

# Instructor's Manual

Containing Solutions to  
Over 280 Problems  
Selected from

## Statistical Mechanics

Third Edition

By

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# Preface

This instructor's manual for the third edition of *Statistical Mechanics* is based on RKP's instructor's manual for the second edition. Most of the solutions here were retypeset into TeX from that manual. PDB is responsible for the solutions of the new problems added in the third edition. The result is a manual containing solutions to some 280 problems selected from the third edition.

The original idea of producing an instructor's manual first came from RKP's friend and colleague Wing-Ki Liu in the 1990's when RKP had just embarked on the task of preparing the second edition of *Statistical Mechanics*.

This should provide several benefits to the statistical mechanics instructor. First of all, there is the obvious advantage of saving time that one would otherwise spend on solving these problems oneself. Secondly, before one selects problems either for homework or for an exam, one can consult the manual to determine the level of difficulty of the various problems and make one's selection accordingly. Thirdly, one may even use some of these solved problems, especially the ones appearing in later chapters, as lecture material, thereby supplementing the text. We hope that this manual will enhance the usefulness of the text – both for the instructors and (indirectly) for the students.

We implore that instructors not share copies of any of the material in this manual with students or post any part of this manual on the web. Students learn best when they work together and struggle over difficult problems. Readily available solutions interfere with this crucial aspect of graduate physics training.

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# Chapter 1

- 1.1.** (a) We expand the quantity  $\ln \Omega^{(0)}(E_1)$  as a Taylor series in the variable  $(E_1 - \bar{E}_1)$  and get

$$\begin{aligned} \ln \Omega^{(0)}(E_1) &\equiv \ln \Omega_1(E_1) + \ln \Omega_2(E_2) & (E_2 = E^{(0)} - E_1) \\ &= \{\ln \Omega_1(\bar{E}_1) + \ln \Omega_2(\bar{E}_2)\} + \\ &\quad \left\{ \frac{\partial \ln \Omega_1(E_1)}{\partial E_1} + \frac{\partial \ln \Omega_2(E_2)}{\partial E_2} \frac{\partial E_2}{\partial E_1} \right\}_{E_1=\bar{E}_1} (E_1 - \bar{E}_1) + \\ &\quad \frac{1}{2} \left\{ \frac{\partial^2 \ln \Omega_1(E_1)}{\partial E_1^2} + \frac{\partial^2 \ln \Omega_2(E_2)}{\partial E_2^2} \left( \frac{\partial E_2}{\partial E_1} \right)^2 \right\}_{E_1=\bar{E}_1} (E_1 - \bar{E}_1)^2 + \dots \end{aligned}$$

The first term of this expansion is a constant, the second term vanishes as a result of equilibrium ( $\beta_1 = \beta_2$ ), while the third term may be written as

$$\frac{1}{2} \left\{ \frac{\partial \beta_1}{\partial E_1} + \frac{\partial \beta_2}{\partial E_2} \right\}_{eq.} (E_1 - \bar{E}_1)^2 = -\frac{1}{2} \left\{ \frac{1}{kT_1^2(C_v)_1} + \frac{1}{kT_2^2(C_v)_2} \right\} (E_1 - \bar{E}_1)^2,$$

with  $T_1 = T_2$ . Ignoring the subsequent terms (which is justified if the systems involved are *large*) and taking the exponentials, we readily see that the function  $\Omega^{(0)}(E_1)$  is a Gaussian in the variable  $(E_1 - \bar{E}_1)$ , with variance  $kT^2(C_v)_1(C_v)_2/\{(C_v)_1 + (C_v)_2\}$ . Note that if  $(C_v)_2 \gg (C_v)_1$  — corresponding to system 1 being in thermal contact with a very large reservoir — then the variance becomes simply  $kT^2(C_v)_1$ , regardless of the nature of the reservoir; cf. eqn. (3.6.3).

- (b) If the systems involved are ideal classical gases, then  $(C_v)_1 = \frac{3}{2}N_1k$  and  $(C_v)_2 = \frac{3}{2}N_2k$ ; the variance then becomes  $\frac{3}{2}k^2T^2 \cdot N_1N_2/(N_1 + N_2)$ . Again, if  $N_2 \gg N_1$ , we obtain the simplified expression  $\frac{3}{2}N_1k^2T^2$ ; cf. Problem 3.18.

- 1.2.** Since  $S$  is additive and  $\Omega$  multiplicative, the function  $f(\Omega)$  must satisfy the condition

$$f(\Omega_1\Omega_2) = f(\Omega_1) + f(\Omega_2). \quad (1)$$

Differentiating (1) with respect to  $\Omega_1$  (and with respect to  $\Omega_2$ ), we get

$$\Omega_2 f'(\Omega_1 \Omega_2) = f'(\Omega_1) \quad \text{and} \quad \Omega_1 f'(\Omega_1 \Omega_2) = f'(\Omega_2),$$

so that

$$\Omega_1 f'(\Omega_1) = \Omega_2 f'(\Omega_2). \quad (2)$$

Since the left-hand side of (2) is independent of  $\Omega_2$  and the right-hand side is independent of  $\Omega_1$ , each side must be equal to a constant,  $k$ , independent of *both*  $\Omega_1$  and  $\Omega_2$ . It follows that  $f'(\Omega) = k/\Omega$  and hence

$$f(\Omega) = k \ln \Omega + \text{const.} \quad (3)$$

Substituting (3) into (1), we find that the constant of integration is zero.

**1.4.** Instead of eqn. (1.4.1), we now have

$$\Omega \propto V(V - v_0)(V - 2v_0) \dots (V - \overline{N-1}v_0),$$

so that

$$\ln \Omega = C + \ln V + \ln (V - v_0) + \ln (V - 2v_0) + \dots + \ln (V - \overline{N-1}v_0),$$

where  $C$  is independent of  $V$ . The expression on the right may be written as

$$C + N \ln V + \sum_{j=1}^{N-1} \ln \left( 1 - \frac{jv_0}{V} \right) \simeq C + N \ln V + \sum_{j=1}^{N-1} \left( -\frac{jv_0}{V} \right) \simeq C + N \ln V - \frac{N^2 v_0}{2V}.$$

Equation (1.4.2) is then replaced by

$$\begin{aligned} \frac{P}{kT} &= \frac{N}{V} + \frac{N^2 v_0}{2V^2} = \frac{N}{V} \left( 1 + \frac{Nv_0}{2V} \right), \text{ i.e.} \\ PV \left( 1 + \frac{Nv_0}{2V} \right)^{-1} &= NkT. \end{aligned}$$

Since  $Nv_0 \ll V$ ,  $(1 + Nv_0/2V)^{-1} \simeq 1 - Nv_0/2V$ . Our last result then takes the form:  $P(V - b) = NkT$ , where  $b = \frac{1}{2}Nv_0$ .

A little reflection shows that  $v_0 = (4\pi/3)\sigma^3$ , with the result that

$$b = \frac{1}{2}N \cdot \frac{4\pi}{3}\sigma^3 = 4N \cdot \frac{4\pi}{3} \left( \frac{1}{2}\sigma \right)^3.$$

**1.5.** This problem is essentially solved in Appendix A; all that remains to be done is to substitute from eqn. (B.12) into (B.11), to get

$$\Sigma_1(\varepsilon^*) = \frac{(\pi\varepsilon^{*1/2}/L)^3}{6\pi^2} V \mp \frac{(\pi\varepsilon^{*1/2}/L)^2}{16\pi} S.$$

Substituting  $V = L^3$  and  $S = 6L^2$ , we obtain eqns. (1.4.15 and 16).

The expression for  $T$  now follows straightforwardly; we get

$$\frac{1}{T} = k \left( \frac{\partial \ln \Omega}{\partial E} \right)_N = \frac{k}{h\nu} \left( \frac{\partial \ln \Omega}{\partial R} \right)_N = \frac{k}{h\nu} \ln \left( \frac{R+N}{R} \right) = \frac{k}{h\nu} \ln \left( 1 + \frac{Nh\nu}{E} \right),$$

so that

$$T = \frac{h\nu}{k} \left/ \ln \left( 1 + \frac{Nh\nu}{E} \right) \right.$$

For  $E \gg Nh\nu$ , we recover the classical result:  $T = E/Nk$ .

**1.9.** Since the function  $S(N, V, E)$  of a given thermodynamic system is an *extensive* quantity, we may write

$$S(N, V, E) = Nf \left( \frac{V}{N}, \frac{E}{N} \right) = Nf(v, \varepsilon) \quad \left( v = \frac{V}{N}, \varepsilon = \frac{E}{N} \right).$$

It follows that

$$\begin{aligned} N \left( \frac{\partial S}{\partial N} \right)_{v, \varepsilon} &= N \left[ f + N \left( \frac{\partial f}{\partial v} \right)_{\varepsilon} \cdot \frac{-V}{N^2} + N \left( \frac{\partial f}{\partial \varepsilon} \right)_{v} \cdot \frac{-E}{N^2} \right], \\ V \left( \frac{\partial S}{\partial V} \right)_{N, \varepsilon} &= VN \left( \frac{\partial f}{\partial v} \right)_{\varepsilon} \cdot \frac{1}{N} \quad \text{and} \quad E \left( \frac{\partial S}{\partial E} \right)_{N, v} = EN \left( \frac{\partial f}{\partial \varepsilon} \right)_{v} \cdot \frac{1}{N}. \end{aligned}$$

Adding these expressions, we obtain the desired result.

**1.11.** Clearly, the initial temperatures and the initial particle densities of the two gases (and hence of the mixture) are the same. The entropy of mixing may, therefore, be obtained from eqn. (1.5.4), with  $N_1 = 4N_A$  and  $N_2 = N_A$ . We get

$$\begin{aligned} (\Delta S)^* &= k[4N_A \ln(5/4) + N_A \ln 5] \\ &= R[4 \ln(5/4) + \ln 5] = 2.502 R, \end{aligned}$$

which is equivalent to about 0.5  $R$  per mole of the mixture.

**1.12.** (a) The expression in question is given by eqn. (1.5.3a). Without loss of generality, we may keep  $N_1$ ,  $N_2$  and  $V_1$  fixed and vary only  $V_2$ . The first and second derivatives of this expression are then given by

$$k \left[ \frac{N_1 + N_2}{V_1 + V_2} - \frac{N_2}{V_2} \right] \quad \text{and} \quad k \left[ -\frac{N_1 + N_2}{(V_1 + V_2)^2} + \frac{N_2}{V_2^2} \right] \quad (1a, b)$$

respectively. Equating (1a) to zero gives the desired condition, viz.  $N_1V_2 = N_2V_1$ , i.e.  $N_1/V_1 = N_2/V_2 = n$ , say. Expression (1b) then reduces to

$$k \left[ -\frac{n}{V_1 + V_2} + \frac{n}{V_2} \right] = \frac{knV_1}{V_2(V_1 + V_2)} > 0.$$

Clearly,  $(\Delta S)_{1=2}$  is at its *minimum* when  $N_1/V_1 = N_2/V_2$ , and it is straightforward to check that the value at the minimum is zero.

- (b) The expression now in question is given by eqn. (1.5.4). With  $N_1 = \alpha N$  and  $N_2 = (1 - \alpha)N$ , where  $N = N_1 + N_2$  (which is fixed), the expression for  $(\Delta S)^*/k$  takes the form

$$-\alpha N \ln \alpha - (1 - \alpha)N \ln (1 - \alpha).$$

The first and second derivatives of this expression with respect to  $\alpha$  are

$$[-N \ln \alpha + N \ln(1 - \alpha)] \quad \text{and} \quad \left[ -\frac{N}{\alpha} - \frac{N}{1 - \alpha} \right] \quad (2a,b)$$

respectively. Equating (2a) to zero gives the condition  $\alpha = 1/2$ , which reduces (2b) to  $-4N$ . Clearly,  $(\Delta S)^*/k$  is at its *maximum* when  $N_1 = N_2 = (1/2)N$ , and it is straightforward to check that the value at the maximum is  $N \ln 2$ .

- 1.13.** Proceeding with eqn. (1.5.1), with  $T$  replaced by  $T_i$ , it is straightforward to see that the extra contribution to  $\Delta S$ , owing to the fact that  $T_1 \neq T_2$ , is given by the expression

$$\frac{3}{2}N_1k \ln (T_f/T_1) + \frac{3}{2}N_2k \ln(T_f/T_2),$$

where  $T_f = (N_1T_1 + N_2T_2)/(N_1 + N_2)$ . It is worth checking that this expression is always greater than or equal to zero, the equality holding if and only if  $T_1 = T_2$ . Furthermore, the result quoted here does not depend on whether the two gases were different or identical.

- 1.14.** By eqn. (1.5.1a), given on page 19 of the text, we get

$$(\Delta S)_v = \frac{3}{2}Nk \ln(T_f/T_i).$$

Now, since  $PV = NkT$ , the same equation may also be written as

$$S = Nk \ln \left( \frac{kT}{P} \right) + \frac{3}{2}Nk \left\{ \frac{5}{3} + \ln \left( \frac{2\pi mkT}{h^2} \right) \right\}. \quad (1b)$$

It follows that

$$(\Delta S)_P = \frac{5}{2}Nk \ln(T_f / T_i) = \frac{5}{3}(\Delta S)_v.$$

A numerical verification of this result is straightforward.

It should be noted that, quite generally,

$$\frac{(\Delta S)_P}{(\Delta S)_v} = \frac{T(\partial S / \partial T)_P}{T(\partial S / \partial T)_v} = \frac{C_P}{C_v} = \gamma$$

which, in the present case, happens to be  $5/3$ .



**1.15.** For an ideal gas,  $C_P - C_V = nR$ , where  $n$  is the number of moles of the gas. With  $C_P/C_V = \gamma$ , one gets

$$C_P = \gamma nR / (\gamma - 1) \quad \text{and} \quad C_V = nR / (\gamma - 1).$$

For a mixture of two ideal gases,

$$C_V = \frac{n_1 R}{\gamma_1 - 1} + \frac{n_2 R}{\gamma_2 - 1} = \left( \frac{f_1}{\gamma_1 - 1} + \frac{f_2}{\gamma_2 - 1} \right) (n_1 + n_2) R.$$

Equating this to the conventional expression  $(n_1 + n_2)R/(\gamma - 1)$ , we get the desired result.

**1.16.** In view of eqn. (1.3.15),  $E - TS + PV = \mu N$ . It follows that

$$dE - TdS - SdT + PdV + VdP = \mu dN + Nd\mu.$$

Combining this with eqn. (1.3.4), we get

$$-SdT + VdP = Nd\mu, \text{ i.e. } dP = (N/V)d\mu + (S/V)dT.$$

Clearly, then,

$$(\partial P / \partial \mu)_T = N/V \text{ and } (\partial P / \partial T)_\mu = S/V.$$

Now, for the ideal gas

$$P = \frac{NkT}{V} \text{ and } \mu = kT \ln \left\{ \frac{N}{V} \left( \frac{h^2}{2\pi mkT} \right)^{3/2} \right\};$$

see eqn. (1.5.7). Eliminating  $(N/V)$ , we get

$$P = kT \left( \frac{2\pi mkT}{h^2} \right)^{3/2} e^{\mu/kT},$$

which is the desired expression. It follows quite readily now that for this system

$$\left( \frac{\partial P}{\partial \mu} \right)_T = \frac{1}{kT} P.$$

which is indeed equal to  $N/V$ , whereas

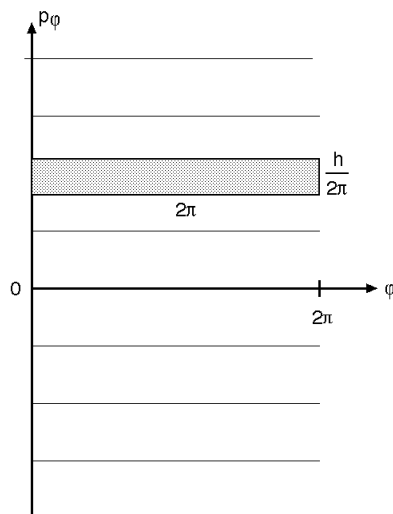
$$\left( \frac{\partial P}{\partial T} \right)_\mu = \frac{5}{2T} P - \frac{\mu}{kT^2} P = \left[ \frac{5}{2} - \ln \left\{ \frac{N}{V} \left( \frac{h^2}{2\pi mkT} \right)^{3/2} \right\} \right] \frac{Nk}{V}$$

which, by eqn. (1.5.1a), is precisely equal to  $S/V$ .

## Chapter 2

**2.3.** The rotator in this problem may be regarded as confined to the ( $z = 0$ )-plane and its position at time  $t$  may be denoted by the azimuthal angle  $\varphi$ . The conjugate variable  $p_\varphi$  is then  $m\rho^2\dot{\varphi}$ , where the various symbols have their usual meanings. The energy of rotation is given by

$$E = \frac{1}{2}m(\rho\dot{\varphi})^2 = p_\varphi^2 / 2m\rho^2.$$



Lines of constant energy in the  $(\varphi, p_\varphi)$ -plane are “straight lines, running parallel to the  $\varphi$ -axis from  $\varphi = 0$  to  $\varphi = 2\pi$ ”. The basic cell of area  $h$  in this plane is a “rectangle with sides  $\Delta\varphi = 2\pi$  and  $\Delta p_\varphi = h/2\pi$ ”. Clearly, the eigenvalues of  $p_\varphi$ , starting with  $p_\varphi = 0$ , are  $n\hbar$  and those of  $E$  are  $n^2\hbar^2/2I$ , where  $I = m\rho^2$  and  $n = 0, \pm 1, \pm 2, \dots$

The eigenvalues of  $E$  obtained here are precisely the ones given by quantum mechanics for the energy “associated with the  $z$ -component of the rotational motion”.

**2.4.** The rigid rotator is a model for a diatomic molecule whose internuclear distance  $r$  may be regarded as fixed. The orientation of the molecule in

space may be denoted by the angles  $\theta$  and  $\varphi$ , the conjugate variables being  $p_\theta = mr^2\dot{\theta}$  and  $p_\varphi = mr^2 \sin^2 \theta \dot{\varphi}$ . The energy of rotation is given by

$$E = \frac{1}{2}m(r\dot{\theta})^2 + \frac{1}{2}m(r \sin \theta \dot{\varphi})^2 = \frac{p_\theta^2}{2mr^2} + \frac{p_\varphi^2}{2mr^2 \sin^2 \theta} = \frac{M^2}{2I},$$

where  $I = mr^2$  and  $M^2 = p_\theta^2 + (p_\varphi^2 / \sin^2 \theta)$ .

The “volume” of the relevant region of the phase space is given by the integral  $\int' dp_\theta dp_\varphi d\theta d\varphi$ , where the region of integration is constrained by the value of  $M$ . A little reflection shows that in the subspace of  $p_\theta$  and  $p_\varphi$  we are restricted by an elliptical boundary with semi-axes  $M$  and  $M \sin \theta$ , the enclosed area being  $\pi M^2 \sin \theta$ . The “volume” of the relevant region, therefore, is

$$\int_{\theta=0}^{\pi} \int_{\varphi=0}^{2\pi} (\pi M^2 \sin \theta) d\theta d\varphi = 4\pi^2 M^2.$$

The number of microstates available to the rotator is then given by  $4\pi^2 M^2 / h^2$ , which is precisely  $(M/h)^2$ . At the same time, the number of microstates associated with the quantized value  $M_j^2 = j(j+1)\hbar^2$  may be estimated as

$$\frac{1}{h^2} [M_{j+\frac{1}{2}}^2 - M_{j-\frac{1}{2}}^2] = \left(j + \frac{1}{2}\right) \left(j + \frac{3}{2}\right) - \left(j - \frac{1}{2}\right) \left(j + \frac{1}{2}\right) = 2j + 1.$$

This is precisely the degeneracy arising from the eigenvalues that the azimuthal quantum number  $m$  has, viz.  $j, j-1, \dots, -j+1, -j$ .

**2.6.** In terms of the variables  $\theta$  and  $L(=m\ell^2\dot{\theta})$ , the state of the simple pendulum is given by, see eqns. (2.4.9),

$$\theta = (A/\ell) \cos(\omega t + \varphi), \quad L = -m\ell\omega A \sin(\omega t + \varphi),$$

with  $E = \frac{1}{2}m\omega^2 A^2$  and  $\tau = 2\pi/\omega$ . The trajectory in the  $(\theta, L)$ -plane is given by the equation

$$\frac{\theta^2}{(A/\ell)^2} + \frac{L^2}{(m\ell\omega A)^2} = 1,$$

which is an ellipse — just like in Fig. 2.2. The enclosed area turns out to be  $\pi m\omega A^2$ , which is precisely equal to the product  $E\tau$ .

**2.7.** Following the argument developed on page 68–69 of the text, the number of microstates for a given energy  $E$  turns out to be

$$\Omega(E) = (R + N - 1)! / R!(N - 1)!, \quad R = \left(E - \frac{1}{2}N\hbar\omega\right) / \hbar\omega. \quad (1)$$

For  $R \gg N$ , we obtain the asymptotic result

$$\Omega(E) \approx R^{N-1} / (N-1)!, \text{ where } R \approx E / \hbar\omega. \quad (3.8.25a)$$

The corresponding expression for  $\Gamma(E; \Delta)$  would be

$$\Gamma(E; \Delta) \approx \frac{(E / \hbar\omega)^{N-1}}{(N-1)!} \cdot \frac{\Delta}{\hbar\omega} = \frac{E^{N-1} \Delta}{(N-1)! (\hbar\omega)^N}. \quad (1)$$

The “volume” of the relevant region of the phase space may be derived from the integral

$$\int' \prod_{i=1}^N (dq_i dp_i), \text{ with } \sum_{i=1}^N \left( \frac{1}{2} k q_i^2 + \frac{1}{2m} p_i^2 \right) \leq E.$$

This is equal to, see eqn. (7a) of Appendix C,

$$\left( \frac{2}{k} \right)^{\frac{1}{2}N} (2m)^{\frac{1}{2}N} \cdot \frac{\pi^N}{N!} E^N = \left( \frac{2\pi}{\omega} \right)^N \frac{E^N}{N!},$$

where  $\omega = \sqrt{k/m}$ . The “volume” of the shell in question is then given by

$$\left( \frac{2\pi}{\omega} \right)^N \frac{NE^{N-1}}{N!} \cdot \Delta = \left( \frac{2\pi}{\omega} \right)^N \frac{E^{N-1} \Delta}{(N-1)!}. \quad (2)$$

Dividing (2) by (1), we see that the conversion factor  $\omega_0$  is precisely  $h^N$ .

**2.8.** We write  $V_{3N} = AR^{3N}$ , so that  $dV_{3N} = A \cdot 3NR^{3N-1} dR$ . At the same time, we have

$$\int_0^\infty \dots \int_0^\infty e^{-\sum_{i=1}^N r_i} \prod_{i=1}^N r_i^2 dr_i = \prod_{i=1}^N \int_0^\infty e^{-r_i} r_i^2 dr_i = 2^N. \quad (1)$$

The integral on the left may be written as

$$\int_0^\infty e^{-R} (4\pi)^{-N} dV_{3N} = \int_0^\infty e^{-R} (4\pi)^{-N} A \cdot 3NR^{3N-1} dR = (4\pi)^{-N} A \cdot 3N \Gamma(3N). \quad (2)$$

Equating (1) and (2), we get:  $A = (8\pi)^N / (3N)!$ , which yields the desired result for  $V_{3N}$ .

The “volume” of the relevant region of the phase space is given by

$$\int' \prod_{i=1}^{3N} dq_i dp_i = V^N \int' \prod_{i=1}^N (4\pi p_i^2 dp_i) = V^N (8\pi E^3 / c^3)^N / (3N)!,$$

so that

$$\Sigma(n, V, E) = V^N (8\pi E^3 / h^3 c^3)^N / (3N)!,$$

which is a function of  $N$  and  $VE^3$ . An *isentropic* process then implies that  $VE^3 = \text{const.}$

The temperature of the system is given by

$$\frac{1}{T} = \left( \frac{\partial(k \ln \Sigma)}{\partial E} \right)_{N,V} = \frac{3Nk}{E}, \text{ i.e. } E = 3NkT.$$

The equation for the isentropic process then becomes  $VT^3 = \text{const.}$ , i.e.  $T \propto V^{-1/3}$ ; this implies that  $\gamma = 4/3$ . The rest of the thermodynamics follows straightforwardly. See also Problems 1.7 and 3.15.

# Chapter 3

**3.4.** For the first part, we use eqn. (3.2.31) with all  $\omega_r = 1$ . We get

$$\frac{k}{\mathcal{N}} \ln \Gamma = k \ln \left\{ \sum_r e^{-\beta E_r} \right\} + k\beta U,$$

which is indeed equal to  $-(A/T) + (U/T) = S$ .

For the second part, we use eqn. (3.2.5), with the result that

$$\begin{aligned} \frac{k}{\mathcal{N}} \ln W \{n_r^*\} &= \frac{k}{\mathcal{N}} \left[ \mathcal{N} \ln \mathcal{N} - \sum_r n_r^* \ln n_r^* \right] \\ &= -k \sum_r \frac{n_r^*}{\mathcal{N}} \ln \frac{n_r^*}{\mathcal{N}} = -k \left\langle \ln \frac{n_r^*}{\mathcal{N}} \right\rangle. \end{aligned}$$

Substituting for  $n_r^*$  from eqn. (3.2.10), we get

$$\frac{k}{\mathcal{N}} \ln W \{n_r^*\} = k\beta \langle E_r \rangle + k \ln \left\{ \sum_r e^{-\beta E_r} \right\},$$

which is precisely the result obtained in the first part.

**3.5.** Since the function  $A(N, V, T)$  of a given thermodynamic system is an *extensive* quantity, we may write

$$A(N, V, T) = Nf(v, T) \quad (v = V / N).$$

It follows that

$$N \left( \frac{\partial A}{\partial N} \right)_{V,T} = N \left[ f + N \left( \frac{\partial f}{\partial v} \right)_T \cdot \frac{-V}{N^2} \right], \text{ and } V \left( \frac{\partial A}{\partial V} \right)_{N,T} = VN \left( \frac{\partial f}{\partial v} \right)_T \cdot \frac{1}{N}.$$

Adding these expressions, we obtain the desired result.

**3.6.** Let's go to part (c) right away. Our problem here is to *maximize* the expression  $S/k = - \sum_{r,s} P_{r,s} \ln P_{r,s}$ , subject to the constraints  $\sum_{r,s} P_{r,s} =$

1,  $\sum_{r,s} E_s P_{r,s} = \bar{E}$  and  $\sum_{r,s} N_r P_{r,s} = \bar{N}$ . Varying  $P$ 's and using the method of Lagrange's undetermined multipliers, we are led to the condition

$$\sum_{r,s} \{-(1 + \ln P_{r,s}) - \gamma - \beta E_s - \alpha N_r\} \delta P_{r,s} = 0.$$

In view of the arbitrariness of the  $\delta P$ 's in this expression, we require that

$$-(1 + \ln P_{r,s}) - \gamma - \beta E_s - \alpha N_r = 0$$

for *all*  $r$  and  $s$ . It follows that

$$P_{r,s} \propto \exp(-\beta E_s - \alpha N_r).$$

The parameters  $\alpha$  and  $\beta$  are to be determined by the given values of  $\bar{N}$  and  $\bar{E}$ .

In the absence of the constraint imposed by  $\bar{N}$ , the parameter  $\alpha$  does not even figure in the calculation, and we obtain

$$P_r \propto \exp(-\beta E_r),$$

as desired in part (b). And if the constraint imposed by  $\bar{E}$  is also absent, we obtain

$$P_r = \text{const.},$$

as desired in part (a).

**3.7.** From thermodynamics,

$$C_P - C_V = T \left( \frac{\partial P}{\partial T} \right)_V \left( \frac{\partial V}{\partial T} \right)_P = -T \left( \frac{\partial P}{\partial T} \right)_V^2 / \left( \frac{\partial P}{\partial V} \right)_T > 0. \quad (1)$$

From Sec. 3.3,

$$P = - \left( \frac{\partial A}{\partial V} \right)_{N,T} = kT \left( \frac{\partial \ln Q}{\partial V} \right)_{N,T}. \quad (2)$$

Substituting (2) into (1), we obtain the desired result.

For the ideal gas,  $Q \propto V^N T^{3N/2}$ . Therefore,  $(\partial \ln Q / \partial V)_T = N/V$ . We then get

$$C_P - C_V = -k \frac{(N/V)^2}{-N/V^2} = Nk.$$

**3.8.** For an ideal gas,

$$Q_1 = V \frac{(2\pi mkT)^{3/2}}{h^3} = \frac{NkT}{P} \frac{(2\pi mkT)^{3/2}}{h^3}.$$

It follows that  $T(\partial \ln Q_1/\partial T)_P = 5/2$ ; the expression on the right-hand side of the given equation then is

$$\ln \left\{ \frac{V}{N} \frac{(2\pi mkT)^{3/2}}{h^3} \right\} + \frac{5}{2}$$

which, by eqn. (3.5.13), is indeed equal to the quantity  $S/Nk$ .

**3.12.** We start with eqn. (3.5.5), substitute  $H(\mathbf{q}, \mathbf{p}) = \sum_i (p_i^2/2m) + U(\mathbf{q})$  and

integrate over the  $p_i$ 's, to get

$$Q_N(V, T) = \frac{1}{N!} \left( \frac{2\pi mkT}{h^2} \right)^{3N/2} Z_N(V, T), \text{ where } Z_N(V, T) = \int e^{-U(\mathbf{q})/kT} d^{3N} q.$$

It follows that, for  $N \gg 1$ ,

$$A = NkT \left[ \ln \left\{ N \left( \frac{h^2}{2\pi mkT} \right)^{3/2} \right\} - 1 \right] - kT \ln Z, \text{ whence}$$

$$S = Nk \left[ \ln \left\{ \frac{1}{N} \left( \frac{2\pi mkT}{h^2} \right)^{3/2} \right\} + \frac{5}{2} \right] + k \ln Z + kT \left( \frac{\partial \ln Z}{\partial T} \right)_{N, V}.$$

Now

$$kT \left( \frac{\partial \ln Z}{\partial T} \right)_{N, V} = \frac{kT \int e^{-U/kT} (U/kT^2) d^{3N} q}{\int e^{-U/kT} d^{3N} q} = \frac{\bar{U}}{T}, \text{ while}$$

$$k \ln Z = k \ln \left\{ \bar{V}^N e^{-\bar{U}/kT} \right\} = Nk \ln \bar{V} - \frac{\bar{U}}{T}.$$

Substituting these results into the above expression for  $S$ , we obtain the desired result for  $S$ . In passing, we note that  $\langle H \rangle \equiv A + TS = \frac{3}{2} NkT + \bar{U}$ .

For the second part of the question, we write  $U(\mathbf{q}) = \sum_{i < j} u(r_{ij})$ , so that

$$e^{-\beta U(\mathbf{q})} = \prod_{i < j} e^{-\beta u(r_{ij})} = \prod_{i < j} (1 + f_{ij}),$$

and follow Problems 3.23 and 1.4. The quantity  $\bar{V}$  then appears to be in the nature of a “free volume” for the molecules of the system.

**3.14.** a) The Lagrangian is given by

$$\mathcal{L} = K - V = \sum_{i\alpha} \frac{1}{2} m \dot{r}_{i\alpha}^2 - \sum_{i < j} u(r_{ij}) - \sum_{i\alpha} [u_w(r_{i\alpha}) + u_w(L - r_{i\alpha})],$$

where  $i = 1, \dots, N$  denotes the particle number,  $\alpha = x, y, z$  denotes the cartesian directions, and  $r_{ij}^2 = \sum_{\alpha} (r_{i\alpha} - r_{j\alpha})^2$ . The canonical momenta are

$$p_{i\alpha} = \frac{\partial \mathcal{L}}{\partial \dot{r}_{i\alpha}} = m \dot{r}_{i\alpha}.$$



The Hamiltonian is given by

$$\begin{aligned}\mathcal{H} &= \sum_{i\alpha} p_{i\alpha} \dot{r}_{i\alpha} - \mathcal{L} \\ &= \sum_{i\alpha} \frac{p_{i\alpha}^2}{2m} + \sum_{i<j} u(r_{ij}) + \sum_{i\alpha} [u_w(r_{i\alpha}) + u_w(L - r_{i\alpha})].\end{aligned}$$

The canonical pressure can be written

$$P = -\frac{\partial \mathcal{H}}{\partial V} = -\frac{1}{3L^2} \frac{\partial \mathcal{H}}{\partial L} = -\frac{1}{3L^2} \sum_{i\alpha} u'_w(L - r_{i\alpha}) = \frac{1}{3L^2} (F_x + F_y + F_z).$$

This is clearly the instantaneous force per unit area on the right, back, and top walls.

b) The cartesian coordinates for the scaled position inside the box are  $s_{i\alpha} = r_{i\alpha}/L$  so the Lagrangian becomes

$$\mathcal{L} = \sum_{i\alpha} \frac{1}{2} m L^2 \dot{s}_{i\alpha}^2 - \sum_{i<j} u(Ls_{ij}) - \sum_{i\alpha} [u_w(Ls_{i\alpha}) + u_w(L - Ls_{i\alpha})].$$

In this case the canonical momenta are

$$\tilde{p}_{i\alpha} = \frac{\partial \mathcal{L}}{\partial \dot{s}_{i\alpha}} = mL^2 \dot{s}_{i\alpha}.$$

This leads to a Hamiltonian of the form

$$\mathcal{H} = \sum_{i\alpha} \frac{\tilde{p}_{i\alpha}^2}{2mL^2} + \sum_{i<j} u(Ls_{ij}) + \sum_{i\alpha} [u_w(Ls_{i\alpha}) + u_w(L - Ls_{i\alpha})],$$

with canonical pressure is

$$\begin{aligned}P &= + \frac{1}{3L^2} \sum_{i\alpha} \frac{\tilde{p}_{i\alpha}^2}{mL^3} \\ &\quad - \frac{1}{3L^2} \sum_{i<j} u'(Ls_{ij}) s_{ij} \\ &\quad - \frac{1}{3L^2} \sum_{i\alpha} [u'_w(Ls_{i\alpha}) s_{i\alpha} + u'_w(L - Ls_{i\alpha})(1 - s_{i\alpha})].\end{aligned}$$

Converting back to normal cartesian coordinates and momenta gives

$$\begin{aligned}P &= + \frac{2}{3V} \sum_{i\alpha} \frac{p_{i\alpha}^2}{2m} \\ &\quad - \frac{1}{3V} \sum_{i<j} u'(r_{ij}) r_{ij} \\ &\quad - \frac{1}{3V} \sum_{i\alpha} [u'_w(r_{i\alpha}) r_{i\alpha} + u'_w(L - r_{i\alpha})(L - r_{i\alpha})].\end{aligned}$$

The first term is  $(2/3)(N/V)$  times the kinetic energy per particle so is  $O(N)$ . The second term is  $(1/3)(N/V)$  times the virial per particle so is also  $O(N)$ . On the other hand, third term is proportional to the force on the walls divided by the volume so is  $O(N^{2/3})$  which is negligible in the thermodynamic limit.

Comparing to equation (3.7.15) for the average pressure we see that

$$\frac{P}{nkT} = 1 - \frac{1}{3NkT} \left\langle \sum_{i < j} u'_w(r_{ij}) r_{ij} \right\rangle.$$

**3.15.** Here,  $Q_N(V, T) = (1/N!)Q_1^N(V, T)$ , while

$$Q_1(V, T) = \int_0^\infty e^{-\beta pc} \frac{V \cdot 4\pi p^2 dp}{h^3} = \frac{8\pi V}{h^3} \frac{1}{\beta^3 c^3},$$

which yields the desired result for  $Q_N$ . The thermodynamics of the system now follows straightforwardly.

As regards the density of states, the expression

$$Q_1(V, T) = \int_0^\infty e^{-\beta \varepsilon} g(\varepsilon) d\varepsilon = \frac{8\pi V}{h^3} \frac{1}{\beta^3 c^3}$$

leads to

$$g(\varepsilon) = \frac{4\pi V}{h^3 c^3} \varepsilon^2$$

for a single particle, while the expression for  $Q_N(V, T)$  leads to

$$g(E) = \frac{1}{N!} \left( \frac{8\pi V}{h^3 c^3} \right)^N \frac{E^{3N-1}}{\Gamma(3N)}$$

for the  $N$ -particle system; cf. the expression for  $\Sigma(E)$  derived in Problem 2.8.

**3.17.** Differentiate the stated result with respect to  $\beta$ , to get

$$\int \left\{ \frac{\partial U}{\partial \beta} - H(U - H) \right\} e^{-\beta H} d\omega = 0.$$

This means that

$$\left\langle \frac{\partial U}{\partial \beta} - HU + H^2 \right\rangle = 0,$$

which amounts to the desired result:  $\langle H^2 \rangle - \langle H \rangle^2 = -(\partial U / \partial \beta)$ .

**3.18.** We start with eqn. (3.6.2), viz.

$$\frac{\partial U}{\partial \beta} = -\frac{\sum_r E_r^2 e^{-\beta E_r}}{\sum_r e^{-\beta E_r}} + U^2, \quad (1)$$

and differentiate it with respect to  $\beta$ , keeping the  $E_r$  fixed. We get

$$\frac{\partial^2 U}{\partial \beta^2} = \langle E^3 \rangle - \langle E^2 \rangle \langle E \rangle + 2U \frac{\partial U}{\partial \beta}.$$

Substituting for  $(\partial U / \partial \beta)$  from eqn. (1), we get

$$\frac{\partial^2 U}{\partial \beta^2} = \langle E^3 \rangle - 3\langle E^2 \rangle U + 2U^3,$$

which is precisely equal to  $\langle (E - U)^3 \rangle$ . As for  $\partial^2 U / \partial \beta^2$ , we note that, since

$$\begin{aligned} \left( \frac{\partial U}{\partial \beta} \right)_{E_r} &= -kT^2 \left( \frac{\partial U}{\partial T} \right)_V = -kT^2 C_V, \\ \left( \frac{\partial^2 U}{\partial \beta^2} \right)_{E_r} &= -kT^2 \left[ \frac{\partial}{\partial T} (-kT^2 C_V) \right]_V = k^2 T^2 \left[ 2TC_V + T^2 \left( \frac{\partial C_V}{\partial T} \right)_V \right]. \end{aligned}$$

Hence the desired result.

For the ideal classical gas,  $U = \frac{3}{2}NkT$  and  $C_V = \frac{3}{2}Nk$ , which readily yield the stated results.

**3.19.** Since  $G = \sum_i q_i p_i$ ,  $\dot{G} = \sum_i (\dot{q}_i p_i + q_i \dot{p}_i)$ . Averaging over a time interval  $\tau$ , we get

$$\frac{1}{\tau} \int_t^{t+\tau} \sum_i (\dot{q}_i p_i + q_i \dot{p}_i) dt = \frac{1}{\tau} \int_t^{t+\tau} \dot{G} dt = \frac{G(t+\tau) - G(t)}{\tau}. \quad (1)$$

For a finite  $V$  and finite  $E$ , the quantity  $G$  is *bounded*; therefore, in the limit  $\tau \rightarrow \infty$ , the right-hand side of (1) vanishes. The left-hand side then gives

$$\left\langle \sum_i (\dot{q}_i p_i + q_i \dot{p}_i) \right\rangle = 0.$$

which leads to the desired result.

**3.20.** The virial of the noninteracting system, by eqn. (3.7.12), is  $-3PV$ . The contribution from interparticle interactions, by eqn. (3.7.15), is given by the “expectation value of the sum of the quantity  $-r(\partial u / \partial r)$  over *all* pairs of particles in the system”. If  $u(r)$  is a homogeneous function (of degree  $n$ ) of the particle coordinates, this contribution will be  $-nU$ , where  $U$  is

the mean potential energy (*not* the internal energy) of the system. The total virial is then given by

$$\mathcal{V} = -3PV - nU.$$

The relation  $K = -\frac{1}{2}\mathcal{V}$  still holds, and the rest of the results follow straightforwardly.

**3.21.** All systems considered here are localized. The pressure term, therefore, drops out, and we are left with the result

$$K = \frac{n}{2}U = \frac{n}{n+2}E.$$

Example (a) pertains to  $n = 2$ , while examples (b) and (c) pertain to  $n = -1$ . In the former case,  $K = U = \frac{1}{2}E$ ; in the latter,  $K = -\frac{1}{2}U = -E$ .

The next problem pertains to  $n = 4$ .

**3.22.** Note that a force proportional to  $q^3$  implies a potential energy proportional to  $q^4$ . Thus

$$H = \frac{1}{2m}p^2 + cq^4 \quad (c > 0).$$

It follows that

$$\left\langle \frac{1}{2m}p^2 \right\rangle = \frac{\int_{-\infty}^{\infty} e^{-\beta p^2/2m} (p^2/2m) dp}{\int_{-\infty}^{\infty} e^{-\beta p^2/2m} dp} = \frac{1}{2\beta};$$

for the values of these integrals, see eqns. (13a) of Appendix B. Next,

$$\langle cq^4 \rangle = \frac{\int_{-\infty}^{\infty} e^{-\beta cq^4} (cq^4) dq}{\int_{-\infty}^{\infty} e^{-\beta cq^4} dq} = -\frac{\partial}{\partial \beta} \ln I(B),$$

where  $I(\beta)$  denotes the integral in the denominator. It is straightforward to see that  $I(\beta)$  is proportional to  $\beta^{-1/4}$ , whence  $\langle cq^4 \rangle = 1/4\beta$ , which proves the desired result.

**3.23.** The key to this derivation is writing the partition function in terms of position integrals over scaled coordinates. Assume a cubic box of size  $L$  and volume  $V = L^3$ . The scaled position for particle  $i$  is  $\mathbf{s}_i = \mathbf{r}_i/L$ . The

partition function is

$$\begin{aligned} Q_N(V, T) &= \frac{1}{\lambda^{3N} N!} \int \exp \left( -\beta \sum_{i < j} u(r_{ij}) \right) d^N \mathbf{r} \\ &= \frac{V^N}{\lambda^{3N} N!} \int \exp \left( -\beta \sum_{i < j} u(V^{1/d} s_{ij}) \right) d^N \mathbf{s}. \end{aligned}$$

Now the pressure is

$$\begin{aligned} P &= - \left( \frac{\partial A}{\partial V} \right)_{N, T} \\ &= \frac{kT}{Q_N} \left[ \frac{NQ_N}{V} - \frac{\beta V^N}{dV \lambda^{3N} N!} \int \left( \sum_{i < j} V^{1/d} s_{ij} u'(V^{1/d} s_{ij}) \right) \exp \left( -\beta \sum_{i < j} u(V^{1/d} s_{ij}) \right) d^N \mathbf{s} \right]. \end{aligned}$$

This can be simplified by going back to integrals over the normal position variables to give equation (3.7.15).

**3.24.** By eqn. (3.7.5), we have, for a single particle,

$$\left\langle \sum_{i=1}^3 p_i \dot{q}_i \right\rangle = 3kT. \quad (1)$$

The left-hand side of (1) is the expectation value of the quantity  $\mathbf{p} \cdot \mathbf{u}$ , i.e. pu which, for a relativistic particle, is equal to  $m_0 u^2 (1 - u^2/c^2)^{-1/2}$ . The desired result follows readily.

In the non-relativistic limit ( $u \ll c$ ), one obtains:  $\langle \frac{1}{2} m_0 u^2 \rangle \approx \frac{3}{2} kT$ ; in the extreme relativistic limit ( $u \rightarrow c$ ), one obtains:  $\langle mc^2 \rangle \approx 3kT$ . Note that, in the latter case,  $m_0 c^2$  is negligible in comparison with  $mc^2$ , so there is no significant difference between the kinetic energy and the total energy of the particle.

**3.25.** For the first part of this problem, see Sec. 6.4 — especially the derivation of the formula (6.4.9). For the second part, equate the result obtained in the first part with the one stated in eqn. (3.7.5).

**3.26.** The multiplicity  $w(j) \{ = (j + s - 1)! / j!(s - 1)! \}$  arises from the variety of ways in which  $j$  indistinguishable quanta can be divided among the  $s$  dimensions of the oscillator:  $j = j_1 + \dots + j_s$ ; this is similar to the calculation done on page 68–69 of the text.

As for the partition function,  $Q_N^{(s)}(\beta) = [Q_1^{(s)}(\beta)]^N$ , where

$$\begin{aligned} Q_1^{(s)}(\beta) &= \sum_{j=0}^{\infty} \frac{(j + s - 1)!}{j!(s - 1)!} e^{-\beta(j + \frac{1}{2}s)\hbar\omega} \\ &= e^{-\frac{1}{2}s\beta\hbar\omega} (1 - e^{-\beta\hbar\omega})^{-s}. \end{aligned}$$

Calculation of the various thermodynamic quantities is now straightforward. The results are found to be essentially the same as for a system of  $sN$  one-dimensional oscillators. However, since

$$Q_N^{(s)}(\beta) = Q_{Ns}^{(1)}(\beta),$$

the chemical potential  $\mu_s$  will turn out to be  $s$  times  $\mu_1$ .

- 3.28.** (a) When one of the oscillators is in the quantum state  $n$ , the energy left for the remaining  $(N-1)$  oscillators is  $E - (n + \frac{1}{2})\hbar\omega$ ; the corresponding number of quanta to be distributed among these oscillators is  $R-n$ ; see eqn. (3.8.24). The relevant number of microstates is then given by the expression  $(R-n+N-2)!/(R-n)!(N-2)!$ . Combined with expression (3.8.25), this gives

$$p_n = \frac{(R-n+N-2)!}{(R-n)!(N-2)!} \div \frac{(R+N-1)!}{R!(N-1)!}. \quad (1)$$

It follows that

$$\frac{p_{n+1}}{p_n} = \frac{R-n}{R-n+N-2} \simeq \frac{R}{R+N} = \frac{\bar{n}}{\bar{n}+1}.$$

By iteration,  $p_n = p_0\{\bar{n}/(\bar{n}+1)\}^n$ .

Going back to eqn. (1), we note that

$$p_0 = \frac{N-1}{R+N-1} \simeq \frac{N}{R+N} = -\frac{1}{\bar{n}+1},$$

which completes the desired calculation.

- (b) The probability in question is proportional to  $g_{N-1}(E-\varepsilon)$ , i.e. to  $(E-\varepsilon)^{\frac{3}{2}(N-1)-1}$ . For  $1 \ll N$ , this is essentially proportional to  $(1-\varepsilon/E)^{\frac{3}{2}N}$  and, for  $\varepsilon \ll -E$ , to  $e^{-3N\varepsilon/2E}$ .

- 3.29.** The partition function of the *anharmonic* oscillator is given by

$$Q_1(\beta) = \frac{1}{h} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{-\beta H} dq \, dp \quad \left\{ H = \frac{p^2}{2m} + cq^2 - gq^3 - fq^4 \right\}.$$

The integration over  $p$  gives a factor of  $\sqrt{2\pi m/\beta}$ . For integration over  $q$ , we write

$$e^{-\beta cq^2} e^{\beta(gq^3 + fq^4)} = e^{-\beta cq^2} \left[ 1 + \beta(gq^3 + fq^4) + \frac{1}{2}\beta^2(gq^3 + fq^4)^2 + \dots \right];$$

the integration then gives

$$\sqrt{\frac{\pi}{\beta c}} + \beta f \cdot \frac{3}{4} \sqrt{\frac{\pi}{\beta^5 c^5}} + \frac{1}{2} \beta^2 g^2 \cdot \frac{15}{8} \sqrt{\frac{\pi}{\beta^7 c^7}} + \dots$$

It follows that

$$Q_1(\beta) = \frac{\pi}{\beta h} \sqrt{\frac{2m}{c}} \left[ 1 + \frac{3f}{4\beta c^2} + \frac{15g^2}{16\beta c^3} + \dots \right],$$

so that

$$\ln Q_1(\beta) = \text{const.} - \ln \beta + \frac{3f}{4\beta c^2} + \frac{15g^2}{16\beta c^3} + \dots,$$

whence

$$U(\beta) = \frac{1}{\beta} + \frac{3f}{4\beta^2 c^2} + \frac{15g^2}{16\beta^2 c^3} + \dots$$

and

$$C(\beta) = k + \frac{3f}{2c^2} \frac{k^2 T}{\beta} + \frac{15g^2}{8c^3} \frac{k^2 T}{\beta} + \dots$$

Next, the mean value of the displacement  $q$  is given by

$$\langle q \rangle = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \exp(-\beta H) q \, dp \, dq / \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \exp(-\beta H) \, dp \, dq.$$

In the desired approximation, we get

$$\begin{aligned} \langle q \rangle &\simeq \beta g \int_{-\infty}^{\infty} e^{-\beta c q^2} q^4 \, dq / \int_{-\infty}^{\infty} e^{-\beta c q^2} \, dq \\ &= \beta g \cdot \frac{3}{4} \sqrt{\frac{\pi}{\beta^5 c^5}} / \sqrt{\frac{\pi}{\beta c}} = \frac{3g}{4\beta c^2}. \end{aligned}$$

**3.30.** The single-oscillator partition function is now given by

$$Q_1(\beta) = \sum_{n=0}^{\infty} e^{-\beta(n+\frac{1}{2})\hbar\omega + \beta x(n+\frac{1}{2})^2 \hbar\omega}.$$

For  $x \ll 1$ , we may write

$$Q_1(\beta) = \sum_{n=0}^{\infty} e^{-\beta(n+\frac{1}{2})\hbar\omega} \left[ 1 + \beta x \left( n + \frac{1}{2} \right)^2 \hbar\omega + \dots \right].$$

With  $u = \beta\hbar\omega$ , the sums involved are

$$S_1(u) = \sum_{n=0}^{\infty} e^{-u(n+\frac{1}{2})} = \left[ 2 \sinh \left( \frac{1}{2} u \right) \right]^{-1}, \text{ and}$$

$$S_2(u) = \sum_{n=0}^{\infty} e^{-u(n+\frac{1}{2})} \left( n + \frac{1}{2} \right)^2 = \frac{d^2}{du^2} S_1(u) = \left[ 4 \sinh \left( \frac{1}{2} u \right) \right]^{-1} \left\{ \coth^2 \left( \frac{1}{2} u \right) - \frac{1}{2} \right\}.$$

It follows that

$$\begin{aligned}\ln Q_1 &= \ln[S_1 + xuS_2 + \dots] \simeq \ln S_1 + xu(S_2/S_1) \\ &= -\ln \left[ 2 \sinh \left( \frac{1}{2}u \right) \right] + \frac{1}{2}xu \left\{ \coth^2 \left( \frac{1}{2}u \right) - \frac{1}{2} \right\}.\end{aligned}$$

The first part of this expression leads to the standard results (3.8.20 and 21). The second part may, for simplification, be expressed as a power series in  $u$ , viz.

$$x \left( \frac{2}{u} + \frac{u}{12} + \frac{u^3}{120} + \dots \right).$$

The resulting contribution to the internal energy per oscillator turns out to be

$$x\hbar\omega \left( \frac{2}{u^2} - \frac{1}{12} - \frac{u^2}{40} - \dots \right)$$

and the corresponding contribution to the specific heat is given by

$$xk \left( \frac{4}{u} + \frac{u^3}{20} + \dots \right).$$

**3.31.** This problem is essentially the same as Problem 3.32, with  $g_1 = g_2 = 1$ ,  $\varepsilon_1 = 0$  and  $\varepsilon_2 = \varepsilon$ .

**3.32.** We use formula (3.3.13), with  $P_r = p_1/g_1$  for each of the states in group 1 and  $p_2/g_2$  for each of the states in group 2. We get

$$S = -k \left[ g_1 \left( \frac{p_1}{g_1} \ln \frac{p_1}{g_1} \right) + g_2 \left( \frac{p_2}{g_2} \ln \frac{p_2}{g_2} \right) \right]. \quad (1)$$

(a) In thermal equilibrium,

$$p_i = \frac{g_i e^{-\beta\varepsilon_i}}{\sum_i g_i e^{-\beta\varepsilon_i}} \quad (i = 1, 2).$$

With  $x = \beta(\varepsilon_2 - \varepsilon_1)$ , we have:  $p_1 = g_1/(g_1 + g_2 e^{-x})$  and  $p_2 = g_2/(g_1 e^x + g_2)$ . Substituting these results into (1), we obtain

$$S = k \left[ \frac{g_1}{g_1 + g_2 e^{-x}} \ln (g_1 + g_2 e^{-x}) + \frac{g_2}{g_1 e^x + g_2} \ln (g_1 e^x + g_2) \right].$$

Writing the first log as  $\ln g_1 + \ln\{1 + (g_2/g_1)e^{-x}\}$  and the second log as  $\ln g_1 + x + \ln\{1 + (g_2/g_1)e^{-x}\}$ , we obtain the stated expression for  $S$ .

(b) With  $Q = g_1 e^{-\beta\varepsilon_1} + g_2 e^{-\beta\varepsilon_2}$ , it is straightforward to see that

$$\begin{aligned}A &= -kT \ln\{g_1 e^{-\beta\varepsilon_1} + g_2 e^{-\beta\varepsilon_2}\} \text{ and} \\ U &= \{g_1 \varepsilon_1 e^{-\beta\varepsilon_1} + g_2 \varepsilon_2 e^{-\beta\varepsilon_2}\} / \{g_1 e^{-\beta\varepsilon_1} + g_2 e^{-\beta\varepsilon_2}\}.\end{aligned}$$

The formula  $S = (U - A)/T$  then leads to the desired result.



- (c) As  $T \rightarrow 0$ ,  $x \rightarrow \infty$  and  $S$  indeed tends to the value  $k \ln g_1$ . This corresponds to the fact that the probabilities  $p_1$  and  $p_2$  in this limit tend to the values 1 and 0, respectively.

**3.35.** The partition function of the system is given by

$$Q_N = \frac{1}{N!} Q_1^N, \text{ where } Q_1 = \frac{V}{\lambda^3} \cdot Z,$$

$Z$  being the factor that arises from the rotational/orientational degrees of freedom of the molecule:

$$\begin{aligned} Z &= \int \exp \left[ -\beta \left\{ \frac{p_\theta^2}{2I} + \frac{p_\varphi^2}{2I \sin^2 \theta} - \mu E \cos \theta \right\} \right] \frac{dp_\theta dp_\varphi d\theta d\varphi}{h^2} \\ &= \int_0^\pi \left( \frac{2\pi I}{\beta} \right)^{1/2} \left( \frac{2\pi I \sin^2 \theta}{\beta} \right)^{1/2} e^{\beta \mu E \cos \theta} \frac{2\pi d\theta}{h^2} \\ &= \frac{I}{\beta \hbar^2} \cdot \frac{2 \sinh(\beta \mu E)}{\beta \mu E}. \end{aligned}$$

The study of the various thermodynamical quantities of the system is now straightforward.

Concentrating on the electrical quantities alone, we obtain for the *net* dipole moment of the system

$$M_z = N \langle \mu \cos \theta \rangle = \frac{N}{\beta} \frac{\partial \ln Z}{\partial E} = N \mu \left[ \coth(\beta \mu E) - \frac{1}{\beta \mu E} \right];$$

cf. eqns. (3.9.4 and 6). For  $\beta \mu E \ll 1$ ,

$$M_z \approx N \mu \cdot \frac{1}{3} \beta \mu E.$$

The polarization  $P$ , per unit volume, of the system is then given by

$$P \approx n \mu^2 E / 3kT \quad (n = N/V),$$

and the dielectric constant  $\varepsilon$  by

$$\varepsilon = \frac{E + 4\pi P}{E} \approx 1 + \frac{4\pi n \mu^2}{3kT}.$$

The numerical part of the problem is straightforward.

