B = 0$ and the Fermi energy of the A particles is less than $\varepsilon_o/2$. It is given by setting $n_A = n_o$. That is

$$\varepsilon_F = (3n_o/4\gamma)^{2/3} \quad (\text{S7.157})$$

Exercise 7.23 Redo the previous exercise for two-dimensional Fermi–Dirac and Bose–Einstein gases at finite temperature, assuming that $\varepsilon_o = 0$, so that $M = 2m$, and determine the density of fermions in the limits of high and low temperature at fixed n_o .

Solution The most important difference between the two- and three-dimensional cases is that in two dimensions there is no Bose–Einstein condensation. Exercises 2.25 and 2.26 give the relationship between particle density and affinity for fermions and bosons in two dimensions. Equation (S2.114) is written for spinless fermions. For the spin- $\frac{1}{2}$ A particles the relation becomes

$$n_A = \frac{mkT}{\pi\hbar^2} [\log(1 + e^{\alpha_A}) - \alpha_A] \quad (\text{S7.158})$$

For the B particles the relation between n_B and α_B is given by Eq. (S2.118), with m replaced by $2m$.

$$n_B = \frac{mkT}{\pi\hbar^2} [\alpha_B - \log(e^{\alpha_B} - 1)] \quad (\text{S7.159})$$

n_A and n_B are to be determined by the two equations

$$n_A + 2n_B = n_o \quad \text{and} \quad 2\alpha_A = \alpha_B \quad (\text{S7.160})$$

The first equation expresses the conservation of A -atoms and the second is the condition for reaction equilibrium. The fermion affinity can be any real number, but the boson affinity must be positive in order to keep the argument of the logarithm in Eq. (S7.159) positive. However, the condition for reaction equilibrium then demands that the fermion affinity must also be positive. Setting $\alpha_B = 2\alpha_A$, writing α_A simply as α , and defining a parameter $\nu_o = \pi\hbar^2 n_o / mkT$, the particle conservation equation, $n_A + 2n_B = n_o$, can be written in the form

$$\log(e^\alpha + 1) + 3\alpha - 2\log(e^{2\alpha} - 1) = \nu_o \quad (\text{S7.161})$$

As $T \rightarrow 0$ at fixed n_o , the parameter $\nu_o \rightarrow \infty$. Equation (S7.161) then requires that $\alpha \rightarrow 0$. For very small values of α ,

$$n_A \approx \frac{mkT}{\pi\hbar^2} \log 2 \quad (\text{S7.162})$$

and

$$n_B = \frac{1}{2}(n_o - n_A) \approx \frac{n_o}{2} - \frac{mkT}{2\pi\hbar^2} \log 2 \quad (\text{S7.163})$$

Thus, at low temperature, the reaction equilibrium shifts more and more towards the bosons.

At high temperatures $\nu_o \rightarrow 0$ and Eq. (S7.161) requires that $\alpha \rightarrow \infty$. This can be seen by assuming that α is very large and using the following expansions.

$$\log(e^\alpha + 1) = \log[e^\alpha(1 + e^{-\alpha})] \approx \alpha + e^{-\alpha} \quad (\text{S7.164})$$

$$\log(e^{2\alpha} - 1) = \log[e^{2\alpha}(1 - e^{-2\alpha})] \approx 2\alpha - e^{-2\alpha} \quad (\text{S7.165})$$

But $e^{-2\alpha}$ is negligible in comparison with $e^{-\alpha}$ for large α . Thus Eq. (S7.161) becomes

$$e^{-\alpha} = \nu_o \tag{S7.166}$$

or

$$\alpha = -\log \nu_o \tag{S7.167}$$

In that limit the density of fermions is

$$\begin{aligned} n_A &= \frac{mkT}{\pi\hbar^2} \left[\log\left(1 + \frac{1}{\nu_o}\right) + \log \nu_o \right] \\ &= \frac{mkT}{\pi\hbar^2} \log(1 + \nu_o) \\ &\approx \frac{mkT}{\pi\hbar^2} \nu_o \\ &= n_o \end{aligned} \tag{S7.168}$$

Thus $n_B \approx 0$. This could have been predicted. At fixed n_o and high T the particles can be treated as classical particles. Since the binding energy is zero, the “molecules” all dissociate at high T .

Exercise 7.24 In a particular frame, a system of particles has an energy

$$E = \frac{1}{2} \sum m_i v_i^2 + U(\mathbf{r}_1, \dots, \mathbf{r}_N) \tag{S7.169}$$

and a momentum

$$\mathbf{P} = \sum m_i \mathbf{v}_i \tag{S7.170}$$

The frame mentioned moves with velocity \mathbf{V} through another Galilean inertial frame. Show that the energy and momentum of the system, as measured in the second frame, are

$$E' = E + \mathbf{V} \cdot \mathbf{P} + \frac{1}{2}MV^2 \tag{S7.171}$$

and

$$\mathbf{P}' = \mathbf{P} + M\mathbf{V} \tag{S7.172}$$

where $M = \sum m_i$ is the total mass of the system. This *Galilean transformation* of energy and momentum will be needed in order to calculate the normal fluid density in liquid helium at low temperature.

Solution In the new frame, particle i will have velocity $\mathbf{v}_i + \mathbf{V}$. Since in a Galilean transformation relative distances of particles do not change, the potential energy is unchanged and therefore

$$\begin{aligned} E' - E &= \frac{1}{2} \sum m_i [(\mathbf{v}_i + \mathbf{V})^2 - v_i^2] \\ &= \mathbf{V} \cdot \sum m_i \mathbf{v}_i + \frac{1}{2}V^2 \sum m_i \\ &= \mathbf{V} \cdot \mathbf{P} + \frac{1}{2}MV^2 \end{aligned} \tag{S7.173}$$

Also

$$\mathbf{P}' = \sum m_i (\mathbf{v}_i + \mathbf{V}) = \mathbf{P} + M\mathbf{V} \tag{S7.174}$$

Exercise 7.25 Use the Galilean transformation equations to determine the energy and momentum of an excitation of wave vector \mathbf{k} in a sample of liquid helium that is flowing with velocity \mathbf{v} .

Solution Consider a bulk sample of the helium, at rest, containing a single excitation of wave vector \mathbf{k} . Its energy and momentum are

$$E = E_g + \varepsilon_{\mathbf{p}} \quad \text{and} \quad \mathbf{p} = \hbar\mathbf{k} \tag{S7.175}$$

where E_g is the ground-state energy of the fluid at rest. Viewed in a frame in which the liquid is moving at velocity \mathbf{v} , its energy and momentum are

$$\begin{aligned} E' &= E + \mathbf{v} \cdot \mathbf{p} + \frac{1}{2}Mv^2 \\ &= E_g + \frac{1}{2}Mv^2 + \varepsilon_{\mathbf{p}} + \mathbf{v} \cdot \mathbf{p} \end{aligned} \quad (\text{S7.176})$$

and

$$\mathbf{P}' = M\mathbf{v} + \mathbf{p} \quad (\text{S7.177})$$

Clearly, the first two terms in E' , namely $E_g + MV^2/2$, represent the energy of the liquid without the excitation. Thus

$$\varepsilon'_{\mathbf{p}} = \varepsilon_{\mathbf{p}} + \mathbf{v} \cdot \mathbf{p} \quad (\text{S7.178})$$

is the added energy, due to the existence of the excitation. But that is what we call the excitation energy. Similarly, since $M\mathbf{v}$ represents the momentum of the fluid without the excitation, the momentum of the excitation in the new frame is still $\mathbf{p} = \hbar\mathbf{k}$, just as it was in the old frame.

Exercise 7.26 At very low temperature, one can assume that the excitations in liquid helium constitute a low-density quasiparticle gas of simple phonons. With this assumption, calculate the normal fluid mass density ρ_n as a function of temperature.