**3.36.** The mean force  $\langle \mathbf{F} \rangle$  between the two dipoles is given by

$$\langle \mathbf{F} \rangle = \left\langle -\frac{\partial U}{\partial \mathbf{R}} \right\rangle = \frac{\int e^{-\beta U} (-\partial U / \partial \mathbf{R}) \sin \theta d\theta d\varphi \cdot \sin \theta' d\theta' d\varphi'}{\int e^{-\beta U} \sin \theta d\theta d\varphi \cdot \sin \theta' d\theta' d\varphi'} \quad (1)$$

$$= \frac{1}{\beta} \frac{\partial}{\partial \mathbf{R}} \ln Z. \quad (2)$$

where  $Z$  denotes the integral in the denominator of (1). At high temperatures, we may write

$$Z = \int \left[ 1 - \beta U + \frac{1}{2} \beta^2 U^2 - \dots \right] \sin \theta \, d\theta d\varphi \cdot \sin \theta' \, d\theta' \, d\varphi'.$$

The linear term vanishes on integration and we are left with

$$\begin{aligned} Z &= \int \left[ 1 + \frac{1}{2} \beta^2 \frac{(\mu\mu')^2}{R^6} \{ 2 \cos \theta \cos \theta' - \sin \theta \sin \theta' \cos(\varphi - \varphi') \}^2 - \dots \right] \\ &\quad \sin \theta \, d\theta d\varphi \cdot \sin \theta' \, d\theta' \, d\varphi' \\ &= 16\pi^2 \left[ 1 + \frac{1}{2} \beta^2 \frac{(\mu\mu')^2}{R^6} \left\{ 4 \cdot \frac{1}{3} \cdot \frac{1}{3} - 0 + \frac{2}{3} \cdot \frac{2}{3} \cdot \frac{1}{2} \right\} - \dots \right]. \end{aligned}$$

It follows that

$$\ln Z = \text{const.} + \frac{1}{3} \beta^2 \frac{(\mu\mu')^2}{R^6} - \dots$$

and hence, at high temperatures,

$$\langle \mathbf{F} \rangle \approx -2\beta \frac{(\mu\mu')^2}{R^7} \hat{\mathbf{R}}.$$

**3.37.** By eqns. (3.9.17 and 18), we have, for a single dipole,

$$\bar{\mu}_z = \frac{\sum_{m=-J}^J (g\mu_B m) \exp(\beta g\mu_B mH)}{\sum_{m=-J}^J \exp(\beta g\mu_B mH)}.$$

At high temperatures, the exponential may be approximated by  $(1 + \beta g\mu_B mH)$  which yields, to the leading order in  $H$ ,

$$\bar{\mu}_z = \beta g^2 \mu_B^2 H \overline{m^2}.$$

One readily obtains for the Curie constant (per unit volume) of the system

$$C_J = N_0 (g^2 \mu_B^2 / k) \overline{m^2}.$$

Writing  $m = J \cos \theta$ , one obtains the desired result.

For the second part, we simply note that, for a given  $J$ ,

$$\overline{m^2} = \frac{\sum_{m=-J}^J m^2}{2J+1} = \frac{J(J+1)(2J+1)/3}{2J+1} = \frac{1}{3} J(J+1).$$

**3.38.** Treating  $m$  as a continuous variable, the partition function of a magnetic dipole assumes the form

$$Q_1(\beta) = \int_{-J}^J e^{\beta g \mu_B H m} dm = \frac{2}{\beta g \mu_B H} \sinh(\beta g \mu_B H J);$$

cf. eqn. (3.9.5). It is clear that this approximation will lead essentially to the same results as the ones following from the Langevin theory — except for the fact that the role of  $\mu$  will be played by  $g \mu_B J$ , which should be contrasted with the expression (3.9.16) of the quantum theory.

**3.40.** (a) By definition,  $C_H = T(\partial S/\partial T)_H$  and  $C_M = T(\partial S/\partial T)_M$ . Now

$$\left(\frac{\partial S}{\partial T}\right)_H = \left(\frac{\partial S}{\partial T}\right)_M + \left(\frac{\partial S}{\partial M}\right)_T \left(\frac{\partial M}{\partial T}\right)_H; \quad (1)$$

at the same time,  $dA \equiv dU - TdS - SdT = HdM - SdT$ , with the result that  $(\partial H/\partial T)_M = -(\partial S/\partial M)_T$ . Equation (1) then becomes

$$\left(\frac{\partial S}{\partial T}\right)_H = \left(\frac{\partial S}{\partial T}\right)_M - \left(\frac{\partial H}{\partial T}\right)_M \left(\frac{\partial M}{\partial T}\right)_H. \quad (2)$$

Multiplying (2) by  $T$ , we obtain the desired result for  $C_H - C_M$ .

(b) The Curie law implies that  $M = CH/T$ . This means that  $(\partial H/\partial T)_M = H/T$ , while  $(\partial M/\partial T)_H = -CH/T^2$ . It follows that  $C_H - C_M = CH^2/T^2$ .

**3.42.** Let  $N_1(N_2)$  be the number of dipoles aligned parallel (opposite) to the field. Then

$$N_1 + N_2 = N, \text{ while } -N_1\varepsilon + N_2\varepsilon = E.$$

It follows that

$$N_1 = \frac{1}{2}(N - E/\varepsilon), \quad N_2 = \frac{1}{2}(N + E/\varepsilon).$$

The number of microstates associated with this macrostate is given by

$$\Omega(N, E) = \frac{N!}{\left\{\frac{1}{2}(N - E/\varepsilon)\right\}! \left\{\frac{1}{2}(N + E/\varepsilon)\right\}!}$$

The entropy of the system is then given by the expression

$$S = k \ln \Omega \approx k \left[ N \ln N - \frac{1}{2} \left( N - \frac{E}{\varepsilon} \right) \ln \left\{ \frac{1}{2} \left( N - \frac{E}{\varepsilon} \right) \right\} - \frac{1}{2} \left( N + \frac{E}{\varepsilon} \right) \ln \left\{ \frac{1}{2} \left( N + \frac{E}{\varepsilon} \right) \right\} \right],$$

which is essentially the same as eqn. (3.10.9).

For the temperature of the system, we get

$$\frac{1}{T} = \left( \frac{\partial S}{\partial E} \right)_N = \frac{k}{2\varepsilon} \ln \left\{ \frac{N - E/\varepsilon}{N + E/\varepsilon} \right\},$$

which agrees with eqn. (3.10.8).

**3.43.** The partition function of this system is given by the usual expression (3.5.5), except for the fact that the Hamiltonian of the system is now a function of the quantities  $\mathbf{p}_j + (e_j / c)\mathbf{A}(\mathbf{r}_j)$ , and not of the  $\mathbf{p}_j$  as such. However, on integration over *any* component of  $\mathbf{p}_j$ , from  $-\infty$  to  $+\infty$ , we obtain the same standard factor  $\sqrt{2\pi mkT}$  — regardless of the value of the corresponding component of  $\mathbf{A}$ . The partition function is, therefore, independent of the applied field and hence the net magnetization of the system is zero.

**3.44.** The Shannon information for a single message is given by  $I_1 = -\sum_r P_r \ln P_r$  where  $P_r$  is the *a priori* probability of message  $r$  from among all  $\Omega$  possible messages. The maximum information is obtained from varying the probabilities, using a Lagrange multiplier  $\mu$  to maintain the normalization  $\sum_r P_r = 1$ , and demanding the solution is stationary.

$$0 = \delta I_1 - \mu \delta \left( \sum_r P_r \right) = - \sum_r \delta P_r [\ln p_r - 1 - \mu].$$

This implies the  $P_r = \text{const}$ , i.e. all messages are equally likely. Therefore  $P_r = 1/\Omega$ , which gives  $I_1 = \ln \Omega$ . Any other set of probabilities gives smaller information per message.

Keeping to the general cases in which probabilities of individual messages do not need to be equal, consider a sequence of two messages. The *a priori* probability of message  $r$  followed by message  $r'$  is  $P_{rr'} = P_r P_{r'} G_{rr'}$ . The quantity  $G_{rr'}$  is the correlation between the two messages. A value of  $G_{rr'}$  greater than unit implies that the first message  $r$  increases the probability of finding the second message  $r'$  above  $P_{r'}$ . The two message probabilities have the following properties:  $\sum_r P_{rr'} = P_{r'}$  and  $\sum_{r'} P_{rr'} = P_r$ , i.e.  $\sum_r P_r G_{rr'} = 1$  and  $\sum_{r'} P_{r'} G_{rr'} = 1$ . The information contained in two messages is given by

$$I_2 = \sum_{rr'} P_{rr'} \ln P_{rr'} = \sum_{rr'} P_r P_{r'} G_{rr'} \ln (P_r P_{r'} G_{rr'}).$$

Expanding the logarithm and using the above summation properties gives

$$I_2 = 2I_1 - \sum_{rr'} P_r P_{r'} G_{rr'} \ln G_{rr'} = 2I_1 + \sum_{rr'} P_r P_{r'} G_{rr'} \ln \left( \frac{1}{G_{rr'}} \right).$$

Now, using  $\ln x \leq x - 1$  for all  $x > 0$ , we get

$$I_2 \leq 2I_1 + \sum_{rr'} P_r P_{r'} [1 - G_{rr'}] = 2I_1.$$

The information contained in two correlated messages is reduced compared to sum of the information contained in two uncorrelated messages. Analysis of the first 65536 digits of  $\pi$  results in an information per character of  $I_1 \approx 2.3 = \ln 10$ . That makes sense because the characters  $0, \dots, 9$  are evenly distributed in the digital representation of  $\pi$ . Furthermore, since the digits of  $\pi$  are uncorrelated, the information per pair of characters is  $I_2 \approx 4.6 = 2I_1$ . Analysis of the first 15,000 characters of *A Christmas Carol* by Charles Dickens gives  $I_1 \approx 3.08 \approx \ln 21.75$ . This value is reasonable since most of the characters are lower case letters of the alphabet and blanks. The nonuniformity of the distribution of letters reduces the information below  $\ln 27$ . When analyzed two characters at a time, the information is  $I_2 \approx 5.45 \approx 2 \ln 15.25$ . The strong correlations between characters in English text reduces the information well below  $2I_1$ .

# Chapter 4

**4.1.** By eqns. (4.1.9), (4.3.10) and (4.1.8), we get

$$\begin{aligned} \sum_{r,s} P_{r,s} \ln P_{r,s} &\equiv \langle \ln P_{r,s} \rangle = -\alpha \bar{N} - \beta \bar{E} - \beta PV \\ &= (\mu \bar{N} - U - PV)/kT. \end{aligned} \quad (1)$$

Since  $\mu \bar{N} = G = U + PV - TS$ , the right-hand side of (1) equals  $-S/k$ . Hence the result.

**4.2.** According to the *grand canonical ensemble* theory,

$$PV = kT \ln \left\{ \sum_{N_r} z^{N_r} Q_{N_r}(V, T) \right\}. \quad (1)$$

Now, the largest term in the sum pertains to the value  $N^*$ , of  $N_r$ , which is determined by the condition

$$\frac{\partial}{\partial N_r} \{N_r \ln z - \ln Q_{N_r}\}_{N_r=N^*} = 0.$$

By Sec. 3.3, this is equivalent to the statement:  $z = \exp(\mu^*/kT)$ , where  $\mu^*$  is the chemical potential of the given system in a *canonical ensemble* (with  $N = N^*$ ). If we replace the sum in (1) by its largest term, we would get

$$PV \approx N^* \mu^* - A^* = P^* V,$$

where  $P^*$  is the pressure of the system in the canonical ensemble (with  $N = N^*$ ). How different would  $P$  be from  $P^*$  depends essentially on how different the particle density  $\bar{n}$  is from  $n^*$  — a question thoroughly discussed in Sec. 4.5.

**4.3.** The probability distribution in question is the *binomial distribution*

$$P(N, V) = \frac{N^{(0)!}}{N!(N^{(0)} - N)!} p^N q^{N^{(0)} - N} \quad \left( p = \frac{V}{V^{(0)}}, q = 1 - \frac{V}{V^{(0)}} \right).$$

We note that

$$\sum_{N=0}^{N^{(0)}} P(N, V) = (q + p)^{N^{(0)}} = 1.$$

For part (i), we have

$$\begin{aligned} \bar{N} &= \sum_{N=0}^{N^{(0)}} N P(N, V) = N^{(0)} p (q + p)^{N^{(0)}-1} = N^{(0)} p, \text{ while} \\ \overline{N(N-1)} &= \sum_{N=0}^{N^{(0)}} N(N-1) P(N, V) = N^{(0)} (N^{(0)} - 1) p^2 (q + p)^{N^{(0)}-2} = N^{(0)} (N^{(0)} - 1) p^2. \end{aligned}$$

It follows that

$$\begin{aligned} \overline{N^2} &= \overline{N(N-1)} + \bar{N} = (N^{(0)} p)^2 - N^{(0)} p^2 + N^{(0)} p, \text{ whence} \\ \overline{(\Delta N)^2} &\equiv \overline{N^2} - \bar{N}^2 = N^{(0)} p (1 - p), \text{ etc.} \end{aligned}$$

For part (ii), we shift the origin to  $N = N^{(0)} p$ , write

$$N = N^{(0)} p + x, \quad N^{(0)} - N = N^{(0)} q - x$$

and examine the function

$$\ln P(x) = \ln N^{(0)}! - \ln(N^{(0)} p + x)! - \ln(N^{(0)} q - x)! + (N^{(0)} p + x) \ln p + (N^{(0)} q - x) \ln q.$$

Since  $N^{(0)} p$  and  $N^{(0)} q$  are both  $\gg 1$ , we apply Stirling's formula,  $\ln v! \approx v \ln v - v$ , and get (after some reduction)

$$\ln P(x) \approx -(N^{(0)} p + x) \ln \left( 1 + \frac{x}{N^{(0)} p} \right) - (N^{(0)} q - x) \ln \left( 1 - \frac{x}{N^{(0)} q} \right).$$

For  $x \ll N^{(0)} p$  and  $N^{(0)} q$ , we expand this expression in powers of  $x$ , with the result that  $\ln P(x) \approx -x^2 / 2 N^{(0)} p q$ . It follows that the distribution  $P(x)$ , under the stated conditions, is a Gaussian, with  $\overline{(\Delta N)^2} = N^{(0)} p q$ .

For part (iii), we write

$$P(N) = \frac{N^{(0)} (N^{(0)} - 1) \dots (N^{(0)} - N + 1)}{N!} p^N (1 - p)^{N^{(0)} - N}.$$

Now, if  $p \ll 1$  and  $N \ll N^{(0)}$ , we obtain the Poisson distribution

$$P(N) \approx \frac{[N^{(0)}]^N}{N!} p^N e^{-N^{(0)} p} = \frac{(\bar{N})^N}{N!} e^{-\bar{N}},$$

with  $\overline{(\Delta N)^2} = \bar{N}$ .

**4.4.** For obvious reasons,

$$P(N_r) = \sum_s P_{r,s} = \frac{e^{-\alpha N_r} \sum_s e^{-\beta E_s}}{\mathcal{Q}(\alpha, \beta, V)} = \frac{z^{N_r} Q_{N_r}(V, T)}{\mathcal{Q}(z, V, T)}. \quad (1)$$

For an ideal classical gas, see Sec. 4.4,

$$z = \frac{\bar{N} \lambda^3}{V}, \quad Q_N = \frac{1}{N!} \left( \frac{V}{\lambda^3} \right)^N, \quad \mathcal{Q} \equiv e^{PV/kT} = e^{\bar{N}}. \quad (2)$$

Substituting (2) into (1), we get

$$P(N) = \frac{(\bar{N})^N}{N!} e^{-\bar{N}},$$

which is a Poisson distribution, with  $\overline{(\Delta N)^2} = \bar{N}$ .

We note that the variance of  $N$ , calculated from the general formula (4.5.3), also turns out to be the same:

$$\overline{(\Delta N)^2} = - \left( \frac{\partial \bar{N}}{\partial \alpha} \right)_{T,V} = z \left( \frac{\partial \bar{N}}{\partial z} \right)_{T,V} = z \left[ \frac{\partial}{\partial z} \left( \frac{zV}{\lambda^3} \right) \right]_{T,V} = z \frac{V}{\lambda^3} = \bar{N}.$$

**4.5.** The first term on the right-hand side of (4.3.20) may be written as

$$\begin{aligned} kT \left( \frac{\partial q}{\partial T} \right)_{z,V} &= kT \left[ \left( \frac{\partial q}{\partial T} \right)_{\mu,V} + \left( \frac{\partial q}{\partial \mu} \right)_{T,V} \left( \frac{\partial \mu}{\partial T} \right)_{z,V} \right] \\ &= kT \left( \frac{\partial q}{\partial T} \right)_{\mu,V} + kT \cdot \frac{\bar{N}}{kT} \cdot k \ln z \quad (\text{for } \mu = kT \ln z). \end{aligned}$$

Equation (4.3.20) then reduces to

$$S = kT \left( \frac{\partial q}{\partial T} \right)_{\mu,V} + kq = k \left[ \frac{\partial}{\partial T} (Tq) \right]_{\mu,V}.$$

Note that this result is directly related to the formula, see Problem 1.16,

$$d(PV) = PdV + Nd\mu + SdT,$$

whence

$$S = \left[ \frac{\partial}{\partial T} (PV) \right]_{\mu,V}.$$

**4.6.** The Gibbs free energy is

$$G(N, P, T) = -kT \ln(Y_N(P, T)).$$



For example

$$\left(\frac{\partial G}{\partial P}\right)_{N,T} = \frac{1}{Y_N(P,T)} \int_0^\infty V Q(N,V,T) e^{-\beta PV} = \langle V \rangle.$$

The ideal gas gives

$$\begin{aligned} Y_N(P,T) &= \frac{1}{(\beta P \lambda^3)^{N+1}}, \\ G(N,P,T) &\approx NkT \ln(\beta P \lambda^3), \\ V &= \left(\frac{\partial G}{\partial P}\right)_{N,T} = \frac{NkT}{P}. \end{aligned}$$

**4.10.** The partition function of the adsorbed molecules, assumed noninteracting, is given by

$$Q_N(N_0, T) = g(N) a^N = \frac{N_0!}{N!(N_0 - N)!} a^N \quad [a = a(T)]. \quad (1)$$

Using Stirling's formula (B.29), we get

$$\ln Q_N \approx N_0 \ln N_0 - N \ln N - (N_0 - N) \ln(N_0 - N) + N \ln a,$$

with the result that

$$\mu = -kT \frac{\partial \ln Q_N}{\partial N} = kT \ln \frac{N}{(N_0 - N)a}. \quad (2)$$

Alternatively, the grand partition function of the system consisting of *all*  $N_0$  sites (of which some are empty while others are occupied by a *single* molecule) is given by

$$\mathcal{Q}(z, N_0, T) = [\mathcal{Q}(z, 1, T)]^{N_0} = [1 + za(T)]^{N_0}; \quad (3)$$

see eqn. (4.4.15), with  $N_r = 0$  or 1. Note that expression (3) could also be obtained by using the standard definition  $\mathcal{Q}(z, N_0, T) = \sum_{N=0}^{N_0} z^N Q_N(N_0, T)$  and employing expression (1) for  $Q_N$ . The mean value of  $N$  now turns out to be

$$\bar{N} = z \frac{\partial}{\partial z} \ln \mathcal{Q} = N_0 \frac{za}{1 + za}, \text{ whence } z = \frac{1}{a} \frac{\bar{N}}{N_0 - \bar{N}}, \quad (4)$$

which agrees with (2).

**4.11.** By eqn. (4) of the preceding problem, the fraction  $\theta$  of the adsorption sites that *are* occupied is given by

$$\theta = \frac{\bar{N}}{N_0} = \frac{za}{1 + za}, \text{ whence } z = \frac{1}{a} \frac{\theta}{1 - \theta}. \quad (1)$$

Now, if the molecules in the adsorbed phase are in equilibrium with those in the gaseous phase, then their fugacity  $z$  would be equal to the fugacity  $z_g$  of the gaseous phase. The latter is given by eqns. (4.4.5 and 29), whereby

$$z_g = \frac{P_g}{kT} \frac{h^3}{(2\pi mkT)^{3/2}}. \quad (2)$$

Equating (1) and (2), we obtain the desired result

$$P_g = \frac{\theta}{1-\theta} \times \frac{1}{a(T)} kT \frac{(2\pi mkT)^{3/2}}{h^3}.$$

**4.12.** From eqn. (4.5.1), we get

$$\left( \frac{\partial \bar{N}}{\partial \beta} \right)_{\alpha, V} = -\overline{NE} + \bar{N} \bar{E}.$$

The left-hand side here is equal to, see eqns. (4.5.3 and 12),

$$\begin{aligned} -kT^2 \left( \frac{\partial \bar{N}}{\partial T} \right)_{z, V} &= -kT \left( \frac{\partial U}{\partial \mu} \right)_{T, V} = -kT \left( \frac{\partial U}{\partial \bar{N}} \right)_{T, V} \left( \frac{\partial \bar{N}}{\partial \mu} \right)_{T, V} \\ &= - \left( \frac{\partial U}{\partial \bar{N}} \right)_{T, V} \overline{(\Delta N)^2}. \end{aligned}$$

Hence the result.

**4.13.** With  $\mu$  fixed (as it is in the grand canonical ensemble),

$$\overline{(\Delta J)^2} = \overline{(\Delta E)^2} - 2\mu \overline{(\Delta E)(\Delta N)} + \mu^2 \overline{(\Delta N)^2}.$$

Substituting from eqn. (4.5.14) and from the previous problem, we get

$$\overline{(\Delta J)^2} = \langle (\Delta E)^2 \rangle_{can} + \left\{ \left( \frac{\partial U}{\partial \bar{N}} \right)_{T, V}^2 - 2\mu \left( \frac{\partial U}{\partial \bar{N}} \right)_{T, V} + \mu^2 \right\} \overline{(\Delta N)^2},$$

which is the desired result.

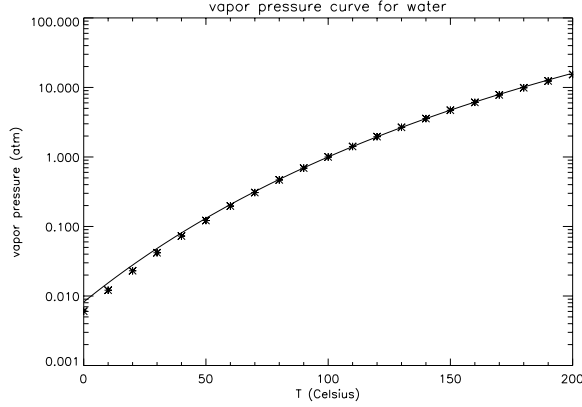
**4.14.** The Clausius–Clapeyron equation (4.7.7) can be integrated to give

$$P_\sigma(T) = P_\sigma(T_0) \exp \left[ \frac{L}{k} \left( \frac{1}{T_0} - \frac{1}{T} \right) \right],$$

where  $T_0 = 373 \text{ K}$ ,  $P_\sigma(T_0) = 1 \text{ atm}$  and

$$\frac{L}{k} = \frac{(2260 \text{ kJ/kg})(18 \text{ kg/kmol})}{(6.02 \times 10^{26} \text{ kmol}^{-1})(1.38 \times 10^{-23} \text{ J/K})} = 4890 \text{ K}.$$

This gives  $P_\sigma(273 \text{ K}) \simeq 0.0082 \text{ atm}$  and  $P_\sigma(473 \text{ K}) \simeq 16 \text{ atm}$ . The experimental values are  $0.006 \text{ atm}$  and  $15.3 \text{ atm}$  respectively.



**4.15.** The correct value for the latent heat of sublimation near the triple point is  $2833 \text{ kJ/kg}$ . Following the solution to problem 4.14,

$$P_\sigma(T) = P_\sigma(T_0) \exp \left[ \frac{L}{k} \left( \frac{1}{T_0} - \frac{1}{T} \right) \right],$$

where  $T_0 = 273 \text{ K}$ ,  $P_\sigma(T_0) = 612 \text{ Pa}$  and

$$\frac{L}{k} = \frac{(2833 \text{ kJ/kg})(18 \text{ kg/kmol})}{(6.02 \times 10^{26} \text{ kmol}^{-1})(1.38 \times 10^{-23} \text{ J/K})} = 6138 \text{ K}.$$

This gives  $P_\sigma(193 \text{ K}) \simeq 0.055 \text{ Pa}$  which corresponds nearly exactly with the experimental value.

**4.16.** The slope of the melting line is

$$\frac{dP_m}{dT} = \frac{L_m}{T(\Delta v)} \simeq \frac{(80 \text{ cal/g})(4.18 \text{ J/cal})(10^6 \text{ cm}^3/\text{m}^3)}{(273 \text{ K})(-0.09 \text{ cm}^3/\text{g})} \simeq -1.3 \times 10^7 \text{ Pa/K}.$$

This gives  $T_m(100 \text{ atm}) = -0.77^\circ \text{C}$ .

**4.17.** The slopes at the triple point are of the form

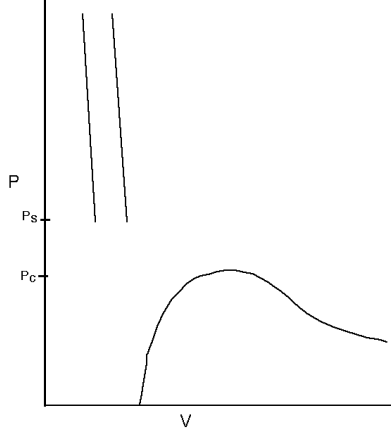
$$\left( \frac{dP_\sigma}{dT} \right)_{ij} = \frac{s_i - s_j}{v_i - v_j} = \frac{\Delta y}{\Delta x},$$

so the vectors

$$[(v_1 - v_2)\hat{x} + (s_1 - s_2)\hat{y}] + [(v_2 - v_3)\hat{x} + (s_2 - s_3)\hat{y}] + [(v_3 - v_1)\hat{x} + (s_3 - s_1)\hat{y}] = 0$$

sum to zero. This makes the third vector the negative of the sum of the first two vectors in each case, guaranteeing the stated geometry.

- 4.18.** The liquid–vapor lines will appear much like in figure 6.2 but the liquid branch will extend to  $P = 0$ . The upper end of the solid–liquid lines will appear as in figure 6.2 but the lines will end at  $P_s$ .



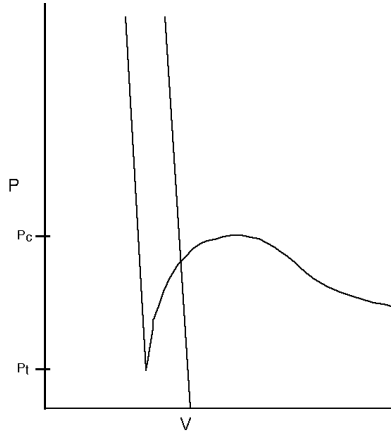
- 4.19.** Since  $p_1(\mu_\sigma(T), T) = p_2(\mu_\sigma(T), T)$  on the coexistence line

$$\left(\frac{\partial p_1}{\partial \mu}\right)_T \frac{d\mu_\sigma}{dT} + \left(\frac{\partial p_1}{\partial T}\right)_\mu = \left(\frac{\partial p_2}{\partial \mu}\right)_T \frac{d\mu_\sigma}{dT} + \left(\frac{\partial p_2}{\partial T}\right)_\mu,$$

which gives

$$\frac{d\mu_\sigma}{dT} = -\frac{s_1 - s_2}{n_1 - n_2} = \frac{-L}{T\Delta n}.$$

- 4.20.** The liquid–vapor lines will appear much like in figure 6.2 but with the liquid branch ending abruptly at  $P_t$ . The liquid side of solid–liquid lines will start at  $P_t$  and extend upward as in figure 6.2 but the solid side of the solid–liquid transition will be to the right of the liquid line (since the solid has lower density) and will extend to  $P = 0$ .



# Chapter 5

**5.1.** On transformation, a given operator  $\hat{A}$  would become

$$\hat{A}' = \hat{U} \hat{A} \hat{U}^{-1} = \begin{pmatrix} 1/\sqrt{2} & 1/\sqrt{2} \\ -1/\sqrt{2} & 1/\sqrt{2} \end{pmatrix} \begin{pmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{pmatrix} \begin{pmatrix} 1/\sqrt{2} & -1/\sqrt{2} \\ 1/\sqrt{2} & 1/\sqrt{2} \end{pmatrix}.$$

Equations (2), (3) and (4) of Sec. 5.3 would then be replaced by

$$\hat{\sigma}'_x = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \quad \hat{\sigma}'_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \hat{\sigma}'_z = \begin{pmatrix} 0 & -1 \\ -1 & 0 \end{pmatrix},$$

$$\hat{\rho}' = \frac{1}{e^{\beta\mu_B B} + e^{-\beta\mu_B B}} \begin{pmatrix} \cosh(\beta\mu_B B) & -\sinh(\beta\mu_B B) \\ -\sinh(\beta\mu_B B) & \cosh(\beta\mu_B B) \end{pmatrix}$$

and

$$\langle \sigma'_z \rangle = \text{Tr}(\hat{\rho}' \hat{\sigma}'_z) = \frac{1}{e^{\beta\mu_B B} + e^{-\beta\mu_B B}} \cdot 2 \sinh(\beta\mu_B B) = \tanh(\beta\mu_B B),$$

with no change in the final result.

**5.2.** For a formal solution to this problem, see Kubo (1965), problem 2.32, pp. 178–80.

**5.4.** If we use the *unsymmetrized* wave function (5.4.3), rather than the *symmetrized* wave function (5.5.7), the density matrix of the system turns out to be, cf. eqn. (5.5.11),

$$\begin{aligned} \langle 1, \dots, N | e^{-\beta \hat{H}} | 1', \dots, N' \rangle &= \sum_{\mathbf{K}} e^{-\beta \hbar^2 K^2 / 2m} \{u_{k_1}(1) \dots u_{k_N}(N)\} \{u_{k_1}^*(1') \dots u_{k_N}^*(N')\} \\ &= \sum_{\mathbf{k}_1, \dots, \mathbf{k}_N} e^{-\beta \hbar^2 (k_1^2 + \dots + k_N^2) / 2m} [\{u_{\mathbf{k}_1}(1) u_{\mathbf{k}_1}^*(1')\} \dots \{u_{\mathbf{k}_N}(N) u_{\mathbf{k}_N}^*(N')\}] \\ &= \prod_{j=1}^N \left[ \sum_{\mathbf{k}_j} e^{-\beta \hbar^2 k_j^2 / 2m} \{u_{\mathbf{k}_j}(j) u_{\mathbf{k}_j}^*(j')\} \right]. \end{aligned}$$

Replacing the summation over  $\mathbf{k}_j$  by an integration, one gets [see the corresponding passage from eqn. (5.5.12) to (5.5.14)]

$$\langle 1, \dots, N | e^{-\beta \hat{H}} | 1', \dots, N' \rangle = \left( \frac{m}{2\pi\beta\hbar^2} \right)^{3N/2} \exp \left\{ -\frac{m}{2\beta\hbar^2} (\xi_1^2 + \dots + \xi_N^2) \right\}, \quad (1)$$

where  $\xi_j = |\mathbf{r}_j - \mathbf{r}'_j|$ . The diagonal elements of the density matrix then are

$$\langle 1, \dots, N | e^{-\beta \hat{H}} | 1, \dots, N \rangle = (m/2\pi\beta\hbar^2)^{3N/2} = 1/\lambda^{3N}, \quad (2)$$

where  $\lambda$  is the mean thermal wavelength of the particles. The structure of expressions (1) and (2) shows that there is *no* spatial correlation among the particles of this system.

The partition function now turns out to be

$$Q_N(V, T) \equiv \text{Tr}(e^{-\beta \hat{H}}) = \int \frac{1}{\lambda^{3N}} d^{3N}r = \frac{v^N}{\lambda^{3N}},$$

with *no* Gibbs' correction factor.

**5.5.** By eqn. (5.5.17), we have

$$Q_N(V, T) \equiv \text{Tr}(e^{-\beta \hat{H}}) = \frac{1}{N! \lambda^{3N}} Z_N(V, T),$$

where

$$Z_N(V, T) = \int \sum_P \{ \dots \} d^{3N}r. \quad (1)$$

In the *zeroth* approximation,  $\sum_P = 1$ ; see eqn. (5.5.19). So,  $Z_N(V, T) = V^N$ . In the *first* approximation,

$$\sum_P = 1 \pm \sum_{i < j} f_{ij} f_{ji} = 1 \pm \sum_{i < j} e^{-2\pi r_{ij}^2 / \lambda^2}. \quad (2)$$

If  $\lambda$  is much smaller than the mean interparticle distance, we may write

$$\sum_P \approx \prod_{i < j} \left( 1 \pm e^{-2\pi r_{ij}^2 / \lambda^2} \right) = \prod_{i < j} e^{-\beta v_s(r_{ij})} = \exp \left\{ -\beta \sum_{i < j} v_s(r_{ij}) \right\},$$

which leads to the desired result.

For the second part, we substitute (2) into (1) and integrate over the position coordinates of the particles. We obtain, on assembling contributions from *all* pairs of particles,

$$Z_N(V, T) = V^N \pm \frac{N(N-1)}{2} \cdot V^{N-2} \frac{V \cdot \lambda^3}{2^{3/2}}.$$

The case  $N = 2$  corresponds to eqn. (5.5.25) for  $Q_2(V, T)$ . For  $N \gg 1$  and  $N\lambda^3 \ll V$ , we may write

$$Z_N(V, T) = V^N \left[ 1 \pm N^2 \frac{\lambda^3}{2^{5/2}V} \right] \approx V^N \left[ 1 \pm \frac{N\lambda^3}{2^{5/2}V} \right]^N.$$

It follows that

$$\ln Q_N(V, T) \approx -N \ln N + N + N \ln \left( \frac{V}{\lambda^3} \right) + N \left( \pm \frac{N\lambda^3}{2^{5/2}V} \right),$$

whence

$$\frac{P}{kT} \equiv \left( \frac{\partial \ln Q_N}{\partial V} \right)_{N,T} \approx \frac{N}{V} \mp \frac{N^2 \lambda^3}{2^{5/2}V^2} = \frac{1}{v} \mp \frac{1}{2^{5/2}} \frac{\lambda^3}{v^2},$$

where  $v = V/N$ ; cf. eqns. (7.1.13) and (8.1.17).

**5.7 and 8.** For solutions to these problems, consult the references cited in Notes 10 and 11.

# Chapter 6

**6.1.** We start with eqn. (6.1.19) and write it in the form

$$S = k \sum_i \left[ n_i^* \ln \left( \frac{g_i}{n_i^*} \right) + \left( n_i^* - \frac{g_i}{a} \right) \ln \left( 1 - a \frac{n_i^*}{g_i} \right) \right]. \quad (1)$$

Now, setting all  $g_i = 1$  and identifying  $(n_i^*/g_i)$  with  $\langle n_\varepsilon \rangle$ , see eqns. (6.1.18a) and (6.2.22), we get

$$S = k \sum_\varepsilon \left[ -\langle n_\varepsilon \rangle \ln \langle n_\varepsilon \rangle + \left( \langle n_\varepsilon \rangle - \frac{1}{a} \right) \ln (1 - a \langle n_\varepsilon \rangle) \right]. \quad (2)$$

Choosing  $a = -1$  or  $+1$ , we obtain the desired results.

Next we have to verify that

$$S = -k \sum_\varepsilon \left\{ \sum_n p_\varepsilon(n) \ln p_\varepsilon(n) \right\} = -k \sum_\varepsilon \langle \ln p_\varepsilon(n) \rangle. \quad (3)$$

Substituting for  $p_\varepsilon(n)$  from eqn. (6.3.10) into (3) leads to the desired result (2), with  $a = -1$ ; substituting from eqn. (6.3.11) instead leads to the desired result (2), with  $a = +1$ .

**6.2.** In the *B.E.* case, see eqn. (6.3.10),

$$p_\varepsilon(n) = (1-r)r^n \quad [r = \langle n_\varepsilon \rangle / (\langle n_\varepsilon \rangle + 1); n = 0, 1, 2, \dots].$$

It follows that

$$\begin{aligned} \langle n_\varepsilon \rangle &= (1-r) \sum_{n=0}^{\infty} n r^n = r/(1-r), \\ \langle n_\varepsilon^2 \rangle &= (1-r) \sum_{n=0}^{\infty} n^2 r^n = r(1+r)/(1-r)^2, \text{ so that} \\ \langle n_\varepsilon^2 \rangle - \langle n_\varepsilon \rangle^2 &= r/(1-r)^2 = \langle n_\varepsilon \rangle + \langle n_\varepsilon \rangle^2. \end{aligned} \quad (1)$$



In the *F.D.* case, see eqn. (6.3.11),

$$\begin{aligned}\langle n_\varepsilon^2 \rangle &= \sum_{n=0}^1 n^2 p_\varepsilon(n) = p_\varepsilon(1) = \langle n_\varepsilon \rangle, \text{ so that} \\ \langle n_\varepsilon^2 \rangle - \langle n_\varepsilon \rangle^2 &= \langle n_\varepsilon \rangle - \langle n_\varepsilon \rangle^2\end{aligned}\quad (2)$$

In the *M.B.* case, see eqn. (6.3.12), one can readily see that

$$\begin{aligned}\langle n_\varepsilon(n_\varepsilon - 1) \rangle &= \sum_n n(n-1) \frac{\langle n_\varepsilon \rangle^n}{n!} e^{-\langle n_\varepsilon \rangle} = \langle n_\varepsilon \rangle^2 \sum_n \frac{\langle n_\varepsilon \rangle^{n-2}}{(n-2)!} e^{-\langle n_\varepsilon \rangle} = \langle n_\varepsilon \rangle^2, \text{ so that} \\ \langle n_\varepsilon^2 \rangle - \langle n_\varepsilon \rangle^2 &= \langle n_\varepsilon \rangle.\end{aligned}\quad (3)$$

For the second part, we note, from eqn. 6.2.22, that

$$\langle n_\varepsilon \rangle^{-1} = e^{(\varepsilon - \mu)/kT} + a.$$

Differentiating this result with respect to  $\mu$ , we get

$$-\langle n_\varepsilon \rangle^{-2} \left[ \frac{\partial \langle n_\varepsilon \rangle}{\partial \mu} \right]_T = -\frac{1}{kT} e^{(\varepsilon - \mu)/kT} = -\frac{1}{kT} [\langle n_\varepsilon \rangle^{-1} - a].$$

It follows that

$$kT \left[ \frac{\partial \langle n_\varepsilon \rangle}{\partial \mu} \right]_T = \langle n_\varepsilon \rangle - a \langle n_\varepsilon \rangle^2. \quad (4)$$

Comparing (4) with our previous results (1)–(3), and with formula (6.3.9), we infer that, quite generally,

$$\langle n_\varepsilon^2 \rangle - \langle n_\varepsilon \rangle^2 = kT [\partial \langle n_\varepsilon \rangle / \partial \mu]_T.$$

**6.3.** Starting with eqn. (6.2.15), we now have

$$\mathcal{Q}(z, V, T) = \prod_\varepsilon \left[ \sum_{n_\varepsilon=0}^\ell (ze^{-\beta\varepsilon})^{n_\varepsilon} \right] = \prod_\varepsilon \left[ \frac{1 - (ze^{-\beta\varepsilon})^{\ell+1}}{1 - ze^{-\beta\varepsilon}} \right],$$

so that

$$q(z, V, T) = \sum_\varepsilon [\ln\{1 - (ze^{-\beta\varepsilon})^{\ell+1}\} - \ln\{1 - ze^{-\beta\varepsilon}\}];$$

cf. eqn. (6.2.17). It follows that

$$\begin{aligned}\langle n_\varepsilon \rangle &= -\frac{1}{\beta} \left( \frac{\partial q}{\partial \varepsilon} \right)_{z, T, \text{all other } \varepsilon} \\ &= -\frac{(\ell+1)(ze^{-\beta\varepsilon})^\ell (ze^{-\beta\varepsilon})}{1 - (ze^{-\beta\varepsilon})^{\ell+1}} + \frac{ze^{-\beta\varepsilon}}{1 - ze^{-\beta\varepsilon}} \\ &= \frac{1}{z^{-1}e^{\beta\varepsilon} - 1} - \frac{\ell+1}{(z^{-1}e^{\beta\varepsilon})^{\ell+1} - 1}\end{aligned}$$

For  $\ell = 1$ , we obtain the Fermi-Dirac result; for  $\ell \rightarrow \infty$  and  $z^{-1}e^{\beta\varepsilon} > 1$  [see eqn. (6.2.16a)], we obtain the Bose-Einstein result.

**6.4.** To determine the state of equilibrium of the given system, we minimize its free energy,  $U - TS$ , under the constraint that the total number of particles,  $N$ , is fixed. For this, we vary the particle distribution from  $n(\mathbf{r})$  to  $n(\mathbf{r}) + \delta n(\mathbf{r})$  and require that the resulting variation

$$\delta(U - TS) = \frac{e^2}{2} \iint \frac{n(\mathbf{r})\delta n(\mathbf{r}') + n(\mathbf{r}')\delta n(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}d\mathbf{r}' + e \int \delta n(\mathbf{r})\varphi_{ext}(\mathbf{r})d\mathbf{r} + kT \int [1 + \ln n(\mathbf{r})]\delta n(\mathbf{r})d\mathbf{r} = 0,$$

while  $\delta N = \int \delta n(\mathbf{r})d\mathbf{r}$  is, of necessity, zero. Introducing the Lagrange multiplier  $\lambda$ , our requirement takes the form

$$\int \left[ e^2 \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + e\varphi_{ext}(\mathbf{r}) + kT[1 + \ln n(\mathbf{r})] - \lambda \right] \delta n(\mathbf{r})d\mathbf{r} = 0.$$

Since the variation  $\delta n(\mathbf{r})$  in this expression is arbitrary, the condition for equilibrium turns out to be

$$e^2 \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + e\varphi_{ext}(\mathbf{r}) + kT \ln n(\mathbf{r}) - \mu = 0, \quad (1)$$

where  $\mu = \lambda - kT$ .

Introducing the total potential  $\varphi(\mathbf{r})$ , viz.

$$\varphi(\mathbf{r}) = \varphi_{ext}(\mathbf{r}) + e \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}', \quad (2)$$

condition (1) takes the Boltzmannian form

$$n(\mathbf{r}) = \exp[\{\mu - e\varphi(\mathbf{r})\}/kT]. \quad (3)$$

Choosing  $n(\mathbf{r})$  to be  $n_0$  at the point where  $\varphi(\mathbf{r}) = 0$ , eqn. (3) may be written as

$$n(\mathbf{r}) = n_0 \exp[-e\varphi(\mathbf{r})/kT]. \quad (4)$$

With  $\varphi_{ext}(\mathbf{r})$  given, the coupled equations (2) and (4) together determine the desired functions  $n(\mathbf{r})$  and  $\varphi(\mathbf{r})$ .

**6.5.** The (un-normalized) distribution function for the variable  $\varepsilon$  in this problem is given by

$$f(\varepsilon)d\varepsilon \sim e^{-\beta\varepsilon}\varepsilon^{1/2}d\varepsilon,$$

where use has been made of expression (2.4.7) for the density of states of a free particle. It is now straightforward to show that

$$\bar{\varepsilon} = \frac{\beta^{-5/2}\Gamma(5/2)}{\beta^{-3/2}\Gamma(3/2)} = \frac{3}{2\beta} \text{ and } \overline{\varepsilon^2} = \frac{\beta^{-7/2}\Gamma(7/2)}{\beta^{-3/2}\Gamma(3/2)} = \frac{15}{4\beta^2}.$$

It follows that

$$\frac{(\Delta\varepsilon)_{r.m.s.}}{\bar{\varepsilon}} \equiv \frac{\sqrt{(\varepsilon^2 - \bar{\varepsilon}^2)}}{\bar{\varepsilon}} = \frac{\sqrt{(3/2)\beta^2}}{(3/2\beta)} = \sqrt{(2/3)}.$$

**6.6.** We have to show that, for *any* law of distribution of molecular speeds [say,  $F(u)du$ ],

$$\begin{aligned} & \frac{\int_0^\infty u F(u) du}{\int_0^\infty F(u) du} \cdot \frac{\int_0^\infty u^{-1} F(u) du}{\int_0^\infty F(u) du} \geq 1, \text{ i.e.} \\ & \int_0^\infty u F(u) du \cdot \int_0^\infty u^{-1} F(u) du \geq \left[ \int_0^\infty F(u) du \right]^2. \end{aligned}$$

For this, we employ Schwarz's inequality (see Abramowitz and Stegun, 1964),

$$\left[ \int_a^b f(x)g(x)dx \right]^2 \leq \int_a^b [f(x)]^2 dx \cdot \int_a^b [g(x)]^2 dx,$$

which holds for arbitrary functions  $f(x)$  and  $g(x)$  — so long as the integrals exist; the equality holds if and only if  $f(x) = c g(x)$ , where  $c$  is a constant. Now, with  $f(u) = \sqrt{uF(u)}$  and  $g(u) = \sqrt{u^{-1}F(u)}$ , we obtain the desired result.

For the Maxwellian distribution,

$$F(u)du \sim e^{-\frac{1}{2}\beta m u^2} u^2 du.$$

It is then straightforward to see, with the help of the formulae (B.13), that

$$\langle u \rangle = \frac{I_3}{I_2} = \left( \frac{8}{\pi\beta m} \right)^{1/2} \text{ and } \langle u^{-1} \rangle = \frac{I_1}{I_2} = \left( \frac{2\beta m}{\pi} \right)^{1/2},$$

whence  $\langle u \rangle \langle u^{-1} \rangle = 4/\pi$ , in conformity with the inequality stated.

**6.7.** For light emitted in the  $x$ -direction, only the  $x$ -component of the molecular velocity  $\mathbf{u}$  will contribute to the Doppler effect. Moreover, for  $u_x \ll c$ ,  $(\nu - \nu_0)/\nu_0 \simeq u_x/c$ , which means that  $(\lambda - \lambda_0)/\lambda_0 \simeq -u_x/c$ . Now, the distribution of  $u_x$  among the molecules of the gas is governed by the Boltzmann factor  $\exp(-\frac{1}{2}mu_x^2/kT)$ ; the distribution of  $\lambda$  in the light emerging from the window will, therefore, be determined by the factor  $\exp\{-\frac{1}{2}mc^2(\lambda - \lambda_0)^2/\lambda_0^2 kT\}$ .

**6.8.** The partition function  $Q_N(\beta) = (1/N!)Q_1^N(\beta)$ , where  $Q_1(\beta)$  is given by

$$\begin{aligned} Q_1(\beta) &= \frac{1}{h^3} \int \exp \left\{ -\beta \left( \frac{p^2}{2m} + mgz \right) \right\} dp_x dp_y dp_z dx dy dz \\ &= \left( \frac{2\pi m}{\beta h^2} \right)^{3/2} \cdot A \frac{1 - e^{-\beta mgL}}{\beta mg}, \end{aligned} \quad (1)$$

$A$  being the area of cross-section of the cylinder. In the limit  $L \rightarrow \infty$ ,

$$Q_1(\beta) = \left( \frac{2\pi m}{\beta h^2} \right)^{3/2} \frac{A}{\beta mg} \propto T^{5/2}. \quad (2)$$

The thermodynamic properties of the system now follow straightforwardly. In particular,  $U$  turns out to be  $\frac{5}{2}NkT$  and hence  $C_v = \frac{5}{2}Nk$ . The extra contribution comes from the potential energy of the system, which also rises with  $T$ . Note, from eqns. (1) and (2), that the *effective* height of the gas molecules is  $(1 - e^{-\beta mgL})/\beta mg$  which for small heights is essentially  $L$  itself but for large heights is essentially  $kT/mg$  — making the total potential energy of the gas equal to  $NkT$ .

**6.9.** Correction to the first printing of third edition: the correct Hamiltonian is

$$\mathcal{H}(p_r, p_\theta, p_z, r, \theta, z) = \frac{p_r^2}{2m} + \frac{(p_\theta^2 - mr^2\omega)^2}{2mr^2} + \frac{p_z^2}{2m} - \frac{mr^2\omega^2}{2}.$$

This gives for the partition function

$$Q_1(V, T) = \frac{2\pi H}{\lambda^3} \int_0^R \exp \left( \frac{\beta mr^2\omega^2}{2} \right) r dr = \frac{2\pi HkT}{\lambda^3 m\omega^2} \left[ \exp \left( \frac{\beta mR^2\omega^2}{2} \right) - 1 \right]$$

In the limit of small rotation rate, this becomes  $Q_1 = \pi HR^2/\lambda^3 = V/\lambda^3$  as expected.

The density is determined from  $\langle \delta(z - z_1)\delta(\theta - \theta_1)\delta(r - r_1)/r \rangle$ . This gives

$$n(r) = n(0) \exp \left( \frac{\beta m\omega^2 r^2}{2} \right).$$

Since the  $^{238}\text{UF}_6$  molecules are heavier, their concentration is enhanced at  $r = R$ , while the concentration of the  $^{235}\text{UF}_6$  is enhanced near  $r = 0$ . The ratio at  $r = 0$  is given by

$$\begin{aligned} \frac{n_{235}(0)}{n_{238}(0)} &= \frac{m_{235}N_{235}}{m_{238}N_{238}} \left[ \frac{\exp \left( \frac{1}{2}\beta m_{238}\omega^2 R^2 \right) - 1}{\exp \left( \frac{1}{2}\beta m_{235}\omega^2 R^2 \right) - 1} \right] \\ &\approx \frac{m_{235}N_{235}}{m_{238}N_{238}} \exp \left[ \frac{1}{2}\beta (m_{238} - m_{235})\omega^2 R^2 \right]. \end{aligned}$$

A value of  $\omega R = 500 \text{ m/s}$  gives a 16% enhancement compared to the input fraction. Drawing the uranium hexafluoride gas from near the center of the cylinder results in a sample that is isotopically enhanced with  $^{235}\text{U}$  compared to the input concentration. This process may be repeated as often as needed to achieve the isotopic fraction needed.

**6.10.** Consider a layer of the gas confined between heights  $z$  and  $z + dz$ . For hydrostatic equilibrium, we must have

$$P(z + dz) + \rho g dz = P(z),$$

where  $\rho$  is the mass density of the gas. In differential form, one gets

$$dP/dz = -\rho g = (-mg/kT)P. \quad (1)$$

(a) If  $T$  is uniform, eqn. (1) can be readily integrated, with the result

$$\ln P = -(mg/kT)z + \text{const.}, \quad (2)$$

which yields the desired formula:  $P(z) = P(0) \exp(-mgz/kT)$ .

(b) If, on the other hand, the equilibrium is attained *adiabatically*, then  $T$  is related to  $P$ ; in fact,  $T \propto P^{(\gamma-1)/\gamma}$ . We now get

$$\frac{dT}{T} = \frac{\gamma-1}{\gamma} \frac{dP}{P} = -\frac{\gamma-1}{\gamma} \frac{mg}{kT} dz. \quad (3)$$

This means that  $T$  now decreases essentially *linearly* with height. The pressure  $P$  and the density  $\rho$  go hand in hand with  $T$  — varying as  $T^{\gamma/\gamma-1}$  and  $T^{1/\gamma-1}$ , respectively.

**6.11.** (a) For the given system,

$$f(\mathbf{p})d\mathbf{p} = \text{const.} e^{-\beta\varepsilon(p)} (4\pi p^2 dp) = C e^{-\beta c(p^2+m_0^2c^2)^{1/2}} p^2 dp.$$

The normalization constant  $C$  is determined by the condition

$$\int f(\mathbf{p})d\mathbf{p} = C \int_0^\infty e^{-\beta c(p^2+m_0^2c^2)^{1/2}} p^2 dp = 1.$$

Substituting  $p = m_0c \sinh \theta$ , we get for the left-hand side of this equation

$$\begin{aligned} & C \int_0^\infty e^{-\beta m_0c^2 \cosh \theta} m_0^3 c^3 \sinh^2 \theta \cosh \theta d\theta \\ &= C m_0^3 c^3 \left[ \frac{e^{-\beta m_0c^2 \cosh \theta}}{-\beta m_0c^2} \sinh \theta \cosh \theta \Big|_0^\infty + \int_0^\infty \frac{e^{-\beta m_0c^2 \cosh \theta}}{\beta m_0c^3} \cosh(2\theta) d\theta \right] \\ &= C m_0^3 c^3 \cdot (\beta m_0c^2)^{-1} K_2(\beta m_0c^2). \end{aligned}$$

Equating this result with 1, we obtain the desired expression for  $C$ .

(b) Using the limiting forms

$$K_2(x) \approx \begin{cases} (\pi/2x)^{1/2} e^{-x} & (x \gg 1) \\ 2/x^2 & (x \ll 1) \end{cases},$$

we obtain, rather straightforwardly, the nonrelativistic and the extreme relativistic limits of the distribution.

(c) Since

$$\begin{aligned} u &= \frac{d\varepsilon}{dp} = \frac{m_0 c^2 d(\cosh \theta)}{m_0 c d(\sinh \theta)} = c \tanh \theta, \\ \langle pu \rangle &= C \int_0^\infty \{m_0 c^2 \sinh \theta \tanh \theta\} e^{-\beta m_0 c^2 \cosh \theta} m_0^3 c^3 \sinh^2 \theta \cosh \theta d\theta \\ &= C m_0^4 c^5 \int_0^\infty e^{-\beta m_0 c^2 \cosh \theta} \sinh^4 \theta d\theta. \end{aligned}$$

Once again, integrating by parts (this time *twice*), we obtain

$$\langle pu \rangle = C m_0^4 c^5 \cdot 3(\beta m_0 c^2)^{-2} K_2(\beta m_0 c^2).$$

Substituting for  $C$ , we obtain:  $\langle pu \rangle = 3/\beta$  — regardless of the severity of the relativistic effects and in conformity with the results of Secs. 3.7 and 6.4.

**6.12.** Ordinarily, when a molecule is reflected from a *stationary* wall that is perpendicular to the  $z$ -direction, the  $z$ -component of its velocity  $\mathbf{u}$  simply changes sign, i.e.  $u'_z = -u_z$ . If the wall is *receding* at velocity  $v$  in the direction of its normal, the above result changes to  $(u'_z - v) = -(u_z - v)$ , so that  $u'_z = -(u_z - 2v)$ . This results in a change in the translational energy of the molecule which, for small  $v$ , is given by

$$\Delta\varepsilon = \frac{1}{2} m u_z'^2 - \frac{1}{2} m u_z^2 \simeq -2m u_z v.$$

If  $A$  is the area of the wall, the net change in the energy of the gas, in

time  $\delta t$ , is then given by, cf. eqn. (6.4.10),

$$\begin{aligned}
\delta E &= A\delta t \cdot n \int_{u_x=-\infty}^{\infty} \int_{u_y=-\infty}^{\infty} \int_{u_z=-\infty}^{\infty} (-2mu_z v) u_z f(\mathbf{u}) du_x du_y du_z \\
&= -Av\delta t \cdot n \int_{\phi=0}^{2\pi} \int_{\theta=0}^{\pi/2} \int_{u=0}^{\infty} \{2mu^2 \cos^2 \theta f(\mathbf{u})\} (u^2 \sin \theta du d\theta d\phi) \\
&= -\delta V \cdot n \frac{1}{3} \int_0^{\infty} \{mu^2 f(\mathbf{u})\} (4\pi u^2 du) \\
&= -\delta V \cdot \frac{2}{3} n \bar{\epsilon}_k = -\delta V \cdot \frac{2}{3} \frac{E_k}{V},
\end{aligned} \tag{1}$$

where  $E_k$  is the total kinetic energy of the gas. Note that, since the gas continues to be in a state of (quasi-static) equilibrium, the change  $\delta E$  (even though it originates in the translational motion of the molecules) becomes eventually a change in the internal energy  $U$  of the gas (which may well have contributions from degrees of freedom other than translational). If  $U = aE_k$ , we may write

$$\delta E_k = \frac{1}{a} \delta U = -\frac{2}{3a} E_k \frac{\delta V}{V}. \tag{2}$$

Next, since  $PV = (2/3)E_k$ , we get

$$\frac{\delta P}{P} + \frac{\delta V}{V} = \frac{\delta E_k}{E_k} = -\frac{2}{3a} \frac{\delta V}{V}. \tag{3}$$

Re-arranging (3) and integrating it, we obtain the desired result.

In the extreme relativistic case, the factor  $2/3$  is replaced throughout by  $1/3$ , leading to the alternate value of  $\gamma$ .