Solution We consider a sample of helium, flowing steadily with a velocity \mathbf{v} through a stationary pipe. The energy of an excitation of momentum \mathbf{p} is $\varepsilon_{\mathbf{p}} = cp + \mathbf{v} \cdot \mathbf{p}$, where c is the velocity of sound in the liquid. Since the excitations are nonconserved bosons, $\alpha = 0$, and thus the average number of excitations per quantum state at temperature T is

$$(e^{\beta(cp + \mathbf{v} \cdot \mathbf{p})} - 1)^{-1} \equiv f(\beta cp + \beta \mathbf{v} \cdot \mathbf{p}) \quad (\text{S7.179})$$

The number of quantum states in the momentum range $d^3\mathbf{p}$ is $(V/h^3)d^3\mathbf{p}$. Therefore, the momentum density due to the phonon gas is

$$\vec{\pi} = \frac{1}{h^3} \int \mathbf{p} f(\beta cp + \beta \mathbf{v} \cdot \mathbf{p}) d^3\mathbf{p} \quad (\text{S7.180})$$

If we choose the x axis in the direction of \mathbf{v} , then, by symmetry, the only nonzero component of $\vec{\pi}$ must be π_x . We can then write Eq. (S7.180) as a scalar equation

$$\pi = \frac{1}{h^3} \int p_x f(\beta cp + \beta vp_x) d^3\mathbf{p} \quad (\text{S7.181})$$

If $v \ll c$, which we may assume, since we are interested in calculating the ratio of π to v for small v , then we can expand the integrand to first order in v .

$$\begin{aligned} \pi &= \frac{\beta v}{h^3} \int p_x^2 f'(\beta cp) d^3\mathbf{p} \\ &= \frac{2\pi\beta v}{h^3} \int_{-1}^1 \cos^2\theta d(\cos\theta) \int_0^\infty p^2 f'(\beta cp) p^2 dp \\ &= \frac{4\pi\beta v}{3h^3} \int_0^\infty f'(\beta cp) p^4 dp \\ &= \frac{4\pi v}{3h^3 c^5 \beta^4} \int_0^\infty f'(x) x^4 dx \\ &= -\frac{16\pi(kT)^4 v}{3h^3 c^5} \int_0^\infty f(x) x^3 dx \\ &= -\frac{16\pi(kT)^4 v}{3h^3 c^5} \int_0^\infty \frac{x^3 dx}{e^x - 1} \\ &= -\frac{16\pi(kT)^4 v}{3h^3 c^5} 3!\zeta(4) \\ &= -\frac{16\pi^5(kT)^4 v}{45h^3 c^5} \\ &= -\frac{2\pi^2(kT)^4 v}{45h^3 c^5} \end{aligned} \quad (\text{S7.182})$$

The normal fluid mass density is the ratio of $\vec{\pi}$ to the pipe velocity, calculated in the superfluid rest frame. Recall that it is the pipe, not the superfluid, that is dragging along the gas of excitations. In the superfluid rest frame the pipe velocity is $-v\hat{x}$. Thus the phonon contribution to the normal fluid mass density is

$$\rho_n(\text{ph}) = \frac{2\pi^2(kT)^4}{45\hbar^3 c^5} \quad (\text{S7.183})$$

It should be noted that it was necessary to compute the phonon distribution function in the rest frame of the pipe rather than the rest frame of the superfluid. In the superfluid frame the moving pipe interacts with the phonon gas, and therefore the phonon gas cannot be considered as an isolated system. In the pipe frame, on the other hand, the moving superfluid does not interact with the phonon gas as long as v is less than the critical velocity, because, as we have seen in Section 7.11, the two systems cannot exchange energy and momentum and still satisfy the fundamental conservation laws. Thus, in the pipe frame, the existence of the superfluid can be ignored except for its effect on changing the excitation spectrum of the phonons from $\varepsilon_{\mathbf{p}} = cp$ to $\varepsilon_{\mathbf{p}} = cp + \mathbf{v} \cdot \mathbf{p}$.