**6.13.** We refer to expression (6.4.11) of the text. For part (a) of the question, we integrate only over  $u$  and  $\varphi$ , to get

$$dR_\theta = n(\bar{u}/4\pi) \cdot 2\pi \sin \theta \cos \theta d\theta = \frac{1}{2} n \bar{u} \sin \theta \cos \theta d\theta.$$

For part (b), we integrate only over  $\theta$  and  $\varphi$ , to get

$$dR_u = n\pi \cdot f(\mathbf{u}) u^3 du, \text{ where } f(\mathbf{u})|_{M.B.} = \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-mu^2/2kT}.$$

For part (c), we refer to expression (6.4.10) instead and get

$$\begin{aligned}
R_E &= n \left(\frac{m}{2\pi kT}\right)^{3/2} \int_{u_x=-\infty}^{\infty} \int_{u_y=-\infty}^{\infty} \int_{u_z=\sqrt{2E/m}}^{\infty} e^{-m(u_x^2+u_y^2+u_z^2)/2kT} u_z du_x du_y du_z \\
&= n \left(\frac{kT}{2\pi m}\right)^{1/2} e^{-E/kT}.
\end{aligned}$$

It follows that

$$\frac{R_E(T_2)}{R_E(T_1)} = \left(\frac{T_2}{T_1}\right)^{1/2} \exp \left\{ \frac{-E}{k} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) \right\}.$$

With  $T_1 = 300\text{ K}$ ,  $T_2 = 310\text{ K}$  and  $E = 10^{-19}\text{ J}$ , this ratio turns out to be about 2.2.

- 6.14.** (a) We start by calculating the kinetic energy associated with the  $z$ -component of the motion of the effused molecules. Proceeding as Section 6.4 of the text, we get [see eqn. (6.4.11)]

$$\begin{aligned} \left\langle \frac{1}{2} m u_z^2 \right\rangle &= \frac{1}{2} m \langle u^2 \cos^2 \theta \rangle = \frac{1}{2} m \frac{\int_0^{\pi/2} \int_0^\infty (u^3 \cos^3 \theta) f(\mathbf{u}) u^2 \sin \theta du d\theta}{\int_0^{\pi/2} \int_0^\infty (u \cos \theta) f(\mathbf{u}) u^2 \sin \theta du d\theta} \\ &= \frac{1}{4} m \frac{\langle u^3 \rangle}{\langle u \rangle}; \end{aligned}$$

note that the averages on the right-hand side are taken over the gas *inside* the vessel. It is not difficult to show, see the corresponding calculation in Problem 6.6 and the formulae (B.13b), that

$$\frac{\langle u^3 \rangle}{\langle u \rangle} = \frac{I_5}{I_3} = \frac{4}{\beta m},$$

so that  $\langle \frac{1}{2} m u_z^2 \rangle$ , for the effused molecules,  $= 1/\beta = kT$ . The kinetic energy associated with the  $x$ - and  $y$ -components of the molecular motion will be the same as inside the vessel, viz.  $\frac{1}{2} kT$  each. It follows that the mean energy  $\varepsilon$  of an effused molecule is  $2 kT$ .

- (b) Assuming quasi-static equilibrium, the relations  $E = (3/2)NkT$  and  $P = NkT/V$  will continue to hold for the gas inside the vessel. However, in view of the result obtained in part (a), we shall also have

$$\frac{dE}{dt} \equiv \frac{d}{dt} \left( \frac{3}{2} NkT \right) = 2kT \frac{dN}{dt}.$$

It follows that

$$\frac{dT}{T} = \frac{1}{3} \frac{dN}{N} \text{ and hence } T \propto N^{1/3};$$

it further follows that  $P \propto N^{4/3}$ .

As for explicit variations with  $t$ , we make use of eqn. (6.4.13) and write

$$\frac{dN}{dt} = -\frac{1}{4} a n \langle u \rangle = -\frac{1}{4} \frac{aN}{V} \left( \frac{8kT}{\pi m} \right)^{1/2}.$$



Combining the last two results, we get

$$\frac{dT}{T} = -\frac{1}{3} \frac{a}{V} \left( \frac{kT}{2\pi m} \right)^{1/2} dt,$$

so that  $T = T_0(1+ct)^{-2}$ , where  $c = (a/6V)(kT_0/2\pi m)^{1/2}$ . The variations of  $N$  and  $P$  with  $t$  follow straightforwardly.

**6.15.** If  $n_H$  is the number of holes per unit area of the surface of the balloon (of radius  $r$ ),  $a$  the area of each hole and  $t$  the duration of the leak, then the total number of molecules leaking is given by

$$\Delta N = \frac{1}{4} n_H \cdot n_H (4\pi r^2) at \quad \left[ \bar{u} = (8kT/\pi m)^{1/2} \right].$$

The fraction of the molecules leaking is thus given by

$$\frac{\Delta N}{N} = \frac{1}{4V} \left( \frac{8kT}{\pi m} \right)^{1/2} \cdot n_H (4\pi r^2) at.$$

Since  $V = (4\pi/3)r^3$ , we get

$$n_H = \frac{\Delta N}{N} \cdot \frac{r}{3at} \left( \frac{2\pi m}{kT} \right)^{1/2}.$$

Substituting the data given, we obtain:  $n_H \simeq 187$  holes/m<sup>2</sup>.

**6.16.** The rate of effusion of molecules from side  $A$  to side  $B$ , through a hole of cross-section  $S$ , is given by the expression

$$R_{A \rightarrow B} = \frac{1}{4} n_A \sqrt{\frac{8kT_A}{\pi m_A}} S = \frac{P_A}{\sqrt{2\pi m_A k T_A}} S;$$

the same from side  $B$  to side  $A$  is given by

$$R_{B \rightarrow A} = \frac{1}{4} n_B \sqrt{\frac{8kT_B}{\pi m_B}} S = \frac{P_B}{\sqrt{2\pi m_B k T_B}} S.$$

In the stationary state, these two expressions will be equal — which leads to the condition of dynamic equilibrium

$$P_A/P_B = (m_A T_A / m_B T_B)^{1/2}.$$

If the two gases are samples of the same gas, the condition simplifies to

$$P_A/P_B = (T_A/T_B)^{1/2}.$$

**6.18.** The (un-normalized) velocity distribution for a pair of molecules is given by

$$F(\mathbf{u}_1, \mathbf{u}_2) d^3 u_1 d^3 u_2 \sim e^{-\frac{1}{2}\beta m(u_1^2 + u_2^2)} d^3 u_1 d^3 u_2.$$

We define the relative velocity,  $\mathbf{v}$ , and the velocity of the centre-of-mass,  $\mathbf{V}$ , in the usual manner, viz.

$$\mathbf{v} = \mathbf{u}_2 - \mathbf{u}_1, \quad \mathbf{V} = \frac{1}{2}(\mathbf{u}_1 + \mathbf{u}_2).$$

This results in a new distribution for the variables  $\mathbf{v}$  and  $\mathbf{V}$ :

$$F(\mathbf{v}, \mathbf{V}) d^3 v d^3 V \sim e^{-\frac{1}{4}\beta m v^2} d^3 v \cdot e^{-\beta m V^2} d^3 V.$$

It is now straightforward to show that  $\langle v \rangle = (16/\pi\beta m)^{1/2} = \sqrt{2}\langle u \rangle$ , while  $\langle v^2 \rangle = (6/\beta m) = 2\langle u^2 \rangle$ . The latter result implies that  $v_{r.m.s.} = \sqrt{2} u_{r.m.s.}$ .

We note that, since

$$v^2 = u_1^2 + u_2^2 + u_2^2 - 2\mathbf{u}_1 \cdot \mathbf{u}_2,$$

$\langle v^2 \rangle = 2\langle u^2 \rangle$ , regardless of the law of distribution of velocities — so long as it is *isotropic*, making  $\langle \mathbf{u}_1 \cdot \mathbf{u}_2 \rangle = 0$ .

**6.19.** The (un-normalized) joint distribution for the molecular energies  $\varepsilon_1$  and  $\varepsilon_2$  is

$$f(\varepsilon_1, \varepsilon_2) d\varepsilon_1 d\varepsilon_2 \sim e^{-\beta(\varepsilon_1 + \varepsilon_2)} \varepsilon_1^{1/2} \varepsilon_2^{1/2} d\varepsilon_1 d\varepsilon_2.$$

To obtain the desired distribution, we set  $\varepsilon_2 = E - \varepsilon_1$  and integrate over all relevant values of  $\varepsilon_1$ , with the result that

$$\begin{aligned} P(E) dE &\sim e^{-\beta E} \int_0^E \{\varepsilon_1(E - \varepsilon_1)\}^{1/2} d\varepsilon_1 dE \\ &\sim e^{-\beta E} E^2 dE; \end{aligned}$$

cf. eqns. (3.4.3) and (3.5.16), with  $N = 2$ . It is now straightforward to check that

$$\langle E \rangle = \frac{\beta^{-4} \Gamma(4)}{\beta^{-3} \Gamma(3)} = \frac{3}{\beta}.$$

**6.20.** The relative fraction of the excited atoms in the given sample of the helium gas would be  $3e^{-\beta\varepsilon_1}$ , where

$$\beta\varepsilon_1 = \frac{hc}{kT\lambda_1} \simeq 38.22.$$

The desired fraction turns out to be extremely small — about  $7 \times 10^{-17}$ .

**6.21.** We extend the treatment of Problem 3.14 to the reaction  $AB + CD \leftrightarrow AD + CB$  and obtain, in equilibrium,

$$\frac{n_{AD}n_{CB}}{n_{AB}n_{CD}} = \frac{f_{AD}f_{CB}}{f_{AB}f_{CD}} = K(T).$$

For the given reaction,

$$K(T) = \frac{f_{HD}^2}{f_{HH}f_{DD}},$$

where each  $f$  is a product of three factors — the translational, the rotational and the vibrational.

Now, for a *heteronuclear* molecule like HD we have, at high temperatures,

$$f_{HD} \approx V \left( \frac{m_{HD}kT}{2\pi\hbar^2} \right)^{3/2} \cdot \frac{2I_{HD}kT}{\hbar^2} \cdot \frac{kT}{\hbar\omega_{HD}},$$

while for a *homonuclear* molecule like HH we have instead

$$f_{HH} \approx V \left( \frac{m_{HH}kT}{2\pi\hbar^2} \right)^{3/2} \cdot \frac{I_{HH}kT}{\hbar^2} \cdot \frac{kT}{\hbar\omega_{HH}};$$

see Note 11 of the text. It follows that, at high temperatures,

$$K(T) \approx 4 \frac{m_{HD}^3}{m_{HH}^{3/2}m_{DD}^{3/2}} \cdot \frac{I_{HD}^2}{I_{HH}I_{DD}} \cdot \frac{I_{HD}^2}{I_{HH}I_{DD}} \cdot \frac{\omega_{HH}\omega_{DD}}{\omega_{HD}^2}. \quad (1)$$

Assuming the internuclear distances to be the same, the  $I$ 's here will be proportional to the reduced masses of the molecules; the  $\omega$ 's, on the other hand, are inversely proportional to the square roots of the reduced masses. Accordingly,

$$\frac{I_{HD}^2}{I_{HH}I_{DD}} \cdot \frac{\omega_{HH}\omega_{DD}}{\omega_{HD}^2} = \frac{\mu_{HD}^3}{\mu_{HH}^{3/2}\mu_{DD}^{3/2}} = \frac{\{m_H m_D / (m_H + m_D)\}^3}{(\frac{1}{2}m_H)^{3/2}(\frac{1}{2}m_D)^{3/2}}. \quad (2)$$

At the same time,

$$\frac{m_{HD}^3}{m_{HH}^{3/2}m_{DD}^{3/2}} = \frac{(m_H + m_D)^3}{(2m_H)^{3/2}(2m_D)^{3/2}}. \quad (3)$$

Substituting (2) and (3) into (1), we see that  $K(T) \approx 4$ .

**6.23.** The potential  $V(r)$  is *minimum* at  $r = r_0$ , which determines the equilibrium value of  $r$ . Accordingly, the quantum of the rotational motion of the molecule is  $\hbar^2/2I$ , where  $I = \mu r_0^2$ . This gives for  $\Theta_r$  the expression  $\hbar^2/2\mu r_0^2 k = \hbar^2/mr_0^2 k$  because the reduced mass  $\mu$  in this case is equal to  $m/2$ . Substituting the given data,  $\Theta_r$  turns out to be about 75 K. This gives a fairly clear idea of the “temperature range” where the rotational

motion of the hydrogen molecules begins to contribute towards the specific heat of the gas.

Next we expand  $V(r)$  in the neighborhood of  $r = r_0$  and write

$$V(r) = -V_0 + (V_0/a^2)(r - r_0)^2 + \dots$$

This gives an  $\omega$  equal to  $(2V_0/\mu a^2)^{1/2} = (4V_0/ma^2)^{1/2}$  and hence a  $\Theta_v$  equal to  $\hbar(4V_0/ma^2)^{1/2}/k$ . Substituting the given data,  $\Theta_v$  turns out to be about 6260 K. Again, this gives a fairly clear idea of the “temperature range” where the vibrational motion of the hydrogen molecules begins to contribute towards the specific heat of the gas.

**6.24.** The effective potential of a diatomic molecule (including both rotation and vibration) is given by

$$V(r) = -V_0 + \frac{1}{2}\mu\omega^2(r - r_0)^2 + \frac{\hbar^2}{2\mu r^2}J(J+1).$$

The equilibrium value of  $r$  is obtained by minimizing  $V(r)$ , with the result

$$(r_{eq} - r_0) = \frac{\hbar^2}{\mu^2\omega^2 r_{eq}^3}J(J+1) \simeq \frac{\hbar^2}{\mu^2\omega^2 r_0^3}J(J+1).$$

It follows that

$$\frac{\Delta r_0}{r_0} \simeq \frac{\hbar^2}{\mu^2\omega^2 r_0^4}J(J+1) = 4 \left( \frac{\Theta_r}{\Theta_v} \right)^2 J(J+1).$$

Using data from the preceding problem, we find that for a hydrogen molecule the fractional change in  $r_0$  is  $O(10^{-3})$ .

**6.25.** The occupation number  $N_J$  is proportional to  $(2J+1)e^{-\varepsilon_J/kT}$ . It follows that

$$\frac{N_0}{N_2} = \frac{1}{5}e^{-(\varepsilon_0 - \varepsilon_2)/kT}, \quad \frac{N_1}{N_2} = \frac{3}{5}e^{-(\varepsilon_1 - \varepsilon_2)/kT}.$$

Substituting the given data, we get

$$\frac{N_0}{N_2} = \frac{1}{5}e^{-1.086} \simeq 0.0675, \quad \frac{N_1}{N_2} = \frac{3}{5}e^{-0.760} \simeq 0.2806;$$

in other words,

$$N_0 : N_1 : N_2 :: 0.050 : 0.208 : 0.742.$$

**6.29.** The various contributions to the molar specific heat of the gas at 300 K are:

- (i) translational — the amount being  $(3/2)R$ .

- (ii) rotational — since the characteristic values of the parameter  $\Theta_r$  in this case are of the order of 10 K, these degrees of freedom may be treated classically, which yields a contribution of  $(3/2)R$ ; see eqn. (6.5.42).
- (iii) vibrational — here, the parameters  $\Theta_v$  are such that the various contributions have to be calculated quantum-mechanically, using formula (6.5.44). We find that

$$\frac{\Theta_{1,2}}{T} \simeq 16.00, \quad \frac{\Theta_{3,4}}{T} \simeq 4.56, \quad \frac{\Theta_5}{T} \simeq 16.37, \quad \frac{\Theta_6}{T} \simeq 7.80,$$

with the result that only modes 3 and 4 make appreciable contributions to the specific heat of the gas; it turns out that each of these contributions is about  $0.22R$ . The contribution from mode 6 is about  $0.02R$ , while those from modes 1,2 and 5 are entirely negligible.

The net result is:  $3.46R$ .

**6.30.** Equation (6.6.3) can be written  $\sum_{\alpha} \nu_{\alpha} \mu_{\alpha} = 0$  where the stoichiometric coefficients are understood to be positive if they appear on the right hand side of equation (6.6.1) and negative if on the left. Using equation (6.6.5) gives

$$\sum_{\alpha} \nu_{\alpha} [\epsilon_{\alpha} + kT \ln (n_{\alpha} \lambda_{\alpha}^3) - kT \ln j_{\alpha}] = 0,$$

which gives

$$\sum_{\alpha} \nu_{\alpha} \left[ \epsilon_{\alpha} + kT \ln (n_0 \lambda_{\alpha}^3) - kT \ln j_{\alpha} + kT \ln \left( \frac{n_{\alpha}}{n_0} \right) \right] = 0.$$

Rearranging gives

$$\begin{aligned} \sum_{\alpha} \nu_{\alpha} \ln \left( \frac{n_{\alpha}}{n_0} \right) &= -\beta \sum_{\alpha} \nu_{\alpha} [\epsilon_{\alpha} + kT \ln (n_0 \lambda_{\alpha}^3) - kT \ln j_{\alpha}] \\ &= -\beta \sum_{\alpha} \nu_{\alpha} \mu_{\alpha}^{(0)}, \end{aligned}$$

where  $\mu_{\alpha}^{(0)}$  is the chemical potential of species  $\alpha$  at temperature  $T$  and standard density  $n_0$ . Equation (6.6.6) follows from exponentiating both sides.

**6.31.** Equation (6.6.11) gives

$$\frac{[\text{CO}]}{[\text{CO}_2]} = \sqrt{\frac{1}{K(T) [\text{O}_2]}}$$

where

$$K(T) = \exp \left( -2\beta\mu_{\text{CO}_2}^{(0)} + 2\beta\mu_{\text{CO}}^{(0)} + \beta\mu_{\text{O}_2}^{(0)} \right).$$

For the parameters given in the problem  $K(1500 \text{ K}) = 4 \times 10^{10}$  which yields  $[\text{CO}] / [\text{CO}_2] \simeq 5 \times 10^{-5} = 50 \text{ ppm}$ , while  $K(600 \text{ K}) = 1.7 \times 10^{40}$  which yields  $[\text{CO}] / [\text{CO}_2] \simeq 7 \times 10^{-20}$  which yields a negligible  $[\text{CO}]$  concentration.

**6.32.** The equilibrium constant for  $\text{N}_2 + \text{O}_2 \rightarrow 2\text{NO}$  is

$$\frac{[\text{NO}]^2}{[\text{N}_2][\text{O}_2]} = K(T) = e^{-\beta\Delta\varepsilon} \frac{j_{\text{NO}}^2}{j_{\text{N}_2}j_{\text{O}_2}} \frac{\lambda_{\text{N}_2}^3\lambda_{\text{O}_2}^3}{\lambda_{\text{NO}}^6}.$$

The internal partition functions are of the form

$$j = \begin{cases} \left( \frac{T}{\Theta_r} \right) & \text{for } kT \ll \hbar\omega \\ \left( \frac{T}{\Theta_r} \right) \left( \frac{kT}{\hbar\omega} \right) & \text{for } kT \gg \hbar\omega \end{cases}$$

which leads to

$$K(T) = \begin{cases} e^{-\beta\Delta\varepsilon} \left( \frac{\Theta_{\text{N}_2}\Theta_{\text{O}_2}}{\Theta_{\text{NO}}^2} \right) \left( \frac{30^3}{28^{3/2}32^{3/2}} \right) & \text{for } kT \ll \hbar\omega \\ e^{-\beta\Delta\varepsilon} \left( \frac{\Theta_{\text{N}_2}\Theta_{\text{O}_2}}{\Theta_{\text{NO}}^2} \right) \left( \frac{30^3}{28^{3/2}32^{3/2}} \right) \left( \frac{\omega_{\text{N}_2}\omega_{\text{O}_2}}{\omega_{\text{NO}}^2} \right) & \text{for } kT \gg \hbar\omega \end{cases}$$

**6.33.** The equilibrium relation is

$$\frac{[\text{CO}_2][\text{H}_2\text{O}]^2}{[\text{CH}_4][\text{O}_2]^2} = K$$

Let  $[\text{excess}]$  be the initial excess amount of  $\text{O}_2$  above stoichiometry, and  $[\text{unburned}]$  be the unburned amount of  $\text{CH}_4$ . Then

$$\frac{[\text{CO}_2][\text{H}_2\text{O}]^2}{[\text{CH}_4][\text{O}_2]^2} = \frac{4([\text{CH}_4]_0 - [\text{unburned}])^3}{[\text{unburned}]([\text{excess}] + 2[\text{unburned}])^2} = K$$

Since  $K \gg 1$ , at the stoichiometric point  $[\text{excess}] = 0$  so

$$[\text{unburned}] \approx \frac{[\text{CH}_4]_0}{K^{1/3}}.$$

On the lean side of the stoichiometric point  $[\text{excess}] > 0$  so

$$[\text{unburned}] \approx \frac{4[\text{CH}_4]_0^2}{[\text{excess}]K}.$$

Finally, on the rich side of the stoichiometric point  $[\text{excess}] < 0$  so

$$[\text{unburned}] \approx -\frac{[\text{excess}]}{2}.$$

**6.34.** Equation (6.6.3) gives  $\mu_{\text{Na}} = \mu_{\text{Na}^+} + \mu_e$  where

$$\begin{aligned}\mu_{\text{Na}} &= -\varepsilon_b - kT \ln 2 + kT \ln (n_{\text{Na}} \lambda_{\text{Na}}^3), \\ \mu_{\text{Na}^+} &= kT \ln (n_{\text{Na}^+} \lambda_{\text{Na}}^3), \\ \mu_e &= -kT \ln 2 + kT \ln (n_e \lambda_e^3),\end{aligned}$$

where  $\varepsilon_b$  is the ionization energy of Na. These lead to

$$\frac{n_{\text{Na}}}{n_{\text{Na}^+} n_e} = e^{\beta \varepsilon_b} \lambda_e^3.$$

If the total density is  $n_0 = n_{\text{Na}} + n_{\text{Na}^+}$ , the ionized fraction  $f = n_{\text{Na}^+}/n_0$ , and the system is charge neutral, then

$$\frac{1-f}{f^2} = e^{\beta \varepsilon_b} n_0 \lambda_e^3 = s,$$

which has solution

$$f = \frac{\sqrt{1+4s} - 1}{2s}.$$

# Chapter 7

**7.2.** With  $N_0 \ll N$ , eqn. (7.1.8) reads

$$n\lambda^3 = g_{3/2}(z) = z + 2^{-3/2}z^2 + 3^{-3/2}z^3 + 4^{-3/2}z^4 + \dots, \quad (1)$$

where  $n$  is the particle density. To invert this series, we write

$$z = c_1(n\lambda^3) + c_2(n\lambda^3)^2 + c_3(n\lambda^3)^3 + c_4(n\lambda^3)^4 + \dots \quad (2)$$

and substitute into (1). Equating coefficients of like powers of  $(n\lambda^3)$  on the two sides of the resulting equation, we get

$$\begin{aligned} 1 &= c_1, \quad 0 = c_2 + 2^{-3/2}c_1^2, \quad 0 = c_3 + 2^{-3/2} \cdot 2c_1c_2 + 3^{-3/2}c_1^3, \\ 0 &= c_4 + 2^{-3/2}(c_2^2 + 2c_1c_3) + 3^{-3/2} \cdot 3c_1^2c_2 + 4^{-3/2}c_1^4, \dots \end{aligned}$$

It follows that

$$\begin{aligned} c_1 &= 1, \quad c_2 = -2^{-3/2}, \quad c_3 = (1/4) - 3^{-3/2}, \\ c_4 &= 5 \cdot 6^{-3/2} - 5 \cdot 2^{-9/2} - (1/8), \dots \end{aligned}$$

We now write eqn. (7.1.7) in the form

$$\frac{PV}{NkT} = \frac{1}{n\lambda^3}(z + 2^{-5/2}z^2 + 3^{-5/2}z^3 + 4^{-5/2}z^4 + \dots)$$

and substitute expression (2) into it. This leads to the desired result (7.1.13), with

$$\begin{aligned} a_1 &= c_1 = 1, \quad a_2 = c_2 + 2^{-5/2}c_1^2 = -2^{-5/2}, \\ a_3 &= c_3 + 2^{-5/2} \cdot 2c_1c_2 + 3^{-5/2}c_1^3 = (1/8) - 2 \cdot 3^{-5/2}, \\ a_4 &= c_4 + 2^{-5/2}(c_2^2 + 2c_1c_3) + 3^{-5/2} \cdot 3c_1^2c_2 + 4^{-5/2}c_1^4 \\ &= 3 \cdot 6^{-3/2} - 5 \cdot 2^{-11/2} - (3/32), \end{aligned}$$

in agreement with the values quoted in expressions (7.1.14).



**7.3.** By eqns. (7.1.24) and (7.1.26),  $n\lambda^3 = g_{3/2}(z)$  while  $n\lambda_c^3 = \zeta(3/2)$ . It follows that

$$\frac{T}{T_c} \equiv \left( \frac{\lambda}{\lambda_c} \right)^{-2} = \left( \frac{g_{3/2}(z)}{\zeta(3/2)} \right)^{-2/3}.$$

The right-hand side of this equation may be approximated with the help of formula (D.9), with the result that

$$\frac{T}{T_c} = \left( \frac{\zeta(3/2) - 2\pi^{1/2}\alpha^{1/2} + \dots}{\zeta(3/2)} \right)^{-2/3} \approx 1 + \frac{4\pi^{1/2}\alpha^{1/2}}{3\zeta(3/2)},$$

valid for  $\alpha \ll 1$  and hence for  $T \gtrsim T_c$ . The desired result now follows readily.

**7.4.** By eqn. (7.1.7),  $P = cT^{5/2}g_{5/2}(z)$ , where  $c$  is a constant. Differentiating this result with respect to  $T$  at *constant*  $P$ , we get

$$0 = \frac{5}{2}cT^{3/2}g_{5/2}(z) + cT^{5/2}\frac{\partial g_{5/2}(z)}{\partial z} \left( \frac{\partial z}{\partial T} \right)_P,$$

so that

$$\left( \frac{\partial z}{\partial T} \right)_P = -\frac{5}{2T} \frac{g_{5/2}(z)}{\{ \partial g_{5/2}(z) / \partial z \}}.$$

Using the recurrence relation (D.10), we get the desired result

$$\frac{1}{z} \left( \frac{\partial z}{\partial T} \right)_P = -\frac{5}{2T} \frac{g_{5/2}(z)}{g_{3/2}(z)}. \quad (1)$$

Now,  $C_P = T(\partial S / \partial T)_{P,N}$  and  $C_V = T(\partial S / \partial T)_{V,N}$ . In view of the fact that  $S$ , at *constant*  $N$ , is a function of  $z$  only, see eqn. (7.1.44a), we may write

$$C_P = T \left( \frac{\partial S}{\partial z} \right)_N \left( \frac{\partial z}{\partial T} \right)_P \quad \text{and} \quad C_V = T \left( \frac{\partial S}{\partial z} \right)_N \left( \frac{\partial z}{\partial T} \right)_V.$$

It follows that

$$\gamma = \frac{C_P}{C_V} = \frac{(\partial z / \partial T)_P}{(\partial z / \partial T)_V}.$$

Substituting from eqn. (1) above and from eqn. (7.1.36), we obtain the desired result

$$C_P / C_V = (5/3) [g_{5/2}(z)g_{1/2}(z) / \{g_{3/2}(z)\}^2].$$

For  $T \gg T_c$ , which implies  $z \ll 1$ , we recover the classical result:  $\gamma = 5/3$ . As  $T \rightarrow T_c$ ,  $z \rightarrow 1$  and the function  $g_{1/2}(z)$  diverges as  $\alpha^{-1/2}$ ; see eqn. (D.8). Along with it, both  $\gamma$  and  $C_P$  diverge as  $(T - T_c)^{-1}$ ; see the relation established in Problem 7.3.

**7.5.** (a) We have to evaluate the quantities

$$\kappa_T = \frac{1}{n} \left( \frac{\partial n}{\partial P} \right)_T \quad \text{and} \quad \kappa_S = \frac{1}{n} \left( \frac{\partial n}{\partial P} \right)_z,$$

where  $n = N/V$ . For  $N_0 \ll N$ ,  $n(T, z) = aT^{3/2}g_{3/2}(z)$ , where  $a$  is a constant; see eqn. (7.1.8). It follows that

$$dn = \frac{3}{2} a T^{1/2} g_{3/2}(z) dT + a T^{3/2} \left\{ \frac{1}{z} g_{1/2}(z) \right\} dz.$$

Similarly, since  $P = cT^{5/2}g_{5/2}(z)$ , where  $c$  is a constant,

$$dP = \frac{5}{2} c T^{3/2} g_{5/2}(z) dT + c T^{5/2} \left\{ \frac{1}{z} g_{3/2}(z) \right\} dz.$$

The quantities  $\kappa_T$  and  $\kappa_S$  are then given by

$$\kappa_T = \frac{1}{n} \frac{a}{cT} \frac{g_{1/2}(z)}{g_{3/2}(z)} \quad \text{and} \quad \kappa_S = \frac{1}{n} \frac{3a}{5cT} \frac{g_{3/2}(z)}{g_{5/2}(z)}.$$

Since  $c = ak$ , the desired results follow readily.

Note that, as  $z \rightarrow 1$ ,  $\kappa_T$  diverges in the same manner as  $\gamma$  and  $C_P$ .

(b) Since  $P = 2U/3V$ ,  $(\partial P/\partial T)_V = 2C_V/3V$ . It follows that

$$C_P - C_V = TV \cdot \frac{1}{nkT} \frac{g_{1/2}(z)}{g_{3/2}(z)} \cdot \frac{4C_V^2}{9V^2} = \frac{4C_V^2}{9Nk} \frac{g_{1/2}(z)}{g_{3/2}(z)},$$

in agreement with eqn. (7.1.48a). The other result follows straightforwardly.

**7.6.** For  $T > T_c$ , we employ expression (7.1.37) and write

$$\frac{1}{Nk} \left( \frac{\partial C_V}{\partial T} \right)_V = \frac{\partial}{\partial \ln z} \left( \frac{C_V}{Nk} \right) \cdot \left( \frac{\partial \ln z}{\partial T} \right)_V.$$

The first factor turns out to be

$$\begin{aligned} & \frac{15}{4} \frac{g_{3/2}(z)g_{3/2}(z) - g_{5/2}(z)g_{1/2}(z)}{\{g_{3/2}(z)\}^2} - \frac{9}{4} \frac{g_{1/2}(z)g_{1/2}(z) - g_{3/2}(z)g_{-1/2}(z)}{\{g_{1/2}(z)\}^2} \\ &= \frac{3}{2} - \frac{15}{4} \frac{g_{5/2}(z)g_{1/2}(z)}{\{g_{3/2}(z)\}^2} + \frac{9}{4} \frac{g_{3/2}(z)g_{-1/2}(z)}{\{g_{1/2}(z)\}^2}. \end{aligned}$$

The second factor is given by eqn. (7.1.36). Multiplying the two, we obtain the desired result.

For  $T < T_c$ , we employ expression (7.1.31) instead. Since  $C_V$  is now proportional to  $T^{3/2}$ ,

$$\frac{1}{Nk} \left( \frac{\partial C_V}{\partial T} \right)_V = \frac{3}{2T} \frac{C_V}{Nk},$$

which leads to the result quoted in the problem.

As  $T \rightarrow T_c$  from above, the quantity under study approaches the limiting value

$$\frac{1}{T_c} \left[ \frac{45}{8} \frac{\zeta(5/2)}{\zeta(3/2)} - 0 - \frac{27}{8} \frac{\{\zeta(3/2)\}^2 \cdot \Gamma(3/2) \alpha^{-3/2}}{\{\Gamma(1/2) \alpha^{-1/2}\}^3} \right];$$

on the other hand, as  $T \rightarrow T_c$  from below, we obtain simply

$$\frac{1}{T_c} \cdot \frac{45}{8} \frac{\zeta(5/2)}{\zeta(3/2)}.$$

The discontinuity in the slope of the specific heat curve at  $T = T_c$  is, therefore, given by

$$\frac{Nk}{T_c} \cdot \frac{27}{8} \left\{ \zeta \left( \frac{3}{2} \right) \right\}^2 \cdot \frac{(\pi^{1/2}/2)}{\pi^{3/2}} = \frac{27Nk}{16\pi T_c} \left\{ \zeta \left( \frac{3}{2} \right) \right\}^2.$$

**7.7.** Since  $P = 2U/3V$ ,  $(\partial^2 P / \partial T^2)_v = (2/3V)(\partial C_v / \partial T)_v$ . An explicit expression for this quantity can be written down using the result quoted in Problem 7.6.

Next, since  $\mu = kT \ln z$ , we obtain using eqn. (7.1.36)

$$\begin{aligned} \left( \frac{\partial \mu}{\partial T} \right)_v &= k \ln z + \frac{kT}{z} \cdot \left( \frac{\partial z}{\partial T} \right)_v = k \ln z - \frac{3}{2} k \frac{g_{3/2}(z)}{g_{1/2}(z)}, \\ \left( \frac{\partial^2 \mu}{\partial T^2} \right)_v &= \left[ k - \frac{3}{2} k \frac{g_{1/2}(z)g_{1/2}(z) - g_{3/2}(z)g_{-1/2}(z)}{\{g_{1/2}(z)\}^2} \right] \left( \frac{\partial \ln z}{\partial T} \right)_v \\ &= \frac{3k}{4T} \frac{g_{3/2}(z)}{g_{1/2}(z)} - \frac{9k}{4T} \frac{\{g_{3/2}(z)\}^2 g_{-1/2}(z)}{\{g_{1/2}(z)\}^3} \end{aligned}$$

Similarly, using a result from Problem 7.4, we obtain

$$\left( \frac{\partial^2 \mu}{\partial T^2} \right)_P = \frac{15k}{4T} \frac{g_{5/2}(z)}{g_{3/2}(z)} - \frac{25k}{4T} \frac{\{g_{5/2}(z)\}^2 g_{1/2}(z)}{\{g_{3/2}(z)\}^3}.$$

We also note, see eqns. (7.1.37) and (7.1.48b), that

$$\frac{C_P}{Nk} = \frac{25}{4} \frac{\{g_{5/2}(z)\}^2 g_{1/2}(z)}{\{g_{3/2}(z)\}^3} - \frac{15}{4} \frac{g_{5/2}(z)}{g_{3/2}(z)}.$$

It is now straightforward to see that the stated thermodynamic relations are indeed satisfied. The critical behavior of these quantities is also straightforward to check.

**7.8.** One readily sees that

$$w^2 = \left( \frac{\partial P}{\partial(nm)} \right)_S = \frac{1}{mn\kappa_S},$$

where  $\kappa_S$  is the adiabatic compressibility of the fluid. Using a result from Problem 7.5, we get for the ideal Bose gas

$$w^2 = \frac{5kT}{3m} \frac{g_{5/2}(z)}{g_{3/2}(z)}.$$

Next,

$$\langle u^2 \rangle = \left\langle \frac{2\varepsilon}{m} \right\rangle = \frac{2}{m} \frac{U}{N} = \frac{3kT}{m} \frac{g_{5/2}(z)}{g_{3/2}(z)};$$

see eqns. (7.1.8) and (7.1.11). Clearly,  $w^2 = (5/9) < u^2 >$ .

**7.9.** We start by calculating the expectation values of the quantities  $\varepsilon^{1/2}$  and  $\varepsilon^{-1/2}$ :

$$\langle \varepsilon^{1/2} \rangle = \frac{\int_0^\infty \langle n_\varepsilon \rangle \varepsilon^{1/2} a(\varepsilon) d\varepsilon}{\int_0^\infty \langle n_\varepsilon \rangle a(\varepsilon) d\varepsilon}, \quad \langle \varepsilon^{-1/2} \rangle = \frac{\int_0^\infty \langle n_\varepsilon \rangle \varepsilon^{-1/2} a(\varepsilon) d\varepsilon}{\int_0^\infty \langle n_\varepsilon \rangle a(\varepsilon) d\varepsilon}.$$

The integral in the denominator has been evaluated in Section 7.1; those in the numerator can be evaluated like-wise, with the results

$$\langle \varepsilon^{1/2} \rangle = (kT)^{1/2} \frac{\Gamma(2)g_2(z)}{\Gamma(3/2)g_{3/2}(z)}, \quad \langle \varepsilon^{-1/2} \rangle = (kT)^{-1/2} \frac{\Gamma(1)g_1(z)}{\Gamma(3/2)g_{3/2}(z)}.$$

It follows that

$$\begin{aligned} \langle u \rangle &= \sqrt{\frac{2}{m}} \langle \varepsilon^{1/2} \rangle = \sqrt{\frac{8kT}{\pi m}} \frac{g_2(z)}{g_{3/2}(z)}, \text{ while} \\ \langle u^{-1} \rangle &= \sqrt{\frac{m}{2}} \langle \varepsilon^{-1/2} \rangle = \sqrt{\frac{2m}{\pi kT}} \frac{g_1(z)}{g_{3/2}(z)}. \end{aligned}$$

Multiplying the last two expressions, we obtain the desired result.

For  $z \rightarrow 0$ , we recover the classical result stated in Problem 6.6. For  $z \rightarrow 1$ , we encounter divergence of the quantity  $\langle u^{-1} \rangle$ , which arises from the contribution made by the particles in the condensate (for which  $u = 0$ ).

**7.11.** Under the conditions of this problem, the summation in eqn. (7.1.2) has to be carried out over the states of the *internal* spectrum as well as over the translational states. Expression (7.1.16) is then replaced by

$$N_e = (N_e)_0 + (N_e)_1 = \frac{V}{\lambda^3} g_{3/2} \left\{ \exp \left( \frac{\mu}{kT} \right) \right\} + \frac{V}{\lambda^3} g_{3/2} \left\{ \exp \left( \frac{\mu - \varepsilon_1}{kT} \right) \right\}.$$

The critical temperature  $T_c$  is then determined by the condition

$$\frac{V}{\lambda_c^3} g_{3/2}(1) + \frac{V}{\lambda_c^3} g_{3/2}(x) = N, \text{ where } x = e^{-\varepsilon_1/kT_c}. \quad (1)$$

For  $x \ll 1$ ,  $g_{3/2}(x) \simeq x$  and eqn. (1) gives

$$\lambda_c^3 \simeq (V/N)[\zeta(3/2) + x].$$

Comparing this with the standard result  $(\lambda_c^0)^3 = (V/N)\zeta(3/2)$ , we get

$$\frac{T_c}{T_c^0} \equiv \left( \frac{\lambda_c^0}{\lambda_c} \right)^2 \simeq \left[ 1 + \frac{x}{\zeta(3/2)} \right]^{-2/3} \simeq 1 - \frac{2/3}{\zeta(3/2)} x \simeq 1 - \frac{2/3}{\zeta(3/2)} e^{-\varepsilon_1/kT_c^0}.$$

For  $x \lesssim 1$ , on the other hand,  $g_{3/2}(x) \simeq \zeta(3/2) - 2\pi^{1/2}(-\ln x)^{1/2}$ ; eqn. (1) now gives

$$\begin{aligned} \lambda_c^3 &\simeq (2V/N)[\zeta(3/2) - \pi^{1/2}(\varepsilon_1/kT_c)^{1/2}], \text{ whence} \\ \frac{T_c}{T_c^0} &\simeq \left\{ 2 \left[ 1 - \frac{\pi^{1/2}}{\zeta(3/2)} \left( \frac{\varepsilon_1}{kT_c} \right)^{1/2} \right] \right\}^{-2/3} \\ &\simeq 2^{-2/3} \left[ 1 + \frac{2}{3} \frac{\pi^{1/2}}{\zeta(3/2)} 2^{1/3} \left( \frac{\varepsilon_1}{kT_c^0} \right)^{1/2} \right]. \end{aligned}$$

**7.12.** The relative mean-square fluctuation in  $N$  is given by the general formula (4.5.7),

$$\frac{(\overline{\Delta N})^2}{N^2} = \frac{kT}{V} \kappa_T, \quad (1)$$

while  $\kappa_T$  for the ideal Bose gas is given in Problem 7.5. As  $T \rightarrow T_c$  from above, the function  $g_{1/2}(z)$  and, along with it, both  $\kappa_T$  and the relative fluctuation in  $N$  diverge!

The mean-square fluctuation in  $E$  is given by the general formula (4.5.14), viz.

$$(\overline{\Delta E})^2 = kT^2 C_V + \{(\partial U/\partial N)_{T,V}\}^2 (\overline{\Delta N})^2. \quad (2)$$

The first term in (2), for the ideal Bose gas, is determined by eqn. (7.1.37) and stays finite at *all*  $T$ . The second term can be evaluated with the help of eqns. (7.1.8 and 11), whereby

$$\left( \frac{\partial U}{\partial N} \right)_{T,V} = \left( \frac{\partial g_{5/2}(z)}{\partial g_{3/2}(z)} \right)_{T,V} = \frac{g_{3/2}(z)}{g_{3/2}(z)}. \quad (3)$$

The second term in (2) is, therefore, *inversely* proportional to  $g_{1/2}(z)$  and hence vanishes as  $T \rightarrow T_c$ ; this happens because the energy associated with the Bose condensate (which is, in fact, the component responsible for the dramatic rise in the fluctuation of  $N$ ) is zero. Thus, all in all, the relative fluctuation in  $E$  is negligible at *all*  $T$ .

**7.13.** It is straightforward to see that for a Bose gas in two dimensions

$$N_e = \int_0^\infty \frac{1}{z^{-1}e^{\beta\varepsilon}-1} \frac{A \cdot 2\pi p \, dp}{h^2} = \frac{A \cdot 2\pi mkT}{h^2} \int_0^\infty \frac{dx}{z^{-1}e^x - 1} = \frac{A^2}{\lambda} g_1(z),$$

while

$$N_0 = \frac{z}{1-z}.$$

Since Bose-Einstein condensation requires that  $z \rightarrow 1$ , the critical temperature  $T_c$ , by the usual argument, is given by

$$\left(\frac{N}{A}\right) \lambda_c^2 = g_1(1) = \infty \quad [\text{for } g_1(z) = -\ln(1-z)].$$

It follows that  $T_c = 0$ .

More accurately, the phenomenon of condensation requires that both  $N_e$  and  $N_0$  be of order  $N$ . This means that, while  $z \simeq 1$ ,  $(1-z)$  be of order  $N^{-1}$  and hence  $\lambda^2$  be of order  $(A \ln N/N)$ . Since the ratio  $(A/N) \sim \ell^2$ , the condition for condensation takes the form  $(\lambda^2/\ell^2) = O(\ln N)$ . It follows that

$$T \equiv \frac{h^2}{2\pi m k \lambda^2} \sim \frac{h^2}{m k \ell^2} \frac{1}{\ln N}.$$

**7.14.** With energy spectrum  $\varepsilon = Ap^s$ , the density of states in the system is given by, see formula (C.7b),

$$a(\varepsilon)d\varepsilon = \frac{V}{h^n} \frac{2\pi^{n/2}}{\Gamma(n-2)} p^{n-1} dp = \frac{V}{h^n} \frac{2\pi^{n/2}}{sA^{n/s}\Gamma(n/2)} \varepsilon^{(n/s)-1} d\varepsilon. \quad (1)$$

This leads to the expression

$$\begin{aligned} N - N_0 &= \frac{V}{h^n} \frac{2\pi^{n/2}}{sA^{n/s}\Gamma(n/2)} \int_0^\infty \frac{\varepsilon^{(n/2)-1}}{z^{-1}e^{\beta\varepsilon} - 1} d\varepsilon \\ &= \frac{V}{h^n} \frac{2\pi^{n/2}\Gamma(n/s)}{sA^{n/s}\Gamma(n/2)} (kT)^{n/s} g_{n/s}(z), \end{aligned} \quad (2)$$

while  $N_0 = z/(1-z)$ . Similarly,

$$P = \frac{1}{h^n} \frac{2\pi^{n/2}\Gamma(n/s)}{sA^{n/s}\Gamma(n/2)} (kT)^{(n/s)+1} g_{(n/s)+1}(z). \quad (3)$$

Next, following the derivation of eqn. (7.1.11), we get

$$U = kT^2 \left\{ \frac{\partial}{\partial T} \left( \frac{PV}{kT} \right) \right\}_{z,v} = \frac{n}{s} PV, \quad (4)$$

so that  $P = sU/nV$ .

The onset of Bose-Einstein condensation requires that  $z \rightarrow 1$  at a finite temperature  $T_c$ . A glance at eqn. (2) tells us that this will happen only if  $n > s$  and that the critical temperature  $T_c$  will then be determined by the equation

$$N = \frac{V}{h^n} \frac{2\pi^{n/2}\Gamma(n/s)}{sA^{n/s}\Gamma(n/2)} (kT_c)^{n/s} \zeta\left(\frac{n}{s}\right). \quad (5)$$

For  $T < T_c$ ,  $N_e$  will be equal to  $N(T/T_c)^{n/s}$  while  $N_0$  will be given by the balance  $(N - N_e)$ .

To study the specific heats we first observe, from eqns. (2)–(4), that for  $T > T_c$  (when  $N_0 \ll N$ )

$$U = \frac{n}{s} NkT \cdot g_{(n/s)+1}(z)/g_{n/s}(z) \quad (6)$$

Next, using eqns. (2) and (3), and the recurrence relation (D.10), we get

$$\frac{1}{2} \left( \frac{\partial z}{\partial T} \right)_v = -\frac{n}{s} \frac{1}{T} \frac{g_{n/s}(z)}{g_{(n/s)-1}(z)} \quad \text{and} \quad \frac{1}{z} \left( \frac{\partial z}{\partial T} \right)_P = -\left( \frac{n}{s} + 1 \right) \frac{1}{T} \frac{g_{(n/s)+1}(z)}{g_{n/s}(z)}. \quad (7)$$

It is now straightforward to show that

$$\frac{C_v}{Nk} = \frac{n}{s} \left( \frac{n}{s} + 1 \right) \frac{g_{(n/s)+1}(z)}{g_{n/s}(z)} - \left( \frac{n}{s} \right)^2 \frac{g_{n/s}(z)}{g_{(n/s)-1}(z)} \quad (8)$$

and

$$\frac{C_P}{Nk} = \left( \frac{n}{s} + 1 \right)^2 \frac{\{g_{(n/s)+1}(z)\}^2 g_{(n/s)-1}(z)}{\{g_{n/s}(z)\}^3} - \frac{n}{s} \left( \frac{n}{s} + 1 \right) \frac{g_{(n/s)+1}(z)}{g_{n/s}(z)}. \quad (9)$$

The limiting cases suggested in the problem follow quite easily.

**7.15.** The position and momentum representations of the Schrodinger equation after the potential is turned off at time  $t = 0$  is

$$\begin{aligned} -\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} &= i\hbar \frac{\partial \psi}{\partial t}, \\ \frac{p^2}{2m} \hat{\psi} &= i\hbar \frac{\partial \hat{\psi}}{\partial t}. \end{aligned}$$

The momentum representation is easily solved

$$\hat{\psi}(p, t) = \exp \left( \frac{p^2 t}{2i\hbar m} \right) \hat{\psi}(p, 0),$$

where

$$\hat{\psi}(p, 0) = \frac{1}{\sqrt{2\pi\hbar}} \int e^{ipx/\hbar} \psi(x, 0) dx.$$

This leads to (suppressing the normalization factor)

$$\hat{\psi}(p, t) \sim \exp \left[ -\frac{p^2}{2\hbar^2} \left( a^2 + \frac{i\hbar t}{m} \right) \right].$$

Inverse Fourier transforming gives

$$\psi(x, t) = \frac{\sqrt{a}}{\pi^{1/4} \sqrt{a^2 + i\hbar t/m}} \exp \left( -\frac{1}{2} \frac{x^2}{a^2 + i\hbar t/m} \right).$$

This solves the Schrodinger equation and leads to the one-dimensional density

$$|\psi(x, t)|^2 = \frac{1}{\pi^{1/2}a} \frac{1}{\sqrt{1 + (\hbar t/ma^2)^2}} \exp\left(-\frac{x^2}{a^2(1 + (\hbar t/ma^2)^2)}\right).$$

This gives the spatial distribution for one cartesian direction once you note that  $\hbar/ma^2 = \omega_0$ . At long-time, the width of the distribution grows linearly in time.

**7.16.** The one-dimensional normalized joint momentum–position density at time  $t = 0$  is given by

$$f(p, x, 0) = \frac{\omega}{2\pi kT} \exp\left(-\frac{\beta p^2}{2m} - \frac{\beta m\omega^2 x^2}{2}\right).$$

After the potential is turned off at  $t = 0$ , the particles move ballistically so the density becomes

$$f(p, x, t) = f(p, x + pt/m, 0) = \frac{\omega}{2\pi kT} \exp\left(-\frac{\beta p^2}{2m} - \frac{\beta m\omega^2 (x + pt/m)^2}{2}\right).$$

The spatial density is then given by

$$n(x, t) = \int f(p, x + pt/m, 0) dp = \frac{\omega}{2\pi kT} \sqrt{\frac{2\pi m kT}{1 + \omega^2 t^2}} \exp\left(-\frac{1}{2} \frac{\beta m\omega^2 x^2}{1 + \omega^2 t^2}\right).$$

The high-temperature limit of equation (7.2.15) is given by the first term in the series since at high temperature the chemical potential is large and negative.

**7.17.** The ground state density at the center of the trap is  $N_0/(\pi^3/2a^3)$ ; see problem 7.15. Using  $N_0/N = 1 - (T/T_c)^3$ ,  $a = \sqrt{\hbar/(m\omega)}$ , and  $kT_c/(\hbar\omega) = (N/\zeta(3))^{1/3}$ , we get

$$n(0)\lambda^3 = 7\zeta(3)^{1/2} N^{1/2} \gg 1.$$

**7.18.** Integrating equation (7.2.15) gives

$$\int n_{\text{ex}}(\mathbf{r}) d\mathbf{r} = \frac{1}{\lambda^3} \sum_{j=1}^{\infty} \frac{e^{\beta\mu j} (kT)^{3/2}}{j^3 m^{3/2} \omega_0^3} = \left(\frac{kT}{\hbar\omega_0}\right)^3 \sum_{j=1}^{\infty} \frac{e^{\beta\mu j}}{j^3}.$$

The excited particles can be counted using the density of states and the Bose-Einstein factor,

$$N_{\text{ex}} = \int a(\varepsilon) \frac{1}{e^{\beta(\varepsilon-\mu)} - 1} d\varepsilon = \frac{(kT)^3}{2(\hbar\omega)^3} \int x^2 \sum_{j=1}^{\infty} e^{-x} e^{\beta\mu j} dx = \left(\frac{kT}{\hbar\omega_0}\right)^3 \sum_{j=1}^{\infty} \frac{e^{\beta\mu j}}{j^3}.$$

Above  $T_c$  when  $\mu < 0$  this counts all of the particles. Below  $T_c$  when  $\mu = 0$ , this counts the particles that are not in the ground state.



**7.19.** The density of states for a two-dimensional harmonic oscillator is  $a(\varepsilon) = \varepsilon/(\hbar\omega_0)^2$  so the number particles in the trap is given by

$$N(T, \mu) = \int d\varepsilon \frac{\varepsilon}{(\hbar\omega)^2} \frac{1}{e^{\beta(\varepsilon-\mu)} - 1}.$$

As  $T \rightarrow T_c$ ,  $\mu \rightarrow 0$  so

$$N = \int d\varepsilon \frac{\varepsilon}{(\hbar\omega)^2} \frac{1}{e^{\beta\varepsilon} - 1} = \left(\frac{kT_c}{\hbar\omega_0}\right)^2 \int \frac{x dx}{e^x - 1} = \zeta(2) \left(\frac{kT_c}{\hbar\omega_0}\right)^2 = \frac{\pi^2}{6} \left(\frac{kT_c}{\hbar\omega_0}\right)^2.$$

so  $kT_c = \hbar\omega\sqrt{6N/\pi^2}$ . The condensate fraction for  $T \leq T_c$  is  $N_0/N = 1 - (T/T_c)^2$ . For this two-dimensional theory to be valid, the occupancy of the first excited z-state must be negligible which requires  $\hbar\omega_z \gg kT_c \sim \sqrt{N}\hbar\omega_0$ , i.e.  $\omega_z \gg \sqrt{N}\omega_0$ .

**7.20.** By eqn. (3.8.14),

$$-kT \ln Q_1 = kT \ln(e^{\beta\hbar\omega/2} - e^{-\beta\hbar\omega/2}) = \frac{\hbar\omega}{2} + kT \ln(1 - e^{-\beta\hbar\omega}).$$

Now, concentrating on the *thermal* part alone and utilizing eqn. (7.3.2), we get

$$A(V, T) \equiv -kT \ln Q(V, T) = \frac{VkT}{\pi^2 c^3} \int_0^\infty \ln(1 - e^{-\beta\hbar\omega}) \omega^2 d\omega.$$

After an integration by parts, we obtain

$$A(V, T) = -\frac{V\hbar}{3\pi^2 c^3} \int_0^\infty \frac{\omega^3 d\omega}{e^{\beta\hbar\omega} - 1} = -\frac{\pi^2 V k^4 T^4}{45 \hbar^3 c^3};$$

cf. eqns. (7.3.17 and 18). We also get

$$S = -\left(\frac{\partial A}{\partial T}\right)_V = -\frac{4A}{T} \quad \text{and} \quad U = A + TS = -3A = 3PV.$$

Other results of Sec. 7.3 follow straightforwardly.

**7.21.** Using expressions (7.3.12) and (7.3.23), we readily get

$$\frac{U}{N} = \frac{\pi^4}{30\zeta(3)} kT \simeq 2.7 kT.$$

Note that the numerical factor appearing here is actually  $\Gamma(4)\zeta(4)/\Gamma(3)\zeta(3)$ .

**7.22.** Since  $\omega = 2\pi c/\lambda$ , the characteristic frequencies of the vibrational modes of a radiation cavity (and hence the energy eigenvalues of these modes) are proportional to  $L^{-1}$ , i.e. to  $V^{-1/3}$ . Just as in Problem 1.7, we infer that the entropy of this system is a function of the combination  $(V^{1/3}U)$ . It then follows that during an *isentropic* process the quantity  $(V^{1/3}U)$  stays constant, i.e.

$$\left(\frac{1}{3}V^{-2/3}dV\right)U + V^{1/3}dU = 0.$$

Consequently, the pressure of the system is given by

$$P \equiv -\left(\frac{\partial U}{\partial V}\right)_S = \frac{1}{3}\frac{U}{V}.$$

**7.24.** The number density of photons in the cosmic microwave background (CMB) follows from equation (7.3.23)

$$n = \frac{2\zeta(3)}{\pi^2} \left(\frac{kT}{\hbar c}\right)^3 \simeq 4.10 \times 10^8 \text{ m}^{-3} \simeq 410. \text{ cm}^{-3}$$

The energy density is

$$u = \frac{\pi^2}{15} \frac{(kT)^4}{(\hbar c)^3} \simeq 4.17 \times 10^{-14} \text{ J/m}^3.$$

The entropy density is

$$s = \frac{4\pi^2 k}{45} \left(\frac{kT}{\hbar c}\right)^3 \simeq 1.48 \times 10^9 k \text{ m}^{-3} \simeq 2.04 \times 10^{-14} \text{ J/m}^3 \text{K}.$$

**7.25.** According to Sec. 7.4,

$$C_V(T) = \int_{\omega} \frac{\partial}{\partial T} \left\{ \frac{\hbar\omega}{e^{\hbar\omega/kT} - 1} \right\} g(\omega) d\omega, \text{ while } C_V(\infty) = \int_{\omega} k g(\omega) d\omega.$$

It follows that

$$\int_0^{\infty} \{C_V(\infty) - C_V(T)\} dT = \int_{\omega} \left[ kT - \frac{\hbar\omega}{e^{\hbar\omega/kT} - 1} \right]_0^{\infty} g(\omega) d\omega.$$

It is easy to show that

$$\lim_{T \rightarrow \infty} \frac{\hbar\omega}{e^{\hbar\omega/kT} - 1} \approx kT - \frac{1}{2}\hbar\omega;$$

see Section 3.8 as well as Fig. 3.4 of the text. The integral on the right-hand side then becomes

$$\int_{\omega} \frac{1}{2} \hbar\omega \cdot g(\omega) d\omega,$$

which is indeed equal to the zero-point energy of the solid.

The physical interpretation of this result lies in noting that the actual amount of heat required to raise the temperature of a solid is less than the value predicted classically because the solid already possesses a finite amount of energy even at  $T = 0K$ .

**7.26.** Using the Debye spectrum (7.4.15), we have for the zero-point energy of the solid

$$\int_0^{\omega_D} \frac{1}{2} \hbar \omega \cdot \frac{9N}{\omega_D^3} \omega^2 d\omega = \frac{9}{8} N \hbar \omega_D = \frac{9}{8} N k \Theta_D.$$

Indeed,

$$\bar{\omega} = \frac{\int_0^{\omega_D} \omega \cdot \omega^2 d\omega}{\int_0^{\omega_D} \omega^2 d\omega} = \frac{3}{4} \omega_D$$

and hence the mean energy per mode is equal to  $\frac{1}{2} \hbar \bar{\omega} = \frac{3}{8} \hbar \omega_D = \frac{3}{8} k \Theta_D$ .

**7.27.** We'll show that if the entropy of a system is given by  $S = aVT^n$ , where  $a$  is a constant, then the quantity  $(C_P - C_V)$  of that system is proportional to  $T^{2n+1}$ . For the Debye solid, at  $T \ll \Theta_D$ , this indeed is the case, the parameter  $n$  being equal to 3. Hence the stated result.

We know that

$$C_P - C_V = T \left( \frac{\partial P}{\partial T} \right)_V \left( \frac{\partial V}{\partial T} \right)_P = -T \left( \frac{\partial V}{\partial P} \right)_T \left( \frac{\partial P}{\partial T} \right)_V.$$

Since

$$S \equiv - \left( \frac{\partial A}{\partial T} \right)_V = aVT^n,$$

we must have

$$A = -aVT^{n+1}/(n+1) + f(V),$$

where  $f(V)$  is a function of  $V$  alone. It follows that

$$P \equiv - \left( \frac{\partial A}{\partial V} \right)_T = a \frac{T^{n+1}}{n+1} - f'(V),$$

so that

$$\left( \frac{\partial P}{\partial V} \right)_T = -f''(V), \quad \left( \frac{\partial P}{\partial T} \right)_V = aT^n;$$

clearly,  $f''(V)$  must be non-negative. We thus get

$$C_P - C_V = -T \cdot \frac{-1}{f''(V)} (aT^n)^2 = \frac{a^2}{f''(V)} T^{2n+1}.$$

**7.33.** The specific heat of the system is given by the general expression (7.4.8), which may in the present case be written as

$$C_V(T) = k \int_0^{\omega_D} \frac{(\hbar\omega/kT)^2 e^{\hbar\omega/kT}}{(e^{\hbar\omega/kT} - 1)^2} g(\omega) d\omega. \quad (1)$$

The mode density,  $g(\omega)$ , is given by the relation

$$g(\omega) d\omega = 3 \cdot V(4\pi p^2 dp)/h^3,$$

where  $p = \hbar k = \hbar(A^{-1}\omega)^{1/s}$ . It follows that

$$g(\omega) d\omega = C \omega^{(3/s)-1} d\omega \quad [C = 3V/(2s\pi^2 A^{3/s})]. \quad (2)$$

Substituting (2) into (1) and introducing the variable  $x = \hbar\omega/kT$ , we get

$$C_V(T) \sim T^{3/s} \int_0^{x_0} \frac{x^{(3/s)+1} e^x}{(e^x - 1)^2} dx \quad \left(x_0 = \frac{\hbar\omega_D}{kT}\right).$$

At low temperatures, the upper limit of this integral may be replaced by infinity — making the integral essentially  $T$ -independent; this leads to the desired result  $C_V \sim T^{3/s}$ .

**7.34.** The mode density in this case is given by, see eqn. (C.7b),

$$g(\omega) d\omega \sim k^{n-1} dk \sim \omega^{n-1} d\omega.$$

The rest of the argument is similar to the one made in the previous problem; the net result is that the specific heat of the given system, at low temperatures, is proportional to  $T^n$ .

It is not difficult to see that if the dispersion relation were  $\omega \sim k^s$  and the dimensionality of the system were  $n$ , then the low-temperature specific heat of the system would be proportional to  $T^{n/s}$ .

**7.35.** The Hamiltonian of this system is given by eqn. (7.4.6); the partition function then turns out to be, see eqn. (3.8.14),

$$Q = e^{-\beta\Phi_0} \prod_i \left\{ 2 \sinh \left( \frac{1}{2} \beta \hbar \omega_i \right) \right\}^{-1},$$

with the result that

$$A = -kT \ln Q = \Phi_0 + kT \sum_i \ln \{ 2 \sinh(\hbar\omega_i/2kT) \}, \text{ and hence}$$

$$P = - \left( \frac{\partial A}{\partial V} \right)_T = - \frac{\partial \Phi_0}{\partial V} - \frac{1}{2} \hbar \sum_i \coth \left( \frac{\hbar\omega_i}{2kT} \right) \cdot \frac{\partial \omega_i}{\partial V}.$$

Recognizing that (i) the total vibrational energy  $U'$  of this system is given by the expression  $\sum_i \left(\frac{1}{2}\hbar\omega_i\right) \coth(\hbar\omega_i/2kT)$ , see eqn. (3.8.20), and (ii) the coefficient  $\partial\omega_i/\partial V = -\gamma\omega_i/V$ , the expression for  $P$  may be written as

$$P = \frac{\partial\Phi_0}{\partial V} + \gamma \frac{U'}{V} \quad (U' = U - \Phi_0); \quad (1)$$

see eqn. (7.4.7). With  $\Phi_0(V) = (V - V_0)^2/2\kappa_0 V_0$ , eqn. (1) takes the form

$$P = -\frac{V - V_0}{\kappa_0 V_0} + \gamma \frac{U'}{V}. \quad (2)$$

Now, the coefficient of thermal expansion of any thermodynamic system is given by

$$\alpha \equiv \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T \left( \frac{\partial P}{\partial T} \right)_V = \kappa_T \left( \frac{\partial P}{\partial T} \right)_V, \quad (3)$$

where  $\kappa_T$  is the isothermal compressibility. In the present case, eqn. (2) gives

$$\kappa_T^{-1} \equiv -V \left( \frac{\partial P}{\partial V} \right)_T = \frac{V}{\kappa_0 V_0} + \gamma \frac{U'}{V} - \gamma \left( \frac{\partial U'}{\partial V} \right)_T;$$

using the thermodynamic formula  $(\partial U/\partial V)_T = T(\partial P/\partial T)_V - P$ , where  $U = \Phi_0 + U'$ , we get

$$\kappa_T^{-1} = \frac{V}{\kappa_0 V_0} + \gamma \frac{U'}{V} - \gamma T \left( \frac{\partial P}{\partial T} \right)_V + \gamma P + \gamma \frac{\partial\Phi_0}{\partial V}.$$

Next, since

$$\left( \frac{\partial P}{\partial V} \right)_V = \gamma \frac{C_V}{V}, \quad (4)$$

we get

$$\kappa_T^{-1} = \frac{V}{\kappa_0 V_0} + (1 + \gamma) \left[ P + \frac{V - V_0}{\kappa_0 V_0} \right] - \frac{\gamma^2 T C_V}{V} \quad (5)$$

Under the conditions of the problem, all terms on the right-hand side of (5), except the first one, can be neglected; the term retained may also be approximated by  $\kappa_0^{-1}$  — with the result that  $\kappa_T \approx \kappa_0$ . Equations (3) and (4) then lead to the desired result for  $\alpha$ .

Finally, the quantity  $(C_P - C_V)$  is given by

$$C_P - C_V = T \left( \frac{\partial P}{\partial T} \right)_V \left( \frac{\partial V}{\partial T} \right)_P = T \left( \frac{\partial P}{\partial T} \right)_V \cdot \alpha V \approx \frac{\gamma^2 \kappa_0 T C_V^2}{V_0}.$$

Note that, at low temperatures,  $(C_P - C_V) \sim T^7$  — as in Problem 7.27.

**7.36.** For rotons,  $\varepsilon = \Delta + (p - p_0)^2/2\mu$ . Therefore,  $u \equiv d\varepsilon/dp = (p - p_0)/\mu$ . Consequently,

$$\begin{aligned} P &= \frac{1}{3} n \langle p(p - p_0)/\mu \rangle \\ &= \frac{1}{3} n \frac{\int e^{-(p-p_0)^2/2\mu kT} \{p(p - p_0)/\mu\} p^2 dp}{\int e^{-(p-p_0)^2/2\mu kT} p^2 dp}. \end{aligned}$$

Substituting  $p = p_0 + \sqrt{2\mu kT} x$ , we get

$$P = \frac{1}{3} n \frac{\int e^{-x^2} (p_0 + \sqrt{2\mu kT} x)^3 (2kT/\mu)^{1/2} x dx}{\int e^{-x^2} (p_0 + \sqrt{2\mu kT} x)^2 dx}.$$

As explained in Section 7.6, these integrals are well-approximated by letting the range of  $x$  extend from  $-\infty$  to  $+\infty$ ; also remembering that  $\sqrt{2\mu kT} \ll p_0$ , we get

$$\begin{aligned} P &\simeq \frac{1}{3} n \left( \frac{2kT}{\mu} \right)^{1/2} \frac{3p_0^2 \sqrt{2\mu kT} \cdot (\sqrt{\pi}/2)}{p_0^2 \cdot \sqrt{\pi}} \\ &= nkT. \end{aligned}$$

**7.37.** Following Secs. 7.5 and 7.6, the free energy  $A(\mathbf{v})$  of a roton gas in mass motion is given by

$$A(\mathbf{v}) = -\bar{N}kT = -kT \cdot \frac{V}{h^3} \int n(\varepsilon - \mathbf{v} \cdot \mathbf{p}) 2\pi p^2 \cdot \sin \theta dp d\theta.$$

As explained in Section 7.6, though rotons obey Bose-Einstein statistics, their distribution function is practically Boltzmannian; see eqns. (7.6.6 and 7). We may, therefore, write

$$A(\mathbf{v}) = -kT \cdot \frac{V}{h^3} \int e^{-\beta\varepsilon + \beta\mathbf{v}\mathbf{p} \cos \theta} 2\pi p^2 \sin \theta dp d\theta.$$

Integrating over  $\theta$ , we get

$$A(\mathbf{v}) = -kT \cdot \frac{V}{h^3} \int_0^\infty e^{-\beta\varepsilon} \frac{\sinh(\beta\mathbf{v}p)}{\beta\mathbf{v}p} 4\pi p^2 dp.$$

Integration over  $p$  is now carried out the same way as in eqn. (7.6.9); with appropriate approximation, we end up with the result

$$A(\mathbf{v}) = A(0) \sinh(\beta\mathbf{v}p_0)/(\beta\mathbf{v}p_0).$$

Next, the inertial density of the roton gas is given by

$$\begin{aligned} \rho(\mathbf{v}) &= \frac{1}{\mathbf{v}} \cdot \frac{1}{h^3} \int n(\varepsilon - \mathbf{v} \cdot \mathbf{p}) p \cos \theta 2\pi p^2 \sin \theta dp d\theta \\ &\simeq \frac{1}{\mathbf{v}h^3} \int e^{-\beta\varepsilon + \beta\mathbf{v}\mathbf{p} \cos \theta} 2\pi p^3 \cos \theta \sin \theta dp d\theta \end{aligned}$$

Integration over  $\theta$  now gives

$$\begin{aligned}\rho(v) &= \frac{1}{vh^3} \int_0^\infty e^{-\beta\varepsilon} \left\{ \frac{\cosh(\beta vp)}{\beta vp} - \frac{\sinh(\beta vp)}{(\beta vp)^2} \right\} 4\pi p^3 dp \\ &= \frac{\beta}{h^3} \int_0^\infty e^{-\beta\varepsilon} \frac{(\beta vp) \cosh(\beta vp) - \sinh(\beta vp)}{(\beta vp)^3} 4\pi p^4 dp.\end{aligned}$$

Finally, integrating over  $p$  (under appropriate approximation) and comparing the resulting expression with eqn. (7.6.19), we obtain

$$\rho(v) = \rho(0) \frac{3\{(\beta vp_0) \cosh(\beta vp_0) - \sinh(\beta vp_0)\}}{(\beta vp_0)^3}.$$

**7.38.** We write eqn. (7.6.17) in the form

$$\rho_0 = -\frac{4\pi}{3h^3} \int_0^\infty \frac{\partial n(p)}{\partial p} \left( p^4 \frac{dp}{d\varepsilon} \right) dp$$

and integrate it by parts, to get

$$\rho_0 = -\frac{4\pi}{3h^3} \left[ n(p) p^4 \frac{dp}{d\varepsilon} \Big|_0^\infty - \int_0^\infty n(p) \frac{d}{dp} \left( p^4 \frac{dp}{d\varepsilon} \right) dp \right].$$

The integrated part vanishes at both limits, and we are left with

$$\rho_0 = \frac{4\pi}{3h^3} \int_0^\infty n(p) \frac{d}{dp} \left( p^4 \frac{dp}{d\varepsilon} \right) dp.$$

Comparing this with the standard result for the equilibrium number of excitations in the system, viz.

$$\bar{N} = \frac{4\pi V}{h^3} \int_0^\infty n(p) p^2 dp,$$

we obtain for the effective mass of an excitation

$$m_{eff} = \frac{\rho_0 V}{\bar{N}} = \frac{1}{3} \left\langle \frac{1}{p^2} \frac{d}{dp} \left( p^4 \frac{dp}{d\varepsilon} \right) \right\rangle.$$

For ideal-gas particles,  $\varepsilon = p^2/2m$ ; the effective mass then turns out to be precisely equal to  $m$ . For phonons,  $\varepsilon = pc$ ; we then get

$$(m_{eff})_{ph} = 4 < \varepsilon > / 3c^2,$$

in agreement with eqn. (7.5.15). Unfortunately, in the case of rotons this expression presents certain problems of analyticity at the point  $p = p_0$ ; we then resort to direct calculation — leading to eqn. (7.6.19), whereby  $(m_{eff})_{rot} \simeq p_0^2/3kT$ .

# Chapter 8

**8.1.** Referring to Fig. 8.11 and noting that the slope of the tangent at the point  $x = \xi$  is  $-1/4$ , the approximate distribution is given by

$$f(x) = \begin{cases} 1 & 0 \leq x \leq (\xi - 2) \\ (\xi + 2 - x)/4 & (\xi - 2) \leq x \leq (\xi + 2) \\ 0 & (\xi + 0) \leq x, \end{cases}$$

where  $x = \varepsilon/kT$  and  $\xi = \mu/kT$ . Accordingly,

$$N = g \cdot \frac{2\pi V}{h^3} (2m)^{3/2} \int_0^\infty n(\varepsilon) \varepsilon^{1/2} d\varepsilon = C \int_0^\infty f(x) x^{1/2} dx,$$

where  $C = g(2\pi V/h^3)(2mkT)^{3/2}$ . After some algebra, one gets

$$N = \frac{1}{5} C \{(\xi + 2)^{5/2} - (\xi - 2)^{5/2}\} = \frac{2}{3} C \xi^{3/2} \left\{ 1 + \frac{1}{2} \xi^{-2} + \dots \right\} \quad (\xi \gg 1). \quad (1)$$

Comparing (1) with eqn. (8.1.24), which may be written as

$$N = \frac{2}{3} C \left( \frac{\varepsilon_F}{kT} \right)^{3/2},$$

we get

$$\xi = \frac{\varepsilon_F}{kT} \left\{ 1 - \frac{1}{3} \left( \frac{kT}{\varepsilon_F} \right)^2 + \dots \right\}. \quad (2)$$

Similarly,

$$\begin{aligned} U &= CkT \int_0^\infty f(x) x^{3/2} dx = \frac{1}{35} CkT \{(\xi + 2)^{7/2} - (\xi - 2)^{7/2}\} \\ &= \frac{2}{5} CkT \xi^{5/2} \left\{ 1 + \frac{5}{2} \xi^{-2} + \dots \right\}. \end{aligned} \quad (3)$$

Combining (1) and (3), and then making use of (2), we get

$$U = \frac{3}{5} NkT \xi \left\{ 1 + 2\xi^{-2} + \dots \right\} = \frac{3}{5} N\varepsilon_F \left\{ 1 + \frac{5}{3} (kT/\varepsilon_F)^2 + \dots \right\}.$$



It follows that, at temperatures much less than  $\varepsilon_F/k$ ,

$$C_V = 2Nk(kT/\varepsilon_F),$$

which is “correct” insofar as the dependence on  $T$  is concerned but is numerically less than the true value, given by eqn. (8.1.39), by a factor of  $4/\pi^2$ .

The reason for the numerical discrepancy lies in the fact that the present approximation takes into account *only* a fraction of the particles that are thermally excited; see Fig. 8.11. In fact, the ones that are not taken into account have a higher  $\Delta\varepsilon$  than the ones that are, which explains why the magnitude of the discrepancy is so large.

**8.2.** By eqns. (8.1.4) and (8.1.5), the temperature  $T_0$  is given by

$$T_0 = \left( \frac{N}{gV f_{3/2}(1)} \right)^{2/3} \left( \frac{h^2}{2\pi mk} \right). \quad (1)$$

At the same time, the Fermi temperature  $T_F$  is given by, see eqn. (8.1.24),

$$T_F \equiv \frac{\varepsilon_F}{k} = \left( \frac{3N}{4\pi gV} \right)^{2/3} \frac{h^2}{2mk}. \quad (2)$$

It follows that

$$\frac{T_0}{T_F} = \left( \frac{4\pi}{3 f_{3/2}(1)} \right)^{2/3} \frac{1}{\pi}. \quad (3)$$

Now, by eqn. (E. 16),  $f_{3/2}(1) = (1-2^{-1/2})\zeta(3/2) \simeq 0.765$ . Substituting this into (3), we get:  $T_0/T_F \simeq 0.989$ .

**8.3.** This problem is similar to Problem 7.4 of the Bose gas and can be done the same way — only the functions  $g_\nu(z)$  get replaced by  $f_\nu(z)$ .

To obtain the low-temperature expression for  $\gamma$ , we make use of expansions (8.1.30–32), with the result

$$\begin{aligned} \gamma &= \left\{ 1 + \frac{5\pi^2}{8}(\ln z)^{-2} + \dots \right\} \left\{ 1 - \frac{\pi^2}{24}(\ln z)^{-2} + \dots \right\} \left\{ 1 + \frac{\pi^2}{8}(\ln z)^{-2} + \dots \right\}^{-2} \\ &= 1 + \frac{\pi^2}{3}(\ln z)^{-2} + \dots \simeq 1 + \frac{\pi^2}{3} \left( \frac{kT}{\varepsilon_F} \right)^2. \end{aligned}$$

**8.4.** This problem is similar to Problem 7.5 of the Bose gas and can be done the same way. To obtain the various low-temperature expressions, we make use of expansions (8.1.30–32). Thus

$$\begin{aligned} \kappa_T &= \frac{3}{2n(kT \ln z)} \left\{ 1 - \frac{\pi^2}{24}(\ln z)^{-2} + \dots \right\} \left\{ 1 + \frac{\pi^2}{8}(\ln z)^{-2} + \dots \right\}^{-1} \\ &= \frac{3}{2n(kT \ln z)} \left\{ 1 - \frac{\pi^2}{6}(\ln z)^{-2} + \dots \right\}. \end{aligned}$$

We now employ eqn. (8.1.35) and get

$$\begin{aligned}\kappa_T &= \frac{3}{2n\varepsilon_F} \left\{ 1 - \frac{\pi^2}{12} \left( \frac{kT}{\varepsilon_F} \right)^2 + \dots \right\}^{-1} \left\{ 1 - \frac{\pi^2}{6} \left( \frac{kT}{\varepsilon_F} \right)^2 + \dots \right\} \\ &\simeq \frac{3}{2n\varepsilon_F} \left\{ 1 - \frac{\pi^2}{12} \left( \frac{kT}{\varepsilon_F} \right)^2 \right\},\end{aligned}\quad (1)$$

which is the desired result.

Similarly, using appropriate expansions, we get

$$\begin{aligned}\kappa_s &= \frac{3}{2n(kT \ln z)} \left\{ 1 - \frac{\pi^2}{2} (\ln z)^{-2} + \dots \right\} \\ &\simeq \frac{3}{2n\varepsilon_F} \left\{ 1 - \frac{5\pi^2}{12} \left( \frac{kT}{\varepsilon_F} \right)^2 \right\}.\end{aligned}\quad (2)$$

Dividing (1) by (2), we obtain the low-temperature expression for  $\gamma$ , the same as the one quoted in the previous problem; this also yields the desired result for  $(C_P - C_V)/C_V$ , which is simply  $(\gamma - 1)$ .

**8.6.** This problem is similar to Problem 7.8 of the Bose gas and can be done the same way. In the limit  $z \rightarrow \infty$ , which corresponds to  $T \rightarrow 0K$ ,

$$w^2 \approx 2kT \ln z / 3m,$$

which tends to the limiting value  $2\varepsilon_F/3m$ . Thus

$$w_0 = (2\varepsilon_F/3m)^{1/2}.$$

For comparison, the Fermi velocity  $u_F = (2\varepsilon_F/m)^{1/2}$ . It follows that  $w_0 = u_F/\sqrt{3}$ .

**8.7.** This problem is similar to Problem 7.9 of the Bose gas and can be done the same way. At low temperatures, using formula (E. 17), we get

$$\begin{aligned}\langle u \rangle \langle u^{-1} \rangle &= \frac{9}{8} \left\{ 1 + \frac{\pi^2}{3} (\ln z)^{-2} + \dots \right\} \left\{ 1 + \frac{\pi^2}{8} (\ln z)^{-2} + \dots \right\}^{-2} \\ &= \frac{9}{8} \left\{ 1 + \frac{\pi^2}{12} (\ln z)^{-2} + \dots \right\} \simeq \frac{9}{8} \left\{ 1 + \frac{\pi^2}{12} \left( \frac{kT}{\varepsilon_F} \right)^2 \right\};\end{aligned}$$

cf. Problem 6.6.

**8.8.** (i) Refer to eqns. (8.3.1 and 2) of the text and note that for silver  $n_e = 1$ ,  $n_a = 4$ ,  $a = 4.09 \text{ \AA}$ , while  $m' = m_e$  — giving  $\varepsilon_F = 5.49 \text{ eV}$  and  $T_F = 6.37 \times 10^4 \text{ K}$ . For lead,  $n_e = 4$ ,  $n_a = 4$ ,  $a = 4.95 \text{ \AA}$ , while  $m' = 2.1 m_e$  — giving  $\varepsilon_F = 9.45 \text{ eV}$  and  $T_F = 10.96 \times 10^4 \text{ K}$ . For aluminum,  $n_e = 3$ ,  $n_a = 4$ ,  $a = 4.05 \text{ \AA}$ , while  $m' = 1.6 m_e$  — giving  $\varepsilon_F = 11.63 \text{ eV}$  and  $T_F = 13.50 \times 10^4 \text{ K}$ .

- (ii) The nuclear radius for  ${}_{80}\text{Hg}^{200}$  is about  $8.4 \times 10^{-13}$  cm. Taking all the nucleons together, this gives a particle density of about  $8.06 \times 10^{37} \text{ cm}^{-3}$ . Substituting this into eqn. (8.1.34), we get:  $\varepsilon_F = 3.7 \times 10^7 \text{ eV}$  and  $T_F = 4.3 \times 10^{11} \text{ K}$ .
- (iii) For liquid  $\text{He}^3$ , the particle density is about  $1.59 \times 10^{22} \text{ cm}^{-3}$ . This yields an  $\varepsilon_F$  of about  $4.1 \times 10^{-4} \text{ eV}$  and a  $T_F$  of about  $4.8 \text{ K}$ .

**8.9.** By eqns. (8.1.4, 5 and 24), the Fermi energy  $\varepsilon_F$  is given by

$$\varepsilon_F = \left\{ \frac{3}{4\pi} f_{3/2}(z) \right\}^{2/3} \frac{h^2}{2m\lambda^2} = \left\{ \frac{3\pi^{1/2}}{4} f_{3/2}(z) \right\}^{2/3} kT.$$

With the help of Sommerfeld's lemma (E.17), this becomes

$$\begin{aligned} \varepsilon_F &= kT \ln z \left\{ 1 + \frac{\pi^2}{8} (\ln z)^{-2} + \frac{7\pi^4}{640} (\ln z)^{-4} + \dots \right\}^{2/3} \\ &= kT \ln z \left\{ 1 + \frac{\pi^2}{12} (\ln z)^{-2} + \frac{\pi^4}{180} (\ln z)^{-4} + \dots \right\}. \end{aligned} \quad (1)$$

To invert this series, we write

$$kT \ln z \equiv \mu = \varepsilon_F \left\{ 1 + a_2 \left( \frac{kT}{\varepsilon_F} \right)^2 + a_4 \left( \frac{kT}{\varepsilon_F} \right)^4 + \dots \right\} \quad (2)$$

and substitute into (1), to get

$$1 - a_2 \left( \frac{kT}{\varepsilon_F} \right)^2 + (a_2^2 - a_4) \left( \frac{kT}{\varepsilon_F} \right)^4 + \dots = 1 + \frac{\pi^2}{12} \left( \frac{kT}{\varepsilon_F} \right)^2 + \left( \frac{\pi^4}{180} - \frac{\pi^2}{6} a_2 \right) \left( \frac{kT}{\varepsilon_F} \right)^4 + \dots$$

Equating coefficients on the two sides of this equality, we get:  $a_2 = -\pi^2/12$ ,  $a_4 = -\pi^4/80, \dots$  Equation (2) then gives the desired result (8.1.35a).

Next, we have from eqns. (8.1.7) and (E.17)

$$\begin{aligned} \frac{U}{N} &= \frac{3}{5} kT \ln z \left\{ 1 + \frac{5\pi^2}{8} (\ln z)^{-2} - \frac{7\pi^4}{384} (\ln z)^{-4} + \dots \right\} \\ &\quad \left\{ 1 + \frac{\pi^2}{8} (\ln z)^{-2} + \frac{7\pi^4}{640} (\ln z)^{-4} + \dots \right\}^{-1} \\ &= \frac{3}{5} kT \ln z \left\{ 1 + \frac{\pi^2}{2} (\ln z)^{-2} - \frac{11\pi^4}{120} (\ln z)^{-4} + \dots \right\}. \end{aligned} \quad (3)$$

Substituting from eqn. (8.1.35a) into (3), we get

$$\begin{aligned} \frac{U}{N} &= \frac{3}{5} \varepsilon_F \left\{ 1 - \frac{\pi^2}{12} \left( \frac{kT}{\varepsilon_F} \right)^2 - \frac{\pi^4}{80} \left( \frac{kT}{\varepsilon_F} \right)^4 + \dots + \right\} \\ &\quad \left\{ 1 + \frac{\pi^2}{2} \left( \frac{kT}{\varepsilon_F} \right)^2 - \frac{\pi^4}{120} \left( \frac{kT}{\varepsilon_F} \right)^4 + \dots \right\} \\ &= \frac{3}{5} \varepsilon_F \left\{ 1 + \frac{5\pi^2}{12} \left( \frac{kT}{\varepsilon_F} \right)^2 - \frac{\pi^4}{16} \left( \frac{kT}{\varepsilon_F} \right)^4 + \dots \right\}. \end{aligned} \quad (4)$$

The specific heat of the gas is then given by

$$\frac{C_V}{Nk} = \frac{\pi^2}{2} \frac{kT}{\varepsilon_F} - \frac{3\pi^4}{20} \left( \frac{kT}{\varepsilon_F} \right)^3 + \dots \quad (5)$$

We note that the ratio of the  $T^3$ -term here to the Debye expression (7.3.23) is  $(1/16)(\Theta_D/T_F)^3$ . For a typical metal, this is  $O(10^{-8}-10^{-9})$ .

**8.10.** This problem is similar to Problem 7.14 of the Bose gas and can be done the same way.

Parts (i) and (ii) are straightforward. For part (iii), we have to show that

$$\frac{C_P}{C_V} = 1 + \left( \frac{s}{n} \right)^2 \frac{C_V}{Nk} \frac{f_{(n/s)-1}(z)}{f_{n/s}(z)} = \left( 1 + \frac{s}{n} \right) \frac{f_{(n/s)+1}(z) f_{(n/s)-1}(z)}{\{f_{n/s}(z)\}^2}, \quad (1)$$

which can be done quite easily; see eqns. (7)–(9) of the solution to Problem 7.14. For part (iv), we observe that, since the quantity  $S/N$  is a function of  $z$  only, an *isentropic* process implies that  $z = \text{const.}$  Accordingly, for such a process,

$$VT^{n/s} = \text{const.} \quad \text{and} \quad P/T^{(n/s)+1} = \text{const.};$$

see eqns. (2) and (3) of the solution to Problem 7.14. Eliminating  $T$  among these relations, we obtain the desired equation of an adiabat. For part (v), we proceed as follows.

In this limit  $z \rightarrow 0$ , eqn. (1) gives

$$C_P/C_V \rightarrow 1 + (s/n). \quad (1a)$$

For  $z \gg 1$ , on the other hand, we obtain [see formula (E.17)]

$$\begin{aligned} \frac{C_P}{C_V} &= \left\{ 1 + \left( \frac{n}{s} + 1 \right) \frac{n}{s} \frac{\pi^2}{6} (\ln z)^{-2} + \dots \right\} \left\{ 1 + \left( \frac{n}{s} - 1 \right) \left( \frac{n}{s} - 2 \right) \frac{\pi^2}{6} (\ln z)^{-2} + \dots \right\} \\ &\quad \times \left\{ 1 + \frac{n}{s} \left( \frac{n}{s} - 1 \right) \frac{\pi^2}{6} (\ln z)^{-2} + \dots \right\}^{-2} \\ &= 1 + \frac{\pi^2}{3} (\ln z)^{-2} + \dots \simeq 1 + \frac{\pi^2}{3} (kT/\varepsilon_F)^2, \end{aligned}$$

regardless of the values of  $s$  and  $n$ .

**8.11.** For  $T \gg T_F$ , we get

$$\frac{C_V}{Nk} \simeq \frac{n}{s}, \quad \frac{C_P - C_V}{Nk} \simeq 1, \quad \text{so that } \frac{C_P}{Nk} \simeq \left(\frac{n}{s} + 1\right).$$

For  $T \ll T_F$ , we obtain [see formula (E.17)]

$$\begin{aligned} \frac{C_V}{Nk} &= \frac{n}{s} \ln z \left\{ 1 + \frac{n}{s} \frac{\pi^2}{3} (\ln z)^{-2} + \dots \right\} - \frac{n}{s} \ln z \left\{ 1 + \left(\frac{n}{s} - 1\right) \frac{\pi^2}{3} (\ln z)^{-2} + \dots \right\} \\ &= \frac{n}{s} \frac{\pi^2}{3} (\ln z)^{-1} + \dots \simeq \frac{n}{s} \frac{\pi^2}{3} \left( \frac{kT}{\varepsilon_F} \right). \end{aligned}$$

To this order of accuracy, the quantity  $C_P/Nk$  has the same value as  $C_V/Nk$ . As for the difference between the two, we obtain

$$\frac{C_P - C_V}{Nk} \simeq \frac{n}{s} \frac{\pi^4}{9} \left( \frac{kT}{\varepsilon_F} \right)^3,$$

consistent with the corresponding value of  $\gamma$  quoted in the previous problem. The non-relativistic case pertains to  $s = 2$  while the extreme relativistic one pertains to  $s = 1$ .

**8.12.** For a Fermi gas confined to a two-dimensional region of area  $A$ ,

$$N = \frac{A}{\lambda^2} f_1(z_F) = \frac{A}{\lambda^2} \ln(1 + z_F), \quad E_F = \frac{AkT}{\lambda^2} f_2(z_F), \quad (1a,b)$$

while the corresponding results for the Bose gas are

$$N = \frac{A}{\lambda^2} g_1(z_B) = \frac{A}{\lambda^2} \ln(1 - z_B), \quad E_B = \frac{AkT}{\lambda^2} g_2(z_B). \quad (2a,b)$$

Equating (1a) and (2a), we get

$$1 + z_F = \frac{1}{1 - z_B}, \quad \text{i.e. } z_F = \frac{z_B}{1 - z_B} \quad \text{or } z_B = \frac{z_F}{1 + z_F}.$$

Next, since  $z \partial f_2(z) / \partial z = f_1(z)$ ,

$$f_2(z_F) = \int_0^{z_F} \frac{1}{z} \ln(1 + z) dz = \int_0^{z_F} \left\{ \frac{1}{1 + z} + \frac{1}{z(1 + z)} \right\} \ln(1 + z) dz.$$

The first part of this integral is readily evaluated; in the second part, we substitute  $z = z'/(1 - z')$ , to get

$$f_2(z_F) = \frac{1}{2} \ln^2(1 + z_F) - \int_0^{z_F/(1+z_F)} \frac{1}{z'} \ln(1 - z') dz' = \frac{1}{2} \ln^2(1 + z_F) + g_2(z_B).$$

Equations (1b) and (2b) then yield the desired result, viz.

$$E_F(N, T) = \frac{N^2 \hbar^2}{4\pi mA} + E_B(N, T), \quad \text{whence } \{C_V(N, T)\}_F = \{C_V(N, T)\}_B.$$

Letting  $T \rightarrow 0$ , we recognize that the constant appearing in the above result must be equal to  $E_F(N, 0)$ . To verify this, we note that, since the Fermi momentum of the gas in two dimensions is given by the equation  $N = A \cdot \pi p_F^2 / h^2$ , the Fermi energy is given by  $\varepsilon_F = p_F^2 / 2m = Nh^2 / 2\pi mA$ . The ground-state energy of the gas then follows readily:

$$E_F(N, 0) = \int_0^{p_F} \frac{p^2}{2m} \frac{A \cdot 2\pi p dp}{h^2} = \frac{A \cdot \pi p_F^4}{4mh^2} = \frac{N^2 h^2}{4\pi mA} = \frac{1}{2} N \varepsilon_F.$$

**8.13.** The Fermi energy of the gas is given by the obvious relation

$$N = \int_0^{\varepsilon_F} a(\varepsilon) d\varepsilon. \quad (1)$$

At the same time, the quantities  $N$  and  $U$ , as functions of  $\mu$  and  $T$ , are given by the standard integrals

$$N = \int_0^\infty \frac{a(\varepsilon) d\varepsilon}{e^{\beta(\varepsilon - \mu)} + 1} \quad \text{and} \quad U = \int_0^\infty \frac{\varepsilon a(\varepsilon) d\varepsilon}{e^{\beta(\varepsilon - \mu)} + 1}.$$

At low temperatures we employ formula (E.18), with  $x = \beta\varepsilon$  and  $\xi = \beta\mu$ , to obtain

$$\begin{aligned} N &= \int_0^\mu a(\varepsilon) d\varepsilon + \frac{\pi^2}{6} (kT)^2 \left\{ \frac{da(\varepsilon)}{d\varepsilon} \right\}_{\varepsilon=\mu} + \dots \\ &\simeq \int_0^{\varepsilon_F} a(\varepsilon) d\varepsilon + (\mu - \varepsilon_F) a(\varepsilon_F) + \frac{\pi^2}{6} (kT)^2 \left\{ \frac{da(\varepsilon)}{d\varepsilon} \right\}_{\varepsilon=\varepsilon_F}, \quad (2) \\ U &= \int_0^\mu \varepsilon a(\varepsilon) d\varepsilon + \frac{\pi^2}{6} (kT)^2 \left\{ \varepsilon a(\varepsilon) + \varepsilon \frac{da(\varepsilon)}{d\varepsilon} \right\}_{\varepsilon=\mu} + \dots \\ &\simeq \int_0^{\varepsilon_F} \varepsilon a(\varepsilon) d\varepsilon + (\mu - \varepsilon_F) \varepsilon_F a(\varepsilon_F) + \frac{\pi^2}{6} (kT)^2 \left\{ a(\varepsilon_F) + \varepsilon_F \left[ \frac{da(\varepsilon)}{d\varepsilon} \right]_{\varepsilon=\varepsilon_F} \right\}. \quad (3) \end{aligned}$$

Comparing (1) and (2), we obtain for the chemical potential of the gas

$$\mu \simeq \varepsilon_F - \frac{\pi^2}{6} \frac{(kT)^2}{a(\varepsilon_F)} \left\{ \frac{da(\varepsilon)}{d\varepsilon} \right\}_{\varepsilon=\varepsilon_F}, \quad (4)$$

which leads to the desired result for  $\mu$ .

Next, substituting (4) into (3), we obtain the remarkably simple expression

$$U \simeq U_0 + (\pi^2/6) k^2 T^2 a(\varepsilon_F),$$

whence

$$C_V \simeq (\pi^2/3) k^2 T a(\varepsilon_F). \quad (5)$$

It follows that

$$S = \int_0^T \frac{C_V dT}{T} \simeq (\pi^2/3) k^2 T a(\varepsilon_F). \quad (6)$$

For a gas with energy spectrum  $\varepsilon \propto p^s$ , confined to a space of  $n$  dimensions,

$$a(\varepsilon) d\varepsilon \sim p^{n-1} dp \sim \varepsilon^{(n/s)-1} d\varepsilon.$$

By eqn. (1), the Fermi energy of the gas is given by

$$N = \int_0^{\varepsilon_F} A \varepsilon^{(n/s)-1} d\varepsilon = \frac{sA}{n} \varepsilon_F^{n/s} = \frac{s\varepsilon_F}{n} a(\varepsilon_F).$$

Substituting this result into (5), we get

$$\frac{C_V}{Nk} \simeq \frac{n}{s} \cdot \frac{\pi^2}{3} \left( \frac{kT}{\varepsilon_F} \right); \quad (7)$$

cf. eqn. (8.1.39), which pertains to the case  $n = 3$ ,  $s = 2$ . See also Problem 8.11.

**8.14.** In the notation of Sec. 3.9, the potential energy of a magnetic dipole in the presence of a magnetic field  $\mathbf{B} = (0, 0, B)$  is given by the expression  $-(g\mu_B m)B$ , where  $m = -J, \dots, +J$ . The total energy  $\varepsilon$  of the dipole is then given by  $\varepsilon = (p^2/2m') - g\mu_B mB$ ,  $m'$  being the (effective) mass of the particle; the momentum of the particle may then be written as

$$p = \{2m'(\varepsilon + g\mu_B mB)\}^{1/2}.$$

At  $T = 0$ , the number of such particles in the gas will be

$$N_m = \frac{4\pi V}{3h^3} \{2m'(\varepsilon_F + g\mu_B mB)\}^{3/2}$$

and hence the net magnetic moment of the gas will be given by

$$M = \sum_m (g\mu_B m) N_m = \frac{4\pi g\mu_B V}{3h^3} (2m')^{3/2} \sum_m m (\varepsilon_F + g\mu_B mB)^{3/2}.$$

We thus obtain for the *low-field* susceptibility (per unit volume) of the system

$$\begin{aligned} \chi_0 &= \lim_{B \rightarrow 0} \left( \frac{M}{VB} \right) = \frac{4\pi g\mu_B}{3h^3} (2m')^{3/2} \cdot \frac{3}{2} g\mu_B \varepsilon_F^{1/2} \sum_{m=-J}^J m^2 \\ &= \frac{2\pi g^2 \mu_B^2}{3h^3} (2m')^{3/2} \varepsilon_F^{1/2} J(J+1)(2J+1). \end{aligned} \quad (1)$$

By eqn. (8.1.24),

$$\varepsilon_F^{3/2} = \frac{3n}{4\pi(2J+1)} \frac{h^3}{(2m')^{3/2}} \quad \left( n = \frac{N}{V} \right). \quad (2)$$

Substituting (2) into (1), we obtain the desired result

$$\chi_0 = \frac{1}{2}n\mu^{*2}/\varepsilon_F \quad \{\mu^{*2} = g^2\mu_B^2 J(J+1)\}.$$

With  $g = 2$  and  $J = 1/2$ , we obtain:  $\chi_0 = (3/2)n\mu_B^2/\varepsilon_F$ , in agreement with eqn. (8.2.6).

The corresponding result in the limit  $T \rightarrow \infty$  is given by

$$\chi_\infty = \frac{1}{2}n\mu^{*2}/kT;$$

see eqn. (3.9.26). We note that the ratio  $\chi_0/\chi_\infty = 3kT/2\varepsilon_F$ , valid for all  $J$ .

**8.15.** We note that the symbol  $\mu_0(xN)$  denotes the chemical potential ( $\equiv kT \ln z$ ) of an ideal gas of  $xN$  “spinless” ( $g = 1$ ) fermions. The corresponding fugacity  $z$  is determined by the equation

$$f_{3/2}(z) = xN\lambda^3/V. \quad (1)$$

Differentiating (1) with respect to  $x$ , we get

$$\frac{\partial f_{3/2}(z)}{\partial \ln z} \frac{\partial \ln z}{\partial x} = \frac{N\lambda^3}{V} = \frac{1}{x} f_{3/2}(z).$$

It follows that

$$\frac{\partial \mu_0}{\partial x} = \frac{kT}{x} \frac{f_{3/2}(z)}{f_{1/2}(z)}.$$

Equation (8.2.20) then assumes the form stated in the problem.

At low temperatures, we get

$$\begin{aligned} \chi &= \frac{n\mu^{*2}}{kT} \cdot \frac{3}{2 \ln z} \left\{ 1 - \frac{\pi^2}{6} (\ln z)^{-2} + \dots \right\} \\ &= \frac{3n\mu^{*2}}{2\varepsilon_F} \left\{ 1 - \frac{\pi^2}{12} \left( \frac{kT}{\varepsilon_F} \right)^2 + \dots \right\}^{-1} \left\{ 1 - \frac{\pi^2}{6} \left( \frac{kT}{\varepsilon_F} \right)^2 + \dots \right\} \\ &\simeq \chi_0 \left\{ 1 - \frac{\pi^2}{12} \left( \frac{kT}{\varepsilon_F} \right)^2 \right\}. \end{aligned} \quad (8.2.24)$$

At high temperatures, on the other hand,

$$\begin{aligned} \chi &= \frac{n\mu^{*2}}{kT} \frac{z - 2^{-1/2}z^2 + \dots}{z - 2^{-3/2}z^2 + \dots} = \frac{n\mu^{*2}}{kT} (1 - 2^{-3/2}z + \dots) \\ &\simeq \chi_\infty (1 - 2^{-5/2}n\lambda^3), \end{aligned} \quad (8.2.27)$$

where use has been made of eqn. (1), with  $f_{3/2}(z) \simeq z$  and  $x = 1/2$ .



**8.18.** The ground-state energy of a relativistic gas of electrons is given by

$$E_0 = \frac{8\pi V}{h^3} \int_0^{p_F} mc^2 [\{1 + (p/mc)^2\}^{1/2} - 1] p^2 dp.$$

Making the substitution (8.5.9), we get

$$E_0 = \frac{8\pi m^4 c^5 V}{h^3} \int_0^{\theta_F} (\cosh \theta - 1) \sinh^2 \theta \cosh \theta d\theta. \quad (1)$$

Now the integral

$$\int_0^{\theta_F} \sinh^2 \theta \cosh^2 \theta d\theta = \frac{1}{3} \sinh^3 \theta \cosh \theta \Big|_0^{\theta_F} - \frac{1}{3} \int_0^{\theta_F} \sinh^4 \theta d\theta. \quad (2)$$

Substituting (2) into (1) and making use of eqn. (8.5.12), we get

$$E_0 = \frac{8\pi m^4 c^5 V}{3h^3} \sinh^3 \theta_F \cosh \theta_F - P_0 V - \frac{8\pi m^4 c^5 V}{3h^3} \sinh^3 \theta_F; \quad (3)$$

note that the last term is simply  $Nmc^2$ . Finally, using the definition  $x = \sinh \theta_F$ , we obtain the desired result.

We observe that eqn. (3) can also be written as

$$E_0 + P_0 V = Nmc^2 (\cosh \theta_F - 1) = N\varepsilon_F \equiv N\mu_0.$$

To verify that the derivative  $(\partial E_0 / \partial V)_N$  is equal to  $-P_0$ , we have to show that

$$\begin{aligned} [\partial \{VB(x)\} / \partial V]_{(Vx^3)} &= -A(x), \text{ i.e. } \partial \{x^{-3}B(x)\} / \partial x^{-3} = -A(x), \text{ i.e.} \\ x^4 \frac{\partial}{\partial x} [8\{(x^2 + 1)^{1/2} - 1\} - x^{-3}A(x)] &= 3A(x), \text{ i.e.} \\ \partial A(x) / \partial x &= 8x^4(x^2 + 1)^{-1/2}, \end{aligned}$$

which can be readily verified with the help of expression (8.5.13).

**8.19.** Utilizing the result obtained in Problem 8.13, we have for a Fermi gas at low temperatures

$$\frac{C_V}{Nk} = \frac{\pi^2}{3} \frac{a(\varepsilon_F)}{N} kT. \quad (1)$$

Now, the density of states for the relativistic gas is given by, see eqn. (8.5.7),

$$a(\varepsilon) = \frac{8\pi V}{h^3} p^2 \frac{dp}{d\varepsilon} = \frac{8\pi m V}{h^3} p \left\{ 1 + \left( \frac{p}{mc} \right)^2 \right\}^{1/2},$$

where  $p = p(\varepsilon)$ . Substituting this result into (1) and making use of eqn. (8.5.4), we get

$$\frac{C_V}{Nk} = \frac{\pi^2 m}{p_F^2} \left\{ 1 + \left( \frac{p_F}{mc} \right)^2 \right\}^{1/2} kT,$$

which leads to the desired result.

In the non-relativistic case ( $p_F \ll mc$  and  $\varepsilon_F = p_F^2/2m$ ), we obtain the familiar expression (8.1.39); in the extreme relativistic case ( $p_F \gg mc$  and  $\varepsilon = pc$ ), we obtain

$$\frac{C_V}{Nk} = \pi^2 \left( \frac{kT}{\varepsilon_F} \right),$$

consistent with expression (7) of the solution to Problem 8.13.

**8.22.** The number of fermions in the trap is

$$N(T, \mu) = \int \frac{d\varepsilon \varepsilon^2}{2(\hbar\omega)^3} \frac{1}{e^{\beta(\varepsilon-\mu)} - 1} = \int_0^{\varepsilon_F} \frac{d\varepsilon \varepsilon^2}{2(\hbar\omega)^3} = \frac{\varepsilon_F^3}{6(\hbar\omega)^3}.$$

Using  $kT_F = \varepsilon_F$  this gives the following relation for the fugacity  $z = e^{-\beta\mu}$ ,

$$3 \left( \frac{T}{T_F} \right)^3 \int \frac{x^2 dx}{e^x e^{-\beta\mu} + 1} = 1.$$

The internal energy is

$$U(T, \mu) = \int \frac{d\varepsilon \varepsilon^3}{2(\hbar\omega)^3} \frac{1}{e^{\beta(\varepsilon-\mu)} - 1} = \frac{(kT)^4}{2(\hbar\omega)^3} \int \frac{x^3}{e^x e^{-\beta\mu} - 1}.$$

When compared to the ground state energy  $U_0 = (kT_F)^4/[8(\hbar\omega)^3]$ , we get

$$\frac{U}{U_0} = 4 \left( \frac{T}{T_F} \right)^4 \int \frac{x^3}{e^x e^{-\beta\mu} - 1}.$$

# Chapter 9

**9.1.** Using the Friedmann equation (9.1.1)

$$\frac{da}{dt} = \sqrt{\frac{8\pi G u}{3c^2}} a,$$

and the connection between scale factor  $a$  and blackbody temperature  $T$ ,  $Ta = T_0 a_0$ , along with (9.3.4b) we get

$$\frac{dT}{dt} = -\sqrt{\frac{8\pi G u}{3c^2}} T = -\sqrt{\frac{8\pi^3 G g k^4}{45 \hbar^3 c^5}} T^3,$$

where  $g = 43/8$  is the effective number of relativistic species from equation (9.3.6b). The solution of the differential equation is

$$T(t) = T_0 \sqrt{\frac{t_0}{T}},$$

where

$$t_0 = \frac{1}{2} \sqrt{\frac{45 \hbar^3 c^5}{8\pi^3 G g (kT_0)^4}} \simeq 0.99 \text{ s}$$

for the case of  $T_0 = 10^{10} \text{ K}$ .

**9.2.** Just use equations (9.3.4) and (9.3.6) with  $T = 10^{10} \text{ K}$ . The pressure and energy density are of order  $10^{25} \text{ J/m}^3$ , and the number density and entropy divided by  $k$  are of order  $10^{38} \text{ m}^{-3}$ .

**9.3.** The average kinetic energy per relativistic electron/positron is of the order of  $u_e/n_e \sim kT$ . The Coulomb energy per electron/positron is of the order of  $u_c \approx e^2/(4\pi\epsilon_0 a)$  where  $a \approx (1/n_e)^{1/3}$  is of the order of the average distance between the charged particles. Using  $n_e \sim (kT/\hbar c)^3$  we get  $u_c/u_e \sim e^2/(4\pi\epsilon_0 \hbar c) \approx 1/137$ . This is the justification for treating the relativistic electrons and positrons as noninteracting.

**9.4.** Correction to the first printing of third edition: The exponent in the result should be  $-3/2$ . For  $\beta mc^2 \gg 1$  but before the time when the

electron density approaches the proton density, the density of electrons and positrons are almost identical so  $\mu \approx 0$ . Equation (9.5.6) gives

$$\begin{aligned} \frac{n_-}{n_\gamma} &\approx \frac{n_+}{n_\gamma} \approx \frac{1}{\zeta(3)} \int_{\beta mc^2}^{\infty} \frac{x \sqrt{x + \beta mc^2} \sqrt{x - \beta mc^2} dx}{e^x + 1} \\ &\approx \frac{e^{-\beta mc^2} (\beta mc^2)^{3/2}}{2\zeta(3)} \int_0^{\infty} \sqrt{y} e^{-y} dy. \end{aligned}$$

**9.5.** Correction to the first printing of third edition: The exponent in the result should be  $-3/2$ . After the density of electrons levels off at the nearly the proton density, you can use equation (9.5.8) to show that the chemical potential  $\mu_- \approx mc^2$ . Then the positron number density is given by equation (9.5.7),

$$\begin{aligned} \frac{n_+}{n_\gamma} &\approx \frac{1}{\zeta(3)} \int_{\beta mc^2}^{\infty} \frac{x \sqrt{x + \beta mc^2} \sqrt{x - \beta mc^2} dx}{e^{x+\beta mc^2} + 1} \\ &\approx \frac{e^{-2\beta mc^2} (\beta mc^2)^{3/2}}{2\zeta(3)} \int_0^{\infty} \sqrt{y} e^{-y} dy \\ &\approx \frac{e^{-2\beta mc^2} (\beta mc^2)^{3/2} \sqrt{\pi}}{4\zeta(3)}. \end{aligned}$$

**9.6.** Correction to the first printing of third edition: the energy density in the statement of the problem should read

$$u_{\text{total}} = (1 + (21/8)(4/11)^{4/3})u_\gamma.$$

After the electron-positron annihilation, the only relativistic species left are the photons and the neutrinos. The factor  $21/8 = (3)(1)(7/8)$  in the energy is because there are three families of neutrinos, the spin degeneracy factor is 1 (all left handed), and  $7/8$  is the Fermi-Dirac factor. The factor  $(4/11)^{4/3}$  is due to the lower temperature of the neutrinos compared to the photons; see equation (9.6.4). Following the solution to problem 9.1, we get

$$t_0 = \frac{1}{2} \sqrt{\frac{45\hbar^3 c^5}{8\pi^3 G \left(1 + \left(\frac{21}{8}\right) \left(\frac{4}{11}\right)^{4/3}\right) (kT_0)^4}} \simeq 1.79 \text{ s}.$$

**9.7.** If the current CMB temperature was 27K rather than 2.7K, the baryon-to-photon ratio would be  $10^3$  times smaller. Equation (9.7.8) implies that the nucleosynthesis temperature would have been about 20% lower which would have delayed the nucleosynthesis by an extra two minutes. This would have given the neutrons a longer time to decay leading to  $q \approx 0.10$  rather than 0.12, leading to a helium content in the universe of about 20%

by weight. If the current CMB temperature were 0.27K, that would have increased the baryon-to-photon ratio by a factor of  $10^3$ . Fewer photons per baryon would have led to an earlier nucleosynthesis, less time for neutrons to decay and an increase of the neutron fraction to  $q \approx 0.135$  leading to about 27% helium content.

**9.8.** The strong interaction exhibits *asymptotic freedom* at high energies justifying treating the quarks and gluons as noninteracting. The effective number of species in equilibrium in these tiny quark-gluon plasmas is accounted for using only the up and down quarks and the gluons. Photons, and leptons, for example, easily escape without interacting with the plasma.

$$\begin{aligned} u_u &= 2 \left( \frac{7}{8} \right) \frac{u_\gamma}{2} & u_{\bar{u}} &= 2 \left( \frac{7}{8} \right) \frac{u_\gamma}{2} & \text{up quarks and antiquarks} \\ u_d &= 2 \left( \frac{7}{8} \right) \frac{u_\gamma}{2} & u_{\bar{d}} &= 2 \left( \frac{7}{8} \right) \frac{u_\gamma}{2} & \text{down quarks and antiquarks} \\ u_g &= (8) 2 \frac{u_\gamma}{2} & & & \text{gluons} \end{aligned}$$

Therefore, the effective number of species is  $g = 8 + 28/8 = 23/2$  and  $u_{\text{QGP}} = gu_\gamma$ . The energy density is  $4 \text{ GeV/fm}^3 = 6.4 \times 10^{35} \text{ J/m}^3$ , so

$$kT \simeq \left( \frac{15(\hbar c)^3}{g\pi^2} \left[ 4 \frac{\text{GeV}}{\text{fm}^3} \right] \right)^{1/4} \simeq 4 \times 10^{-11} \text{ J} \simeq 250 \text{ MeV},$$

and  $T \simeq 3 \times 10^{12} \text{ K}$ . This is the record hottest temperature for matter created in the laboratory.

**9.9.** The strong interaction exhibits *asymptotic freedom* at high energies justifying treating the quarks and gluons as noninteracting. The effective number of species is much larger than during the time near  $t = 1\text{s}$  due to

the muons, quarks and gluons.

$u_\gamma = 2 \frac{u_\gamma}{2}$		photons
$u_{e^-} = 2 \left(\frac{7}{8}\right) \frac{u_\gamma}{2}$	$u_{e^+} = 2 \left(\frac{7}{8}\right) \frac{u_\gamma}{2}$	electrons/positrons
$u_{\nu_e} = \left(\frac{7}{8}\right) \frac{u_\gamma}{2}$	$u_{\bar{\nu}_e} = \left(\frac{7}{8}\right) \frac{u_\gamma}{2}$	electron neutrinos/antineutrinos
$u_{\nu_\mu} = \left(\frac{7}{8}\right) \frac{u_\gamma}{2}$	$u_{\bar{\nu}_\mu} = \left(\frac{7}{8}\right) \frac{u_\gamma}{2}$	muon neutrinos/antineutrinos
$u_{\nu_\tau} = \left(\frac{7}{8}\right) \frac{u_\gamma}{2}$	$u_{\bar{\nu}_\tau} = \left(\frac{7}{8}\right) \frac{u_\gamma}{2}$	tau neutrinos/antineutrinos
$u_{\mu^-} = 2 \left(\frac{7}{8}\right) \frac{u_\gamma}{2}$	$u_{\mu^+} = 2 \left(\frac{7}{8}\right) \frac{u_\gamma}{2}$	muons/antimuons
$u_u = 2 \left(\frac{7}{8}\right) \frac{u_\gamma}{2}$	$u_{\bar{u}} = 2 \left(\frac{7}{8}\right) \frac{u_\gamma}{2}$	up quarks/antiquarks
$u_d = 2 \left(\frac{7}{8}\right) \frac{u_\gamma}{2}$	$u_{\bar{d}} = 2 \left(\frac{7}{8}\right) \frac{u_\gamma}{2}$	down quarks/antiquarks
$u_g = (8)2 \frac{u_\gamma}{2}$		gluons

The result is  $u = (149/8)u_\gamma$ . Proceeding as in problem 9.1 we get

$$T(t) = 10^{10} \text{ K} \sqrt{\frac{0.53 \text{ s}}{T}}.$$

Therefore at  $kT = 300 \text{ MeV}$  ( $T \simeq 3.5 \times 10^{12} \text{ K}$ ), the age of the universe was about  $4 \times 10^{-6} \text{ s}$ .