Exercise 7.27 Calculate the roton contribution to the normal fluid density in liquid helium.

Solution We consider the same situation as was described in Exercise 7.26. The roton spectrum, in the pipe frame, is

$$\varepsilon_{\mathbf{p}} = \varepsilon_o + (p - p_o)^2/2\mu + vp_x \quad (\text{S7.184})$$

Because, below the transition temperature, $kT \ll \varepsilon_o$, we can use the Boltzmann approximation to the Bose–Einstein distribution function. Then

$$\pi = \frac{1}{h^3} \int p_x e^{-\beta[\varepsilon_o + (p-p_o)^2/2\mu + vp_x]} d^3\mathbf{p} \quad (\text{S7.185})$$

At $v = 0$ the integral vanishes. Expanding to first order in v , we get

$$\begin{aligned} \pi &= -\frac{\beta v}{h^3} e^{-\beta\varepsilon_o} \int p_x^2 e^{-\beta(p-p_o)^2/2\mu} d^3\mathbf{p} \\ &= -\frac{2\pi\beta v}{h^3} e^{-\beta\varepsilon_o} \int_{-1}^1 \cos^2\theta d(\cos\theta) \int_o^\infty p^2 e^{-\beta(p-p_o)^2/2\mu} p^2 dp \\ &= -\frac{4\pi\beta v}{3h^3} e^{-\beta\varepsilon_o} \int_o^\infty e^{-\beta(p-p_o)^2/2\mu} p^4 dp \end{aligned} \quad (\text{S7.186})$$

For the reason given after Eq. (7.113), we can extend the integral to $-\infty$, obtaining, with $q \equiv p - p_o$,

$$\begin{aligned} \pi &= -\frac{4\pi\beta v}{3h^3} e^{-\beta\varepsilon_o} \int_{-\infty}^\infty e^{-\beta q^2/2\mu} (q^4 + 6p_o^2 q^2 + p_o^4) dq \\ &= -\frac{4\pi^{3/2}\beta v}{3h^3} e^{-\beta\varepsilon_o} \left[\frac{3}{4}(2\mu kT)^{5/2} + 3p_o^2(2\mu kT)^{3/2} + p_o^4(2\mu kT)^{1/2} \right] \end{aligned} \quad (\text{S7.187})$$

Thus

$$\rho_n(\text{rot}) = \frac{4\pi^{3/2}}{3h^3 kT} e^{-\varepsilon_o/kT} \left[\frac{3}{4}(2\mu kT)^{5/2} + 3p_o^2(2\mu kT)^{3/2} + p_o^4(2\mu kT)^{1/2} \right] \quad (\text{S7.188})$$

Exercise 7.28 (a) Using Eqs. (S7.183) and (S7.188), plot the theoretical prediction for the normal fluid density as a function of T between 1 and 3 K. (b) The transition temperature is the temperature at which the superfluid density becomes zero and thus ρ_n is equal to the mass density of helium, which is about 146 kg/m^3 at T_λ . (It does not vary strongly with temperature.) By finding the point on the curve at which $\rho_n = \rho$, estimate T_λ .

Solution The graph of $\rho_n(T)$ in Fig. S7.4 was drawn using Eqs. (S7.183) and (S7.188) and the experimental values

$$\varepsilon_o/k = 8.6 \text{ K}, \quad p_o = 2.0 \times 10^{-24} \text{ kg m/s}$$