# Chapter 10

**10.1.** By eqn. (10.2.3), the second virial coefficient of the gas with the given interparticle interaction would be

$$\begin{aligned} a_2 &= -\frac{2\pi}{\lambda^3} \left[ \int_0^D -1 \cdot r^2 dr + \int_D^\infty \{e^{\varepsilon(\sigma/r)^6/kT} - 1\} r^2 dr \right] \\ &= \frac{2\pi}{\lambda^3} \left[ \frac{1}{3} D^3 - \int_{r_0}^\infty \sum_{j=1}^\infty \frac{1}{j!} \left( \frac{\varepsilon \sigma^6}{kT r^6} \right)^j r^2 dr \right] \\ &= \frac{2\pi D^3}{3\lambda^3} \left[ 1 - \sum_{j=1}^\infty \frac{1}{(2j-1)j!} \left( \frac{\varepsilon \sigma^6}{kT D^6} \right)^j \right]; \end{aligned}$$

cf. eqn. (10.3.6). For the rest of the question, follow the solution to Problem 10.7.

**10.2.** For this problem, we integrate (10.2.3) by parts and write

$$a_2 \lambda^3 = -\frac{2\pi}{3kT} \int_0^\infty e^{-u(r)/kT} \frac{\partial u(r)}{\partial r} r^3 dr;$$

cf. eqn. (3.7.17) and Problem 3.23. With the given  $u(r)$ , we get

$$\begin{aligned} a_2 \lambda^3 &= \frac{2\pi}{3kT} \int_0^\infty e^{-A/kTr^m} e^{B/kTr^n} \left( \frac{mA}{r^{m-2}} - \frac{nB}{r^{n-2}} \right) dr \\ &= \frac{2\pi}{3kT} \int_0^\infty e^{-A/kTr^m} \sum_{j=0}^\infty \frac{1}{j!} \left( \frac{B}{kT} \right)^j \left( \frac{mA}{r^{m-2+nj}} - \frac{nB}{r^{n-2+nj}} \right) dr \\ &= \frac{2\pi}{3kT} \sum_{j=0}^\infty \frac{1}{j!} \left( \frac{B}{kT} \right)^j \left\{ A \Gamma \left( \frac{m-3+nj}{m} \right) \left( \frac{kT}{A} \right)^{(m-3+nj)/m} - \frac{n}{m} B \Gamma \left( \frac{n-3+nj}{m} \right) \left( \frac{kT}{A} \right)^{(n-3+nj)/m} \right\}. \end{aligned}$$

From the first sum we take the ( $j=0$ )-term out and combine the remaining terms with the second sum (in which the index  $j$  is changed to  $j-1$ );

after considerable simplification, we get

$$a_2\lambda^3 = \frac{2\pi}{3} \left( \frac{A}{kT} \right)^{3/m} \left\{ \Gamma \left( \frac{m-3}{m} \right) - \frac{3}{m} \sum_{j=1}^{\infty} \frac{1}{j!} \Gamma \left( \frac{nj-3}{m} \right) \left[ \frac{B}{kT} \left( \frac{kT}{A} \right)^{n/m} \right]^j \right\}. \quad (1)$$

For comparison with other cases, we set  $A = A'r_0^m$  and  $B = B'r_0^n$  (so that  $A'$  and  $B'$  become direct measures of the energy of interaction). Expression (1) then becomes

$$a_2\lambda^3 = \frac{2\pi}{3} r_0^3 \left( \frac{A'}{kT} \right)^{3/m} \left\{ \Gamma \left( \frac{m-3}{m} \right) - \frac{3}{m} \sum_{j=1}^{\infty} \frac{1}{j!} \Gamma \left( \frac{nj-3}{m} \right) \left[ \frac{B'}{kT} \left( \frac{kT}{A'} \right)^{n/m} \right]^j \right\}. \quad (2)$$

Now, to simulate a *hard-core* repulsive interaction, we let  $m \rightarrow \infty$ , with the result that

$$a_2\lambda^3 = \frac{2\pi}{3} r_0^3 \left\{ 1 - 3 \sum_{j=1}^{\infty} \frac{1}{(nj-3)j!} \left( \frac{B'}{kT} \right)^j \right\}. \quad (2a)$$

With  $n = 6$ , expression (2a) reduces to the one derived in the preceding problem. Furthermore, if terms with  $j > 1$  are neglected, we recover the van der Waals approximation (10.3.8).

For further comparison, we look at the behavior of the coefficient  $B_2 (= a_2\lambda^3)$  at *high* temperatures. While the hard-core expression (2a) predicts a constant  $B_2$  as  $T \rightarrow \infty$ , the soft-core expression (2) predicts a  $B_2$  that ultimately vanishes, as  $T^{-3/m}$ , which agrees qualitatively with the data shown in Fig. 10.2.

**10.3.** (a) Using the thermodynamic relation

$$C_P - C_V = T(\partial P/\partial T)_V(\partial V/\partial T)_P = -T(\partial P/\partial T)_V^2/(\partial P/\partial V)_T$$

and the equation of state (10.3.9), we get

$$\frac{C_P - C_V}{Nk} = -\frac{T(\partial P/\partial T)_V^2}{k(\partial P/\partial V)_T} = -\frac{T\{k/(v-b)\}^2}{k\{-kT/(v-b)^2 + 2a/v^3\}} = \frac{1}{1 - 2a(v-b)^2/kT v^3}.$$

(b) In view of the thermodynamic relation

$$TdS = C_V dT + T(\partial P/\partial T)_V dV$$

and the equation of state (10.3.9), an adiabatic process is characterized by the fact that

$$C_V dT + NkT(v-b)^{-1} dv = 0.$$

Integrating this result, under the assumption that  $C_V = \text{const.}$ , we get

$$T^{C_V/Nk}(v-b) = \text{const.}$$



(c) For this process we evaluate the Joule coefficient

$$\left(\frac{\partial T}{\partial V}\right)_U = \frac{(\partial U/\partial V)_T}{(\partial U/\partial T)_V} = -\frac{T(\partial P/\partial T)_V - P}{C_V} = -\frac{a/v^2}{C_V} = -\frac{N^2 a}{C_V V^2}.$$

Now integrating from state 1 to state 2, we readily obtain the desired result.

**10.4.** Since, by definition,

$$\alpha = v^{-1}(\partial v/\partial T)_P \text{ and } B^{-1} \equiv \kappa_T = -v^{-1}(\partial v/\partial P)_T,$$

we must have:

$$[\partial(\alpha v)/\partial P]_T = -[\partial(vB^{-1})/\partial T]_P. \quad (1)$$

Using the given empirical expressions, we obtain for the left-hand side of (1)

$$\left(\frac{\partial(\alpha v)}{\partial P}\right)_T = \frac{1}{T} \left(\frac{\partial v}{\partial P}\right)_T = -\frac{vB^{-1}}{T} = -\frac{1}{PT} \left(v + \frac{a'}{T^2}\right)$$

and for the right-hand side

$$-\left(\frac{\partial(vB^{-1})}{\partial T}\right)_P = -\frac{1}{P} \left[\left(\frac{\partial v}{\partial T}\right)_P - \frac{2a'}{T^3}\right] = -\frac{1}{P} \left(\alpha v - \frac{2a'}{T^3}\right) = -\frac{1}{P} \left(\frac{v}{T} + \frac{a'}{T^3}\right).$$

The compatibility of the given expressions is thus established.

To determine the equation of state of the gas, we note from the given expression for  $\alpha$  that

$$\left(\frac{\partial v}{\partial T}\right)_P = \frac{v}{T} + \frac{3a'}{T^3}, \text{ i.e. } \left[\frac{\partial}{\partial T} \left(\frac{v}{T}\right)\right]_P = \frac{3a'}{T^4},$$

whence

$$\frac{v}{T} = -\frac{a'}{T^3} + f(P), \text{ i.e. } v = -\frac{a'}{T^2} + Tf(P), \quad (2)$$

where  $f$  is a function of  $P$  only. We then obtain for  $B$

$$vB^{-1} = -Tf'(P). \quad (3)$$

Combining (2) and (3), we get

$$\frac{f'(P)}{f(P)} = -\frac{vB^{-1}}{(v + a'/T)^2} = -\frac{1}{P}.$$

It follows that  $f(P)$  is proportional to  $1/P$  and hence, by (2),

$$P = \text{const. } T(v + a'/T^2)^{-1}.$$

**10.5.** The Joule-Thomson coefficient of a gas is given by

$$\left(\frac{\partial T}{\partial P}\right)_H = -\frac{(\partial H/\partial P)_T}{(\partial H/\partial T)_P} = \frac{1}{C_P} \left[ T \left(\frac{\partial V}{\partial T}\right)_P - V \right] = \frac{N}{C_P} \left[ \left(\frac{\partial v}{\partial T}\right)_P - v \right].$$

By eqn. (10.2.1),

$$\begin{aligned} \frac{Pv}{kT} &= 1 + \frac{a_2\lambda^3}{v} + \dots, \text{ so that} \\ v &= \frac{kT}{P} \left( 1 + \frac{a_2\lambda^3 P}{kT} + \dots \right) = \frac{kT}{P} + a_2\lambda^3 + \dots \end{aligned}$$

It follows that

$$T \left(\frac{\partial v}{\partial T}\right)_P - v = \left[ T \frac{\partial(a_2\lambda^3)}{\partial T} - a_2\lambda^3 \right] + \dots$$

and hence the quoted result for  $(\partial T/\partial P)_H$ .

With the given interparticle interaction, eqn. (10.2.3) gives

$$\begin{aligned} a_2\lambda^3 &= -2\pi \left[ \int_0^D -1 \cdot r^2 dr + \int_D^{r_1} (e^{u_0/kT} - 1) r^2 dr \right] \\ &= \frac{2\pi}{3} \left[ D^3 - (r_1^3 - D^3) e^{u_0/kT} \right], \end{aligned}$$

whence

$$T \frac{\partial(a_2\lambda^3)}{\partial T} - a_2\lambda^3 = \frac{2\pi}{3} \left[ (r_1^3 - D^3) \left( 1 + \frac{u_0}{kT} \right) e^{u_0/kT} - r_1^3 \right].$$

The desired result for  $(\partial T/\partial P)_H$  now follows readily.

We note that the Joule-Thomson coefficient obtained here vanishes at a temperature  $T_0$ , known as the *temperature of inversion*, given by the implicit relationship

$$\left( 1 + \frac{u_0}{kT_0} \right) e^{u_0/kT_0} = \frac{r_1^3}{r_1^3 - D^3}.$$

For  $T < T_0$ ,  $(\partial T/\partial P)_H > 0$ , which means that the Joule-Thomson expansion causes a cooling of the gas. For  $T > T_0$ ,  $(\partial T/\partial P)_H < 0$ ; the expansion now causes a heating instead.

**10.7.** To the desired approximation,

$$\frac{P}{kT} \equiv \frac{1}{V} \ln \mathcal{Q} = \frac{1}{\lambda^3} (z - a_2 z^2), \quad n = \frac{N}{V} = \frac{1}{\lambda^3} (z - 2a_2 z^2), \quad (1a,b)$$

where  $a_2$  is the second virial coefficient of the gas. It follows that

$$z = n\lambda^3(1 + 2a_2 \cdot n\lambda^3), \text{ whence } P = nkT(1 + a_2 \cdot n\lambda^3). \quad (2a,b)$$

Next

$$\begin{aligned} A &= NkT \ln z - PV = NkT \{\ln(n\lambda^3) - 1 + a_2 \cdot n\lambda^3\}, \\ G &= NkT \ln z = NkT \{\ln(n\lambda^3) + 2a_2 \cdot n\lambda^3\}, \\ S &= - \left( \frac{\partial A}{\partial T} \right)_{N,V} = Nk \left\{ \frac{5}{2} - \ln(n\lambda^3) - n \frac{\partial}{\partial T} (Ta_2\lambda^3) \right\}; \end{aligned}$$

remember that the coefficient  $a_2$  is a function of  $T$ . Furthermore,

$$\begin{aligned} U &= A + TS = NkT \left\{ \frac{3}{2} - nT \frac{\partial}{\partial T} (a_2\lambda^3) \right\}, \\ H &= U + PV = NkT \left\{ \frac{5}{2} - nT^2 \frac{\partial}{\partial T} \left( \frac{a_2\lambda^3}{T} \right) \right\}, \\ C_V &= \left( \frac{\partial U}{\partial T} \right)_{N,V} = Nk \left\{ \frac{3}{2} - n \frac{\partial}{\partial T} \left( T^2 \frac{\partial}{\partial T} (a_2\lambda^3) \right) \right\}, \text{ and} \\ C_P - C_V &= -T \frac{(\partial P / \partial T)_{N,V}^2}{(\partial P / \partial V)_{N,T}} = Nk \left\{ 1 + 2nT \frac{\partial}{\partial T} (a_2\lambda^3) \right\}. \end{aligned}$$

For the second part, use the expression for  $a_2\lambda^3$  derived in Problem 10.5 and examine the temperature dependence of the various thermodynamic quantities.

**10.8.** We consider a volume element  $dx_1 dy_1 dz_1$  around the point  $P(x_1, 0, 0)$  in solid 1 and a volume element  $dx_2 dy_2 dz_2$  around the point  $Q(x_2, y_2, z_2)$  in solid 2. The force of attraction between these elements will be

$$-\alpha(n dx_1 dy_1 dz_1)(n dx_2 dy_2 dz_2) \frac{\ell^5}{\{(x_2 - x_1)^2 + y_2^2 + z_2^2\}^{5/2}},$$

directed along the line joining the points  $P$  and  $Q$ . The *normal* component of this force will be

$$-\alpha n^2 (dy_1 dz_1) \ell^5 \frac{(x_2 - x_1)}{\{(x_2 - x_1)^2 + y_2^2 + z_2^2\}^3} dx_1 dx_2 dy_2 dz_2.$$

The net force (per unit area) experienced by solid 1, because of attraction by all the molecules of solid 2, will thus be

$$\begin{aligned} & -\alpha n^2 \ell^5 \int_{x_1=-\infty}^0 \int_{x_2=d}^{\infty} \int_{\rho=0}^{\infty} \frac{(x_2 - x_1)}{\{(x_2 - x_1)^2 + \rho^2\}^3} dx_1 dx_2 \cdot 2\pi\rho d\rho \\ &= -\frac{\pi\alpha n^2 \ell^5}{2} \int_{x_1=-\infty}^0 \int_{x_2=d}^{\infty} \frac{1}{(x_2 - x_1)^3} dx_1 dx_2 = \frac{\pi\alpha n^2 \ell^5}{4d}, \end{aligned}$$

i.e. inversely proportional to  $d$ .

**10.9.** For  $x \ll 1$ , the spherical Bessel function  $j_\ell(x)$  behaves like  $x^\ell/1.3 \dots (2\ell + 1)$  while the spherical Neumann function behaves like  $-1.3 \dots (2\ell - 1)/x^{\ell+1}$ ; see Abramowitz and Stegun (1964). Substituting these results into eqn. (10.5.31), we readily obtain the desired result.

**10.10.** The *symmetrized* wave functions for a pair of non-interacting bosons/fermions are given by

$$\Psi_\alpha(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2V}} (e^{i\mathbf{k}_1 \cdot \mathbf{r}_1} e^{i\mathbf{k}_2 \cdot \mathbf{r}_2} \pm e^{i\mathbf{k}_1 \cdot \mathbf{r}_2} e^{i\mathbf{k}_2 \cdot \mathbf{r}_1}).$$

The probability density operator  $\hat{W}_2$  of the pair is then given through the matrix elements

$$\begin{aligned} \langle 1', 2' | \hat{W}_2 | 1, 2 \rangle &= 2\lambda^6 \sum_\alpha \Psi_\alpha(1', 2') \Psi_\alpha^*(1, 2) e^{-\beta E_\alpha} \\ &= \frac{\lambda^6}{V^2} \sum_\alpha (e^{i\mathbf{k}_1 \cdot \mathbf{r}'_1} e^{i\mathbf{k}_2 \cdot \mathbf{r}'_2} \pm e^{i\mathbf{k}_1 \cdot \mathbf{r}'_2} e^{i\mathbf{k}_2 \cdot \mathbf{r}'_1}) \times \\ &\quad (e^{-i\mathbf{k}_1 \cdot \mathbf{r}_1} e^{-i\mathbf{k}_2 \cdot \mathbf{r}_2} \pm e^{-i\mathbf{k}_1 \cdot \mathbf{r}_2} e^{-i\mathbf{k}_2 \cdot \mathbf{r}_1}) e^{-\beta \hbar^2 (k_1^2 + k_2^2)/2m} \\ &= \frac{\lambda^6}{2V^2} \sum_{\mathbf{k}_1} \sum_{\mathbf{k}_2} \left[ e^{i\mathbf{k}_1 \cdot (\mathbf{r}'_1 - \mathbf{r}_1)} e^{i\mathbf{k}_2 \cdot (\mathbf{r}'_2 - \mathbf{r}_2)} + e^{i\mathbf{k}_1 \cdot (\mathbf{r}'_2 - \mathbf{r}_2)} e^{i\mathbf{k}_2 \cdot (\mathbf{r}'_1 - \mathbf{r}_1)} \pm \right. \\ &\quad \left. e^{i\mathbf{k}_1 \cdot (\mathbf{r}'_2 - \mathbf{r}_1)} e^{i\mathbf{k}_2 \cdot (\mathbf{r}'_1 - \mathbf{r}_2)} \pm e^{i\mathbf{k}_1 \cdot (\mathbf{r}'_1 - \mathbf{r}_2)} e^{i\mathbf{k}_2 \cdot (\mathbf{r}'_2 - \mathbf{r}_1)} \right] \\ &\quad e^{-\beta \hbar^2 k_1^2/2m} e^{-\beta \hbar^2 k_2^2/2m} \\ &= \frac{1}{2} [\langle 1' | \hat{W}_1 | 1 \rangle \langle 2' | \hat{W}_1 | 2 \rangle + \langle 2' | \hat{W}_1 | 2 \rangle \langle 1' | \hat{W}_1 | 1 \rangle \pm \\ &\quad \langle 2' | \hat{W}_1 | 1 \rangle \langle 1' | \hat{W}_1 | 2 \rangle \pm \langle 1' | \hat{W}_1 | 2 \rangle \langle 2' | \hat{W}_1 | 1 \rangle] \\ &= \langle 1' | \hat{W}_1 | 1 \rangle \langle 2' | \hat{W}_1 | 2 \rangle \pm \langle 2' | \hat{W}_1 | 1 \rangle \langle 1' | \hat{W}_1 | 2 \rangle. \end{aligned}$$

Comparing this with eqn. (10.6.18), we obtain the desired result.

**10.11.** A particle with spin  $J$  can be in any one of the  $(2J + 1)$  spin states characterized by the spin functions  $\chi_m (m = -J, \dots, J)$ . For a pair of such particles, we will have  $(2J + 1)^2$  spin states characterized by the symmetrized spin functions

$$\chi_{m_1}(1) \chi_{m_2}(2) \pm \chi_{m_1}(2) \chi_{m_2}(1) \quad (m_{1,2} = -J, \dots, J).$$

Of these,  $(2J + 1)$  functions, for which  $m_1 = m_2$ , can only be symmetric, for the corresponding antisymmetric combinations vanish identically. The remaining  $2J(2J + 1)$  functions, for which  $m_1 \neq m_2$ , can be symmetric or antisymmetric; however, only half of them are *linearly independent* functions (because an interchange of the suffices  $m_1$  and  $m_2$  does not produce anything new). Thus, in all, we have  $J(2J + 1)$  antisymmetric spin functions, and  $(J + 1)(2J + 1)$  symmetric spin functions, that are linearly independent.

Now the total wave function of the pair will be the product of a symmetrized space function (like the ones considered in the previous problem) and a symmetrized spin function (like the ones discussed above). For the total wave function to be symmetric, as required for a pair of bosons, we may associate any of the  $(J+1)(2J+1)$  symmetric spin functions with a symmetric space function *or* any of the  $J(2J+1)$  antisymmetric spin functions with an antisymmetric space function. This will lead to the quoted expression for the coefficient  $b_2^s$ . On the other hand, for the total wave function to be antisymmetric, as required for a pair of fermions, we may associate any of the  $J(2J+1)$  antisymmetric spin functions with a symmetric space function *or* any of the  $(J+1)(2J+1)$  symmetric spin functions with an antisymmetric space function. This will lead to the quoted expression for the coefficient  $b_2^A$ .

**10.12.** To derive the desired results, we make the following observations:

- (i) Since a pair of particles with spin  $J$  has  $(2J+1)^2$  possible spin states while a pair of spinless particles has only one, we have to divide the expression for  $b_2$  pertaining to the former by  $(2J+1)^2$  so that we are talking of the average contribution *per state*.
- (ii) To make a transition from *discreteness* in orientation (that is associated with a finite value of  $J$ ) to *continuity* in orientation, we should take the limit  $J \rightarrow \infty$ .
- (iii) In view of the foregoing, the distinction between the original system being symmetric or antisymmetric is completely lost, and we are led to the results quoted in the problem.

Next, using eqns. (10.5.28, 36 and 37), we obtain for the quantum-mechanical Boltzmannian gas

$$b_2 = - \left( \frac{D}{\lambda} \right)^1 - 3\pi \left( \frac{D}{\lambda} \right)^3 + \frac{22\pi^2}{3} \left( \frac{D}{\lambda} \right)^5 + \dots,$$

which differs *significantly* from the corresponding classical result.

**10.13** Expand the definition of the pair density  $n_2(\mathbf{r}, \mathbf{r}')$  in powers of the fugacity  $z$  using the grand canonical partition function and the Mayer functions  $f_{ij} = \exp(-\beta u(r_{ij})) - 1$ .

$$\begin{aligned} n_2(r_{12}) &= \frac{1}{\mathcal{Q}(\mu, V, T)} \sum_{N=2}^{\infty} \frac{z^N}{(N-2)!} \int d\mathbf{r}_3 \cdots d\mathbf{r}_N \exp(-\beta u(r_{12}) - \beta u(r_{13}) - \cdots) \\ &= e^{-\beta u(r_{12})} \left[ z^2 + z^3 \int (1 + f_{13} + f_{23} + f_{13}f_{23}) d\mathbf{r}_3 - z^3 Q_1 + \cdots \right] \\ &= e^{-\beta u(r_{12})} \left[ \left( z^2 + 2z^3 \int f(r) d\mathbf{r} \right) + z^3 \int f_{13}f_{23} d\mathbf{r}_3 + \cdots \right] \end{aligned}$$

Note every term includes the factor  $e^{-\beta u(r_{12})}$ . The coefficients of those terms are integrals over the Mayer functions that are continuous functions of  $r_{12}$  even for the infinite step function potential; see equation (10.3.19) and discussion in Hansen and McDonald (1986) Chapter 5.

**10.14** The pressure is given by

$$\frac{P}{nkT} = 1 - \frac{n}{2dkT} \int r g(r) \frac{du}{dr} d\mathbf{r},$$

where  $g(r) = y(r)e^{-\beta u(r)}$ . This gives

$$\frac{P}{nkT} = 1 - \frac{n}{2dkT} \int r y(r) \frac{du}{dr} e^{-\beta u(r)} d\mathbf{r} = 1 + \frac{n}{2d} \int r y(r) \frac{d}{dr} \left( e^{-\beta u(r)} \right) d\mathbf{r},$$

For the case of hard spheres,

$$\frac{d}{dr} \left( e^{-\beta u(r)} \right) = \delta(r - D),$$

so

$$\frac{P}{nkT} = 1 + \frac{nD^d}{2d} \Omega_d y(D).$$

where  $\Omega_d$  is the area of the  $d$ -dimensional unit sphere. For hard spheres  $y(D) = g(D^+)$ . In three dimensions  $\eta = \pi n D^3/6$  and  $\Omega_3 = 4\pi$ , so  $P/(nkT) = 1 + 4\eta g(D^+)$ .

**10.15** Let  $P(r)$  be the cumulative probability that no particles are closer than  $r$  to a given particle. Breaking up the interval between zero and  $r$  into small intervals starting at  $r_k = k\Delta r$  with width  $\Delta r$  gives

$$P(r) = \prod_{k=0}^{r/\Delta r} (1 - 4\pi n g(r_k) r_k^2 \Delta r),$$

since each factor represents the probability there are no neighbors in interval  $k$ . This gives

$$\ln(P(r)) \approx \sum_{k=0}^{r/\Delta r} \ln(1 - 4\pi n g(r_k) r_k^2 \Delta r) \approx - \sum_{k=0}^{r/\Delta r} 4\pi n g(r_k) r_k^2 \Delta r.$$

Therefore

$$P(r) = \exp \left( -4\pi n \int_0^r r^2 g(r) dr \right).$$

Finally

$$w(r) = -\frac{dP}{dr}.$$

For an ideal gas  $g(r) = 1$ , so the integrals are easily evaluated.

**10.17 & 10.18.** For a complete solution to these problems, see Landau and Lifshitz (1958), sec. 117, pp. 369–74.

**10.19.** (a) In this problem we are concerned with the integral

$$I = \int_0^{\infty} \frac{\partial u}{\partial r} e^{-\beta u} r^3 dr.$$

Integrating by parts, we get

$$I = -\frac{1}{\beta} [e^{-\beta u} + c] r^3 \Big|_0^{\infty} + \frac{1}{\beta} \int_0^{\infty} (e^{-\beta u} + c) 3r^2 dr.$$

An arbitrary constant  $c$  has been introduced here to secure “proper behavior” at  $r = \infty$ . Since  $\exp(-\beta u) \rightarrow 1$  as  $r \rightarrow \infty$ , we choose  $c = -1$ . The integrated part then vanishes [assuming that  $u(r) \rightarrow 0$  faster than  $1/r^3$ ], and we are left with the result

$$I = \frac{3}{\beta} \int_0^{\infty} [e^{-\beta u} - 1] r^2 dr.$$

This reduces eqn. (10.7.11) to the desired form.

(b) In the case of hard-sphere potential, the function  $f(r) = -1$  for  $r \leq \sigma$  and 0 for  $r > \sigma$ . We then get

$$\frac{PV}{NkT} \simeq 1 + \frac{2\pi n\sigma^3}{3} \quad \left( n = \frac{N}{V} \right).$$

For  $n\sigma^3 \ll 1$ , we may write this result in the approximate form

$$PV \left( 1 - \frac{2\pi n\sigma^3}{3} \right) = NkT.$$

Comparison with Problem 1.4 shows that the parameter  $b$  of that problem is equal to  $(2\pi/3)N\sigma^3$ , which is indeed four times the actual space occupied by the particles.

**10.20** Use

$$\begin{aligned} [\kappa_T(n, T)]^{-1} &= n \left( \frac{\partial p}{\partial n} \right)_T \\ P(n, T) &= n^2 \left( \frac{\partial f}{\partial n} \right)_T \end{aligned}$$

where  $f = A/N$  is the Helmholtz free energy per particle. Then

$$P(n, T) = p(n_0, T) + \int_{n_0}^n \frac{dn'}{n' \kappa(n', T)},$$

$$f(n, T) = f(n_0, T) + \int_{n_0}^n \frac{P(n', T)}{(n')^2} dn'.$$

**10.21** The most general Gaussian distribution of variables  $\{u_1, \dots, u_N\}$  is of the form

$$P(u_1, \dots, u_N) \sim \exp\left(-\frac{1}{2} \mathbf{u}^T A \mathbf{u}\right)$$

where  $A$  is a symmetric positive definite matrix. The matrix has only positive eigenvalues and can be diagonalized into diagonal matrix ( $\tilde{A} = U^T = U^{-1}$ ) using the orthogonal the matrix  $U$ . The eigenvalues  $\{\lambda_1, \dots, \lambda_N\}$  are all positive and  $\det U = 1$ . The normalization is

$$\begin{aligned} \mathcal{N} &= \int d^N u \exp\left(-\frac{1}{2} \mathbf{u}^T A \mathbf{u}\right) = \int d^N y \exp\left(-\frac{1}{2} \mathbf{y}^T \tilde{A} \mathbf{y}\right) \\ &= \sqrt{(2\pi)^N \prod_{i=1}^N \lambda_i} = \sqrt{(2\pi)^N \det A}. \end{aligned}$$

The transformed variables are  $\mathbf{y} = U^T \mathbf{u}$  so the Jacobian is unity. The integral of the average of  $\exp(\mathbf{a}^T \mathbf{u})$  can be determined from completing the square inside the exponential,

$$\int d^N u \exp\left(\mathbf{a}^T \mathbf{u} - \frac{1}{2} \mathbf{u}^T A \mathbf{u}\right) = \mathcal{N} \exp\left(\frac{1}{2} \mathbf{a}^T A^{-1} \mathbf{a}\right).$$

Averaging the quantity  $(\mathbf{a}^T \mathbf{u})^2$  is accomplished by transforming to the  $\mathbf{y}$  variables which, using

$$\int dx x^2 \exp(-\lambda x^2/2) = (2\pi)^{1/2} / \lambda^{3/2},$$

gives

$$\int d^N u (\mathbf{a}^T \mathbf{u})^2 \exp\left(-\frac{1}{2} \mathbf{u}^T A \mathbf{u}\right) = \mathcal{N} \mathbf{a}^T U \tilde{A}^{-1} U^T \mathbf{a} = \mathcal{N} \mathbf{a}^T A^{-1} \mathbf{a}.$$

**10.22** The pressure is given by

$$p = - \left( \frac{\partial A}{\partial V} \right)_{N, T} = n^2 \left( \frac{\partial A/N}{\partial n} \right)_T,$$



and the excess pressure is given by

$$P^{\text{ex}} = P_{cs} - P_{\text{ideal}} = nkT \left( \frac{1 + \eta + \eta^2 - \eta^3}{(1 - \eta)^3} - 1 \right) = nkT \frac{4\eta - 2\eta^2}{(1 - \eta)^3} = n^2 \left( \frac{\partial A^{\text{ex}}/N}{\partial n} \right)_T.$$

This can be integrated to give

$$\frac{\beta A^{\text{ex}}}{N} = \int_0^\eta \frac{4 - 2\eta'}{(1 - \eta')^2} d\eta' = \frac{3 - 2\eta}{(1 - \eta)^2} - 3 = \frac{4\eta - 3\eta^2}{(1 - \eta)^2}.$$

**10.23** The simplest rational approximations are

$$\begin{aligned} \frac{P}{nkT} = \frac{1 + \eta/8}{(1 - \eta)^2} \approx & 1 + 2\eta + 3.125\eta^2 + 4.25\eta^3 + 5.375\eta^4 + 6.5\eta^5 \\ & + 7.625\eta^6 + 8.75\eta^7 + 9.875\eta^8 + 11.000\eta^9 + \dots, \end{aligned}$$

and

$$\begin{aligned} \frac{P}{nkT} = \frac{1 + 0.128018\eta}{(1 - \eta)^2} \approx & 1 + 2\eta + 3.128018\eta^2 + 4.256036\eta^3 + 5.384054\eta^4 + 6.512072\eta^5 \\ & + 7.64009\eta^6 + 8.768108\eta^7 + 9.896126\eta^8 + 11.024144\eta^9 + \dots \end{aligned}$$

The later gets the first two orders exactly correct, and the third and fourth order coefficients correct to better than 1%.

# Chapter 11

**11.4.** The relevant results for  $T < T_c$  are given in eqns. (11.2.13–15). The corresponding results for  $T > T_c$  follow from eqn. (11.2.10) by neglecting  $n_0$  altogether; we get, to the *first* order in  $a$ ,

$$\frac{1}{N}A(N, V, T) = \frac{1}{N}A_{id}(N, V, T) + \frac{4\pi a\hbar^2}{mv}, \quad (13a)$$

$$P = P_{id} + \frac{4\pi a\hbar^2}{mv^2}, \quad (14a)$$

$$\mu = \mu_{id} + \frac{8\pi a\hbar^2}{mv}. \quad (15a)$$

Remembering that  $v_c \propto T^{-3/2}$ , the various quantities of interest turn out to be

$$C_V = -T \left( \frac{\partial^2 A}{\partial T^2} \right)_{N, V} = (C_V)_{id} + N \frac{2\pi a\hbar^2}{mT} \begin{cases} 0 & (T > T_c) \\ \left( -\frac{3}{2v_c} + \frac{6v}{v_c^2} \right) & (T < T_c) \end{cases}$$

$$K = -v \left( \frac{\partial P}{\partial v} \right)_T = K_{id} + \frac{2\pi a\hbar^2}{m} \begin{cases} 4/v^2 & (T > T_c) \\ 2/v^2 & (T < T_c) \end{cases}$$

$$\left( \frac{\partial^2 P}{\partial T^2} \right)_v = \left( \frac{\partial^2 P}{\partial T^2} \right)_{v, id} + \frac{2\pi a\hbar^2}{mT^2} \begin{cases} 0 & (T > T_c) \\ 6/v_c^2 & (T < T_c) \end{cases}$$

$$\left( \frac{\partial^2 \mu}{\partial T^2} \right)_v = \left( \frac{\partial^2 \mu}{\partial T^2} \right)_{v, id} + \frac{4\pi a\hbar^2}{mT^2} \begin{cases} 0 & (T > T_c) \\ 3/4v_c & (T < T_c) \end{cases}$$

The thermodynamic relationship quoted in part (b) of the problem is readily verified.

As for the discontinuities at  $T = T_c$ , we get (setting  $v = v_c$ )

$$\Delta C_V = N \frac{9\pi a\hbar^2}{mT_c} \frac{1}{v_c} = Nk \frac{9a\lambda_c^2}{2} \frac{\zeta(3/2)}{\lambda_c^3} = Nk \frac{9a}{2\lambda_c} \zeta(3/2),$$

$$\Delta K = -\frac{4\pi a\hbar^2}{m} \frac{1}{v_c^2},$$

$$\Delta \left( \frac{\partial^2 P}{\partial T^2} \right)_v = \frac{12\pi a\hbar^2}{mT_c^2 v_c^2}, \quad \Delta \left( \frac{\partial^2 \mu}{\partial T^2} \right)_v = \frac{3\pi a\hbar^2}{mT_c^2 v_c}.$$

- 11.5.** (a) We replace the sum over  $\mathbf{p}$  appearing in eqn. (11.3.14) by an integral, viz.

$$\int_0^\infty \left\{ \varepsilon(\mathbf{p}) - \frac{p^2}{2m} - \frac{4\pi a \hbar^2 N}{mV} + \left( \frac{4\pi a \hbar^2 N}{mV} \right)^2 \frac{m}{p^2} \right\} \frac{V \cdot 4\pi p^2 dp}{h^3}.$$

Substituting  $p = (8\pi a \hbar^2 N/V)^{1/2} x$ , we get

$$\int_0^\infty \left( \frac{4\pi a \hbar^2 N}{mV} \right) \left\{ x(x^2 + 2)^{1/2} - x^2 - 1 + \frac{1}{2x^2} \right\} \frac{4\pi V}{h^3} \left( \frac{8\pi a \hbar^2 N}{V} \right)^{3/2} x^2 dx,$$

which readily leads us from eqn. (11.3.14) to (11.3.15). The resulting integral over  $x$  can be done by elementary means, giving

$$\int_0^\infty \left\{ x(x^2 + 2)^{1/2} - x^2 - 1 + \frac{1}{2x^2} \right\} x^2 dx = \frac{1}{15}(3x^2 - 4)(x^2 + 2)^{3/2} - \frac{1}{5}x^5 - \frac{1}{3}x^3 + \frac{1}{2}x \Big|_0^\infty.$$

For  $x \gg 1$ ,

$$\begin{aligned} \frac{1}{15}(3x^2 - 4)(x^2 + 2)^{3/2} &= \frac{1}{15}(3x^5 - 4x^3) \left\{ 1 + \frac{3}{x^2} + \frac{3}{2x^4} + O\left(\frac{1}{x^6}\right) \right\} \\ &= \frac{1}{5}x^5 + \frac{1}{3}x^3 - \frac{1}{2}x + O\left(\frac{1}{x}\right). \end{aligned}$$

The contribution from the upper limit is, therefore, zero. From the lower limit we get  $\sqrt{128}/15$ , which leads to eqn. (11.3.16).

- (b) Noting that

$$\frac{4\pi V p^2 dp}{h^3} = \frac{4\pi V}{h^3} \left( \frac{8\pi a \hbar^2 N}{V} \right)^{3/2} x^2 dx = N \left\{ \frac{128}{\pi} (na^3) \right\}^{1/2} x^2 dx,$$

we readily obtain eqn. (11.3.23). Now the integral

$$\int_0^\infty \left\{ \frac{x(x^2 + 1)}{(x^2 + 2)^{1/2}} - x^2 \right\} dx = \frac{1}{3}(x^2 - 1)(x^2 + 2)^{1/2} - \frac{1}{3}x^3 \Big|_0^\infty.$$

Again, for  $x \gg 1$ ,

$$\frac{1}{3}(x^2 - 1)(x^2 + 2)^{1/2} = \frac{1}{3}(x^3 - x) \left\{ 1 + \frac{1}{x^2} + O\left(\frac{1}{x^4}\right) \right\} = \frac{1}{3}x^3 + O\left(\frac{1}{x}\right),$$

with the result that the contribution from the upper limit vanishes. From the lower limit we get  $\sqrt{2}/3$ , which leads to eqn. (11.3.24).

- 11.6.** We invert the given equation for  $n$  and write

$$\mu_0 = \frac{4\pi a \hbar^2 n}{m} \left[ 1 + \frac{32}{3\pi^{1/2}} (na^3)^{1/2} + \dots \right].$$

Substituting this into the given expressions for  $E_0$  and  $P_0$ , we get

$$\begin{aligned}\frac{E_0}{V} &= \frac{2\pi a\hbar^2 n^2}{m} \left[ 1 + \frac{32}{3\pi^{1/2}}(na^3)^{1/2} + \dots \right]^2 \left[ 1 - \frac{64}{5\pi^{1/2}}(na^3)^{1/2} + \dots \right] \\ &= \frac{2\pi a\hbar^2 n^2}{m} \left[ 1 + \frac{128}{15\pi^{1/2}}(na^3)^{1/2} + \dots \right], \text{ and} \\ P_0 &= \frac{2\pi a\hbar^2 n^2}{m} \left[ 1 + \frac{32}{3\pi^{1/2}}(na^3)^{1/2} + \dots \right]^2 \left[ 1 - \frac{128}{15\pi^{1/2}}(na^3)^{1/2} + \dots \right] \\ &= \frac{2\pi a\hbar^2 n^2}{m} \left[ 1 + \frac{64}{5\pi^{1/2}}(na^3)^{1/2} + \dots \right],\end{aligned}$$

in complete agreement with eqns. (11.3.16 and 17).

**11.7.** By eqns. (11.3.11), the number operator  $\hat{n}_p$  for the *real* particles is given by

$$\hat{n}_p = a_p^+ a_p = \frac{1}{1 + \alpha_p^2} \{ b_p^+ b_p - \alpha_p (b_{-p} b_p + b_p^+ b_{-p}^+) + \alpha_p^2 b_{-p} b_{-p}^+ \}.$$

The terms linear in  $\alpha_p$  do not contribute to the expectation value of  $\hat{n}_p$  (with  $\mathbf{p} \neq 0$ ) because of the absence of the diagonal matrix elements in  $b_{-p} b_p$  and  $b_p^+ b_{-p}^+$ . Further, since  $b_p^+ b_p = \hat{N}_p$  and  $b_{-p} b_{-p}^+ = \hat{N}_{-p} + 1$ , we get

$$\overline{n}_p = \frac{1}{1 - \alpha_p^2} \{ \bar{N}_p + \alpha_p^2 (\bar{N}_{-p} + 1) \} \quad (\mathbf{p} \neq 0).$$

Finally, in view of the isotropy of the problem,  $\bar{N}_{-p} = \bar{N}_p$  and we get the desired result.

**11.8.** For a solution to this problem, see Feynman (1954).

**11.10 and 11.** For solutions to these problems, see Fetter (1963, 1965).

**11.14.** We set  $x = 1 + \varepsilon$ , where  $|\varepsilon| \ll 1$ , and find that

$$\begin{aligned}2x^4 \ln \frac{x^2}{|x^2 - 1|} &\simeq 2(1 + 4\varepsilon) \ln \frac{1 + 2\varepsilon}{2|\varepsilon|(1 + \frac{1}{2}\varepsilon)} \simeq 2(1 + 4\varepsilon) \left\{ -\ln |\varepsilon| - \ln 2 + \frac{3}{2}\varepsilon \right\}, \\ 10 \left( x - \frac{1}{x} \right) \ln \left| \frac{x+1}{x-1} \right| &\simeq 20\varepsilon \ln \frac{2+\varepsilon}{|\varepsilon|} \simeq 20\varepsilon \{ -\ln |\varepsilon| + \ln 2 \}, \\ \frac{(2-x^2)^{5/2}}{x} \ln \left( \frac{1+x\sqrt{(2-x^2)}}{1-x\sqrt{(2-x^2)}} \right) &= \frac{2(2-x^2)^{5/2}}{x} \ln \left| \frac{x+\sqrt{2-x^2}}{x-\sqrt{2-x^2}} \right| \\ &\simeq \frac{2(1-2\varepsilon)^{5/2}}{1+\varepsilon} \ln \left| \frac{(1+\varepsilon) + (1-\varepsilon-\varepsilon^2)}{(1+\varepsilon) - (1-\varepsilon-\varepsilon^2)} \right| \\ &\simeq 2(1-6\varepsilon) \ln \left| \frac{2}{2\varepsilon + \varepsilon^2} \right| \simeq 2(1-6\varepsilon) \left\{ -\ln |\varepsilon| - \frac{1}{2}\varepsilon \right\}.\end{aligned}$$

Substituting these results into the square bracket appearing in the formula for  $\varepsilon(p)$ , we get, to the desired degree of approximation,

$$\begin{aligned} 11 + \{-2 \ln |\varepsilon| - 2 \ln 2 + 3\varepsilon - 8\varepsilon \ln |\varepsilon| - 8\varepsilon \ln 2\} \\ - \{-20\varepsilon \ln |\varepsilon| + 20\varepsilon \ln 2\} - \{-2 \ln |\varepsilon| - \varepsilon + 12\varepsilon \ln |\varepsilon|\} \\ = (11 - 2 \ln 2) - 4(7 \ln 2 - 1)\varepsilon, \end{aligned}$$

which yields the stated result.

Comparing this result with eqn. (11.8.10), we find that

$$V(p) \simeq \text{const.} - \frac{8}{15\pi^2} (7 \ln 2 - 1) \frac{p_F^3 a^2}{m \hbar^2} (p - p_F).$$

Equation (11.8.11) then gives

$$\frac{1}{m^*} \simeq \frac{1}{m} \left\{ 1 - \frac{8}{15\pi^2} (7 \ln 2 - 1) (k_F a)^2 \right\},$$

which leads to the desired result for the ratio  $m^*/m$ .

**11.15.** At  $T = 0$  K, the chemical potential of a thermodynamic system is given by

$$\mu = \left( \frac{\partial E}{\partial N} \right)_v = \frac{\partial(E/V)}{\partial(N/V)}.$$

It follows that, in the ground state of the given system,

$$E = V \int_0^n \mu(n) dn = \frac{N}{n} \int_0^n \mu(n) dn \quad \left( n = \frac{N}{V} \right).$$

Now, since  $p_F = (3\pi^2 n)^{1/3} \hbar$ , the given expression for  $\mu$  may be written as

$$\mu(n) \simeq (3\pi^2 n)^{2/3} \frac{\hbar^2}{2m} + (2\pi n) \frac{\hbar^2 a}{m} + (3\pi^2 n)^{4/3} \frac{2}{15\pi^2} (11 - 2 \ln 2) \frac{\hbar^2 a^2}{m}.$$

It follows that

$$\frac{E}{N} \simeq \frac{3}{5} (3\pi^2 n)^{2/3} \frac{\hbar^2}{2m} + \frac{1}{2} (2\pi n) \frac{\hbar^2 a}{m} + \frac{3}{7} (3\pi^2 n)^{4/3} \frac{2}{15\pi^2} (11 - 2 \ln 2) \frac{\hbar^2 a^2}{m},$$

which agrees with eqn. (11.7.31).

**11.16.** For a complete solution to this problem, see the first edition of this book — Sec. 10.3, pages 311-5.

**11.17.** Correction to the first printing of third edition: In line 3, the definition of the dimensionless wavefunction should read:  $\psi = a_{\text{osc}}^{3/2} \Psi / \sqrt{N}$ . Using that substitution and  $a_{\text{osc}} = \sqrt{\hbar / (m\omega_0)}$  gives

$$-\frac{1}{2} \tilde{\nabla}^2 \psi + \frac{1}{2} s^2 \psi + \frac{4\pi N a}{a_{\text{osc}}} |\psi|^2 \psi = \tilde{\mu} \psi,$$

where  $\mathbf{s} = \mathbf{r}/a_{\text{osc}}$ ,  $\tilde{\nabla} = \partial/\partial s_x + \dots$  and  $\tilde{\mu} = \mu/(\hbar\omega_0)$ .

**11.18.** The solution for the case  $V = 0$  is  $\Psi = \sqrt{N/V}$  which gives  $\mu = Nu_0/V$  and  $E = (2\pi a\hbar^2 N^2)/(mV)$ .

**11.19.** For the case  $a \rightarrow 0$  the dimensionless G-P equation is

$$-\frac{1}{2}\tilde{\nabla}^2\psi + \frac{1}{2}s^2\psi = \mu\psi,$$

which has solution  $\psi = \frac{1}{\pi^{3/4}} \exp(-\frac{1}{2}s^2)$  with  $E/(N\hbar\omega_0) = 3/2$ , i.e. the zero point energy for  $N$  particles in the trap.

**11.20.** Use the dimensionless form from problem 11.17. Ignoring the kinetic energy term

$$\psi = \frac{\sqrt{\tilde{\mu} - \frac{s^2}{2}}}{\sqrt{4\pi Na/a_0}}.$$

The normalization is

$$1 = \frac{4\pi a_0}{4\pi Na} \int_0^{\sqrt{2\tilde{\mu}}} \left( \tilde{\mu} - \frac{s^2}{2} \right) ds$$

which gives

$$N = \frac{a_0}{15\pi a} (2\tilde{\mu})^{5/2}.$$

Using the definitions for  $u_0$ ,  $\tilde{\mu}$ , and  $a_0$  gives equations (11.2.25) and (11.2.26). Equation (11.2.28) follows from the definition of the dimensionless length scale, and (11.2.27) comes from integrating the dimensionless energy in problem 11.17, again ignoring the kinetic energy term.

# Chapter 12

**12.1.** We assume the equation of state to be

$$P = \frac{kT}{v} \left( 1 - \frac{1}{2}\beta_1 \frac{\lambda^3}{v} - \frac{2}{3}\beta_2 \frac{\lambda^6}{v^2} \right), \quad (1)$$

where  $\beta_1$  and  $\beta_2$  are certain functions of  $T$ . It follows that

$$\begin{aligned} \left( \frac{\partial P}{\partial v} \right)_T &= -\frac{kT}{v^2} + \beta_1 \frac{kT\lambda^3}{v^3} + 2\beta_2 \frac{kT\lambda^6}{v^4}, \text{ and} \\ \left( \frac{\partial^2 P}{\partial v^2} \right)_T &= 2\frac{kT}{v^3} - 3\beta_1 \frac{kT\lambda^3}{v^4} - 8\beta_2 \frac{kT\lambda^6}{v^5}. \end{aligned}$$

At the critical point, both these derivatives vanish — with the result that

$$(\beta_1)_c \frac{\lambda_c^3}{v_c} + 2(\beta_2)_c \frac{\lambda_c^6}{v_c^2} = 1 \text{ and } 3(\beta_1)_c \frac{\lambda_c^3}{v_c} + 8(\beta_2)_c \frac{\lambda_c^6}{v_c^2} = 2,$$

whence

$$(\beta_1)_c = 2v_c/\lambda_c^3 \text{ and } (\beta_2)_c = -v_c^2/2\lambda_c^6. \quad (2)$$

We infer that, at the critical point,  $\beta_1^2 = -8\beta_2$ .

Finally, substituting (2) into (1), we get

$$\left( \frac{Pv}{kT} \right)_c = 1 - \frac{1}{2}(\beta_1)_c \frac{\lambda_c^3}{v_c} - \frac{2}{3}(\beta_2)_c \frac{\lambda_c^6}{v_c^2} = 1 - 1 + \frac{1}{3} = \frac{1}{3}.$$

**12.2.** The given equation of state is

$$P = \frac{kT}{v-b} e^{-a/kTv}. \quad (1)$$

It follows that

$$\begin{aligned} \left( \frac{\partial P}{\partial v} \right)_T &= kT e^{-a/kTv} \left\{ -\frac{1}{(v-b)^2} + \frac{1}{v-b} \cdot \frac{a}{kTv^2} \right\} = P \left\{ -\frac{1}{(v-b)} + \frac{a}{kTv^2} \right\}, \\ \left( \frac{\partial^2 P}{\partial v^2} \right)_T &= \left( \frac{\partial P}{\partial v} \right)_T \left\{ -\frac{1}{(v-b)} + \frac{a}{kTv^2} \right\} + P \left\{ \frac{1}{(v-b)^2} - \frac{2a}{kTv^3} \right\}. \end{aligned}$$

At the critical point, both these derivatives vanish — with the result that

$$\frac{a}{kT_c} = \frac{v_c^2}{v_c - b} \text{ and } \frac{2a}{kT_c} = \frac{v_c^3}{(v_c - b)^2},$$

whence  $v_c = 2b$  and  $kT_c = a/4b$ . Equation (1) then gives:  $P_c = (a/4b^2)e^{-2}$  and hence  $kT_c/P_c v_c = e^2/2 \simeq 3.695$ .

- (a) For large  $v$ , the given equation of state may be approximated as

$$P = \frac{kT}{v} \left(1 - \frac{b}{v}\right)^{-1} e^{-a/kTv} \simeq \frac{kT}{v} \left\{1 + \frac{b}{v} - \frac{a}{kTv}\right\}.$$

Comparing this with eqns. (10.3.7–10), we see that the coefficient  $B_2$  in the present case is formally the same as the one for the van der Waals gas, viz.  $b - (a/kT)$ .

- (b) We note that the derivative  $(\partial P/\partial v)_T$  for the Dietrici gas can be written as

$$\begin{aligned} \left(\frac{\partial P}{\partial v}\right)_T &= -\frac{kT}{v^2(v-b)^2} e^{-a/kTv} \left\{v^2 - \frac{a}{kT}(v-b)\right\} \\ &= -\frac{kT}{v^2(v-b)^2} e^{-a/kTv} \left\{\left(v - \frac{a}{2kT}\right)^2 + \frac{ab}{kT^2}(T - T_c)\right\}. \end{aligned}$$

Clearly, if  $T > T_c$ , then  $(\partial P/\partial v)_T$  is definitely negative; the same is true at  $T = T_c$  — except for the special case  $v = a/2kT_c = 2b$  when  $(\partial P/\partial v)_T$  is zero. In any case, for all  $T \geq T_c$ ,  $P$  is a *monotonically* decreasing function of  $v$  — with the result that, for any given  $T$  and  $P$ , we have a *unique*  $v$ .

- (c) For  $T < T_c$ ,  $P$  is a *non-monotonic* function of  $v$  — generally decreasing with  $v$  but increasing between the values

$$v_{\min} = \frac{a}{2kT} - \sqrt{\frac{ab}{kT^2}(T_c - T)} \text{ and } v_{\max} = \frac{a}{2kT} + \sqrt{\frac{ab}{kT^2}(T_c - T)}.$$

For any given  $T$ , we now have (for a certain range of  $P$ ) *three* possible values of  $v$  such that

$$v_1 > v_{\max} > v_2 > v_{\min} > v_3;$$

see Figs. 12.2 and 12.3. We further note that

$$\frac{v_{\min}}{v_c} = \frac{1}{1 + (1 - T/T_c)^{1/2}} \text{ and } \frac{v_{\max}}{v_c} = \frac{1}{1 - (1 - T/T_c)^{1/2}}.$$

Clearly,  $v_{\min} < v_c < v_{\max}$  and, hence,  $v_3 < v_c < v_1$ .



(d) To examine the critical behavior of the Dietrici gas, we write

$$P = \frac{a}{4e^2b^2}(1 + \pi), \quad v = 2b(1 + \psi), \quad T = \frac{a}{4bk}(1 + t).$$

The equation of state then takes the form

$$1 + \pi = \frac{1 + t}{1 + 2\psi} \exp \left[ 2 \left( 1 - \frac{1}{(1 + t)(1 + \psi)} \right) \right].$$

Taking logarithms, carrying out expansions and retaining the most important terms, we get

$$\pi \approx t - \left( 2\psi - 2\psi^2 + \frac{8}{3}\psi^3 \right) + 2\{1 - (1 - t)(1 - \psi + \psi^2 - \psi^3)\} \approx 3t - \frac{2}{3}\psi^3 - 2t\psi.$$

We now observe that

- (i) at  $t = 0$ ,  $\pi \approx -\frac{2}{3}\psi^3$ , while at  $\psi = 0$ ,  $\pi \approx 3t$ ,
- (ii) for  $t < 0$ , we obtain three values of  $\psi$ : while  $|\psi_2| \ll |\psi_{1,3}|$ , implying once again  $\pi \approx 3t$ ,  $\psi_{1,3} \approx \pm(3|t|)^{1/2}$ ,
- (iii) the quantity  $-\left(\frac{\partial\psi}{\partial\pi}\right)_t \approx \frac{1}{2\psi^2+2t} \approx \begin{cases} 1/2t & (t > 0, \psi = 0) \\ 1/4|t| & (t < 0, \psi = \psi_{1,3}) \end{cases}.$

Comparing these results with the ones derived in Sec. 12.2, we infer that the critical exponents of this gas are precisely the same as those of the van der Waals gas; the amplitudes, however, are different.

**12.3.** The given equation of state (for one mole) of the gas is

$$P = RT/(v - b) - a/v^n \quad (n > 1). \quad (1)$$

Equating  $(\partial P/\partial v)_T$  and  $(\partial^2 P/\partial v^2)_T$  to zero, we get

$$v_c = \frac{n+1}{n-1}b \text{ and } T_c = \frac{4n(n-1)^{n-1}}{(n+1)^{n+1}} \frac{a}{b^{n-1}R}.$$

Equation (1) then gives

$$P_c = \left( \frac{n-1}{n+1} \right)^{n+1} \frac{a}{b^n},$$

whence  $RT_c/P_c v_c = 4n/(n^2 - 1)$ .

To determine the critical behaviour of this gas, we write

$$P = P_c(1 + \pi), \quad v = v_c(1 + \psi), \quad T = T_c(1 + t).$$

The equation of state then takes the form

$$1 + \pi = \frac{4n(1 + t)}{(n^2 - 1)(1 + \psi) - (n - 1)^2} - \frac{n + 1}{(n - 1)(1 + \psi)^n}.$$

Carrying out the usual expansions and retaining only the most important terms, we get

$$\pi \approx \frac{2n}{n-1}t - \frac{n(n+1)^2}{12}\psi^3 - \frac{n(n+1)}{n-1}t\psi.$$

It follows that

- (i) at  $t = 0$ ,  $\pi \approx -\{n(n+1)^2/12\}\psi^3$ , while at  $\psi = 0$ ,  $\pi \approx \{2n/(n-1)\}t$ ,
  - (ii) for  $t < 0$ , we obtain three values of  $\psi$ ; while  $|\psi_2| \ll |\psi_{1,3}|$ , implying once again that  $\pi \approx \{2n/(n-1)\}t$ ,  $\psi_{1,3} \approx \pm\{12/(n^2-1)\}^{1/2}|t|^{1/2}$ ,
  - (iii) the quantity  $-\left(\frac{\partial\psi}{\partial\pi}\right)_t \approx \frac{4(n-1)}{n(n+1)\{(n^2-1)\psi^2+4t\}}$
- $$\approx \begin{cases} (n-1)/n(n+1)t & (t > 0) \\ (n-1)/2n(n+1)|t| & (t < 0) \end{cases}.$$

Clearly, the critical exponents of this gas are the same as those of the van der Waals gas — regardless of the value of  $n$ . The critical amplitudes (as well as the critical constants  $P_c$ ,  $v_c$  and  $T_c$ ), however, do vary with  $n$  and hence are model-dependent.

**12.4.** The partition function of the system may be written as  $\sum_L \exp f(L)$ , where

$$f(L) = \ln N! - \ln(Np)! - \ln(Nq)! + \beta N \left( \frac{1}{2}qJL^2 + \mu BL \right).$$

Using the Stirling approximation (B.29), we get

$$f(L) \approx -Np \ln p - Nq \ln q + \beta N \left( \frac{1}{2}qJL^2 + \mu BL \right).$$

With  $p$  and  $q$  given by eqn. (1) of the problem, the function  $f(L)$  is *maximum* when

$$-\frac{1}{2}N(1 + \ln p) + \frac{1}{2}N(1 + \ln q) + \beta N(qJL + \mu B) = 0.$$

Substituting for  $p$  and  $q$ , the above condition takes the form

$$\frac{1}{2} \ln \frac{1+L}{1-L} = \beta(qJL + \mu B).$$

Comparing this with eqn. (12.5.10), we see that the value,  $L^*$ , of  $L$ , that maximizes the function  $f(L)$  is identical with  $\bar{L}$ .

The free energy and the internal energy of the system are now given by

$$A \approx -kTf(L^*) \approx NkT(p^* \ln p^* + q^* \ln q^*) - N \left( \frac{1}{2}qJL^{*2} + \mu BL^* \right),$$

$$U \approx -\frac{1}{2}NqJL^{*2} - N\mu BL^*,$$

whence

$$S \approx -Nk(p^* \ln p^* + q^* \ln q^*).$$

**12.5.** The relevant results of the preceding problem are

$$\frac{A}{N} = kT \left\{ \frac{1+L^*}{2} \ln \frac{1+L^*}{2} + \frac{1-L^*}{2} \ln \frac{1-L^*}{2} \right\} - \frac{1}{2} qJL^{*2} - \mu BL^*, \quad (1)$$

$$\bar{N}_+ = \frac{1}{2} N(1+L^*), \bar{N}_- = \frac{1}{2} N(1-L^*), \quad (2)$$

where  $L^*$  satisfies the maximization condition

$$\frac{1}{2} \{ \ln(1+L^*) - \ln(1-L^*) \} = \beta(qJL^* + \mu B). \quad (3)$$

Combining (1) and (3), we get

$$\frac{A}{N} = \frac{1}{2} kT \ln \frac{1-L^{*2}}{4} + \frac{1}{2} qJL^{*2}. \quad (4)$$

Now, using the correspondence given in Section 11.4 and remembering that  $L^*$  is identical with  $\bar{L}$ , we obtain from eqns. (2) and (4) the desired results for the quantities  $P$  and  $v$  pertaining to a lattice gas.

For the critical constants of the gas, we first note from eqn. (12.5.13) that  $T_c = qJ/k$ , i.e.  $q\varepsilon_0/4k$ ; the other constants then follow from the stated results for  $P$  and  $v$ , with  $B = 0$  and  $\bar{L} = 0$ .

**12.6.** The Hamiltonian of this model may be written as

$$H = -\frac{1}{2} c \sum_{i \neq j} \sigma_i \sigma_j - \mu B \sum_i \sigma_i.$$

The double sum here is equal to  $\sum_i \sigma_i \sum_j \sigma_j - \sum_i \sigma_i^2 = (NL)^2 - N$  which, for  $N \gg 1$ , is essentially equal to  $N^2 L^2$ . It follows that *asymptotically* our Hamiltonian is of the form

$$H = -\frac{1}{2} (cN) NL^2 - \mu BNL.$$

Now, this is precisely the Hamiltonian of the model studied in Problem 12.4, except for the fact that the quantity  $qJ$  there is replaced by the quantity  $cN$  here. We, therefore, infer that, in the limit  $N \rightarrow \infty$  and  $c \rightarrow 0$  (such that the product  $cN$  is held fixed), the mean-field approach of Problem 12.4 would be exact for the present model — provided that the fixed value of the product  $cN$  is identified with the quantity  $qJ$ . It follows that the critical temperature of this model would be  $cN/k$ .

**12.7 & 8.** Let us concentrate on one particular spin,  $\mathbf{s}_0$ , in the lattice and look at the part of the energy  $E$  that involves this spin, viz.  $-2J \sum_{j=1}^q \mathbf{s}_0 \cdot \mathbf{s}_j - g\mu_B \mathbf{s}_0 \cdot \mathbf{H}$ ; for notation, see Secs. 3.9 and 12.3. In the spirit of the mean field theory, we replace each of the  $\mathbf{s}_j$  by  $\bar{\mathbf{s}}$ , which modifies the foregoing expression to  $-g\mu_B \mathbf{s}_0 \cdot \mathbf{H}_{eff}$ , where

$$\mathbf{H}_{eff} = \mathbf{H} + \mathbf{H}' \quad (H' = 2qJ\bar{\mathbf{s}}/g\mu_B). \quad (1)$$

We now apply the theory of Sec. 3.9. Taking  $\mathbf{H}$  (and hence  $\bar{\mathbf{s}}$ ) to be in the direction of the positive  $z$ -axis, we get from eqn. (3.9.22)

$$\bar{\mu}_z = g\mu_B s B_s(x) \quad [x = \beta(g\mu_B s)H_{eff}], \quad (2)$$

where  $B_s(x)$  is the Brillouin function of order  $s$ . At high temperatures (where  $x \ll 1$ ), the function  $B_s(x)$  may be approximated by  $\{(s+1)/3s\}x$ , with the result that

$$\bar{\mu}_z \approx \frac{g^2 \mu_B^2 s(s+1)}{3kT} \left\{ H + \frac{2qJ\bar{\mu}_z}{g^2 \mu_B^2} \right\}. \quad (3)$$

The net magnetization, per unit volume, of the system is now given by the formula  $M = n\bar{\mu}_z$ , where  $n(= N/V)$  is the spin density in the lattice. We thus get from (3)

$$M \left( 1 - \frac{T_c}{T} \right) \approx \frac{CH}{T}, \text{ i.e. } M \approx \frac{CH}{T - T_c}, \text{ where} \quad (4)$$

$$T_c = \frac{2s(s+1)qJ}{3k}, \quad C = \frac{ng^2 \mu_B^2 s(s+1)}{3k}. \quad (5)$$

The Curie-Weiss law (4) signals the possibility of a phase transition as  $T \rightarrow T_c$  from above. However, this is only a *high-temperature* approximation, so no firm conclusion about a phase transition can be drawn from it. For that, we must look into the possibility of spontaneous magnetization in the system.

To study the possibility of spontaneous magnetization, we let  $H \rightarrow 0$  and write from (2)

$$\bar{\mu}_z = g\mu_B s B_s(x_0) \quad [x_0 = \beta(g\mu_B s)H' = 2sqJ\bar{\mu}_z/g\mu_B kT]. \quad (6)$$

In the close vicinity of the transition temperature, we expect  $\bar{\mu}_z$  to be much less than the saturation value  $g\mu_B s$ , so once again we approximate the function  $B_s(x_0)$  for  $x_0 \ll 1$ . However, this time we need a better approximation than the one employed above; this can be obtained by utilizing the series expansion

$$\coth x = \frac{1}{x} + \frac{x}{3} - \frac{x^3}{45} + \dots \quad (x \ll 1),$$

which yields the desired result:

$$B_s(x) = \frac{s+1}{3s}x - \frac{(s+1)\{s^2 + (s+1)^2\}}{90s^3}x^3 + \dots \quad (x \ll 1). \quad (7)$$

Substituting (7) into (6), we get

$$\bar{\mu}_z = \frac{T_c}{T}\bar{\mu}_z - \frac{b}{g^2\mu_B^2s^2} \left( \frac{T_c}{T}\bar{\mu}_z \right)^3 + \dots, \quad (8)$$

where  $T_c$  is the same as defined in (5), while  $b$  is a positive number given by

$$b = \frac{3}{10} \left\{ 1 + \frac{s^2}{(s+1)^2} \right\}. \quad (9)$$

Clearly, for  $T < T_c$ , a non-zero solution for  $\bar{\mu}_z$  is possible; in fact, for  $T \lesssim T_c$ ,

$$\bar{\mu}_z \approx (g\mu_B s / \sqrt{b})(1 - T/T_c)^{1/2}. \quad (10)$$

The long-range order  $\bar{L}_0$  is then given by

$$\bar{L}_0 \equiv \bar{\mu}_z / (g\mu_B s) \approx (1/\sqrt{b})(1 - T/T_c)^{1/2}. \quad (11)$$

For  $T \ll T_c$ , we employ the approximation

$$\coth x \approx 1 + 2e^{-2x}, \text{ whence } B_s(x) \approx 1 - s^{-1}e^{-x/s} \quad (x \gg 1). \quad (12)$$

Equation (6) now gives

$$\bar{L}_0 \approx 1 - s^{-1} \exp \left( -\frac{2sqJ}{kT} \right) = 1 - s^{-1} \exp \left\{ -\frac{3T_c}{(s+1)T} \right\}. \quad (13)$$

For  $s = 1/2$ , expressions (11) and (13) reduce precisely to eqns. (12.5.14 and 15) of the Ising model; the expression for  $T_c$  is different though.

**12.9 & 10.** We shall consider only the Heisenberg model; the study of the Ising model is somewhat simpler. Following the procedure of Problem 12.7, we find that the “effective field”  $\mathbf{H}_a$  experienced by any given spin  $\mathbf{s}$  on the sub-lattice  $a$  would be

$$\mathbf{H}_a = \mathbf{H} - \frac{2q'J'}{g\mu_B}\bar{\mathbf{s}}_b - \frac{2qJ}{g\mu_B}\bar{\mathbf{s}}_a, \quad (1a)$$

where  $q'$  and  $q$  are, respectively, the number of nearest neighbors on the other and on the same sub-lattice, while  $J'$  and  $J$  are the *magnitudes* of the corresponding interaction energies. Similarly,

$$\mathbf{H}_b = \mathbf{H} - \frac{2q'J'}{g\mu_B}\bar{\mathbf{s}}_a - \frac{2qJ}{g\mu_B}\bar{\mathbf{s}}_b. \quad (1b)$$

The net magnetization, per unit volume, of the sub-lattices  $a$  and  $b$  at high temperatures is then given by, see eqns. (2) and (3) of the preceding problem,

$$\begin{aligned}\mathbf{M}_a &\equiv \frac{1}{2}n(g\mu_B\bar{s}_a) \approx \frac{1}{2}n \cdot \frac{g^2\mu_B^2s(s+1)}{3kT} \left\{ \mathbf{H} - \frac{4q'J'}{ng^2\mu_B^2}\mathbf{M}_b - \frac{4qJ}{ng^2\mu_B^2}\mathbf{M}_a \right\}, \\ \mathbf{M}_b &\equiv \frac{1}{2}n(g\mu_B\bar{s}_b) \approx \frac{1}{2}n \cdot \frac{g^2\mu_B^2s(s+1)}{3kT} \left\{ \mathbf{H} - \frac{4q'J'}{ng^2\mu_B^2}\mathbf{M}_a - \frac{4qJ}{ng^2\mu_B^2}\mathbf{M}_b \right\}.\end{aligned}$$

Adding these two results, we obtain for the total magnetization of the lattice

$$\mathbf{M} \approx \frac{C}{T} \{ \mathbf{H} - (\gamma' + \gamma)\mathbf{M} \} \quad \left[ \gamma' = \frac{2q'J'}{ng^2\mu_B^2}, \gamma = \frac{2qJ}{ng^2\mu_B^2} \right]; \quad (2)$$

the parameter  $C$  here is the same as defined in eqn. (5) of the preceding problem. Equation (2) may be written in the form

$$\mathbf{M} \approx \frac{C}{T + \theta} \mathbf{H}, \text{ where } \theta = (\gamma' + \gamma)C; \quad (3)$$

this yields the desired result for the paramagnetic susceptibility of the lattice. Note that the parameter  $\theta$  here has no direct bearing on the onset of a phase transition in the system; for that, we must examine the possibility of spontaneous magnetization in the two sub-lattices.

To study the possibility of spontaneous magnetization, we let  $\mathbf{H} \rightarrow 0$ ; in that limit, the vectors  $\mathbf{M}_a$  and  $\mathbf{M}_b$  are equal in magnitude but opposite in direction. We may then write:  $\mathbf{M}_a = \mathbf{M}^*$ ,  $\mathbf{M}_b = -\mathbf{M}^*$ , and study only the former. In analogy with eqn. (6) of the preceding problem, we now have

$$M^* = \frac{1}{2}n(g\mu_Bs)B_s(x_0) \quad \left[ x_0 = \frac{4s(q'J' - qJ)M^*}{n g\mu_B kT} \right]. \quad (4)$$

We now employ expansion (7) of the preceding problem and get

$$M^* = \frac{T_N}{T} M^* - \frac{b}{\left(\frac{1}{2}n g\mu_Bs\right)^2} \left( \frac{T_N}{T} M^* \right)^3 + \dots, \quad (5)$$

where

$$T_N = \frac{2s(s+1)}{3k} (q'J' - qJ), \quad (6)$$

while the number  $b$  is the same as given by eqn. (9) of the preceding problem. Clearly, for  $T < T_N$ , a nonzero solution for  $M^*$  is possible. Note that the Néel temperature  $T_N = (\gamma' - \gamma)C$ , which should be contrasted with the parameter  $\theta$  of eqn. (3); moreover, for the antiferromagnetic transition to take place in the given system, we must have  $q'J' > qJ$ , the physical reason for which is not difficult to understand.

**12.11.** To determine the equilibrium distribution  $f(\sigma)$ , we minimize the free energy  $(E - TS)$  of the system under the obvious constraint  $\sum_{\sigma} f(\sigma) = 1$ . For this, we vary the function  $f(\sigma)$  to  $f(\sigma) + \delta f(\sigma)$  and require that the resulting variation

$$\begin{aligned} \delta(E - TS) &= \frac{1}{2} qN \sum_{\sigma', \sigma''} u(\sigma', \sigma'') \{f(\sigma') \delta f(\sigma'') + f(\sigma'') \delta f(\sigma')\} \\ &\quad + NkT \sum_{\sigma'} \{1 + \ln f(\sigma')\} \delta f(\sigma') = 0, \end{aligned}$$

while  $\sum_{\sigma'} \delta f(\sigma')$  is, of necessity, zero. Introducing the Lagrange multiplier  $\lambda$  and remembering that the function  $u(\sigma', \sigma'')$  is symmetric in  $\sigma'$  and  $\sigma''$ , our requirement takes the form

$$\sum_{\sigma'} \left\{ qN \sum_{\sigma''} u(\sigma', \sigma'') f(\sigma'') + NkT \{1 + \ln f(\sigma')\} - \lambda \right\} \delta f(\sigma') = 0.$$

Since the variation  $\delta f(\sigma')$  in this expression is arbitrary, the condition for equilibrium becomes

$$qN \sum_{\sigma''} u(\sigma', \sigma'') f(\sigma'') + NkT \ln f(\sigma') - N\mu = 0,$$

where  $\mu = (\lambda - NkT)/N$ . By a change of notation, we get the desired result

$$f(\sigma) = C \exp \left[ -\beta q \sum_{\sigma'} u(\sigma, \sigma') f(\sigma') \right], \quad (1)$$

where  $C$  is a constant to be determined by the normalization condition  $\sum_{\sigma} f(\sigma) = 1$ .

For the special case  $u(\sigma, \sigma') = -J\sigma\sigma'$ , where the  $\sigma$ 's can be either  $+1$  or  $-1$ , eqn. (1) becomes

$$f(\sigma) = C \exp[\beta q J \sigma \{f(1) - f(-1)\}]. \quad (2)$$

Writing  $f(\sigma) = \frac{1}{2}(1 + \bar{L}_0 \sigma)$ , the quantity  $f(1) - f(-1)$  becomes precisely equal to  $\bar{L}_0$ , and eqn. (2) takes the form

$$f(\sigma) = C \exp[\beta q J \sigma \bar{L}_0]. \quad (3)$$

From equation (3), we obtain

$$f(1) + f(-1) = 2C \cosh(\beta q J \bar{L}_0) = 1, \quad \text{while} \quad (4)$$

$$f(1) - f(-1) = 2C \sinh(\beta q J \bar{L}_0) = \bar{L}_0. \quad (5)$$

Dividing (5) by (4), we obtain the Weiss eqn. (12.5.11) for  $\bar{L}_0$ .

**12.12.** The configurational energy of the lattice is given by

$$\begin{aligned} E &= \frac{1}{2}qN[\varepsilon_{11} \cdot x_A(1+X) \cdot x_A(1-X) + \varepsilon_{12}\{x_A(1+X)(x_B + x_AX) \\ &\quad + x_A(1-X)(x_B - x_AX)\} + \varepsilon_{22}(x_B - x_AX)(x_B + x_AX)] \\ &= \frac{1}{2}qN[(\varepsilon_{11}x_A^2 + 2\varepsilon_{12}x_Ax_B + \varepsilon_{22}x_B^2) - 2\varepsilon x_A^2X^2] \quad \left[ \varepsilon = \frac{1}{2}(\varepsilon_{11} + \varepsilon_{22}) - \varepsilon_{12} \right]. \end{aligned}$$

The entropy, on the other hand, is given by

$$\begin{aligned} S &= k \left[ \ln \left( \frac{1}{2}N \right)! - \ln \left\{ \frac{1}{2}Nx_A(1+X) \right\}! - \ln \left\{ \frac{1}{2}N(x_B - x_AX) \right\}! + \right. \\ &\quad \left. \ln \left( \frac{1}{2}N \right)! - \ln \left\{ \frac{1}{2}Nx_A(1-X) \right\}! - \ln \left\{ \frac{1}{2}N(x_B + x_AX) \right\}! \right] \\ &\approx \frac{1}{2}Nk[-x_A(1+X) \ln\{x_A(1+X)\} - (x_B - x_AX) \ln(x_B - x_AX) \\ &\quad - x_A(1-X) \ln\{x_A(1-X)\} - (x_B + x_AX) \ln(x_B + x_AX)]. \end{aligned}$$

To determine the equilibrium value of  $X$ , we minimize the free energy of the system and obtain

$$\frac{\partial(E - TS)}{\partial X} = -2qN\varepsilon x_A^2X + \frac{1}{2}NkTx_A \ln \left\{ \frac{(1+X)(x_B + x_AX)}{(1-X)(x_B - x_AX)} \right\} = 0. \quad (1)$$

Now, since  $x_A + x_B = 1$ , the argument of the logarithm can be written as  $(1+z)/(1-z)$ , where  $z = X/(x_B + x_AX^2)$ . Equation (1) then takes the form

$$\frac{2q\varepsilon x_AX}{kT} = \frac{1}{2} \ln \frac{1+z}{1-z} = \tanh^{-1} z, \quad (2)$$

which is identical with the result quoted in the problem. For  $x_A = x_B = \frac{1}{2}$ , eqn. (2) reduces to the more familiar result

$$\frac{q\varepsilon X}{kT} = \tanh^{-1} \frac{2X}{1+X^2} = 2 \tanh^{-1} X, \quad (2a)$$

leading to a phase transition at the critical temperature  $T_c^0 = q\varepsilon/2k$ .

To determine the transition temperature  $T_c$  in the general case when  $x_A \neq x_B$ , we go back to eqn. (2) and write it in the form

$$\frac{X}{x_B + x_AX^2} = \tanh \left( \frac{4x_AT_c^0}{T} X \right). \quad (3)$$

For small  $X$ , we get

$$\begin{aligned} \frac{1}{x_B}X - \frac{x_A}{x_B^2}X^3 + \dots &= \frac{4x_AT_c^0}{T}X - \frac{1}{3} \left( \frac{4x_AT_c^0}{T} \right)^3 X^3 + \dots, \text{ i.e.} \\ \frac{1}{x_B} \left( \frac{4x_Ax_BT_c^0}{T} - 1 \right) X - \frac{1}{3x_B^3} \left[ \left( \frac{4x_Ax_BT_c^0}{T} \right)^3 - 3x_Ax_B \right] X^3 + \dots &= 0. \end{aligned}$$



It is now straightforward to see that for  $T < 4x_A x_B T_c^0$ , a non-zero solution for  $X$  is possible whereas for  $T \geq 4x_A x_B T_c^0$ ,  $X = 0$  is the only possibility. The transition temperature  $T_c$  is, therefore, given by  $4x_A(1 - x_A)T_c^0$ .

**12.13.** For a complete solution to this problem, see Kubo (1965), problem 5.6, pp. 335–7.

- 12.14.** (a) Setting  $\bar{N}_{++} + \bar{N}_{--} + \bar{N}_{+-} = \frac{1}{2}qN$ , we find that, *in equilibrium*,  $\gamma = 1/(1 + s\bar{L}^2)$ . So, in general, it may be written as  $1/(1 + sL^2)$ .  
 (b) As in Problem 12.4, we write  $Q(B, T) = \sum_L \exp f(L)$ , where

$$\begin{aligned} f(L) &= \ln N! - \ln N_+! - \ln N_-! - \beta E, \text{ with} \\ N_+ &= \frac{1}{2}N(1 + L), \quad N_- = \frac{1}{2}N(1 - L), \\ \text{and } E &= -J(N_{++} + N_{--} - N_{+-}) - \mu B(N_+ - N_-) \\ &= -J \cdot \frac{1}{2}qN(L^2 + s)/(1 + sL^2) - \mu BNL. \end{aligned}$$

The condition that *maximizes*  $f(L)$  now reads:

$$\frac{1}{2} \ln \frac{1 + L}{1 - L} = \beta \left[ qJ \frac{(1 - s^2)L}{(1 + sL^2)^2} + \mu B \right].$$

In the close vicinity of the critical point,  $L \ll 1$  — with the result that

$$\frac{1}{2} \ln \frac{1 + L}{1 - L} \simeq \beta [qJ(1 - s^2)L + \mu B] \quad (T \simeq T_c).$$

Comparing this with the corresponding equation in the solution to Problem 12.4, we infer that the *critical behavior* of this model is qualitatively the same as one encounters in the Bragg-Williams approximation. Quantitatively, though, the *effective* spin-spin interaction is reduced by the factor  $(1 - s^2)$  — leading to a critical temperature  $T_c = (1 - s^2)qJ/k$ , instead of  $qJ/k$ .

- (c) As for the specific-heat singularity, the limit  $T \rightarrow T_{c-}$  would be identical with the one obtained in Sec. 12.5; see the derivation leading to eqn. (12.5.18) and note that the replacement of  $J$  by  $(1 - s^2)J$  does not affect the final result  $\frac{3}{2}Nk$ . For  $T > T_c$ ,  $\bar{L}_0$  is identically zero. We are then left with a finite configurational energy,  $-\frac{1}{2}qJNs$ , that arises from the (assumed) short-range order in the system; however, unlike in the Bethe approximation, this energy is temperature-independent and hence does not entail any specific heat. The singularity in question is, therefore, precisely the same as the one encountered in Sec. 12.5 and depicted in Fig. 12.8.

**12.15.** Using eqn. (12.6.30), we get

$$\begin{aligned}\frac{S_\infty - S_c}{Nk} &= \frac{1}{Nk} \int_{T_c}^{\infty} \frac{C(T)dT}{T} = \frac{1}{2}q \int_0^{\gamma_c} \gamma \operatorname{sech}^2 \gamma d\gamma \\ &= \frac{1}{2}q(\gamma_c \tanh \gamma_c - \ln \cosh \gamma_c).\end{aligned}$$

Next, we use eqn. (12.6.11) and obtain

$$\begin{aligned}\frac{S_\infty - S_c}{Nk} &= \frac{1}{2}q \left[ \frac{1}{2} \ln \left( \frac{q}{q-2} \right) \frac{1}{q-1} + \frac{1}{2} \ln \left\{ 1 - \left( \frac{1}{q-1} \right)^2 \right\} \right] \\ &= \frac{1}{4} \frac{q}{q-1} \{ \ln q - \ln(q-2) \} + \frac{1}{4} q \{ \ln q + \ln(q-2) - 2 \ln(q-1) \}.\end{aligned}$$

In view of the fact that  $S_\infty = Nk \ln 2$ , we finally get

$$\frac{S_c}{Nk} = \ln 2 - \frac{1}{4} \frac{q^2}{q-1} \ln q + \frac{1}{2} q \ln(q-1) - \frac{1}{4} \frac{q(q-2)}{q-1} \ln(q-2),$$

which leads to the desired result.

For  $q \gg 1$ , the stated expression for  $S_c/Nk$  reduces to

$$\begin{aligned}\ln 2 + \frac{q}{2} \left\{ -\frac{1}{q} + O\left(\frac{1}{q^2}\right) \right\} - \frac{q}{4} \left\{ 1 + O\left(\frac{1}{q}\right) \right\} \left\{ -\frac{2}{q} + O\left(\frac{1}{q^2}\right) \right\} \\ = \ln 2 + O\left(\frac{1}{q}\right),\end{aligned}$$

which tends to the limit  $\ln 2$  as  $q \rightarrow \infty$ .

**12.16.** Using eqn. (12.6.14), we get

$$\begin{aligned}\chi \equiv \left( \frac{\partial \bar{M}}{\partial B} \right)_T &= \frac{N\mu^2}{kT} \left( \frac{\partial \bar{L}}{\partial \alpha} \right)_T = \frac{2N\mu^2}{kT} \frac{1 + \exp(-2\gamma) \cosh(2\alpha + 2\alpha')}{\{\cosh(2\alpha + 2\alpha') + \exp(-2\gamma)\}^2} \\ &\quad \left\{ 1 + \left( \frac{\partial \alpha'}{\partial \alpha} \right)_T \right\}.\end{aligned}\tag{1}$$

To determine  $(\partial \alpha' / \partial \alpha)_T$ , we differentiate (12.6.8) logarithmically and obtain after some simplification

$$\left( \frac{\partial \alpha'}{\partial \alpha} \right)_T = \frac{(q-1) \{ \tanh(\alpha + \alpha' + \gamma) - \tanh(\alpha + \alpha' - \gamma) \}}{2 - (q-1) \{ \tanh(\alpha + \alpha' + \gamma) - \tanh(\alpha + \alpha' - \gamma) \}}.\tag{2}$$

Substituting (2) into (1) and letting  $\alpha \rightarrow 0$ , we get

$$\begin{aligned}\chi_0 &= \frac{4N\mu^2}{kT} \frac{1 + \exp(-2\gamma) \cosh(2\alpha')}{\{\cosh(2\alpha') + \exp(-2\gamma)\}^2} \\ &\quad \frac{1}{2 - (q-1) \{ \tanh(\alpha' + \gamma) - \tanh(\alpha' - \gamma) \}}.\end{aligned}\tag{3}$$

To study the critical behavior of  $\chi_0$ , we let  $\alpha' \rightarrow 0$  and  $\gamma \rightarrow \gamma_c$ . Using eqn. (12.6.11), we see that, while the first two factors of expression (3) reduce to

$$\frac{4N\mu^2}{kT_c} \frac{1}{1 + \exp(-2\gamma_c)} = \frac{2N\mu^2}{kT_c} \frac{q}{q-1}, \quad (4)$$

the last factor diverges. To determine the nature of the divergence, we write  $\gamma = \gamma_c(1-t)$  and carry out expansions in powers of  $t$  and  $\alpha'$ . Thus

$$\begin{aligned} \tanh(\gamma \pm \alpha') &= \tanh \gamma_c + \operatorname{sech}^2 \gamma_c (-\gamma_c t \pm \alpha') \\ &\quad - \operatorname{sech}^2 \gamma_c \tanh \gamma_c (-\gamma_c t \pm \alpha')^2 + \dots, \end{aligned}$$

so that

$$\begin{aligned} \tanh(\gamma + \alpha') + \tanh(\gamma - \alpha') &\approx 2 \tanh \gamma_c - 2 \operatorname{sech}^2 \gamma_c \cdot \gamma_c t \\ &\quad - 2 \operatorname{sech}^2 \gamma_c \tanh \gamma_c \cdot \alpha'^2; \end{aligned}$$

note that we have dropped terms of order  $t^2$  and higher. It now follows that

$$\begin{aligned} 2 - (q-1)\{\tanh(\gamma + \alpha') + \tanh(\gamma - \alpha')\} \\ \approx 2(q-1)\operatorname{sech}^2 \gamma_c (\gamma_c t + \tanh \gamma_c \cdot \alpha'^2). \end{aligned} \quad (5)$$

Substituting (4) and (5) into (3), we finally obtain

$$\chi_0 \approx \frac{N\mu^2}{kT_c} \frac{1}{(q-2)(\gamma_c t + \tanh \gamma_c \cdot \alpha'^2)}. \quad (6)$$

For  $t > 0$ ,  $\alpha' = 0$ ; eqn. (6) then gives

$$\chi_0 \approx \frac{N\mu^2}{kT_c} \frac{1}{(q-2)\gamma_c t}. \quad (7a)$$

For  $t < 0$ ,  $\alpha'$  is given by eqn. (12.6.13), whence  $\alpha'^2 \simeq -3(q-1)\gamma_c t$ ; we now get

$$\chi_0 \approx \frac{N\mu^2}{kT_c} \frac{1}{2(q-2)\gamma_c |t|}. \quad (7b)$$

Note that, for large  $q$ , the quantity

$$(q-2)\gamma_c = \frac{1}{2}(q-2) \ln \left( \frac{q}{q-2} \right) = 1 + O\left(\frac{1}{q}\right);$$

eqns. (7) then reduce to eqns. (12.5.22) of the Bragg-Williams approximation.

**12.19.** We refer to the solutions to Problems 12.4 and 12.5, whereby

$$\begin{aligned}
 \psi_0 &\equiv \left( \frac{A}{NkT} \right)_{B=0} = \frac{1+m_0}{2} \ln \frac{1+m_0}{2} + \frac{1-m_0}{2} \ln \frac{1-m_0}{2} - \frac{1}{2} \frac{qJ}{kT} m_0^2 \\
 &= \frac{1}{2} \ln \frac{1-m_0^2}{4} + \frac{m_0}{2} \ln \frac{1+m_0}{1-m_0} - \frac{1}{2} \frac{T_c}{T} m_0^2 \\
 &= -\ln 2 + \frac{1}{2} \left( -m_0^2 - \frac{m_0^4}{2} - \dots \right) + m_0 \left( m_0 + \frac{m_0^3}{3} + \dots \right) \\
 &\quad - \frac{1}{2} (1-t+\dots) m_0^2 \\
 &\approx -\ln 2 + \frac{1}{2} t m_0^2 + \frac{1}{12} m_0^4.
 \end{aligned}$$

Comparing this expression with eqn. (12.9.5), we infer that in the Bragg-Williams approximation  $r_1 = 1/2$  and  $s_0 = 1/12$ . Now, substituting these values of  $r_1$  and  $s_0$  into eqns. (12.9.4, 9–11 and 15), we see that the corresponding eqns. (12.5.14, 22, 24 and 18) are readily verified.

A similar calculation under the Bethe approximation is somewhat tedious; the answer, nevertheless, is

$$r_1 = \frac{q-2}{4} \ln \frac{q}{q-2}, \quad s_0 = \frac{(q-1)(q-2)}{12q^2}.$$

**12.20.** The equilibrium values of  $m$  in this case are given by the equation

$$\psi'_h = -h + 2rm + 4sm^3 + 6um^5 = 0 \quad (u > 0). \quad (1)$$

With  $h = 0$ , we get:  $m_0 = 0, \pm\sqrt{A_+}$  or  $\pm\sqrt{A_-}$ , where

$$A_{\pm} = \frac{-s \pm \sqrt{s^2 - 3ur}}{3u}. \quad (2)$$

First of all, we note that, for  $A_{\pm}$  to be real,  $s^2$  must be  $\geq 3ur$ . This presents no problem if  $r \leq 0$ ; however, if  $r > 0$ , then  $s$  must be either  $\geq \sqrt{3ur}$  or  $\leq -\sqrt{3ur}$ . We also observe that

$$A_+ A_- = \frac{r}{3u} \quad \text{and} \quad A_+ + A_- = -\frac{2s}{3u}.$$

It follows that (i) if  $r < 0$ , then one of the  $A$ 's will be positive, the other negative (in fact, since  $A_- < A_+$ ,  $A_-$  will be negative and  $A_+$  positive), (ii) if  $r = 0$ , then for  $s > 0$ ,  $A_-$  will be negative and  $A_+ = 0$ , for  $s = 0$  both  $A_-$  and  $A_+$  will be zero whereas for  $s < 0$ ,  $A_-$  will be zero while  $A_+$  will be positive (and equal to  $2|s|/3u$ ), (iii) if  $r > 0$ , then for  $s \geq \sqrt{3ur}$  both  $A_+$  and  $A_-$  will be negative whereas for  $s \leq -\sqrt{3ur}$  both  $A_+$  and  $A_-$  will be positive. We must, in this context, remember that only a *positive*  $A$  will yield a *real*  $m_0$ . Finally, since

$$\psi''_0 = 2r + 12sm_0^2 + 30um_0^4, \quad (3)$$

the extremum at  $m_0 = 0$  is a *maximum* if  $r < 0$ , a *minimum* if  $r > 0$ . It follows that for  $r < 0$  the function  $\psi_0$  is minimum at  $m_0 = \pm\sqrt{A_+}$  and for  $r > 0$  (and  $s \leq -\sqrt{3ur}$ ) it is maximum at  $m_0 = \pm\sqrt{A_-}$  and minimum at  $m_0 = \pm\sqrt{A_+}$ . We, therefore, have to contend only with  $A_+$ .

The foregoing observations should suffice to prove statements (a), (e), (f) and (g) of this problem. For the rest, we note that the function  $\psi_0(m_0)$  may be written as

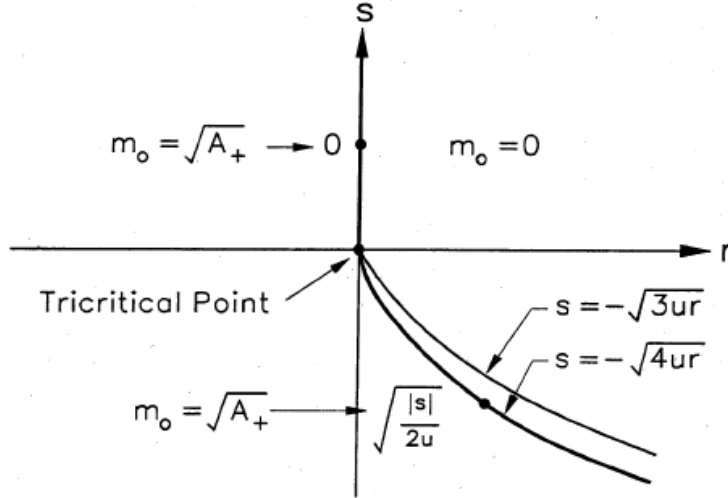
$$\psi_0(m_0) = q + (rm_0^2 + sm_0^4 + um_0^6) - \frac{1}{4}m_0(2rm_0 + 4sm_0^3 + 6um_0^5) \quad (4a)$$

$$= q + \frac{1}{2}m_0^2(r - um_0^4); \quad (4b)$$

note that in writing (4a) we have added an expression which, by the minimization condition, is identically zero. It now follows from eqn. (4b) that  $\psi_0(m_0 = 0)$  is less than, equal to or greater than  $\psi_0(m_0 \neq 0)$  according as  $m_0^2$  is less than, equal to or greater than  $\sqrt{r/u}$ . The dividing line corresponds to  $A_+ = \sqrt{r/u}$ , i.e.

$$\frac{-s + \sqrt{s^2 - 3ur}}{3u} = \sqrt{\frac{r}{u}}, \text{ i.e. } s = -\sqrt{4ur};$$

see the accompanying figure. We also note that, in reference to the dividing line,  $m_0^2$  decreases monotonically towards the limiting value  $\sqrt{r/3u}$  as  $s \rightarrow -\sqrt{3ur}$  and increases monotonically as  $s$  decreases below  $-\sqrt{4ur}$ . These observations should suffice to prove statements (b), (c) and (d).



**12.21.** With  $s = 0$ , the order parameter  $m$  is given by the equation

$$\psi'_h = -h + 2rm + 6um^5 = 0.$$

For  $|t| \ll 1$ , we set  $r \approx r_1 t$ ; the equation of state then takes the form

$$h \approx 2r_1 t m + 6um^5.$$

With  $t < 0$  and  $h \rightarrow 0$ , we get:  $m_0 \approx (r_1/3u)^{1/4}|t|^{1/4}$ , giving  $\beta = 1/4$ . With  $t = 0$ , we get:  $h \approx 6um^5$ , giving  $\delta = 5$ . For susceptibility, we have

$$\chi \sim \left( \frac{\partial m}{\partial h} \right)_t \approx \frac{1}{2r_1 t + 30um^4}.$$

It follows that

$$\chi_0 \approx \begin{cases} 1/2 r_1 t & (t > 0, m \rightarrow 0) \\ 1/8 r_1 |t| & (t < 0, m \rightarrow m_0), \end{cases}$$

giving  $\gamma = \gamma' = 1$ . Finally, using the scaling relation  $\alpha + 2\beta + \gamma = 2$ , we get:  $\alpha = 1/2$ .

**12.22.** (a) We introduce the variable  $\psi = (v_g - v_c)/v_c \simeq (v_c - v_\ell)/v_c$  and obtain

$$\psi \sim \left( \frac{\partial G^{(s)}}{\partial \pi} \right)_t \sim |t|^{2-\alpha-\Delta} g' \left( \frac{\pi}{|t|^\Delta} \right). \quad (2)$$

With  $t < 0$  and  $\pi \rightarrow 0$ , we get:  $\psi \sim |t|^\beta$ , where  $\beta = 2 - \alpha - \Delta$ . It follows that the quantities  $(\rho_\ell - \rho_c)$ ,  $(\rho_c - \rho_g)$  and  $(\rho_\ell - \rho_g)$  all vary as  $|t|^\beta$ .

(b) Writing  $g'(x)$  as  $x^{\beta/\Delta} f(x)$ , eqn. (1) takes the form

$$\psi \sim \pi^{\beta/\Delta} f(\pi/|t|^\Delta). \quad (2)$$

It follows that the quantity  $|t|^\Delta/\pi$  is a universal function of the quantity  $\pi^{\beta/\Delta}/\psi$ , i.e.

$$|t| \sim \pi^{1/\Delta} \times \text{a universal function of } (\pi/\psi^{\Delta/\beta}).$$

It is now clear that, at  $t = 0$ ,  $\pi \sim \psi^\delta$ , where  $\delta = \Delta/\beta$ .

(c) For the isothermal compressibility of the system, we have from (1)

$$\kappa_T \equiv -\frac{1}{v} \left( \frac{\partial v}{\partial P} \right)_T \sim \left( \frac{\partial \psi}{\partial \pi} \right)_t \sim |t|^{\beta-\Delta} g'' \left( \frac{\pi}{|t|^\Delta} \right).$$

It follows that, in the limit  $\pi \rightarrow 0$ ,  $\kappa_T \sim |t|^{-\gamma}$ , where  $\gamma = \Delta - \beta = \beta(\delta - 1)$ . As for the coefficient of volume expansion, we have the relationship

$$\alpha_P = \frac{1}{v} \left( \frac{\partial v}{\partial T} \right)_P = -\frac{1}{v} \left( \frac{\partial v}{\partial P} \right)_T \left( \frac{\partial P}{\partial T} \right)_v = \kappa_T \left( \frac{\partial P}{\partial T} \right)_v.$$

In the region of phase transition,  $(\partial P/\partial T)_v$  is simply  $(dP/dT)$ , which is *non-singular*. Accordingly,  $\alpha_P \sim \kappa_T \sim |t|^{-\gamma}$ . Similarly, in view of the

relation  $C_P = VT(dP/dT)^2\kappa_T$ , established in Problem 13.25, we infer that  $C_P \sim \kappa_T \sim |t|^{-\gamma}$ .

For  $C_V$ , we go back to the given expression for  $G^{(s)}$  and write

$$\begin{aligned} S^{(s)} &= - \left( \frac{\partial G^{(s)}}{\partial T} \right)_P \sim |t|^{1-\alpha} \times \text{a universal function of } \left( \frac{\pi}{|t|^\Delta} \right) \\ &\sim |t|^{1-\alpha} \times \text{a universal function of } \left( \frac{\psi}{|t|^\beta} \right). \end{aligned}$$

It then follows that

$$C_V^{(s)} = T \left( \frac{\partial S^{(s)}}{\partial T} \right)_V \sim |t|^{-\alpha} \times \text{a universal function of } \left( \frac{\psi}{|t|^\beta} \right).$$

Now, letting  $\psi \rightarrow 0$ , we obtain:  $C_V^{(s)} \sim |t|^{-\alpha}$ . And, in view of the relation  $C_V = VT(dP/dT)^2\kappa_S$ , also established in Problem 13.25, we infer that  $\kappa_S \sim C_V \sim |t|^{-\alpha}$ .

Finally, for the latent heat of vaporization  $\ell$ , we invoke the Clapeyron equation,

$$\frac{dP_\sigma}{dT} = \frac{\ell}{T(v_g - v_\ell)},$$

and conclude that  $\ell \sim |t|^\beta$ .

**12.23.** We make the following observations:

- (i) With  $h = 0$  and  $t < 0$ ,  $m_0 = 0$  or  $\pm(b^{-1}|t|)^{1/2}$ , giving  $\beta = 1/2$ .
- (ii) With  $t = 0$ ,  $h = abm^{2\Theta+1}$ , giving  $\delta = 2\Theta + 1$ .
- (iii) The quantity

$$\left( \frac{\partial m}{\partial h} \right)_t = \frac{1}{a(1 + 3bm^2)(t + bm^2)^{\Theta-1}}.$$

With  $t > 0$  and  $h \rightarrow 0$ ,  $m \rightarrow 0$  and we are left with

$$\left( \frac{\partial m}{\partial h} \right)_t \approx \frac{1}{at^\Theta}, \text{ giving } \gamma = \Theta.$$

The scaling relation (12.10.22) is readily verified.

**12.24.** For  $\mathbf{r}_i \neq \mathbf{r}_j$ , eqns. (12.11.22 and 26) give

$$(\nabla^2 - \xi^{-2})g(\mathbf{r}) = 0. \quad (1)$$

Now, if  $g(\mathbf{r})$  is a function of  $r$  only then

$$\begin{aligned}\nabla g &= \frac{dg}{dr} \nabla r = \frac{dg}{dr} \frac{\mathbf{r}}{r} = \frac{dg}{dr} \left( \frac{x_1}{r}, \dots, \frac{x_d}{r} \right), \text{ whence} \\ \nabla \cdot \nabla g &= \sum_{i=1}^d \frac{\partial}{\partial x_i} \left( \frac{dg}{dr} \frac{x_i}{r} \right) = \sum_{i=1}^d \left\{ \frac{dg}{dr} \frac{1}{r} + \left( \frac{d^2 g}{dr^2} \frac{1}{r} - \frac{dg}{dr} \frac{1}{r^2} \right) \frac{x_i^2}{r} \right\} \\ &= \frac{d^2 g}{dr^2} + \frac{dg}{dr} \frac{1}{r} (d-1).\end{aligned}\quad (2)$$

Substituting (2) into (1), we obtain the desired differential equation — of which (12.11.26) is the *exact* solution.

Substituting (12.11.27) into the left-hand side of the given differential equation, we get

$$\text{const.} \frac{e^{-r/\xi}}{r^{(d-1)/2}} \left[ \left( \frac{1}{\xi^2} + \dots \right) + (\dots) - \frac{1}{\xi^2} \right];$$

the ratio of the terms omitted to the ones retained is  $O(\xi/r)$ . Clearly, the equation is satisfied for  $r \gg \xi$ . Similarly, substituting (12.11.28) instead, we get

$$\text{const.} \frac{1}{r^{d-2}} \left[ \frac{(2-d)(1-d)}{r^2} + \frac{d-1}{r} \frac{2-d}{r} - (\dots) \right];$$

the ratio of the term omitted to the ones retained is now  $O(r/\xi)^2$ . Clearly, the equation is again satisfied but this time for  $r \ll \xi$ .

**12.25.** By the scaling hypothesis of Sec. 12.10, we expect that, for  $h > 0$  and  $t > 0$ ,

$$\begin{aligned}\xi(t, h) &= \xi(t, 0) \times \text{a universal function of } (h/t^\Delta) \\ &= \xi(t, 0) \times \text{a universal function of } (t/h^{1/\Delta}).\end{aligned}$$

Now, in view of eqn. (11.12.1), we may write

$$\begin{aligned}\xi(t, h) &\sim t^{-\nu} (t/h^{1/\Delta})^\nu \times \text{a universal function of } (t/h^\Delta) \\ &= h^{-\nu/\Delta} \times \text{a universal function of } (t/h^{1/\Delta}).\end{aligned}$$

At  $t = 0$ , we obtain:  $\xi(0, h) \sim h^{-\nu^c}$ , where  $\nu^c = \nu/\Delta$ .

By a similar argument,  $\chi(0, h) \sim h^{-\gamma^c}$ , where

$$\gamma^c = \gamma/\Delta = \beta(\delta - 1)/\beta\delta = (\delta - 1)/\delta.$$

**12.26.** Clearly, the ratio  $(\rho_0/\rho_s) \sim |t|^{2\beta-\nu}$ . In view of the scaling relations  $\alpha + 2\beta + \gamma = 2$ ,  $\gamma = (2 - \eta)\nu$  and  $d\nu = 2 - \alpha$ , we get

$$2\beta - \nu = (2 - \alpha - \gamma) - \nu = \{d\nu - (2 - \eta)\nu\} - \nu = (d - 3 + \eta)\nu.$$

Setting  $d = 3$ , we obtain the desired result.



**12.27.** By definition,

$$\sigma \equiv \psi_A(t) \sim |t|^\mu \quad (t \lesssim 0). \quad (1)$$

By an argument similar to the one that led to eqn. (12.12.14), we get

$$\psi_A(t) \sim A^{-1} \sim \xi^{-(d-1)}, \quad (2)$$

where  $A$  is the “area of a typical domain in the liquid-vapor interface”. Now, for a *scalar* model ( $n = 1$ ), to which the liquid-vapor transition belongs,  $\xi \sim |t|^{-\nu}$ . Equations (1) and (2) then lead to the desired result

$$\mu = (d-1)\nu = (2-\alpha)(d-1)/d.$$

# Chapter 13

**13.1.** Since  $\bar{M} = (\bar{N}_+ - \bar{N}_-)\mu$  and  $\bar{N}_+ + \bar{N}_- = N$ , we readily see that

$$\bar{N}_\pm = \frac{1}{2}N \left( 1 \pm \frac{\bar{M}}{N\mu} \right) = \frac{1}{2}N \frac{P(\beta, B) \pm \sinh x}{P(\beta, B)} \quad (x = \beta\mu B). \quad (1)$$

Next, comparing eqns. (12.3.19) and (13.2.12), and keeping in mind that  $q = 2$ , we get

$$\bar{N}_+ - \bar{N}_{++} = N \frac{e^{-4\beta J}}{2D(\beta, B)} = N \frac{P^2(\beta, B) - \sinh^2 x}{2D(\beta, B)}. \quad (2)$$

It follows from eqns. (1) and (2) that

$$\begin{aligned} \bar{N}_{++} &= (N/2D) \{ (P + \sinh x)(P + \cosh x) - (P^2 - \sinh^2 x) \} \\ &= (N/2D) \{ (P + \sinh x)(\cosh x + \sinh x) \}, \end{aligned} \quad (3)$$

which is the desired result. Equation (12.3.17) now gives

$$\bar{N}_{+-} = 2(\bar{N}_+ - \bar{N}_{++}) \text{ and } \bar{N}_{--} = N - 2\bar{N}_+ + \bar{N}_{++} = \bar{N}_{++} - (\bar{M}/\mu).$$

The number  $\bar{N}_{+-}$  is just twice the expression (2). The number  $\bar{N}_{--}$  is given by

$$\begin{aligned} \bar{N}_{--} &= (N/2D) \{ (P + \sinh x)(\cosh x + \sinh x) - \sinh x \cdot 2(P + \cosh x) \} \\ &= (N/2D) \{ (P - \sinh x)(\cosh x - \sinh x) \}, \end{aligned} \quad (4)$$

which is the desired result.

It is straightforward to check that the sum

$$\bar{N}_{++} + \bar{N}_{--} = (N/D)(P \cosh x + \sinh^2 x) = (N/D) \{ P \cosh x + (P^2 - e^{-4\beta J}) \};$$

adding  $\bar{N}_{+-}$ , one obtains the expected result  $N$ . Finally, the product

$$\bar{N}_{++}\bar{N}_{--} = (N/2D)^2 \{ P^2 - \sinh^2 x \} = (N/2D)^2 e^{-4\beta J}.$$

Equation (12.6.22) is now readily verified.

- 13.2.** (a) In view of eqn. (12.3.18), the quantity  $(N_{++} + N_{--} - N_{+-})$  that appears in the Hamiltonian (12.3.19) of the lattice may be written as  $(\frac{1}{2}qN - 2N_{+-})$ . The partition function (12.3.20) then assumes the form stated here.
- (b) A complete solution to this problem can be found in the first edition of this book — Sec. 12.9A, pp. 414–8. In any case, this problem is a special case,  $q = 2$ , of the next problem which is treated here at sufficient length.

**13.3.** In the notation of Problem 13.2, we now have

$$\begin{aligned} \ln g_N(N_+, N_{+-}) &\approx \frac{1}{2}qN \ln \left( \frac{1}{2}qN \right) - N_{++} \ln N_{++} - N_{--} \ln N_{--} \\ &\quad - N_{+-} \ln \left( \frac{1}{2}N_{+-} \right) + (q-1)\{N_+ \ln N_+ + N_- \ln N_- - N \ln N\}, \end{aligned} \quad (1)$$

where, by virtue of eqn. (12.3.17),

$$N_{++} = \frac{1}{2}qN_+ - \frac{1}{2}N_{+-}, \quad N_{--} = \frac{1}{2}qN_- - \frac{1}{2}N_{+-} \quad \text{and} \quad N_- = N - N_+. \quad (2)$$

Now, as usual, the logarithm of the partition function may be approximated by the logarithm of the largest term in the sum over  $N_+$  and  $N_{+-}$ , with the result that

$$\ln Q_N(B, T) \approx \ln g_N(N_+^*, N_{+-}^*) + \beta J \left( \frac{1}{2}qN - 2N_{+-}^* \right) + \beta \mu B (2N_+^* - N), \quad (3)$$

where  $N_+^*$  and  $N_{+-}^*$  are the values of the variables  $N_+$  and  $N_{+-}$  that *maximize* the summand (or the log of it). The maximizing conditions turn out to be

$$\begin{aligned} \frac{\partial}{\partial N_+}(\dots) &= -(1 + \ln N_{++}) \left( \frac{1}{2}q \right) - (1 + \ln N_{--}) \left( -\frac{1}{2}q \right) + \\ &\quad (q-1)\{(1 + \ln N_+) + (1 + \ln N_-)(-1)\} + 2\beta \mu B \\ &= \ln \left\{ \left( \frac{N_{--}}{N_{++}} \right)^{q/2} \left( \frac{N_+}{N_-} \right)^{q-1} \right\} + 2\beta \mu B = 0, \quad \text{and} \end{aligned} \quad (4)$$

$$\begin{aligned} \frac{\partial}{\partial N_{+-}}(\dots) &= -(1 + \ln N_{++}) \left( -\frac{1}{2} \right) - (1 + \ln N_{--}) \left( -\frac{1}{2} \right) - \\ &\quad \left\{ 1 + \ln \left( \frac{1}{2}N_{+-} \right) \right\} - 2\beta J \\ &= \ln \left\{ \frac{N_{++}^{1/2} N_{--}^{1/2}}{(\frac{1}{2}N_{+-})} \right\} - 2\beta J = 0. \end{aligned} \quad (5)$$

Equations (4) and (5), with the help of eqns. (2), determine the equilibrium values of all the numbers involved in the problem; eqn. (3) then determines the rest of the properties of the system.

To compare these results with the ones following from the Bethe approximation, we first observe that eqn. (5) here is identical with the corresponding eqn. (12.6.22) of that treatment. As for eqn. (4), we go back to eqns. (12.6.4 and 8) of the Bethe approximation, whereby

$$\frac{\bar{N}_+}{\bar{N}_-} = e^{2\alpha} \left[ \frac{\cosh(\alpha + \alpha' + \gamma)}{\cosh(\alpha + \alpha' - \gamma)} \right]^q = e^{2\alpha + 2\alpha'q/(q-1)}$$

and to eqn. (12.6.21), whereby

$$\frac{\bar{N}_{--}}{\bar{N}_{++}} = e^{-4(\alpha + \alpha')}.$$

It follows that

$$\left( \frac{\bar{N}_{--}}{\bar{N}_{++}} \right)^{q/2} \left( \frac{\bar{N}_+}{\bar{N}_-} \right)^{q-1} = e^{-2q(\alpha + \alpha') + 2\alpha(q-1) + 2\alpha'q} = e^{-2\alpha} \quad (\alpha = \beta\mu B),$$

in complete agreement with eqn. (4). Hence the equivalence of the two treatments.

**13.4.** By eqns. (13.2.8 and 37),

$$\xi^{-1}(B, T) = \ln \left[ \frac{\cosh x + \{e^{-4\beta J} + \sinh^2 x\}^{1/2}}{\cosh x - \{e^{-4\beta J} + \sinh^2 x\}^{1/2}} \right] \quad (x = \beta\mu B).$$

As  $T \rightarrow T_c$  (which, in this case, is 0),

$$\xi^{-1}(B, T_c) \approx \ln \left[ \frac{\cosh x + \sinh x}{\cosh x - \sinh x} \right] = 2x.$$

It follows that  $\xi(B, T_c) \approx (1/2x) \sim B^{-1}$ , which means that the critical exponent  $\nu^c = 1$ . Now, a reference to eqns. (13.2.21 and 35) tells us that  $\nu = \Delta$ . The relation  $\nu^c = \nu/\Delta$  is thus verified.

**13.5.** On integration over  $B$ , our partition function takes the form

$$Q_N(s, T) \sim \left( \frac{2\pi s}{\beta N} \right)^{1/2} \sum_{\{\sigma_i\}} \exp \left\{ \frac{\beta\mu^2 s}{2N} \left( \sum_i \sigma_i \right)^2 + \beta J \sum_i \sigma_i \sigma_{i+1} \right\},$$

which implies an *effective* Hamiltonian given by the expression

$$H_{eff} = -\frac{1}{2}\mu^2 s NL^2 - J \sum_i \sigma_i \sigma_{i+1} \quad \left( L = N^{-1} \sum_i \sigma_i \right).$$

The first term here is equivalent to an *infinite-range* interaction of the type considered in Problem 12.6, with  $\mu^2 s$  playing the role of the quantity  $cN$  of that model. This is also equivalent to the Bragg-Williams model, with  $\mu^2 s \leftrightarrow qJ$ ; see Problem 12.4. It follows that, by virtue of this term, the system will undergo an order-disorder transition at a critical temperature  $T_c = \mu^2 s/k$ . The second term in the Hamiltonian will contribute towards the short-range order in the system.