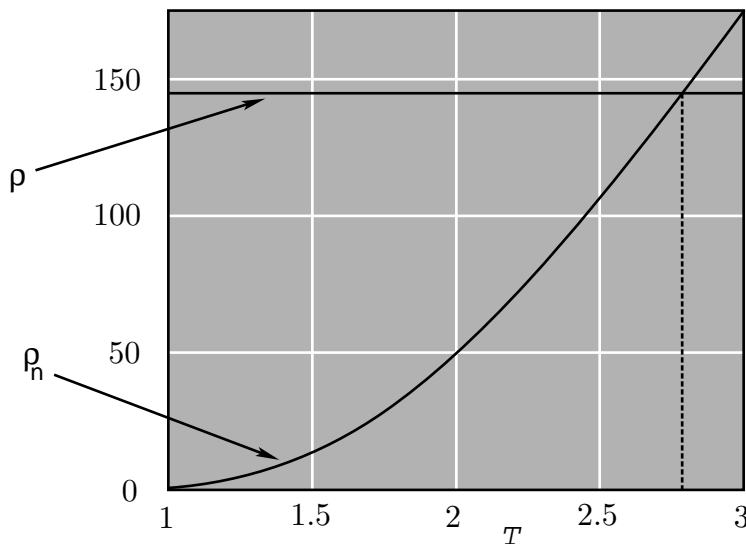


Fig. S7.4 The theoretically predicted value of the normal fluid density equals the experimental value of the total fluid density at about 2.8 K.

$$\mu = 1.0 \times 10^{-27} \text{ kg}, \quad c = 244 \text{ m/s}$$

As shown, $\rho_n = \rho$ at a temperature of about 2.8 K rather than at the actual transition temperature of 2.2 K. It is not surprising that this approximate calculation overestimates T_λ . The approximate excitation energies for both phonons and rotons all lie above the true excitation energy curve; thus the density of excitations at any temperature is underestimated by our approximations. This means that we must go to higher T in order to make $\rho_n = \rho$. Also, the whole theory, based upon noninteracting excitations, becomes less and less accurate as T approaches T_λ and the excitation density becomes very high.

Exercise 7.29 Consider a tall evacuated pipe, standing up in the earth's gravitational field. Taking into account that there is a gravitational force on the radiant energy inside the pipe, determine the equilibrium energy density as a function of height.

Solution Assume that the cross-sectional area of the pipe is A . The radiant energy within a slab of height dz is $E = \varepsilon(z)A dz$, where ε is the energy density. The gravitational force on that radiant energy is

$$F_g = \frac{E}{c^2}g = \frac{\varepsilon g}{c^2}A dz \quad (\text{S7.189})$$

This force must be balanced by the pressure force, which is given by

$$F_p = Ap(z) - Ap(z + dz) = -\frac{dp}{dz}A dz \quad (\text{S7.190})$$

Thus the condition of equilibrium is that

$$\frac{dp}{dz} = -\frac{g}{c^2}\varepsilon(z) \quad (\text{S7.191})$$

Taking into account the fact that for a radiation gas $p = \varepsilon/3$, we obtain a single equation for the energy density.

$$\frac{d\varepsilon(z)}{dz} = -\frac{3g}{c^2}\varepsilon(z) \quad (\text{S7.192})$$

This equation has the solution

$$\varepsilon(z) = \varepsilon(0) e^{-3gz/c^2} \quad (\text{S7.193})$$

Exercise 7.30 Wait a minute! The energy density is proportional to the fourth power of the temperature. If the energy density varies with height as was suggested by the last exercise, then the temperature would

have to vary with height, which is inconsistent with the condition for thermal equilibrium. We now have a flat contradiction between the condition for mechanical equilibrium and the condition for thermal equilibrium. Which one is right?

Solution When faced with a paradox such as this, one must search for some fundamental principle that can be completely relied upon. It cannot be solved by manipulating formulas. The most reliable principle we have is that the total entropy of a system is a maximum at equilibrium. Because of the connection between entropy and probability, that principle simply states that a system will go from less probable to more probable macrostates.

Consider a system composed of two flat boxes, one at height z and the other at height $z + \Delta z$, connected by a thin tube (Fig. S7.5). The inside walls are perfect mirrors so that the radiation gas inside is perfectly isolated. When the system comes to equilibrium, the tube is closed, leaving only the two isolated boxes of radiation. What is the condition that they be in equilibrium? Any discussion that involves moving photons from one box to the other but does not use general relativity has to be viewed with suspicion. We must therefore avoid such an analysis. Instead, in the upper box, we picture a process in which an amount of radiant energy equal to $2m_e c^2$ is converted into an electron–positron pair at rest. The electron and positron are allowed to fall, in the weak gravitational field, to the lower box, where, by pair annihilation, their energy is converted back to radiation. Remembering that $\beta = \partial S / \partial E$ by definition, we see that the entropy of the upper box decreases by an amount $2\beta(z + \Delta z)m_e c^2$. At the lower box, the two particles have an energy $2m_e c^2 + 2m_e g \Delta z$, and so the entropy of the lower box is increased by an amount $2\beta(z)m_e(c^2 + g \Delta z)$. For equilibrium, the total entropy change due to this conceivable but unlikely process must be zero. This gives the equilibrium condition that

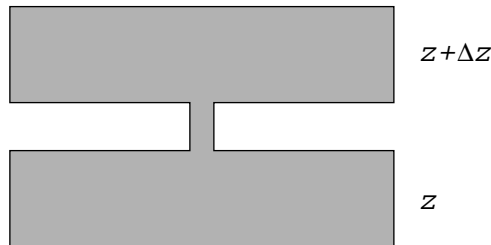


Fig. S7.5 Two flat boxes with mirrored inside surfaces at slightly different elevations are connected by a thin tube.

$$c^2 \beta(z + \Delta z) = (c^2 + g \Delta z) \beta(z) \quad (\text{S7.194})$$

Expanding this to first order in Δz gives the following differential equation for the equilibrium temperature distribution.

$$\frac{d\beta(z)}{dz} = \frac{g}{c^2} \beta(z) \quad (\text{S7.195})$$

When gravitational effects are taken into account, the equilibrium condition is not that the temperature be constant! Now we must check whether this agrees with our previous equation for $\varepsilon(z)$. According to Eq. (7.119),

$$\varepsilon = \frac{\pi^2}{15} \frac{\beta^{-4}}{(\hbar c)^3} \quad (\text{S7.196})$$

Differentiating this with respect to z and using Eq. (S7.195) for $d\beta/dz$ gives the differential equation

$$\frac{d\varepsilon(z)}{dz} = -4 \frac{g}{c^2} \varepsilon(z) \quad (\text{S7.197})$$

We have oversolved the problem by a factor of $4/3!$ Where is our mistake?

In spite of the fact that we have done our best to avoid any situation in which general relativity would have to be invoked, a general relativistic effect has crept in to spoil our solution. Fortunately it is a simple thing that can be understood without the massive mathematical apparatus of general relativity. The

condition for mechanical equilibrium was stated to be that the total force on a slab of radiation gas should vanish. It is better to say that the total momentum delivered to the slab of gas in any finite time interval should vanish. The pressure at heights z and $z+\Delta z$ give the rates at which momentum is delivered through the respective surfaces. But a *rate* unavoidably involves a local clock, and clocks do not run at the same rate at different locations in a gravitational field. If we consistently use a clock at z to define our rates, then, because the clock at $z+\Delta z$ runs faster by a factor of $(1+g\Delta z/c^2)$, the rate at which momentum is delivered to the slab through the upper surface is $p(z+\Delta z)(1+g\Delta z/c^2)$. The correct equation for mechanical equilibrium is

$$p(z) - (1 + g\Delta z/c^2)p(z + \Delta z) = \frac{g}{c^2}\varepsilon(z)\Delta z \quad (\text{S7.198})$$

or

$$\frac{dp}{dz} = -\frac{g}{c^2}[p(z) + \varepsilon(z)] \quad (\text{S7.199})$$

The pressure–energy relation, $p = \varepsilon/3$, then gives the correct differential equation

$$\frac{d\varepsilon}{dz} = -4\frac{g}{c^2}\varepsilon(z) \quad (\text{S7.200})$$

in agreement with Eq. (S7.197). It is Eq. (S7.192) that is wrong.