We also note that the root-mean-square value of  $B$  in this model is  $(s/\beta N)^{1/2}$  which, for a given value of  $s$ , is negligibly small when  $N$  is large. The order-disorder transition is made possible by the fact that the resulting interaction is of an infinite range.

**13.6.** Since the Hamiltonian  $H\{\tau_i\}$  of the present model is formally similar to the Hamiltonian  $H\{\sigma_i\}$  of Sec. 13.2, the partition function of this system can be written down in analogy with eqn. (13.2.10):

$$\frac{1}{N} \ln Q \approx \ln \left[ e^{\beta J_2} \cosh(\beta J_1) + \{e^{-2\beta J_2} + e^{2\beta J_2} \sinh^2(\beta J_1)\}^{1/2} \right],$$

from which the various thermodynamic properties of the system can be derived. In particular, we get

$$\begin{aligned} \overline{\sigma_i \sigma_{i+1}} &= \frac{1}{\beta N} \frac{\partial}{\partial J_1} \ln Q = \frac{\sinh(\beta J_1)}{\{e^{-4\beta J_2} + \sinh^2(\beta J_1)\}^{1/2}}, \text{ and} \\ \overline{\sigma_i \sigma_{i+2}} &= \frac{1}{\beta N} \frac{\partial}{\partial J_2} \ln Q = 1 - \frac{2e^{-4\beta J_2}}{\{e^{-4\beta J_2} + \sinh^2(\beta J_1)\}^{1/2} \left[ \cosh(\beta J_1) + \{e^{-4\beta J_2} + \sinh^2(\beta J_1)\}^{1/2} \right]}. \end{aligned}$$

As a check, we see that in the limit  $J_2 \rightarrow 0$  these expressions reduce to  $\tanh(\beta J_1)$  and  $\tanh^2(\beta J_1)$ , respectively; on the other hand, if  $J_1 \rightarrow 0$ , they reduce to 0 and  $\tanh(\beta J_2)$  instead.

**13.7.** In the symmetrized version of this problem, the transfer matrix  $\mathbf{P}$  is given by

$$\langle \sigma_i, \sigma'_i | \mathbf{P} | \sigma_{i+1}, \sigma'_{i+1} \rangle = \exp \left\{ K_1 (\sigma_i \sigma_{i+1} + \sigma'_i \sigma'_{i+1}) + \frac{1}{2} K_2 (\sigma_i \sigma'_i + \sigma_{i+1} \sigma'_{i+1}) \right\},$$

where  $K_1 = \beta J_1$  and  $K_2 = \beta J_2$ . Since  $(\sigma_i, \sigma'_i) = (1, 1), (1, -1), (-1, 1)$  or  $(-1, -1)$ , we get

$$(\mathbf{P}) = \begin{pmatrix} e^{2K_1+K_2} & 1 & 1 & e^{-2K_1+K_2} \\ 1 & e^{2K_1-K_2} & e^{-2K_1-K_2} & 1 \\ 1 & e^{-2K_1-K_2} & e^{2K_1-K_2} & 1 \\ e^{-2K_1+K_2} & 1 & 1 & e^{2K_1+K_2} \end{pmatrix}$$

The eigenvalues of this matrix are

$$\begin{pmatrix} \lambda_1 \\ \lambda_2 \end{pmatrix} = \frac{1}{2} \left[ (A + B + C + D) \pm \{(A - B + C - D)^2 + 16\}^{1/2} \right],$$

$$\lambda_3 = A - C, \quad \lambda_4 = B - D,$$

where

$$A = e^{2K_1+K_2}, \quad B = e^{2K_1-K_2}, \quad C = e^{-2K_1+K_2}, \quad D = e^{-2K_1-K_2}.$$

Since  $\lambda_1$  is the largest eigenvalue of  $\mathbf{P}$ ,

$$\frac{1}{N} \ln Q \approx \ln \lambda_1 = \ln \left\{ \frac{1}{2} \left[ (A + B + C + D) + \{(A - B + C - D)^2 + 16\}^{1/2} \right] \right\}.$$

Substituting for  $A$ ,  $B$ ,  $C$  and  $D$ , we obtain the quoted result. The study of the various thermodynamic properties of the system is now straightforward.

**13.8.** In the notation of Sec. 13.2, the transfer matrix of this model is

$$\langle \sigma_i | \mathbf{P} | \sigma_{i+1} \rangle = \exp(\beta J \sigma_i \sigma_{i+1}) \quad (\sigma_i = -1, 0, 1).$$

It follows that

$$(\mathbf{P}) = \begin{pmatrix} e^K & 1 & e^{-K} \\ 1 & 1 & 1 \\ e^{-K} & 1 & e^K \end{pmatrix} \quad (K = \beta J),$$

with eigenvalues

$$\begin{pmatrix} \lambda_1 \\ \lambda_2 \end{pmatrix} = \frac{1}{2} \left[ (1 + 2 \cosh K) \pm \{8 + (2 \cosh K - 1)^2\}^{1/2} \right], \quad \lambda_3 = 2 \sinh K.$$

Since  $\lambda_1$  is the largest eigenvalue of  $\mathbf{P}$ ,

$$\frac{1}{N} \ln Q \approx \ln \lambda_1 = \ln \left\{ \frac{1}{2} \left[ (1 + 2 \cosh K) + \{8 + (2 \cosh K - 1)^2\}^{1/2} \right] \right\},$$

which leads to the quoted expression for the free energy  $A$ .

In the limit  $T \rightarrow 0$ ,  $K \rightarrow \infty$ , with the result that  $\cosh K \approx \frac{1}{2}e^K$  and hence  $A \approx -NJ$ ; this corresponds to a state of perfect order in the system, with  $U = -NJ$  and  $S = 0$ . On the other hand, when  $T \rightarrow \infty$ ,  $\cosh K \rightarrow 1$  and hence  $A \rightarrow -NkT \ln 3$ ; this corresponds to a state of complete randomness in a system with  $3^N$  microstates.

**13.9.** (a) Making use of the correspondence established in Sec. 12.4, we obtain for a one-dimensional lattice gas ( $q = 2$ ).

- (i) The fugacity  $z = e^{-4\beta J + 2\beta \mu B} = \eta^2 y$ , where  $\eta = e^{-2\beta J}$  and  $y \leftrightarrow e^{2\beta \mu B}$ .

- (ii) The pressure  $P = -(A/N) - J + \mu B$ ; using eqn. (13.2.11), this becomes

$$P = kT \ln \left[ \cosh(\beta\mu B) + \{e^{-4\beta J} + \sinh^2(\beta\mu B)\}^{1/2} \right] + \mu B. \quad (1)$$

- (iii) The density  $(1/v) = \frac{1}{2}\{1 + (\bar{M}/N\mu)\}$ ; using eqn. (13.2.13), this becomes

$$\frac{1}{v} = \frac{1}{2} \left[ 1 + \frac{\sinh(\beta\mu B)}{\{e^{-\beta J} + \sinh^2(\beta\mu B)\}^{1/2}} \right]. \quad (2)$$

Our next step consists in eliminating the *magnetic* variable  $(\beta\mu B)$  in favor of the *fluid* variable  $y$ . For this, we note that

$$\begin{aligned} \cosh(\beta\mu B) &= \frac{1}{2}(y^{1/2} + y^{-1/2}) = (y+1)/2y^{1/2}, \\ \sinh(\beta\mu B) &= \frac{1}{2}(y^{1/2} - y^{-1/2}) = (y-1)/2y^{1/2}, \end{aligned}$$

while  $\beta\mu B = \frac{1}{2} \ln y$ . Substituting these results into eqns. (1) and (2), we obtain the quoted expressions for  $P/kT$  and  $1/v$ . It may be verified that these expressions satisfy the thermodynamic relation

$$\frac{1}{v} = z \left[ \frac{\partial}{\partial z} \left( \frac{P}{kT} \right) \right]_T = y \left[ \frac{\partial}{\partial y} \left( \frac{P}{kT} \right) \right]_\eta$$

At high temperatures,  $\eta \rightarrow 1$  and we get

$$\frac{P}{kT} \approx \ln(y+1), \quad \frac{1}{v} \approx \frac{y}{y+1}.$$

Moreover, in this limit  $y \simeq z \ll 1$ . One may, therefore, write

$$\frac{P}{kT} \approx y, \quad \frac{1}{v} \approx y \quad \text{and hence} \quad \frac{Pv}{kT} \approx 1.$$

At low temperatures,  $\eta$  becomes very small and  $y$  very large — with the result that

$$\frac{P}{kT} \approx \ln y + \frac{\eta^2}{y}, \quad \frac{1}{v} \approx 1 - \frac{\eta^2}{y}.$$

- (b) For a *hard-core* lattice gas ( $y \rightarrow 0$ ,  $\eta \rightarrow \infty$ ), we get

$$\frac{P}{kT} = \ln \left[ \frac{1 + \sqrt{1+4z}}{2} \right], \quad \rho = \frac{\sqrt{1+4z} - 1}{2\sqrt{1+4z}}.$$

From the second equation, it follows that  $\sqrt{1+4z} = 1/(1-2\rho)$ . Substituting this into the first equation, we obtain the quoted expression for  $P(\rho)$ .

**13.10.** Applying eqn. (12.11.11) to a one-dimensional system, we get

$$\begin{aligned}\frac{\chi_0}{N\beta\mu^2} &= \sum_{x=-\infty}^{\infty} e^{-(a/\xi)|x|} = 1 + 2 \sum_{x=1}^{\infty} e^{-(a/\xi)x} \\ &= 1 + 2 \frac{e^{-a/\xi}}{1 - e^{-a/\xi}} = \frac{1 + e^{-a/\xi}}{1 - e^{-a/\xi}} = \coth\left(\frac{a}{2\xi}\right).\end{aligned}$$

For  $\xi \gg a$ ,  $\coth(a/2\xi) \approx (2\xi/a)$ , making  $\chi_0 \propto \xi^1$  — consistent with the fact that for this system  $(2 - \eta) = 1$ . For  $\xi \ll a$ , we recover the familiar result:  $\chi_0 \approx N\mu^2/kT$ .

For an  $n$ -vector model, eqn. (13.3.17) leads to the result

$$\frac{\chi_0}{N\beta\mu^2} = \frac{1 + I_{n/2}(\beta J)/I_{(n-2)/2}(\beta J)}{1 - I_{n/2}(\beta J)/I_{(n-2)/2}(\beta J)},$$

which agrees with the expression quoted in the problem. For the special case  $n = 1$ , the ratio  $I_{1/2}(x)/I_{-1/2}(x) = \tanh x$ , whence

$$\frac{\chi_0}{N\beta\mu^2} = \frac{1 + \tanh(\beta J)}{1 - \tanh(\beta J)} = \frac{\cosh(\beta J) + \sinh(\beta J)}{\cosh(\beta J) - \sinh(\beta J)} = e^{2\beta J},$$

in agreement with eqn. (13.2.14).

**13.11.** We introduce an extra factor  $\sigma_{k+1}^2 \dots \sigma_{\ell-1}^2 \sigma_{m+1}^2 \dots \sigma_{n-1}^2$ , which is identically equal to 1, and write

$$\overline{\sigma_k \sigma_\ell \sigma_m \sigma_n} = \overline{(\sigma_k \sigma_{k+1}) \dots (\sigma_{\ell-1} \sigma_\ell) (\sigma_m \sigma_{m+1}) \dots (\sigma_{n-1} \sigma_n)}.$$

Following the same procedure that led to eqn. (13.2.31), we now get

$$\overline{\sigma_k \sigma_\ell \sigma_m \sigma_n} = \prod_{i=k}^{\ell-1} \tanh(\beta J_i) \prod_{i=m}^{n-1} \tanh(\beta J_i).$$

Employing a common  $J$ , we obtain the desired result

$$\overline{\sigma_k \sigma_\ell \sigma_m \sigma_n} = \{\tanh(\beta J)\}^{\ell-k} \{\tanh(\beta J)\}^{n-m} = \{\tanh(\beta J)\}^{n-m+\ell-k}$$

**13.12.** For a complete solution to this problem, see Thompson (1972b), sec. 6.1, pp. 147–9.

**13.13.** With  $J' = 0$ , we get a much simpler result, viz.

$$\frac{1}{N} \ln Q = \ln 2 + \frac{1}{2\pi^2} \int_0^\pi \int_0^\pi \ln \{\cosh(2\gamma) - \sinh(2\gamma) - \cos \omega\} d\omega d\omega'.$$



The integration over  $\omega'$  is straightforward; the one over  $\omega$  can be done with the help of the formula

$$\int_0^\pi \ln(a - b \cos \omega) d\omega = \pi \ln \left[ \frac{a + \sqrt{a^2 - b^2}}{2} \right] \quad (|b| < a), \quad (1)$$

which yields the expected result

$$\frac{1}{N} \ln Q = \ln 2 + \frac{1}{2} \ln \left[ \frac{\cosh(2\gamma) + 1}{2} \right] = \ln(2 \cosh \gamma).$$

With  $J' = J$ , we have

$$\frac{1}{N} \ln Q = \ln 2 + \frac{1}{2\pi^2} \int_0^\pi \int_0^\pi \ln \{ \cosh^2(2\gamma) - \sinh 2\gamma (\cos \omega + \cos \omega') \} d\omega d\omega'. \quad (2)$$

We substitute  $\omega = \theta + \varphi$  and  $\omega' = \theta - \varphi$ ; this will replace the sum  $(\cos \omega + \cos \omega')$  by the product  $2 \cos \theta \cos \varphi$  and the element  $d\omega d\omega'$  by  $2d\theta d\varphi$ . As for the limits of integration, the periodicity of the integrand allows us to choose the rectangle  $[0 \leq \theta \leq \pi, 0 \leq \varphi \leq \pi/2]$  without affecting the value of the integral. We thus have

$$\frac{1}{N} \ln Q = \ln 2 + \frac{1}{\pi^2} \int_0^\pi \int_0^{\pi/2} \ln \{ \cosh^2(2\gamma) - 2 \sinh(2\gamma) \cos \varphi \cos \theta \} d\theta d\varphi.$$

Integration over  $\theta$  may now be carried out using formula (1), with the result

$$\begin{aligned} \frac{1}{N} \ln Q &= \ln 2 + \frac{1}{\pi} \int_0^{\pi/2} \ln \left[ \frac{1}{2} \left\{ \cosh^2(2\gamma) + \sqrt{\cosh^4(2\gamma) - 4 \sinh^2(2\gamma) \cos^2 \varphi} \right\} \right] d\varphi \\ &= \ln \left\{ 2 \cdot \frac{1}{\sqrt{2}} \cosh(2\gamma) \right\} + \frac{1}{\pi} \int_0^{\pi/2} \ln \left\{ 1 + \sqrt{1 - \kappa^2 \cos^2 \varphi} \right\} d\varphi, \end{aligned}$$

where  $\kappa$  is given by eqn. (13.4.23). Finally, we replace  $\cos^2 \varphi$  by  $\sin^2 \varphi$  (without affecting the value of the integral) and recover eqn. (13.4.22).

We know that this model is singular at  $\kappa = 1$ . A close look at the integral in (2) shows that the singularity arises when contributions in the neighborhood of the point  $\omega = \omega' = 0$  pile up. Since  $\cos \omega$  and  $\cos \omega'$  are almost unity there, the situation becomes catastrophic when  $\cosh^2 2\gamma = 2 \sinh 2\gamma$ , i.e. when  $\kappa = 1$ . In the *anisotropic* case, a similar observation suggests that the singularity will arise when

$$\cosh(2\gamma) \cosh(2\gamma') = \sinh(2\gamma) + \sinh(2\gamma').$$

Squaring both sides of this equation and simplifying, we get

$$\sinh(2\gamma) \sinh(2\gamma') = 1 \quad (3)$$

as the criterion for the onset of phase transition in this system; cf. eqn. (13.4.18). The study of the thermodynamic behavior of the system in the neighborhood of the critical point in the general case, when  $J' \neq J$ , is highly complicated; the fact, however, remains that the internal energy  $U_0$  is continuous and the specific heat  $C_0$  displays a logarithmic divergence at a critical temperature  $T_c$  given by eqn. (3).

**13.14.** As  $\kappa \rightarrow 1$ , the first integral tends to the limit

$$\int_0^{\pi/2} \frac{1 - \sin \varphi}{\cos \varphi} d\varphi = \int_0^{\pi/2} \frac{\cos \varphi}{1 + \sin \varphi} d\varphi = \ln(1 + \sin \varphi) \Big|_0^{\pi/2} = \ln 2.$$

The second integral diverges as  $\kappa \rightarrow 1$ , so we need to examine it carefully. Setting  $\cos \varphi = x$ , this integral takes the form

$$\int_0^1 \frac{\kappa dx}{\sqrt{(1 - \kappa^2) + \kappa^2 x^2}} \simeq \int_0^1 \frac{dx}{\sqrt{\kappa'^2 + x^2}} = \ln \left\{ x + \sqrt{\kappa'^2 + x^2} \right\} \Big|_0^1.$$

Since  $\kappa$  is close to 1,  $\kappa'^2 \ll 1$ ; we, therefore, get for this integral the asymptotic result  $\ln 2 - \ln |\kappa'|$ . It follows that  $K_1(\kappa) \approx 2 \ln 2 - \ln |\kappa'| = \ln(4/|\kappa'|)$ .

**13.15.** The quantity to be evaluated here is

$$\frac{S_c}{Nk} = \left( \frac{U}{NkT} \right)_c - \left( \frac{A}{NkT} \right)_c.$$

The first term, by eqn. (13.4.28), is  $-K_c \coth(2K_c) = -\sqrt{2}K_c$ . The second, by eqn. (13.4.22), is

$$\begin{aligned} \ln 2 + \frac{1}{\pi} \int_0^{\pi/2} \ln(1 + \cos \varphi) d\varphi \\ = \ln 2 + \frac{1}{\pi} \left[ \varphi \ln(1 + \cos \varphi) \Big|_0^{\pi/2} + \int_0^{\pi/2} \frac{\varphi \sin \varphi}{1 + \cos \varphi} d\varphi \right]. \end{aligned}$$

The integrated part vanishes while the remaining integral has the value  $-(\pi/2) \ln 2 + 2G$ ; see Gradshteyn and Ryzhik (1965), p. 435. Thus, finally,

$$\frac{S_c}{Nk} = -\sqrt{2}K_c + \frac{1}{2} \ln 2 + 2G/\pi \simeq 0.3065.$$

The corresponding result under the Bethe approximation is  $2 \ln 3 - (7/3) \ln 2 \simeq 0.5799$  and that under the Bragg-Williams approximation is  $\ln 2 \simeq 0.6931$ .

**13.16.** Expanding around  $K = K_c$ , we get

$$\begin{aligned}\sinh(2K) &= \sinh(2K_c) + 2\cosh(2K_c)(K - K_c) + 2\sinh(2K_c)(K - K_c)^2 + \dots \\ &= 1 + 2\sqrt{2}(K - K_c) + 2(K - K_c)^2 + \dots\end{aligned}\quad (1)$$

Since  $(K - K_c) = K_c\{(1+t)^{-1} - 1\} = K_c(-t + t^2 - \dots)$ , eqn. (1) becomes

$$\sinh(2K) = 1 - 2\sqrt{2}K_c t + \left(2\sqrt{2}K_c + 2K_c^2\right)t^2 + \dots\quad (2)$$

Raising expression (2) to the power  $-4$ , we get

$$\{\sinh(2K)\}^{-4} = 1 + 8\sqrt{2}K_c t - \left(8\sqrt{2}K_c + 8K_c^2 - 80K_c^2\right)t^2 + \dots,$$

so that

$$\begin{aligned}1 - \{\sinh(2K)\}^{-4} &= -8\sqrt{2}K_c t + \left(8\sqrt{2}K_c - 72K_c^2\right)t^2 + \dots \\ &= 8\sqrt{2}K_c |t| \left\{1 + \left(1 - \frac{9}{\sqrt{2}}K_c\right)|t| + \dots\right\}.\end{aligned}\quad (3)$$

Taking the eighth-root of (3), we obtain the desired result.

**13.17.** Making use of the correspondence established in Sec. 12.4 and utilizing a result obtained in Problem 13.15, we have for a two-dimensional lattice gas ( $q = 4$ )

$$\frac{P_c}{kT_c} = -\left(\frac{A}{NkT}\right)_c - \frac{2J}{kT_c} = \left(\frac{1}{2}\ln 2 + \frac{2G}{\pi}\right) - 2K_c.$$

We also have:  $v_c = 2$  (because, at  $T = T_c$ , the spontaneous magnetization of the corresponding ferromagnet is zero). It follows that

$$\frac{P_c v_c}{kT_c} = \ln 2 + \frac{4G}{\pi} - 4K_c \simeq 0.09659.$$

Taking the reciprocal of this result, we obtain the one stated in the problem.

**13.18.** In one dimension, expression (13.5.31) assumes the form

$$W_1(\varphi) = \int_0^\infty e^{-(1+\varphi)x} I_0(x) dx = \frac{1}{\{(1+\varphi)^2 - 1\}^{1/2}} = \frac{1}{(\lambda^2 - J^2)^{1/2}}.$$

The constraint equation (13.5.19) then becomes

$$\frac{N}{2\beta} \frac{1}{(\lambda^2 - J^2)^{1/2}} + \frac{N\mu^2 \beta^2}{4(\lambda - J)^2} = N, \quad (1)$$

which agrees with the quoted result. Comparing (1) with the *formal* constraint equation (13.5.13), we conclude that

$$\frac{\partial A_\lambda}{\partial \lambda} = \frac{N}{2\beta} \frac{1}{(\lambda^2 - J^2)^{1/2}} + \frac{N\mu^2 B^2}{4(\lambda - J)^2}, \quad (2)$$

It follows that

$$A_\lambda = \frac{N}{2\beta} \ln \left\{ \lambda + (\lambda^2 - J^2)^{1/2} \right\} + \frac{N\mu^2 B^2}{4(\lambda - J)} + C, \quad (2)$$

where  $C$  is a constant of integration. To determine  $C$ , we observe from eqn. (13.5.12a) that, for  $B = 0$  and  $J = 0$ , the partition function  $Q_N = (\pi/\beta\lambda)^{N/2}$  — with the result that  $A_\lambda = (N/2\beta) \ln(\beta\lambda/\pi)$ . It follows that  $C = (N/2\beta) \ln(\beta/2\pi)$ , which leads to the quoted result for  $A_\lambda$ .

With  $B = 0$  but  $J \neq 0$ , eqn. (1) gives:  $(\lambda^2 - J^2)^{1/2} = 1/2\beta$ , and hence  $\lambda = (1 + 4\beta^2 J^2)^{1/2}/2\beta$ . Equation (13.5.15) then gives

$$\frac{\beta A_{\mathcal{J}}}{N} = \frac{\beta A_\lambda}{N} - \beta\lambda = \frac{1}{2} \ln \left\{ \frac{(1 + 4\beta^2 J^2)^{1/2} + 1}{4\pi} \right\} - \frac{1}{2}(1 + 4\beta^2 J^2)^{1/2}.$$

**13.19.** With  $\beta J_i = \beta \cdot nJ' = nK$ , eqn. (13.3.8) becomes

$$Q_N(nK) = \left| \frac{\Gamma(n/2)}{(\frac{1}{2}nK)^{(n-2)/2}} I_{(n-2)/2}(nK) \right|^{N-1}.$$

For  $n, N \gg 1$ , we get

$$\begin{aligned} \frac{1}{nN} \ln Q_N(nK) &\approx \frac{1}{n} \left[ \ln \Gamma \left( \frac{n}{2} \right) - \frac{n}{2} \ln \left( \frac{1}{2}nK \right) + \ln I_{n/2} \left( \frac{n}{2} \cdot 2K \right) \right] \\ &= \frac{1}{n} \left[ \frac{n}{2} \ln \frac{n}{2} - \frac{n}{2} + \dots - \frac{n}{2} \ln \left( \frac{1}{2}nK \right) \right. \\ &\quad \left. + \frac{n}{2} \left\{ (4K^2 + 1)^{1/2} - \ln \left( \frac{(4K^2 + 1)^{1/2} + 1}{2K} \right) \right\} + \dots \right] \\ &\approx \frac{1}{2} \left[ (4K^2 + 1)^{1/2} - 1 - \ln \left( \frac{(4K^2 + 1)^{1/2} + 1}{2} \right) \right]. \end{aligned}$$

**13.20.** By eqn. (13.5.69), we have for the spherical model at  $T < T_c$

$$\chi_0 = \frac{N\mu^2}{2J\varphi} \approx \frac{N^2 \mu^2 (K - K_c)}{J}.$$

Replacing  $(K - K_c)$  by  $m_0^2 K$ , see eqn. (13.5.44), and remembering that  $K = J/k_B T$ , we obtain the desired result.

**13.21.** Before employing the suggested approximation, we observe that the major contribution to the integral over  $\theta_j$  in expression (13.5.58) comes from those values of  $\theta_j$  that are either close to the lower limit 0 or close to the upper limit  $2\pi$ . We, therefore, write this integral in the form

$$2 \int_0^\pi \cos(R_j \theta_j / a) e^{-x+x \cos \theta_j} \frac{N_j}{2\pi} d\theta_j,$$

so that the major contribution now comes *only* from those values of  $\theta$  that are close to 0. We may, therefore, replace  $(1 - \cos \theta_j)$  by  $\theta_j^2/2$  and, at the same time, replace the upper limit of the integral by  $\infty$ . This yields the asymptotic result

$$2 \int_0^\pi \cos(R_j \theta_j / a) e^{-x\theta_j^2/2} \frac{N_j}{2\pi} d\theta_j = \frac{N_j}{\sqrt{2\pi x}} e^{-R_j^2/2a^2 x},$$

where use has been made of formula (B.41). Equation (13.5.57) then becomes

$$G(\mathbf{R}) \approx \frac{1}{2N\beta J} \int_0^\infty \frac{N}{(2\pi x)^{d/2}} e^{-\varphi x - R^2/2a^2 x} dx,$$

which is precisely the expression that led to eqns. (13.5.61 and 62).

In the case of the Bose gas, we are concerned with the expression

$$\frac{1}{(2\pi)^d} \int \frac{\exp(i\mathbf{k} \cdot \mathbf{R})}{e^{\alpha + \beta \hbar^2 k^2 / 2m} - 1} d^d k,$$

see Section 13.6, which may now be approximated by

$$\frac{1}{(2\pi)^d} \int \frac{\exp(i\mathbf{k} \cdot \mathbf{R})}{\alpha + \beta \hbar^2 k^2 / 2m} d^d k.$$

Using the representation (13.5.27), this may be written as

$$\begin{aligned} & \int_0^\infty e^{-\alpha x} \left[ \prod_{n=1}^d \int_{-\infty}^\infty \frac{1}{2\pi} e^{ik_n R_n - \beta \hbar^2 k_n^2 x / 2m} dk_n \right] dx \\ &= \int_0^\infty e^{-\alpha x} \left[ \prod_{n=1}^d \left( \frac{1}{\lambda \sqrt{x}} e^{-\pi R_n^2 / \lambda^2 x} \right) \right] dx \quad \left[ \lambda = \hbar \left( \frac{2\pi\beta}{m} \right)^{1/2} \right] \\ &= \frac{1}{\lambda^d} \int_0^\infty e^{-\alpha x - \pi R^2 / \lambda^2 x} \frac{1}{x^{d/2}} dx, \end{aligned}$$

which is precisely the expression that led to eqns. (13.6.35 and 36).

**13.22.** The constraint equation (13.5.21) now takes the form

$$2N\beta(1 - m^2) = \sum_{\mathbf{k}} \left\{ J \left( \varphi + \frac{1}{2} k^\sigma a^\sigma \right) \right\}^{-1},$$

which may as well be written as

$$2K(1 - m^2) = F(\varphi), \text{ where } K = \beta J \text{ and } F(\varphi) = N^{-1} \sum_{\mathbf{k}} \left( \varphi + \frac{1}{2} k^\sigma a^\sigma \right)^{-1}.$$

To determine the behavior of the function  $F(\varphi)$  at small  $\varphi$ , we look at the derivative

$$F'(\varphi) = -N^{-1} \sum_{\mathbf{k}} \left( \varphi + \frac{1}{2} k^\sigma a^\sigma \right)^{-2}.$$

In view of eqns. (13.5.17) and (C.7b), we obtain

$$\begin{aligned} F'(\varphi) &\approx -N^{-1} \prod_{j=1}^d \left( \frac{N_j a^j}{2\pi} \right) \int_0^\infty \left( \varphi + \frac{1}{2} k^\sigma a^\sigma \right)^{-2} \frac{2\pi^{d/2}}{\Gamma(d/2)} k^{d-1} dk \\ &= -\frac{a^d}{2^{d-1} \pi^{d/2} \Gamma(d/2) \varphi^2} \int_0^\infty \left( 1 + \frac{1}{2\varphi} k^\sigma a^\sigma \right)^{-2} k^{d-1} dk. \end{aligned}$$

We substitute  $k^\sigma = (2\varphi/a^\sigma)x$  and get

$$\begin{aligned} F'(\varphi) &\approx -\frac{(2\varphi)^{d/\sigma}}{2^{d-1} \pi^{d/2} \Gamma(d/2) \sigma \varphi^2} \int_0^\infty \frac{x^{(d/\sigma)-1} dx}{(1+x)^2} \\ &= -\frac{2^{d/\sigma} \Gamma(d/\sigma) \Gamma(2 - d/\sigma)}{2^{d-1} \pi^{d/2} \Gamma(d/2) \sigma} \varphi^{(d-2\sigma)/\sigma} \quad (d < 2\sigma). \end{aligned}$$

Integrating over  $\varphi$ , we obtain

$$F(\varphi) \approx F(0) - \frac{2^{d/\sigma} \Gamma\{(d/\sigma)/\sigma\} \Gamma\{(2\sigma - d)/\sigma\}}{2^{d-1} \pi^{d/2} \Gamma(d/2) \sigma} \varphi^{(d-2\sigma)/\sigma};$$

cf. eqn. (G.7c). The function  $F(0)$  exists for all  $d > \sigma$  and may be identified with  $2K_c$ , leading to the constraint equation

$$2K(1 - m^2) = 2K_c - \text{const. } \varphi^{(d-\sigma)/\sigma} \quad (\sigma < d < 2\sigma).$$

The critical exponents of the model follow straightforwardly from this equation. The first one to emerge is  $\beta = 1/2$ , as before. Next,  $\gamma = \sigma/(d - \sigma)$ , whence  $\alpha = 2 - 2\beta - \gamma = (d - 2\sigma)/(d - \sigma)$ , while  $\delta = 1 + (\gamma/\beta) = (d + \sigma)/(d - \sigma)$ . Next, from the very starting form of the function  $F(\varphi)$ , we infer that the correlation length  $\xi \sim \varphi^{-1/\sigma}$  and hence  $\sim t^{-1/(d-\sigma)}$ ; it follows that  $\nu = 1/(d - \sigma)$ . We then get:  $\eta = 2 - (\gamma/\nu) = 2 - \sigma$ .

For  $d > 2\sigma$ , the derivative  $F'(0)$  exists — with the result that

$$F(\varphi) \approx F(0) - |F'(0)|\varphi.$$

This leads to *mean-field* results for the exponents  $\beta$ ,  $\gamma$ ,  $\alpha$  and  $\delta$ . The correlation length is, once again, given by  $\xi \sim \varphi^{-1/\sigma}$  but now this is  $\sim t^{-1/\sigma}$ , so that  $\nu = 1/\sigma$  (and not  $1/2$ ); accordingly,  $\eta$  is, once again,  $2 - \sigma$  (and not 0).

**13.23.** The derivation of eqns. (13.6.9 and 11) proceeds exactly as of eqns. (7.1.36 and 37). The derivation of eqns. (13.6.10 and 13) proceeds exactly as in Problem 7.4; eqn. (13.6.12) then follows as a product of expressions (13.6.11 and 13): The derivation of eqns. (13.6.14 and 15) proceeds exactly as in Problem 7.5; note that one may first obtain here

$$\kappa_T = \frac{1}{nk_B T} \frac{g_{(d-2)/2}(z)}{g_{d/2}(z)}, \quad \kappa_S = \frac{d}{(d+2)nk_B T} \frac{g_{d/2}(z)}{g_{(d+2)/2}(z)},$$

and then use eqn. (13.6.7) to express these quantities in terms of  $P$ . Finally, the derivation of eqn. (13.6.23) proceeds exactly as in Problem 7.6.

**13.24.** The derivations here proceed exactly as in Problem 7.7. The singularity of these quantities arises from the last term of the two expressions, and is qualitatively similar to the singularity of the quantity  $(\partial C_V / \partial T)$ . Note that the singularity of the combination  $\{v(\partial^2 P / \partial T^2)_v - (\partial^2 \mu / \partial T^2)_v\}$  is relatively mild.

**13.25.** By definition,

$$C_P \equiv T \left( \frac{\partial S}{\partial T} \right)_P = T \left( \frac{\partial S}{\partial V} \right)_P \left( \frac{\partial V}{\partial T} \right)_P.$$

Using the Maxwell relation  $(\partial S / \partial V)_P = (\partial P / \partial T)_S$ , we get

$$C_P = T \left( \frac{\partial P}{\partial T} \right)_S \left( \frac{\partial V}{\partial T} \right)_P = T \left( \frac{\partial P}{\partial T} \right)_S \left\{ - \left( \frac{\partial V}{\partial P} \right)_T \left( \frac{\partial P}{\partial T} \right)_V \right\} = T \left( \frac{\partial P}{\partial T} \right)_S \left\{ V \kappa_T \left( \frac{\partial P}{\partial T} \right)_V \right\}.$$

Next

$$C_V \equiv T \left( \frac{\partial S}{\partial T} \right)_V = T \left( \frac{\partial S}{\partial P} \right)_V \left( \frac{\partial P}{\partial T} \right)_V.$$

Now, using the Maxwell relation  $(\partial S / \partial P)_V = -(\partial V / \partial T)_S$ , we get

$$C_V = -T \left( \frac{\partial V}{\partial T} \right)_S \left( \frac{\partial P}{\partial T} \right)_V = -T \left( \frac{\partial V}{\partial P} \right)_S \left( \frac{\partial P}{\partial T} \right)_S \left( \frac{\partial P}{\partial T} \right)_V = T(V \kappa_S) \left( \frac{\partial P}{\partial T} \right)_S \left( \frac{\partial P}{\partial T} \right)_V.$$

In the two-phase region,  $(\partial P / \partial T)_S = (\partial P / \partial T)_V = dP / dT$ , with the result that

$$C_P = VT(dP / dT)^2 \kappa_T, \quad C_V = VT(dP / dT)^2 \kappa_S.$$

Now, by eqn. (13.6.28),  $dP / dT$ , at  $T < T_c$ ,  $= (d + 2)P / 2T$ . Using this result and eqn. (13.6.15), we get

$$C_V = VT \left\{ \frac{(d + 2)P}{2T} \right\}^2 \frac{d}{(d + 2)P} = \frac{d(d + 2)}{4} \frac{PV}{T}.$$

Substituting for  $P$  from eqn. (13.6.28), we recover expression (13.6.30) for  $C_V$ .

**13.26.** As shown in Problem 1.16,  $d\mu = -sdT + v dP$ . It follows that

$$\kappa_T \equiv -\frac{1}{v} \left( \frac{\partial v}{\partial P} \right)_T = - \left( \frac{\partial v}{\partial \mu} \right)_T.$$

Since  $v = 1/\rho$ , we readily obtain the desired result for  $\kappa_T$ .

For the ideal Bose gas at  $T < T_c$ , the particle numbers  $N_0$  and  $N_e$  are given by eqns. (13.6.24) and (13.6.27). Since  $\alpha \equiv -\mu/k_B T$ , we have

$$\rho = \frac{N}{V} = \frac{N_0}{V} + \frac{N_e}{V} = -\frac{k_B T}{V\mu} + \frac{\zeta(d/2)}{\lambda^d}.$$

It follows that

$$\kappa_T = \frac{1}{\rho^2} \left( \frac{k_B T}{V\mu^2} \right) = \frac{1}{\rho^2} \frac{k_B T}{V} \left( -\frac{N_0}{k_B T} \right)^2 = \frac{N_0^2}{\rho^2 V k_B T} = \frac{V \rho_0^2}{\rho^2 k_B T}.$$

Incidentally, using the relationship between  $C_P$  and  $\kappa_T$ , as developed in Problem 13.25, we can show that, in the two-phase region of the Bose gas,

$$\frac{C_P}{N k_B} = N \left\{ \frac{d + 2}{2} \frac{\zeta\{(d + 2)/2\}}{\zeta(d/2)} \right\}^2 \left( \frac{T}{T_c} \right)^d \left( \frac{\rho_0}{\rho} \right)^2.$$

Comparing this with eqn. (13.6.30), we find that, in this region, the ratio  $C_P / C_V = O(N)$ .

**13.28.** Use the relations  $N/(L - ND) = \beta P$  and

$$\lim_{n \rightarrow \infty} \left( 1 + \frac{z}{n} \right)^n = \exp(z),$$

and collect factors.



**13.29.** Using equation (10.7.20a) and ignoring the delta-function contribution to  $S(k)$  gives

$$S(k) = 1 + \frac{n}{\beta P(1 - nD)} \left[ \sum_{j=1}^{\infty} \frac{1}{(j-1)!} \int_{jD}^{\infty} (\beta P(x - jD))^j \exp(-\beta P(x - jD) + ikx) + \text{c.c.} \right].$$

Using  $n/(\beta P(1 - nD)) = 1$  we get

$$\begin{aligned} S(k) &= 1 + \left( \frac{\beta P e^{ikD}}{\beta P - ik - \beta P e^{ikD}} + \text{c.c.} \right) \\ &= \frac{k^2}{k^2 + 2(\beta P)^2(1 - \cos(kD)) + 2\beta P k \sin(kD)} \end{aligned}$$

**13.30.** The isobaric partition function is

$$\begin{aligned} Y_N(P, T) &= \left[ \frac{1}{\lambda} \int_{-\infty}^{\infty} \exp \left( -\beta P y - \frac{\beta m \omega^2}{2} (y - a)^2 \right) dx \right], \\ G(N, P, T) &= N k T \ln \left( \frac{kT}{\hbar \omega} \right) + N P a - \frac{N P^2}{2 m \omega^2}, \end{aligned}$$

which gives  $L = (\partial G / \partial P)_T = N(a - P / m \omega^2)$ . As  $P \rightarrow 0$  the length goes to  $Na$ , i.e.  $N$  times the equilibrium length of one spring. However, the masses and springs do not form a long-range-ordered lattice since the variance of the neighbor distances grows with  $n$ .

$$\begin{aligned} \langle x_n - x_0 \rangle &= n \langle y \rangle = a - \frac{P}{m \omega^2} \\ \langle (x_n - x_0)^2 \rangle - \langle x_n - x_0 \rangle^2 &= n (\langle y^2 \rangle - \langle y \rangle^2) = n a^2 \frac{kT}{m \omega^2 a^2}. \end{aligned}$$

The heat capacity is  $C_P = Nk$ .

**13.31.** Here is a C code snippet that performs the calculation.

```
int L=4;
int n=L*L;
int* s=new int[n]; //spins: 0 or 1
int* i1 = new int[n]; //neighbors to the right
int* i3 = new int[n]; //neighbors above
for (int i=0;i<n;i++)
{
    i1[i] = i+1; // site to right
    i3[i] = i+L; // site above
    if ((i1[i] % L) == 0) i1[i] -= L; //implement periodic boundary conditions
    if (i3[i] >= n) i3[i] -= n; //implement periodic boundary conditions
}
```

```

}
double* hist=new double[n+1]; // histogram: double since would overflow integers for L>5;
for (int e=0;e<=n;e++) hist[e]=0.0;
double nconfig=pow(2.0,n); // number of configurations is  $2 \wedge n$ 
for (double iconfig=0.0; iconfig < nconfig; iconfig += 1.0)
{
    double state = iconfig;
    for (int i=0;i<n;i++) // determine spins (0 or 1) for each site
    {
        s[i]=(int) fmod(state,2.0);
        state = floor(0.5*state);
    }
    int e=0;
    for (int i=0;i<n;i++) // count energy above ground state (unequal neighbors)
    {
        e += (s[i] != s[i1[i]]);
        e += (s[i] != s[i3[i]]);
    }
    hist[e/2] += 1.0; //increment histogram of energies, only even values needed
}
for (int e=0;e<=n;e++) cout << e << " " << hist[e] << endl; //output the results

```

This code gives the coefficients in the problem. Since the  $L = 6$  case involves  $2^{36}$  configurations, you might try a bitwise calculation with each row represented by an integer between 0 and  $2^L - 1$  and the spins represented by the bits. This is computationally much more efficient since the energy can be determined easily using simple bit rotations and exclusive ors.

**13.32.** Separating off the ground state energy gives

$$T = \begin{pmatrix} 1 & x \\ x & 1 \end{pmatrix}$$

which has eigenvalues  $\lambda = 1 \pm x$ . Therefore

$$Q_N = (1+x)^N + (1-x)^N,$$

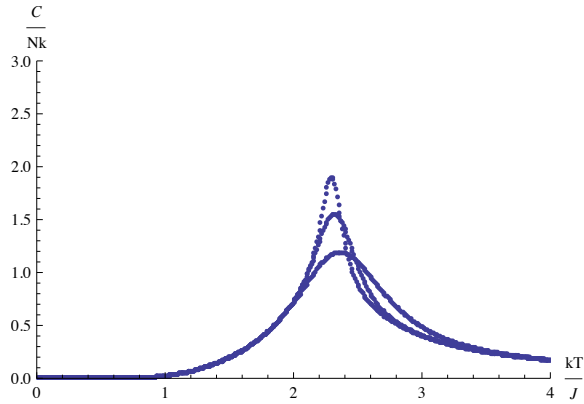
which can be expanded

$$Q_N = \sum_{j=0}^N \left( \frac{N!x^j}{j!(N-j)!} + \frac{N!(-x)^j}{j!(N-j)!} \right) = \sum_{k=0}^{N/2} \left( 2 \frac{n!}{(2k)!(N-2k)!} x^{2k} \right)$$

**13.33.** The  $8 \times 8$  partition function coefficients are

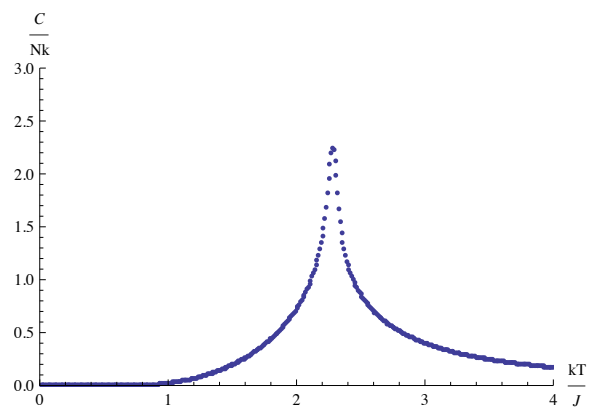
$g = \{2, 0, 128, 256, 4672, 17920, 145408, 712960, 4274576, 22128384, 118551552, 610683392,$   
 $3150447680, 16043381504, 80748258688, 396915938304, 1887270677624, 8582140066816,$   
 $36967268348032, 149536933509376, 564033837424064, 1971511029384704,$   
 $6350698012553216, 18752030727310592, 50483110303426544, 123229776338119424,$   
 $271209458049836032, 535138987032308224, 941564975390477248, 1469940812209435392,$   
 $2027486077172296064, 2462494093546483712, 2627978003957146636,$   
 $2462494093546483712, 2027486077172296064, 1469940812209435392,$   
 $941564975390477248, 535138987032308224, 271209458049836032,$   
 $123229776338119424, 50483110303426544, 18752030727310592, 6350698012553216,$   
 $1971511029384704, 564033837424064, 149536933509376, 36967268348032,$   
 $8582140066816, 1887270677624, 396915938304, 80748258688, 16043381504, 3150447680,$   
 $610683392, 118551552, 22128384, 4274576, 712960, 145408, 17920, 4672, 256, 128, 0, 2\}$

The specific heats for the  $8 \times 8$ ,  $16 \times 16$  and  $32 \times 32$  Ising model are shown below.



Notice that the height of the peak grows linearly with  $\ln(L)$ .

**13.34.** The specific heat for the  $64 \times 64$  Ising model is shown below.



# Chapter 14

**14.1.** We start with expression (13.2.3) for the partition function  $Q_N$  and carry out summation over  $\sigma_2, \sigma_4, \dots$ . The resulting expression will consist of  $\frac{1}{2}N$  factors such as

$$\sum_{\sigma_2} \langle \sigma_1 | \mathbf{P} | \sigma_2 \rangle \langle \sigma_2 | \mathbf{P} | \sigma_3 \rangle = \langle \sigma_1 | \mathbf{P}^2 | \sigma_3 \rangle,$$

and will be formally similar to the expression we started with. Calling the new transfer operator  $\mathbf{P}'\{\mathbf{K}'\}$ , we clearly get eqn. (1) of the problem.

From the given expression for  $\mathbf{P}\{\mathbf{K}\}$ , we readily get

$$\mathbf{P}'\{\mathbf{K}'\} = e^{2K_0} \begin{pmatrix} e^{2(K_1+K_2)} + e^{-2K_1} & e^{K_2} + e^{-K_2} \\ e^{K_2} + e^{-K_2} & e^{2(K_1-K_2)} + e^{-2K_1} \end{pmatrix}.$$

Expressing this in a form similar to eqn. (2), we obtain

$$\begin{aligned} e^{K'_0+K'_1+K'_2} &= e^{2K_0} \{ e^{2(K_1+K_2)} + e^{-2K_1} \} \\ e^{K'_0+K'_1-K'_2} &= e^{2K_0} \{ e^{2(K_1-K_2)} + e^{-2K_1} \}, \text{ and} \\ e^{K'_0-K'_1} &= e^{2K_0} \{ e^{K_2} + e^{-K_2} \}^2 \end{aligned}$$

which are identical with eqns. (14.2.7) and will lead precisely to eqns. (14.2.8).

**14.2.** We'll do the second part only, for it includes the first as a special case. For this, we have to show that the given function  $f(K_1, K_2)$  satisfies the functional equation (14.2.11). Now, the right-hand side of this equation is

$$-\frac{1}{2} \ln \left\{ e^{K'_0} \left[ \frac{e^{K'_1+K'_2} + e^{K'_1-K'_2}}{2} + \left\{ e^{-2K'_1} + \left( \frac{e^{K'_1+K'_2} - e^{K'_1-K'_2}}{2} \right)^2 \right\}^{1/2} \right] \right\}.$$

Substituting from eqns. (14.2.7) with  $K_0 = 0$ , this becomes

$$\begin{aligned} &-\frac{1}{2} \ln [e^{K_2} \cosh(2K_1 + K_2) + e^{-K_2} \cosh(2K_1 - K_2) + \{4 \cosh^2 K_2 + \\ &\quad (e^{K_2} \cosh(2K_1 + K_2) - e^{-K_2} \cosh(2K_1 - K_2))^2\}^{1/2}] \\ &= -\frac{1}{2} \ln [e^{2K_1} \cosh(2K_2) + e^{-2K_1} + \{4 \cosh^2 K_2 + (e^{2K_1} \sinh(2K_2))^2\}^{1/2}]. \end{aligned}$$

The left-hand side of the same equation is

$$\begin{aligned}
& -\ln[e^{K_1} \cosh K_2 + \{e^{-2K_1} + e^{2K_1} \sinh^2 K_2\}^{1/2}] \\
&= -\frac{1}{2} \ln [e^{2K_1} \cosh^2 K_2 + e^{-2K_1} + e^{2K_1} \sinh^2 K_2 \\
&\quad + 2e^{K_1} \cosh K_2 \{e^{-2K_1} + e^{2K_1} \sinh^2 K_2\}^{1/2}] \\
&= -\frac{1}{2} \ln [e^{2K_1} \cosh(2K_2) + e^{-2K_1} + \{4 \cosh^2 K_2 + 4e^{4K_1} \cosh^2 K_2 \sinh^2 K_2\}^{1/2}],
\end{aligned}$$

which is precisely the same as the right-hand side.

**14.3.** We'll do the second part only, for it includes the first as a special case. For this, we have to show that the given function  $f(K_1, K_2, \Lambda)$  satisfies the functional equation (14.2.27). Now, the right-hand side of this equation is

$$-\frac{1}{2}K'_0 + \frac{1}{4} \ln \left[ \frac{\Lambda' + \sqrt{\Lambda'^2 - K_1'^2}}{2\pi} \right] - \frac{K_2'^2}{8(\Lambda' - K_1')}.$$

Substituting from eqns. (14.2.25 and 28) with  $K_0 = 0$ , this becomes

$$\begin{aligned}
& -\frac{1}{4} \ln \left( \frac{\pi}{\Lambda} \right) - \frac{K_2^2}{8\Lambda} + \frac{1}{4} \ln \left[ \frac{(\Lambda - K_1^2/2\Lambda) + \sqrt{\Lambda^2 - K_1^2}}{2\pi} \right] \\
& \quad - \frac{K_2^2}{8(\Lambda - K_1)} \left( 1 + \frac{K_1}{\Lambda} \right) \\
&= \frac{1}{4} \ln \left[ \frac{2\Lambda}{2\pi} \cdot \frac{(\Lambda - K_1^2/2\Lambda) + \sqrt{\Lambda^2 - K_1^2}}{2\pi} \right] \\
& \quad - \frac{K_2^2}{8(\Lambda - K_1)} \left[ \frac{\Lambda - K_1}{\Lambda} + \frac{\Lambda + K_1}{\Lambda} \right] \\
&= \frac{1}{2} \ln \left[ \frac{\Lambda + \sqrt{\Lambda^2 - K_1^2}}{2\pi} \right] - \frac{K_2^2}{4(\Lambda - K_1)}.
\end{aligned}$$

which is precisely  $f(K_1, K_2, \Lambda)$ .

**14.4.** Making the suggested substitution into eqn. (14.2.24), we get

$$Q_N = \int \cdots \int \exp \left[ \sum_{j=1}^{N'} \left\{ K'_0 + K'_1 \cdot \frac{2\Lambda}{K_1} s'_j s'_{j+1} - \Lambda' \cdot \frac{2\Lambda}{K_1} s_j'^2 \right\} \right] \left( \frac{2\Lambda}{K_1} \right)^{N'/2} ds'_1 \cdots ds'_N.$$

In view of eqns. (14.2.25), with  $K_0 = K_2 = 0$ , we now have

$$\begin{aligned}
e^{K'_0} \cdot \left( \frac{2\Lambda}{K_1} \right)^{1/2} &= \left( \frac{\pi}{\Lambda} \right)^{1/2} \cdot \left( \frac{2\Lambda}{K_1} \right)^{1/2} = \left( \frac{2\pi}{K_1} \right)^{1/2} = e^{K''_0}, \text{ say,} \\
K'_1 \cdot \frac{2\Lambda}{K_1} &= K_1, \text{ and } \Lambda' \cdot \frac{2\Lambda}{K_1} = \frac{2\Lambda^2}{K_1} - K_1 = \Lambda'', \text{ say.}
\end{aligned}$$

The resulting expression for  $Q_N$ , when compared with eqn. (14.2.19), leads to the functional equation

$$f(K_1, \Lambda) = -\frac{1}{2}K_0'' + \frac{1}{2}f(K_1, \Lambda''), \quad (1)$$

where

$$K_0'' = \frac{1}{2} \ln \left( \frac{2\pi}{K_1} \right) \text{ and } \Lambda'' = \frac{2\Lambda^2}{K_1} - K_1. \quad (2)$$

To verify that the function (14.2.32) satisfies the functional equation (1), we note that the right-hand side of this equation is

$$\begin{aligned} & -\frac{1}{4} \ln \left( \frac{2\pi}{K_1} \right) + \frac{1}{4} \ln \left[ \frac{\Lambda'' + \sqrt{\Lambda''^2 - K_1^2}}{2\pi} \right] \\ &= \frac{1}{4} \ln \left[ \frac{K_1}{2\pi} \cdot \frac{(2\Lambda^2/K_1 - K_1) + \sqrt{4\Lambda^4/K_1^2 - 4\Lambda^2}}{2\pi} \right] \\ &= \frac{1}{4} \ln \left[ \frac{2\Lambda^2 - K_1^2 + 2\Lambda\sqrt{\Lambda^2 - K_1^2}}{4\pi^2} \right] = \frac{1}{2} \ln \left[ \frac{\Lambda + \sqrt{\Lambda^2 - K_1^2}}{2\pi} \right], \end{aligned}$$

which is precisely  $f(K_1, \Lambda)$ .

**14.5.** For a solution to this problem, see Kadanoff (1976a).

**14.6.** The eigenvalues  $\lambda_1$  and  $\lambda_2$  of the matrix  $\mathcal{A}_\ell^*$  are determined by the equation

$$\begin{vmatrix} a_{11} - \lambda & a_{12} \\ a_{21} & a_{22} - \lambda \end{vmatrix} = 0.$$

Clearly,

$$\lambda_1 + \lambda_2 = a_{11} + a_{22}, \quad \text{while} \quad \lambda_1 \lambda_2 = a_{11}a_{22} - a_{12}a_{21}. \quad (1)$$

The eigenfunctions  $\varphi_1$  and  $\varphi_2$  are given by

$$\varphi_1 = \text{const} \begin{pmatrix} x_1 \\ y_1 \end{pmatrix}, \quad \text{where} \quad \frac{y_1}{x_1} = \frac{\lambda_1 - a_{11}}{a_{12}} = \frac{a_{21}}{\lambda_1 - a_{22}}, \quad \text{and} \quad (2)$$

$$\varphi_2 = \text{const} \begin{pmatrix} x_2 \\ y_2 \end{pmatrix}, \quad \text{where} \quad \frac{y_2}{x_2} = \frac{\lambda_2 - a_{11}}{a_{12}} = \frac{a_{21}}{\lambda_2 - a_{22}}, \quad (3)$$

(a) Now, by eqn. (14.3.13a),

$$\begin{aligned} k_1 &= u_1 x_1 + u_2 x_2, \quad k_2 = u_1 y_1 + u_2 y_2, \quad \text{where} \\ u_1 &= \frac{k_1 y_2 - k_2 x_2}{x_1 y_2 - y_1 x_2}, \quad u_2 = \frac{k_1 y_1 - k_2 x_1}{x_2 y_1 - y_2 x_1}. \end{aligned}$$

It follows that the slope of the line  $u_1 = 0$  in the  $(k_1, k_2)$ -plane is  $m_1 = y_2/x_2$ , which is given by eqn. (3), while the slope of the line

$u_2 = 0$  is  $m_2 = y_1/x_1$ , which is given by eqn. (2). We readily see that the product

$$m_1 m_2 = \frac{\lambda_2 - a_{11}}{a_{12}} \cdot \frac{\lambda_1 - a_{11}}{a_{12}} = \frac{\lambda_2 \lambda_1 - a_{11}(\lambda_2 + \lambda_1) + a_{11}^2}{a_{12}^2}$$

Substituting from eqns. (1), we get

$$m_1 m_2 = \frac{(a_{11}a_{22} - a_{12}a_{21}) - a_{11}(a_{11} + a_{22}) + a_{11}^2}{a_{12}^2} = -\frac{a_{21}}{a_{12}}.$$

It follows that the two lines will be mutually perpendicular if and only if  $a_{12} = a_{21}$ .

- (b) If  $a_{12}$  or  $a_{21} = 0$ , then by eqns. (1),  $\lambda_1 = a_{11}$  and  $\lambda_2 = a_{22}$ . The stated results then follow straightforwardly.
- (c) If  $a_{11} = 0$ , then  $m_1 = -a_{21}/\lambda_1 = \lambda_2/a_{12}$  and  $m_2 = -a_{21}/\lambda_2 = \lambda_1/a_{12}$ . On the other hand, if  $a_{22} = 0$ , then  $m_1 = a_{21}/\lambda_2 = -\lambda_1/a_{12}$  and  $m_2 = a_{21}/\lambda_1 = -\lambda_2/a_{12}$ .

**14.7.** In the limit  $n \rightarrow \infty$ , we obtain from eqns. (14.4.38–40)

$$\begin{aligned} \nu &\approx \frac{1}{2} + \frac{1}{4}\varepsilon, \quad \Delta \approx \frac{3}{2} + \frac{1}{2}\varepsilon, \quad \alpha \approx -\frac{1}{2}\varepsilon, \\ \beta &\approx \frac{1}{2}, \quad \gamma \approx 1 + \frac{1}{2}\varepsilon, \quad \delta \approx 3 + \varepsilon, \quad \eta \approx 0. \end{aligned}$$

At the same time, we obtain directly from eqns. (13.5.47, 66 and 67), with  $d = 4 - \varepsilon$  where  $0 < \varepsilon \ll 1$ ,

$$\begin{aligned} \alpha &\simeq \frac{-\varepsilon}{2}, \quad \beta = \frac{1}{2}, \quad \gamma = \frac{2}{2-\varepsilon} \simeq 1 + \frac{1}{2}\varepsilon, \\ \delta &= \frac{6-\varepsilon}{2-\varepsilon} = 3 \frac{1-\frac{1}{6}\varepsilon}{1-\frac{1}{2}\varepsilon} \simeq 3 \left(1 + \frac{1}{3}\varepsilon\right) = 3 + \varepsilon, \quad \eta = 0, \\ \nu &= \frac{1}{2-\varepsilon} \simeq \frac{1}{2} \left(1 + \frac{1}{2}\varepsilon\right) = \frac{1}{2} + \frac{1}{4}\varepsilon. \end{aligned}$$

To the given order in  $\varepsilon$ , the two sets of results are in complete agreement.

**14.8 & 9.** For  $d = 4 - \varepsilon$  where  $0 < \varepsilon \ll 1$ , eqn. (14.4.46) gives

$$S_d \approx \frac{\sin(\pi - \pi\varepsilon/2)\Gamma(3)}{2\pi\{\Gamma(2)\}^2} \approx \frac{1}{2}\varepsilon.$$

Equations (14.4.43–45) then give

$$\begin{aligned} \eta &\simeq \frac{4\varepsilon \cdot \frac{1}{2}\varepsilon}{4} \frac{1}{n} = \frac{\varepsilon^2}{2n}, \\ \gamma &\simeq \frac{2}{2-\varepsilon} \left(1 - \frac{3\varepsilon}{n}\right) \simeq \left(1 + \frac{1}{2}\varepsilon\right) \left\{1 - \frac{3\varepsilon}{n}\right\} \simeq 1 + \left(\frac{1}{2} - \frac{3}{n}\right)\varepsilon, \\ \alpha &\simeq -\frac{\varepsilon}{2-\varepsilon} \left(1 - \frac{12\varepsilon}{\varepsilon} \frac{1}{n}\right) \simeq -\frac{\varepsilon}{2} \left(1 - \frac{12}{n}\right). \end{aligned}$$



Next, we obtain

$$\begin{aligned}
\beta &= \frac{1}{2}(2 - \alpha - \gamma) = \frac{1}{2} - \frac{2(2d-5)S_d}{d-2} \frac{1}{n} + O\left(\frac{1}{n^2}\right) \\
&\simeq \frac{1}{2} - \frac{3}{2n}\varepsilon, \\
\delta &= 1 + \frac{\gamma}{\beta} = 1 + \frac{4}{d-2} \frac{1 - 6S_d/n + O(1/n^2)}{1 - 4(2d-5)/(d-2) \cdot (S_d/n) + O(1/n^2)} \\
&= 1 + \frac{4}{2-\varepsilon} \left[ 1 + O\left(\frac{1}{n^2}\right) \right] \simeq 1 + 2\left(1 + \frac{1}{2}\varepsilon\right) = 3 + \varepsilon, \\
\nu &= \frac{\gamma}{2-\eta} = \frac{1}{d-2} \frac{1 - 6S_d/n + O(1/n^2)}{1 - 2(4-d)/d \cdot (S_d/n) + O(1/n^2)} \\
&\simeq \frac{1}{2-\varepsilon} \left(1 - \frac{3\varepsilon}{n}\right) \simeq \frac{1}{2} \left(1 + \frac{1}{2}\varepsilon\right) \left(1 - \frac{3\varepsilon}{n}\right) \simeq \frac{1}{2} \left[ 1 + \left(\frac{1}{2} - \frac{3}{n}\right)\varepsilon \right] \\
&= \frac{1}{2} + \frac{1}{4} \left(1 - \frac{6}{n}\right)\varepsilon.
\end{aligned}$$

All these results agree with the corresponding ones following from eqns. (14.4.38–40).

# Chapter 15

- 15.1.** (i) We multiply expression (15.1.11) by  $\Delta T$ , take its average and utilize relations (15.1.14), to obtain  $\overline{(\Delta T \Delta S)} = kT$ .
- (ii) We multiply expression (15.1.12) by  $\Delta V$ , take its average and utilize relations (15.1.14), to obtain  $\overline{(\Delta P \Delta V)} = -kT$ .
- (iii) We multiply expression (15.1.11) by  $\Delta V$ , take its average and utilize relations (15.1.14), to obtain

$$\overline{\Delta S \Delta V} = \left( \frac{\partial P}{\partial T} \right)_V kT \left[ -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T \right] V = kT \left( \frac{\partial V}{\partial T} \right)_P.$$

- (iv) We multiply expression (15.1.12) by  $\Delta T$ , take its average and utilize relations (15.1.14), to obtain  $\overline{(\Delta P \Delta T)} = kT^2 C_V^{-1} (\partial P / \partial T)_V$ .
- 15.2.** If we choose  $\Delta S$  and  $\Delta P$  as our *independent variables*, then

$$\begin{aligned} \Delta T &= \left( \frac{\partial T}{\partial S} \right)_P \Delta S + \left( \frac{\partial T}{\partial P} \right)_S \Delta P = \frac{T}{C_P} \Delta S + \left( \frac{\partial T}{\partial P} \right)_S \Delta P, \text{ and} \\ \Delta V &= \left( \frac{\partial V}{\partial S} \right)_P \Delta S + \left( \frac{\partial V}{\partial P} \right)_S \Delta P = \left( \frac{\partial T}{\partial P} \right)_S \Delta S - V \kappa_S \Delta P. \end{aligned}$$

It follows that

$$-\Delta T \Delta S + \Delta P \Delta V = -\frac{T}{C_P} (\Delta S)^2 - V \kappa_S (\Delta P)^2,$$

which converts expression (15.1.8) into (15.1.15), leading directly to expressions (15.1.16) for  $\overline{(\Delta S)^2}$ ,  $\overline{(\Delta P)^2}$  and  $\overline{(\Delta S \Delta P)}$ .

For an independent evaluation of these averages, we proceed as in Prob-

lem 15.1. From eqns. (15.1.11, 12 and 14), we readily obtain

$$\begin{aligned}\overline{(\Delta S)^2} &= \frac{C_V^2}{T^2} \overline{(\Delta T)^2} + \left( \frac{\partial P}{\partial T} \right)_V^2 \overline{(\Delta V)^2} = k \left[ C_V + TV \kappa_T \left( \frac{\partial P}{\partial T} \right)_V^2 \right] = kC_P, \\ \overline{(\Delta P)^2} &= \left( \frac{\partial P}{\partial T} \right)_V^2 \overline{(\Delta T)^2} + \frac{1}{\kappa_T^2 V^2} \overline{(\Delta V)^2} = \frac{kT}{C_V} \left[ T \left( \frac{\partial P}{\partial T} \right)_V^2 + \frac{C_V}{\kappa_T V} \right] \\ &= \frac{kT}{C_V} \cdot \frac{C_P}{\kappa_T V} = \frac{kT}{\kappa_S V}, \text{ and} \\ \overline{(\Delta S \Delta P)} &= \frac{C_V}{T} \left( \frac{\partial P}{\partial T} \right)_V \overline{(\Delta T)^2} - \left( \frac{\partial P}{\partial T} \right)_V \frac{1}{\kappa_T V} \overline{(\Delta V)^2} = 0.\end{aligned}$$

**15.3.** We start with expression (15.1.6) and eliminate  $\Delta S$  by writing

$$\begin{aligned}\Delta S &= \left( \frac{\partial S}{\partial E} \right)_0 \Delta E + \left( \frac{\partial S}{\partial V} \right)_0 \Delta V + \frac{1}{2} \left[ \left( \frac{\partial^2 S}{\partial E^2} \right)_0 (\Delta E)^2 \right. \\ &\quad \left. + 2 \left( \frac{\partial^2 S}{\partial E \partial V} \right)_0 \Delta E \Delta V + \left( \frac{\partial^2 S}{\partial V^2} \right)_0 (\Delta V)^2 \right] + \dots\end{aligned}$$

Replacing  $(\partial S/\partial E)_0$  by  $1/T$  and  $(\partial S/\partial V)_0$  by  $P/T$ , and retaining terms up to second order only, expression (15.1.6) takes the form

$$p \propto \exp \left[ \frac{1}{2k} \left\{ \left( \frac{\partial \theta}{\partial E} \right)_0 (\Delta E)^2 + 2 \left( \frac{\partial \theta}{\partial V} \text{ or } \frac{\partial \pi}{\partial E} \right)_0 \Delta E \Delta V + \left( \frac{\partial \pi}{\partial V} \right)_0 (\Delta V)^2 \right\} \right],$$

where  $\theta = 1/T$  and  $\pi = P/T$ . The covariance matrix of this distribution is given by

$$\begin{pmatrix} \overline{(\Delta E)^2} & \overline{(\Delta E \Delta V)} \\ \overline{(\Delta V \Delta E)} & \overline{(\Delta V)^2} \end{pmatrix} = k \begin{pmatrix} -\frac{\partial \theta}{\partial E} & -\frac{\partial \theta}{\partial V} \\ -\frac{\partial \pi}{\partial E} & -\frac{\partial \pi}{\partial V} \end{pmatrix}^{-1}.$$

The evaluation of the inverse here is rather tricky; the interested reader may consult Kubo (1965), problem 6.2, pp. 382-5, where a complete solution, along with the desired results for  $\overline{(\Delta E)^2}$ ,  $\overline{(\Delta V)^2}$  and  $\overline{(\Delta E \Delta V)}$ , is given.

In passing, we note that two of the aforementioned results are also given in eqns. (15.1.14 and 18); the third may be obtained as follows: multiply (15.1.17) by  $\Delta V$ , take its average and utilize relations (15.1.14), to get

$$\begin{aligned}\overline{(\Delta E \Delta V)} &= \left( \frac{\partial E}{\partial V} \right)_T \overline{(\Delta V)^2} = \left[ T \left( \frac{\partial P}{\partial T} \right)_V - P \right] kT \kappa_T V \\ &= kT \left[ T \left( \frac{\partial V}{\partial T} \right)_P + P \left( \frac{\partial V}{\partial P} \right)_T \right].\end{aligned}$$

**15.4.** With a given displacement  $y(x)$ , the overall shape of the string would, on an average, be as shown in Fig. 1. This amounts to a strain,  $\Delta\ell$ , in the string given by the expression

$$\Delta\ell = \sqrt{x^2 + y^2} + \sqrt{(\ell - x)^2 + y^2} - \ell;$$

the energy  $\Phi$  associated with this strain is obviously  $F\Delta\ell$ . For small  $y$ ,

$$\Phi(y) \approx F \left[ \frac{y^2}{2x} + \frac{y^2}{2(\ell - x)} \right] = \frac{F\ell}{2x(\ell - x)} y^2,$$

which leads to a probability distribution for  $y$  that is Gaussian, with variance

$$\overline{(\Delta y)^2} = \frac{kT}{F\ell} x(\ell - x).$$

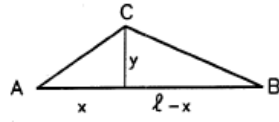


Fig. 1

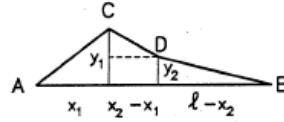


Fig. 2

For the second part, we refer to Fig. 2 for which

$$\begin{aligned} \Delta\ell &= \sqrt{x_1^2 + y_1^2} + \sqrt{(x_2 - x_1)^2 + (y_1 - y_2)^2} + \sqrt{(\ell - x_2)^2 + y_2^2} - \ell \\ &\approx \frac{y_1^2}{2x_1} + \frac{(y_1 - y_2)^2}{2(x_2 - x_1)} + \frac{y_2^2}{2(\ell - x_2)}, \text{ and hence} \end{aligned}$$

$$\Phi(y_1, y_2) \approx \frac{F}{2x_1(x_2 - x_1)(\ell - x_2)} [x_2(\ell - x_2)y_1^2 - 2x_1(\ell - x_2)y_1y_2 + x_1(\ell - x_1)y_2^2].$$

This leads to a bivariate Gaussian distribution in the variables  $y_1$  and  $y_2$ , with the covariance matrix

$$\begin{aligned} \begin{pmatrix} \overline{y_1^2} & \overline{y_1 y_2} \\ \overline{y_2 y_1} & \overline{y_2^2} \end{pmatrix} &= \frac{kT x_1 (x_2 - x_1) (\ell - x_2)}{F} \begin{pmatrix} x_2(\ell - x_2) & -x_1(\ell - x_2) \\ -x_1(\ell - x_2) & x_1(\ell - x_1) \end{pmatrix}^{-1} \\ &= \frac{kT}{F\ell} \begin{pmatrix} x_1(\ell - x_1) & x_1(\ell - x_2) \\ x_1(\ell - x_2) & x_2(\ell - x_2) \end{pmatrix}. \end{aligned}$$

**15.5.** The quantity in question here is

$$\{(\overline{\Delta N_A})^2\}^{1/2} / \bar{N}_A = (kT \kappa_T / V_A)^{1/2}; \quad (1)$$

see eqn. (15.1.20). Assuming the gas to be an ideal one, the compressibility  $\kappa_T$  may be taken as  $1/(nkT)$ , where  $n$  is the particle density in the system; see eqn. (15.2.12). This reduces (1) to the simple expression  $(1/\bar{N}_A)^{1/2}$ .

For this fraction to be 1 per cent, the volume  $V_A$  of the subsystem must be such that it contains, on an average,  $10^4$  particles. At normal temperature and pressure, this volume would be about  $3.7 \times 10^{-22} m^3$  — for instance, a cube of side  $7.2 \times 10^{-8} m$ .

**15.6.** By eqns. (15.2.23) and (15.3.11), and by Note 5, we have

$$\overline{x^2} = 2Dt = 2BkTt = kTt/3\pi\eta a.$$

It follows that

$$k = 3\pi\eta a \overline{x^2}/Tt.$$

Substituting the given data, we get:  $k = 1.18 \times 10^{-16} \text{ erg } K^{-1}$ , which may be compared with the accepted value of  $1.38 \times 10^{-16} \text{ erg } K^{-1}$ .

**15.7.** By eqn. (15.3.2), we have

$$\langle \mathbf{v} \cdot \mathbf{F} \rangle = M \left\langle \mathbf{v} \cdot \frac{d\mathbf{v}}{dt} \right\rangle + \frac{1}{B} \langle \mathbf{v} \cdot \mathbf{v} \rangle = \frac{1}{2} M \frac{d}{dt} \langle v^2 \rangle + \frac{1}{B} \langle v^2 \rangle.$$

Substituting for  $\langle v^2 \rangle$  from eqn. (15.3.29) and remembering that  $B = \tau/M$ , we get

$$\begin{aligned} \langle \mathbf{v} \cdot \mathbf{F} \rangle &= \frac{M}{\tau} \left\{ \frac{3kT}{M} - v^2(0) \right\} e^{-2t/\tau} + \frac{1}{B} \left[ \frac{3kT}{M} - \left\{ \frac{3kT}{M} - v^2(0) \right\} e^{-2t/\tau} \right] \\ &= \frac{3kT}{BM} = \frac{3kT}{\tau}, \end{aligned}$$

which holds at *all*  $t$ . By tacit assumption, the statement  $\langle \mathbf{r} \cdot \mathbf{F} \rangle = 0$  also holds at *all*  $t$ . On the other hand, the quantities  $\langle \mathbf{v} \cdot \mathcal{F} \rangle$  and  $\langle \mathbf{r} \cdot \mathcal{F} \rangle$  behave somewhat differently.

First of all,

$$\langle \mathbf{v} \cdot \mathcal{F} \rangle = M \left\langle \mathbf{v} \cdot \frac{d\mathbf{v}}{dt} \right\rangle = \frac{1}{2} M \frac{d}{dt} \langle v^2 \rangle$$

If the Brownian particle has already attained thermal equilibrium, then  $\langle v^2 \rangle = 3kT/M$  and hence  $\langle \mathbf{v} \cdot \mathcal{F} \rangle = 0$ ; if it hasn't, then

$$\langle \mathbf{v} \cdot \mathcal{F} \rangle = \frac{M}{\tau} \left\{ \frac{3kT}{M} - v^2(0) \right\} e^{-2t/\tau},$$

which decays exponentially with  $t$ . Next, by eqns. (15.3.1 and 5),

$$\langle \mathbf{r} \cdot \mathcal{F} \rangle = M \left\langle \mathbf{r} \cdot \frac{d\mathbf{v}}{dt} \right\rangle = -\frac{M}{\tau} \langle \mathbf{r} \cdot \mathbf{v} \rangle = -\frac{M}{2\tau} \frac{d}{dt} \langle r^2 \rangle.$$

Once again, if the particle has already attained thermal equilibrium, then, by eqn. (15.3.7),

$$\langle \mathbf{r} \cdot \mathcal{F} \rangle = -3kT(1 - e^{-t/\tau}) \xrightarrow[t \gg \tau]{} -3kT;$$

if it hasn't, then, by eqn. (15.3.31),

$$\langle \mathbf{r} \cdot \mathcal{F} \rangle = [-3kT + \{3kT - M\mathbf{v}^2(0)\}e^{-t/\tau}](1 - e^{-t/\tau})$$

which too approaches  $-3kT$  when  $t$  becomes much larger than  $\tau$ .

**15.8.** Integrating eqn. (15.3.14) over  $t$ , we get

$$\mathbf{r}(t) = \int_0^t \mathbf{v}(t') dt' = \mathbf{v}(0) \left[ -\tau e^{-t'/\tau} \right]_0^t + \int_0^t \left[ e^{-t'/\tau} \int_0^{t'} e^{u/\tau} \mathbf{A}(u) du \right] dt'. \quad (1)$$

The remaining integration may be carried out by parts, with the result

$$\begin{aligned} & \left[ (-\tau e^{-t'/\tau}) \int_0^{t'} e^{u/\tau} \mathbf{A}(u) du \right]_0^t - \int_0^t (-\tau e^{-t'/\tau}) \{e^{t'/\tau} \mathbf{A}(t')\} dt' \\ &= -\tau e^{-t/\tau} \int_0^t e^{u/\tau} \mathbf{A}(u) du + \tau \int_0^t \mathbf{A}(t') dt'. \end{aligned} \quad (2)$$

Substituting (2) into (1), we obtain the desired result

$$\mathbf{r}(t) = \mathbf{v}(0)\tau(1 - e^{-t/\tau}) + \tau \int_0^t \{1 - e^{(u-t)/\tau}\} \mathbf{A}(u) du. \quad (3)$$

To obtain an expression for  $\langle r^2(t) \rangle$ , we take the square of (3) and average it over an ensemble. The cross-term vanishes on averaging, and we are left with

$$\begin{aligned} \langle r^2(t) \rangle &= v^2(0)\tau^2(1 - e^{-t/\tau})^2 + \tau^2 \int_0^t \int_0^t \{1 - e^{(u_1-t)/\tau}\} \{1 - e^{(u_2-t)/\tau}\} \\ &\quad \langle \mathbf{A}(u_1) \cdot \mathbf{A}(u_2) \rangle du_1 du_2. \end{aligned} \quad (4)$$

Noting that the autocorrelation function  $\langle \mathbf{A}(u_1) \cdot \mathbf{A}(u_2) \rangle$ , which is the same as the function  $K(s)$  of Sec. 15.3, may be treated as a delta function, see the passage from eqn. (15.3.24) to (15.3.25) along with eqns. (15.3.26 and 28), we may write

$$\langle \mathbf{A}(u_1) \cdot \mathbf{A}(u_2) \rangle = C\delta(u_2 - u_1), \text{ where } C = 6kT/M\tau.$$

The second term in (4) then takes the form

$$\begin{aligned} & \frac{6kT\tau}{M} \int_0^t \{1 - e^{(u-t)/\tau}\}^2 du \\ &= \frac{6kT\tau}{M} \left[ t - \frac{1}{2}\tau(1 - e^{-t/\tau})(3 - e^{-t/\tau}) \right]. \end{aligned} \quad (5)$$

Substituting (5) into (4), we obtain eqn. (15.3.31).

**15.13.** By eqn. (15.5.14), we have in the first case

$$\begin{aligned} w(f) &= 4 \int_0^{\infty} K(0) e^{-\alpha s^2} \cos(2\pi f^* s) \cos(2\pi f s) ds \\ &= 2K(0) \int_0^{\infty} e^{-\alpha s^2} [\cos\{2\pi(f - f^*)s\} + \cos\{2\pi(f + f^*)s\}] ds. \end{aligned}$$

Using formula (B.41), we get the desired result

$$w(f) = K(0) \left( \frac{\pi}{\alpha} \right)^{1/2} [e^{-\pi^2(f-f^*)^2/\alpha} + e^{-\pi^2(f+f^*)^2/\alpha}].$$

In the limit  $\alpha \rightarrow 0$  (with  $f^* > 0$ ),  $w(f) \rightarrow K(0)\delta(f - f^*)$ ; see eqn. (B.43). In the limit  $f^* \rightarrow 0$  (with  $\alpha > 0$ ),  $w(f) \rightarrow 2K(0)(\pi/\alpha)^{1/2} \exp\{-(\pi^2 f^2/\alpha)\}$ . On the other hand, if both  $\alpha$  and  $f^* \rightarrow 0$ ,  $w(f)$  tends to be  $2K(0)\delta(f)$ . In either case, eqn. (15.5.16) is satisfied.

In the second case, we get

$$w(f) = 2K(0) \left[ \frac{\alpha}{\alpha^2 + 4\pi^2(f - f^*)^2} + \frac{\alpha}{\alpha^2 + 4\pi^2(f + f^*)^2} \right].$$

Now, in the limit  $\alpha \rightarrow 0$  (with  $f^* > 0$ ),  $w(f) \rightarrow 2\pi K(0)\delta\{2\pi(f - f^*)\} = K(0)\delta(f - f^*)$ ; see eqn. (B.36). In the limit  $f^* \rightarrow 0$  (with  $\alpha > 0$ ),  $w(f) \rightarrow 4K(0)\alpha/(\alpha^2 + 4\pi^2 f^2)$ . On the other hand, if both  $\alpha$  and  $f^* \rightarrow 0$ ,  $w(f)$  again tends to be  $2K(0)\delta(f)$ .

**15.14.** By eqn. (15.5.14), we get

$$\begin{aligned} w(f) &= 4 \int_0^{\infty} K(0) \frac{\sin(as) \sin(bs)}{abs^2} \cos(2\pi f s) ds \\ &= \frac{2K(0)}{ab} \int_0^{\infty} \sin(as) [\sin\{(b - 2\pi f)s\} + \sin\{(b + 2\pi f)s\}] \frac{ds}{s^2}. \quad (1) \end{aligned}$$

To evaluate the integral in (1), we use the formula, see Gradshteyn and Ryzhik (1965),

$$\int_0^{\infty} \sin(px) \sin(qx) \frac{dx}{x^2} = \begin{cases} p\pi/2 & \text{if } p \leq q \\ q\pi/2 & \text{if } q \leq p \end{cases}.$$

It follows that if  $0 < f \leq (a - b)/2\pi$ , then the integral in (1) is equal to

$$(b - 2\pi f)\pi/2 + (b + 2\pi f)\pi/2 = b\pi. \quad (2)$$

If  $(a - b)/2\pi \leq f \leq (a + b)/2\pi$ , then our integral is equal to

$$(b - 2\pi f)\pi/2 + a\pi/2 = (a + b - 2\pi f)\pi/2. \quad (3)$$

If  $f \geq (a + b)/2\pi$ , then we have

$$-a\pi/2 + a\pi/2 = 0. \quad (4)$$

Substituting (2)–(4) into (1), we obtain the desired result for  $w(f)$ .

It is quite straightforward to check that the function  $w(f)$  obtained here satisfies eqn. (15.5.16).

**15.15.** (a) From the defining equation of the variable  $Y(t)$ , we get

$$\langle Y^2(t) \rangle = \int_u^{u+t} \int_u^{u+t} \langle y(u_1)y(u_2) \rangle du_1 du_2 \quad (1)$$

Since  $y(u)$  is *statistically stationary*, we may write

$$\langle y(u_1)y(u_2) \rangle = \int_0^\infty w(f) \cos(2\pi fs) df \quad (s = u_2 - u_1); \quad (2)$$

see eqn. (15.5.15). Substituting (2) into (1), we get

$$\begin{aligned} \langle Y^2(t) \rangle &= \int_0^\infty w(f) I(f, t) df, \text{ where} \\ I(f, t) &= \int_u^{u+t} \int_u^{u+t} \{ \cos(2\pi fu_2) \cos(2\pi fu_1) + \sin(2\pi fu_2) \sin(2\pi fu_1) \} du_1 du_2 \\ &= \left[ \int_u^{u+t} \cos(2\pi fu) du \right]^2 + \left[ \int_u^{u+t} \sin(2\pi fu) du \right]^2 \\ &= \frac{1}{4\pi^2 f^2} [ [\sin\{2\pi f(u+t)\} - \sin(2\pi fu)]^2 + \\ &\quad [\cos(2\pi fu) - \cos\{2\pi f(u+t)\}]^2 ] \\ &= \frac{1}{2\pi^2 f^2} [1 - \cos(2\pi ft)], \text{ regardless of the initial instant } u. \end{aligned} \quad (4)$$

Substituting (4) into (3), we obtain the desired result for  $\langle Y^2(t) \rangle$ .



Next, it follows that

$$\frac{\partial}{\partial t} \langle Y^2(t) \rangle = \frac{1}{\pi} \int_0^\infty \frac{w(f)}{f} \sin(2\pi ft) df, \text{ and} \quad (5)$$

$$\frac{\partial^2}{\partial t^2} \langle Y^2(t) \rangle = 2 \int_0^\infty w(f) \cos(2\pi ft) df. \quad (6)$$

Taking the sine transform of (5) and the cosine transform of (6), we obtain the other quoted results. Finally, a comparison of eqns. (2) and (6) shows that

$$K_y(s) = \frac{1}{2} \frac{\partial^2}{\partial s^2} \langle Y^2(s) \rangle. \quad (7)$$

- (b) If the variable  $y(u)$  is the  $x$ -component of the velocity of a Brownian particle, with power spectrum (15.5.21), then eqns. (3) and (4) give

$$\begin{aligned} \langle x^2(t) \rangle &= \frac{2kT\tau}{\pi^2 M} \int_0^\infty \frac{1 - \cos(2\pi ft)}{f^2 \{1 + (2\pi f\tau)^2\}} df \\ &= \frac{4kT\tau^2}{\pi M} \int_0^\infty \frac{1 - \cos(xt/\tau)}{x^2(1 + x^2)} dx \\ &= \frac{2kT\tau^2}{M} \left[ \frac{t}{\tau} - (1 - e^{-t/\tau}) \right], \end{aligned} \quad (8)$$

in complete agreement with eqn. (15.3.7) for the quantity  $\langle r^2(t) \rangle$ . We also note that

$$\frac{1}{2} \frac{\partial^2}{\partial s^2} \langle x^2(s) \rangle = \frac{kT}{M} e^{-s/\tau} \quad (s > 0), \quad (9)$$

which indeed is equal to the autocorrelation function  $K(s)$  of the variable  $v_x$ ; see eqn. (15.6.20).

**15.16.** First we'll prove the following lemma.

Lemma:

For a given variable  $x(t)$ , define a complementary function

$$y_x(f, T) = \frac{1}{\sqrt{T}} \int_{-T/2}^{T/2} x(t) e^{-2\pi ift} dt. \quad (1)$$

The power spectrum of the variable  $x(t)$  is then given by

$$w_x(f) = 2 \lim_{T \rightarrow \infty} |y_x(f, T)|^2. \quad (2)$$

Proof:

From (1), it readily follows that

$$|y_x(f, T)|^2 = \frac{1}{T} - \int_{-T/2}^{T/2} \int_{-T/2}^{T/2} x(t_1)x(t_2)e^{2\pi if(t_2-t_1)} dt_1 dt_2.$$

Changing over to the variables  $S$  and  $s$ , as defined in eqns. (15.3.23), we get

$$|y_x(f, T)|^2 = \frac{1}{T} \int \int x\left(S - \frac{1}{2}s\right) x\left(S + \frac{1}{2}s\right) \cos(2\pi fs) dS ds.$$

Integrating over  $S$  and letting  $T \rightarrow \infty$  amounts to taking an ensemble average of the quantity  $x\left(S - \frac{1}{2}s\right) x\left(S + \frac{1}{2}s\right)$ ; this reduces the above expression to

$$\int_{-\infty}^{\infty} K_x(s) \cos(2\pi fs) ds$$

which, by eqn. (15.5.14), is equal to  $\frac{1}{2}w_x(f)$ . Hence the lemma.

We now proceed to establish the stated relation between the power spectra  $w_v(f)$  and  $w_A(f)$ . For this we refer to eqn. (15.3.5) for the variable  $\mathbf{A}(t)$  and construct its complementary function

$$y_A(f, T) = \frac{1}{\sqrt{T}} \int_{-T/2}^{T/2} \left( \frac{d\mathbf{v}}{dt} + \frac{\mathbf{v}}{\tau} \right) e^{-2\pi ift} dt. \quad (3)$$

The first part here gives

$$\frac{1}{\sqrt{T}} \left[ \mathbf{v} e^{-2\pi ift} \Big|_{-T/2}^{T/2} - \int_{-T/2}^{T/2} \mathbf{v}(-2\pi if) e^{-2\pi ift} dt \right].$$

Equation (3) then becomes

$$y_A(f, T) = \frac{1}{\sqrt{T}} \left[ \mathbf{v} \left( \frac{T}{2} \right) e^{-\pi ifT} - \mathbf{v} \left( -\frac{T}{2} \right) e^{\pi ifT} \right] + \left( \frac{1}{\tau} + 2\pi if \right) y_v(f, T).$$

Since the variable  $\mathbf{v}(t)$  is bounded, the limit  $T \rightarrow \infty$  gives

$$|y_A(f, T)|^2 \approx \left| \frac{1}{\tau} + 2\pi if \right|^2 |y_v(f, T)|^2. \quad (4)$$

Using lemma (2), we finally get

$$w_A(f) = \left[ \frac{1}{\tau^2} + (2\pi f)^2 \right] w_v(f), \quad (5)$$

which is the desired result.

Now, by eqn. (15.5.21),

$$w_v(f) = \frac{12kT\tau}{M} \frac{1}{1 + (2\pi f\tau)^2}. \quad (6)$$

Substituting (6) into (5), we readily obtain the stated result for  $w_A(f)$ . Note that this result is consistent with the assertion that, for most practical purposes, the autocorrelation function  $K_A(s)$  may be taken as  $C\delta(s)$ , with  $C = 6kT/M\tau$ ; see eqns. (15.3.26 and 28).

- 15.17.** (a) Using eqn. (15.3.14), we construct the quantity  $\mathbf{v}(t) \cdot \mathbf{v}(t+s)$  and average it over an ensemble. The cross-term vanishes on averaging, and we are left with

$$\langle \mathbf{v}(t) \cdot \mathbf{v}(t+s) \rangle = e^{-2(t+s)/\tau} \left[ v^2(0) + \int_0^t \int_0^{t+s} e^{(u_1+u_2)\tau} \langle \mathbf{A}(u_1) \cdot \mathbf{A}(u_2) \rangle du_1 du_2 \right]. \quad (1)$$

In view of the argument leading from eqn. (15.3.24) to (15.3.25), we may replace the function  $\langle \mathbf{A}(u_1) \cdot \mathbf{A}(u_2) \rangle$  by the singular expression  $C\delta(u_2 - u_1)$ , where  $C = 6kT/M\tau$ . At the same time, we observe that the integral

$$\int_0^t e^{(u_1+u_2)/\tau} \delta(u_1 - u_2) du_1 = \begin{cases} e^{2u_2/\tau} & \text{if } 0 < u_2 < t \\ 0 & \text{otherwise.} \end{cases}$$

The double integral in (1) is then equal to

$$\begin{aligned} \int_0^t C e^{2u_2/\tau} du_2 &= C \frac{\tau}{2} (e^{2t/\tau} - 1) & \text{if } s > 0, \text{ and} \\ \int_0^{t+s} C e^{2u_2/\tau} du_2 &= C \frac{\tau}{2} (e^{2(t+s)/\tau} - 1) & \text{if } s < 0. \end{aligned}$$

Substituting these results into (1), we obtain eqns. (15.6.7) and (15.6.8). Equation (15.6.9) follows straightforwardly.

- (b) To evaluate  $\langle r^2(t) \rangle$ , we write eqn. (15.6.9) in the form

$$K_v(s) = \left( v^2(0) - \frac{3kT}{M} \right) e^{-2S/\tau} + \frac{3kT}{M} e^{-|s|/\tau}, \quad (2)$$

where  $S = \frac{1}{2}(u_1 + u_2)$  and  $s = (u_2 - u_1)$ . Substituting (2) into

eqn. (15.6.6), we get

$$\begin{aligned}\langle r^2(t) \rangle &= \left( v^2(0) - \frac{3kT}{M} \right) \left[ \int_0^{t/2} e^{-2S/\tau} \cdot 4S dS + \int_{t/2}^t e^{-2S/\tau} \cdot 4(t-S) dS \right] \\ &\quad + \frac{3kT}{M} \left[ \int_0^{t/2} 2 \int_0^{2S} e^{-2s/\tau} ds dS + \int_{t/2}^t 2 \int_0^{2(t-S)} e^{-2s/\tau} ds dS \right] \\ &= \left( v^2(0) - \frac{3kT}{M} \right) \cdot \tau^2 (1 - e^{-t/\tau})^2 + \frac{3kT}{M} \cdot 2\tau \{t - \tau(1 - e^{-t/\tau})\},\end{aligned}$$

which is the same as expression (15.3.31). Note that the second part of this result is identical with expression (15.3.7) that pertains to a *stationary* ensemble.

**15.18.** Using equation (15.3.37), the response function is

$$\tilde{\chi}_{vx}(\omega) = \int_0^\infty \chi_{vx}(s) e^{i\omega s} ds$$

which has imaginary part

$$\chi''_{vx}(\omega) = \frac{1}{M} \frac{\omega (\omega^2 - \omega_0^2)}{(\omega^2 - \omega_0^2)^2 + \gamma^2 \omega^2}.$$

The correlation function is

$$G_{vx}(t - t') = \int_{-\infty}^t ds \int_{-\infty}^{t'} ds' \chi_{vx}(t - s) \chi_{xx}(t' - s') \langle F(s) F(s') \rangle$$

Using  $\langle F(s) F(s') \rangle = 2\gamma M k T \delta(s - s')$  and Fourier transforming gives

$$S_{vx}(\omega) = \frac{2kT}{M} \frac{(\omega^2 - \omega_0^2)}{(\omega^2 - \omega_0^2)^2 + \gamma^2 \omega^2}.$$

**15.19.** Just differentiate equation (15.6.29) with respect to  $t$  and equation (15.6.28) drops out.

Correction to the first printing of third edition: 15.20 and 15.21: The correlation function relation should read:

$$G_{AB}(t) = G_{BA}(-t - i\beta\hbar).$$

**15.20.** Since we need to evaluate  $\langle [A(t), B(0)] \rangle$ , we need to relate  $\langle B(0)A(t) \rangle$  to  $\langle A(t)B(0) \rangle$ .

$$\begin{aligned}\langle B(0)A(t) \rangle &= \frac{1}{Q} \text{Tr} \left( B e^{iHt/\hbar} A e^{-iHt/\hbar} e^{-\beta H} \right) \\ &= \frac{1}{Q} \text{Tr} \left( e^{iHt/\hbar + \beta H} A e^{-iHt/\hbar - \beta H} B e^{-\beta H} \right) \\ &= \langle A(t - i\beta\hbar)B(0) \rangle\end{aligned}$$

Now equation (15.6.34) can be evaluated as

$$\begin{aligned}\chi''_{AB}(\omega) &= \frac{1}{2\hbar} \int (\langle A(t)B(0) \rangle - \langle A(t - i\beta\hbar)B(0) \rangle) e^{i\omega t} dt \\ &= \frac{1}{2\hbar} \int (\langle A(t)B(0) \rangle e^{i\omega t} - \langle A(t - i\beta\hbar)B(0) \rangle e^{i\omega(t - i\beta\hbar)} e^{-\beta\hbar\omega}) dt \\ &= \frac{1}{2\hbar} (1 - e^{-\beta\hbar\omega}) S_{AB}(\omega)\end{aligned}$$

**15.21.** Since  $\langle B(0)A(t) \rangle = \langle A(t - i\beta\hbar)B(0) \rangle$ ,

$$\langle A(t)B(0) - B(0)A(t) \rangle \approx i\beta\hbar \left\langle \frac{dA}{dt} B \right\rangle$$

as  $\hbar \rightarrow 0$ . Therefore,

$$\begin{aligned}\chi''_{AB}(\omega) &= \frac{1}{2\hbar} \int \langle A(t)B(0) - B(0)A(t) \rangle e^{i\omega t} dt \approx \frac{i\beta\hbar}{2\hbar} \int \left\langle \frac{dA}{dt} B(0) \right\rangle e^{i\omega t} dt \\ &= \frac{\beta\omega}{2} \int \langle A(t)B(0) \rangle e^{i\omega t} dt = \frac{\omega}{2kT} S_{AB}(\omega)\end{aligned}$$

**15.22.** The self-diffusion term can be written

$$\begin{aligned}S_{\text{self}}(\omega) &= \int \langle e^{-i\mathbf{k} \cdot (\mathbf{r}(t) - \mathbf{r}(0))} \rangle e^{i\omega t} dt \\ &= \int e^{i\omega t - Dk^2|t|} dt,\end{aligned}$$

using the diffusion relation  $\langle (x(t) - x(0))^2 \rangle = 2D|t|$ . Integrating gives

$$S_{\text{self}}(\omega) = \frac{2Dk^2}{\omega^2 + (Dk^2)^2};$$

compare to the heat diffusion term in equation (15.6.45).

**15.23.** The magnitude of the wavevector transfer is  $k = \sqrt{2}k_0 = 7 \times 10^6 \text{ m}^{-1}$  and the width of the Rayleigh peak is  $\Delta\omega = D_T k^2 = 7 \times 10^6 \text{ s}^{-1}$ . The location of the sound peak is at  $\omega = ck = 2.4 \times 10^9 \text{ m}^{-1}$  is well separated from the Rayleigh peak.

**15.24.** The Raman peak has  $\hbar\omega = 0.05 \text{ eV} \simeq 2kT$  at room temperature so the peaks are not symmetric. Since  $\Gamma \sim 10^{12} \text{ s}^{-1}$  and  $\omega \sim 8 \times 10^{13} \text{ s}^{-1}$ , the Raman peak is well resolved.

# Chapter 16

**16.1.** Here is a C code snippet for a pseudorandom number generator based on the L'Ecuyer prime number linear congruential generator discussed in Appendix I.

```
double rand(double seed[])
{
    seed[0] = fmod(seed[0] * 40014., 2147483563.);
    seed[1] = fmod(seed[1] * 40692., 2147483399.);
    double r=seed[0]- seed[1];
    if (r<= 0.0) r += 2147483562.;
    return r/2147483563.;
}
```

For a sequence of  $N$  numbers, one should test that  $\langle x \rangle \approx 0.5 \pm 1/(12\sqrt{N})$  and  $\langle x^2 \rangle - \langle x \rangle^2 \approx 1/12$ .

**16.2** Here is a code snippet for generating gaussian pseudorandom numbers based on the Box-Muller algorithm in Appendix I.

```
double s,w;
do
{
    double x=2.0*rand(seed)-1.0;
    double y=2.0*rand(seed)-1.0;
    s=x*x+y*y;
} while( s >= 1.0);
w=sqrt(-2.0*log(s)/s);
gaussrand = x*w;
```

For efficiency, one can also use  $y*w$  as an independent gaussian pseudorandom number. For a sequence of  $N$  numbers, one should test that  $\langle x \rangle \approx 0.0 \pm 1/\sqrt{N}$  and  $\langle x^2 \rangle \approx 1.0$ . The reader should also determine the expected uncertainty in the value of the variance for  $N$  numbers. The histogram of points for pairs of gaussian random numbers should be centered at 0, be isotropic, and have variance  $\langle x^2 + y^2 \rangle = 2$ .

**16.3** First note that the sum of two gaussian random distributions is also gaussian,

$$P_1(s_1) = \frac{\exp\left(-\frac{s_1^2}{2\sigma_1^2}\right)}{\sqrt{2\pi\sigma_1^2}}, \quad P_2(s_2) = \frac{\exp\left(-\frac{s_2^2}{2\sigma_2^2}\right)}{\sqrt{2\pi\sigma_2^2}},$$

$$P(S = s_1 + s_2) = \int \int \delta(S - s_1 - s_2) P_1(s_1) P_2(s_2) ds_1 ds_2,$$

$$P(S) = \frac{\exp\left(-\frac{S^2}{2(\sigma_1^2 + \sigma_2^2)}\right)}{\sqrt{2\pi(\sigma_1^2 + \sigma_2^2)}}.$$

Iterating the equation defining the correlated random numbers gives

$$s_k = (1 - \alpha) \sum_{j=0}^{\infty} \alpha^j r_{k-j}.$$

This implies that the  $s$ 's are also gaussian. The averages  $\langle s_k \rangle$  are clearly zero and the variance is given by

$$\langle s_k^2 \rangle = (1 - \alpha)^2 \sum_{i=0}^{\infty} \sum_{j=0}^{\infty} \alpha^{i+j} \langle r_{k-i} r_{k-j} \rangle,$$

which is easily evaluated to give

$$\langle s_k^2 \rangle = (1 - \alpha)^2 \sum_{j=0}^{\infty} \alpha^{2j} = \frac{(1 - \alpha)^2}{1 - \alpha^2} = \frac{1 - \alpha}{1 + \alpha}.$$

The correlations are then given by

$$\langle s_k s_{k-l} \rangle = \alpha^{|l|} \frac{1 - \alpha}{1 + \alpha}.$$

**16.4** A Monte Carlo Sweep of an ordered list of  $N$  particles

$x_0 < x_2 < x_3 < \dots < x_{N-1}$  is done with the following C code snippet.

```
xtrial = x[0] + dx*(rand(seed)-0.5);
if (xtrial - (x[n-1] - L) > 1.0 && x[1] - xtrial > 1.0) x[i]=xtrial;
for (int i=1;i<n-1;i++)
{
    xtrial=x[i] + dx*(rand(seed)-0.5);
    if (xtrial - x[i-1] > 1.0 && x[i+1]-xtrial > 1.0) x[i]=xtrial;
}
xtrial = x[n-1] + dx*(rand(seed)-0.5);
if (xtrial - x[n-2] > 1.0 && (x[0] + L) - xtrial > 1.0) x[i]=xtrial;
```

Note the periodic boundary conditions treat particle to the left of particle 0 as particle  $N - 1$  shifted left by  $L$ , and particle to the right of

particle  $N - 1$  as particle 0 shifted to the right by  $L$ . The random step size  $dx$  is typically chosen on the order of  $L/(DN) - 1$  but must be less than 2 to avoid particles getting out of order.

**16.5** Here is a C code snippet for a Monte Carlo of a two-dimensional system of hard spheres in a  $LX \times LY$  periodic box.

```
int i = n*rand(seed); // choose a particle randomly
double xtrial = x[i] + dx*(rand(seed)-0.5);
double ytrial = y[i] + dx*(rand(seed)-0.5);
int collision = 0;
for (int j=0;j<n;j++)
{
    if( j != i)
    {
        double dx = fabs(x[j]-x[i]);
        double dy = fabs(y[j]-y[i]);
        if (dx > halfLX) dx = LX-dx; // use periodic boundary conditions
        if (dy > halfLY) dy = LY-dy; // halfLX=0.5*LX and halfLY=0.5*LY
        if (dx*dx+dy*dy < 1.0) collision=1; // test for collision
    }
    if (collision == 1) break;
}
if (collision == 0) //accept trial position if no collision
{
    x[i] = xtrial;
    y[i] = ytrial;
    if (x[i] > LX) x[i] -= LX; // impose periodic boundary conditions
    if (y[i] > LY) y[i] -= LY;
    if (x[i] < 0.0) x[i] += LX;
    if (y[i] < 0.0) y[i] += LY;
}
```

Here is a C code snippet to collect correlation function information.

```
for (int i=0;i<n;i++) for (int j=i+1;j<n;j++)
{
    double dx = fabs(x[j]-x[i]);
    double dy = fabs(y[j]-y[i]);
    if (dx > halfLX) dx = LX-dx; // use periodic boundary conditions
    if (dy > halfLY) dy = LY-dy; // halfLX=0.5*LX and halfLY=0.5*LY
    int ir=sqrt(dx*dx+dy*dy)/dr; // dr is the binsize
    histogram[ir] ++; //increment the histogram
}
```

**16.6** The new additions to the code accept moves  $\Delta y > 0$  with probability  $\exp(-\beta mg \Delta y)$ , and to reject moves that go outside the vertical boundaries. At low density and small  $\beta mg L_y$ , the density will be proportional to  $\exp(-\beta mgy)$ . Large  $\beta mg L_y$  will result in an interface with a low density phase above a high density phase.



**16.7** Here is a C code snippet for one time step for Lennard-Jones particles in a two dimensional  $LX \times LY$  box with periodic boundary conditions. The arrays `x1` and `x0` store the current and previous positions of the `n` particles respectively.

```
// calculate forces
for (int i=0;i<n;i++)
{
    fx[i]=0.0;
    fy[i]=0.0;
}
for (int i=0;i<n;i++) for (int j=i+1;j<n;j++)
{
    double dx=x1[j]-x1[i];
    double dy=y1[j]-y1[i];
    if (dx > halfLX) dx -= LX; // use periodic boundary conditions
    if (dy > halfLY) dy -= LY; // halfLX=0.5*LX and halfLY=0.5*LY
    if (dx < -halfLX) dx += LX;
    if (dy < -halfLY) dy += LY;
    double r2=1.0/(dx*dx+dy*dy);
    double r4=r2*r2;
    double r6=r2*r4;
    double r8=r4*r4;
    double r14=r8*r6;
    double f0=48.0*r14 - 24.0*r8; // see equation (16.3.5)
    double fx0=f0*dx;
    double fy0=f0*dy;
    fx[j] += fx0; // Use Newtons's third law to update forces on each particle
    fy[j] += fy0;
    fx[i] -= fx0;
    fy[i] -= fy0;
}
//update positions using Verlet
for (int i=0;i<n;i++)
{
    double xnew=2*x1[i]-x0[i]+dtsqr*fx[i];
    double ynew=2*y1[i]-y0[i]+dtsqr*fy[i];
    x0[i]=x1[i];
    x1[i]=xnew;
    y0[i]=y1[i];
    y1[i]=ynew;
}
// impose periodic boundary conditions
for (int i=0;i<n;i++)
{
    if (x1[i] > LX) { x1[i] -= LX; x0[i] -= LX; }
```

```

    if (y1[i] > LY) { y1[i] -= LY; y0[i] -= LY; }
    if (x1[i] < 0.0) { x1[i] += LX; x0[i] += LX; }
    if (y1[i] < 0.0) { y1[i] += LY; y0[i] += LY; }
}

```

**16.8** The new additions are to generate a one-body force  $F_y = -mg$  and repulsive forces with the top and bottom walls. The average kinetic energy per particle will be independent of the position in the box. At low density and small  $\beta mg L_y$ , the density will be proportional to  $\exp(-\beta mgy)$ . Large  $\beta mg L_y$  will result in an interface with a low density phase above a high density phase.

**16.9** Each Monte Carlo step involves determining the energy change of a spin flip with is proportional to  $\Delta = s_i(s_{i+1} + s_{i-1})$  using periodic boundary conditions. If  $\Delta \leq 0$  flip the spin. Otherwise  $\Delta = +2$ , so flip the spin with probability  $\exp(-4K)$ . Due to the periodic boundary conditions the correlation function will also be periodic. You can generalize the calculation of the correlation function in section 13.2 for a finite periodic lattice to show that the zero field correlation function is of form

$$\langle s_i s_j \rangle = \frac{1}{1 + \left(\frac{\lambda_2}{\lambda_1}\right)^N} \left[ \left(\frac{\lambda_2}{\lambda_1}\right)^{|i-j|} + \left(\frac{\lambda_2}{\lambda_1}\right)^{N-|i-j|} \right],$$

so the correlations are minimized halfway across the lattice.

**16.10** Here is a C code snippet for the two dimensional Ising model

```

int L=32; // size of lattice
int n=L*L; // number of sites
double K=-0.5*log(sqrt(2.0)-1); // K=critical value
int nstat = 1000000; // number of Monte Carlo Sweeps
int neq=100000; // number of equilibration sweeps
int* s=new int[n]; // spins: +1 or -1
for (int i=0;i<n;i++) s[i]=1; // all spins initially up (+1)
int* i1 = new int[n]; // arrays i1[], i2[], i3[], i4[]: neighbor sites
int* i2 = new int[n];
int* i3 = new int[n];
int* i4 = new int[n];
for (int i=0;i<n;i++)
{
    i1[i] = i+1; // site to right
    i2[i] = i-1; // site to left
    i3[i] = i+L; // site above
    i4[i] = i-L; // site below
    if ((i1[i] % L) == 0) i1[i] -= L; //implement periodic boundary conditions
    if (((i2[i]+L) % L) == L-1) i2[i] += L; //implement periodic boundary conditions
    if (i3[i] >= n) i3[i] -= n; //implement periodic boundary conditions
    if (i4[i] < 0) i4[i] += n; //implement periodic boundary conditions
}
double* boltz=new double[5]; //precompute spin flip Boltzmann factors for efficiency
boltz[2]=exp(-4.0*K); // energy increase = 4
boltz[4]=exp(-8.0*K); // energy increase = 8
int* e=new int[nstat]; //stored energy after each pass
int* m=new int[nstat]; //stored magnetization after each pass
int energy;
int mag;
for (int iter=0; iter<(nstat+neq);iter++) // perform nstat Monte Carlo Sweeps
    //after neq equilibration steps
{
    for (int ii=0;ii<n;ii++)
    {
        int i=n*rand(seed); //choose a random site
        int neighborsum=s[i1[i]]+s[i2[i]]+s[i3[i]]+s[i4[i]]; //sum of spins on
                                                                    //neighboring sites
        int de = s[i]*neighborsum; // energy change of spin flip is 2*de
        if (de <= 0) s[i]=-s[i]; // accept if energy change is not positive
        else if (rand(seed) < boltz[de]) s[i]=-s[i]; //if energy increase,
                                                                    //accept with Boltzmann factor probability
    }
    if (iter >= neq)
    {

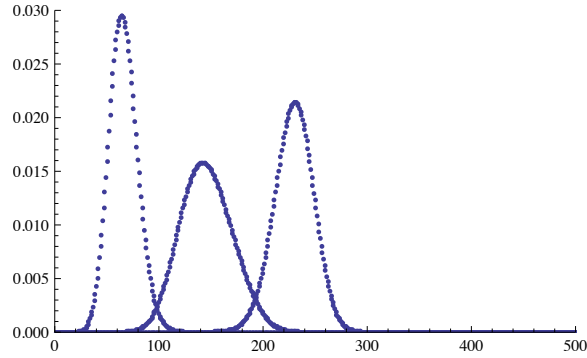
```

```

mag=0;
energy=0;
for (int i=0;i<n;i++)
{
    mag += s[i];
    energy -= s[i]*(s[i1[i]]+s[i3[i]]);
}
e[iter-neq] = energy; //store energy for later analysis
m[iter-neq] = mag; //store magnetization for later analysis
// collect other statistics here, especially for correlations
}
}

```

**16.11** Use the code snippet to collect a histogram of energies. Use the code posted at [www.elsevierdirect.com](http://www.elsevierdirect.com) to calculate the energy distribution at  $K = 0.4, K_c = 0.4406868, 0.5$ . Here is a plot. The horizontal axis is the energy above the ground state in units of  $4J$  and the vertical axis is the probability for each energy.



**16.12** Each Monte Carlo step will involve creating a trial state ( $\theta_{\text{trial}} = \theta_i + \Delta\theta(\text{rand}(\text{seed}) - 0.5)$ ) and calculating the change in energy,

$$\begin{aligned} \Delta\varepsilon = & \cos(\theta_i + \theta_{i+1}) - \cos(\theta_i - \theta_{i-1}) \\ & - \cos(\theta_{\text{trial}} - \theta_{i+1}) - \cos(\theta_{\text{trial}} - \theta_{i-1}). \end{aligned}$$

Accept (i.e. set  $\theta_i = \theta_{\text{trial}}$ ) if  $\Delta\varepsilon < 0$  or  $\text{rand}(\text{seed}) < \exp(-\beta\Delta\varepsilon)$ .

**16.13** Here is is C code snippet for the two dimensional XY model

```

int L=32; // size of lattice
int n=L*L; // number of sites
double K=1.12; // K=critical value
int nstat = 1000000; // number of Monte Carlo Sweeps
int neq=100000; // number of equilibration sweeps
double* theta=new double[n]; // angles of spins
double dtheta=1.0; // range for random angle changes
double twopi=8.0*atan(1.0);
for (int i=0;i<n;i++) theta[i]=0.0; // all spins initially along x direction
int* i1 = new int[n]; // arrays i1[], i2[], i3[], i4[]: neighbor sites
int* i2 = new int[n];
int* i3 = new int[n];
int* i4 = new int[n];
for (int i=0;i<n;i++)
{
    i1[i] = i+1; // site to right
    i2[i] = i-1; // site to left
    i3[i] = i+L; // site above
    i4[i] = i-L; // site below
    if ((i1[i] % L) == 0) i1[i] -= L; //implement periodic boundary conditions
    if (((i2[i]+L) % L) == L-1) i2[i] += L; //implement periodic boundary conditions
    if (i3[i] >= n) i3[i] -= n; //implement periodic boundary conditions
    if (i4[i] < 0) i4[i] += n; //implement periodic boundary conditions
}
double* e=new double[nstat]; //stored energy after each pass
double* mx=new double[nstat]; //stored x component of magnetization after each pass
for (int iter=0; iter<(nstat+neq);iter++) // perform nstat Monte Carlo Sweeps
//after neq equilibration steps
{
    for (int ii=0;ii<n;ii++)
    {
        int i=n*rand(seed); //choose a random site
        double thetatrial = fmod(theta[i] + dtheta*(rand(seed)-0.5) + twopi , twopi);
        double de=cos(theta[i]-theta[i1[i]]) - cos(thetatrial-theta[i1[i]])
            + cos(theta[i]-theta[i2[i]]) - cos(thetatrial-theta[i2[i]])
            + cos(theta[i]-theta[i3[i]]) - cos(thetatrial-theta[i3[i]])
            + cos(theta[i]-theta[i4[i]]) - cos(thetatrial-theta[i4[i]]);
        if (de<0.0) theta[i]=thetatrial; //accept if energy decreases
        else if (rand(seed) < exp(K*de) theta[i]=thetatrial; //or with Boltzmann factor
    }
    if (iter >= neq)
    {
        double magx=0.0;
        double magy=0.0;
    }
}

```

```

double energy=0.0;
for (int i=0;i<n;i++)
{
    magx += cos(theta[i]);
    magy += sin(theta[i]);
    energy -= (cos(theta[i]-theta[i1[i]])+cos(theta[i]-theta[i3[i]]));
}
e[iter-neq] = energy; //store energy for later analysis
mx[iter-neq] = magx; //store x magnetization for later analysis
my[iter-neq] = magy; //store y magnetization for later analysis
// collect other statistics here, especially for correlations
}
}

```