4.34   Modified Joule–Thomson (Boston)

Figure P.4.34 shows container A of variable volume V controlled by a frictionless piston, immersed in a bath at temperature τ. This container is connected by a pipe with a porous plug to another container, B, of fixed volume V'. Container A is initially occupied by an ideal gas at pressure P while container B is initially evacuated. The gas is allowed to flow through the plug, and the pressure on the piston is maintained at the constant value P. When the pressure of the gas in B reaches P, the experiment is terminated. Neglecting any heat conduction through the plug, show that the final temperature of the gas in B is $\tau_1 = (C_P/C_V)\tau$, where C_P and C_V are the molar heats at constant pressure and volume of the gas.
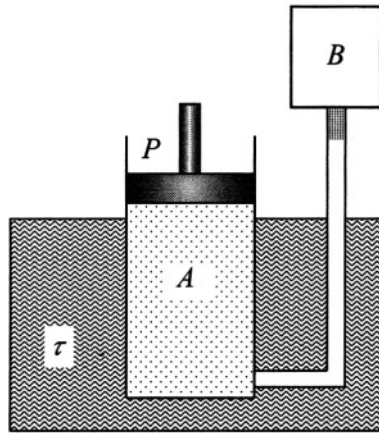

Figure **P.4.34**

Ideal Gas and Classical Statistics

4.35   Poisson Distribution in Ideal Gas (Colorado)

Consider a monatomic *ideal* gas of total $\tilde{N}$ molecules in a volume $\tilde{V}$. Show that the probability, P_N, for the number N of molecules contained in a small element of V is given by the Poisson distribution

$$P_N = \frac{e^{-\langle N \rangle} \langle N \rangle^N}{N!}$$

where $\langle N \rangle = \tilde{N} V / \tilde{V}$ is the average number of molecules found in the volume V.

4.36   Polarization of Ideal Gas (Moscow Phys-Tech)

Calculate the electric polarization $\mathbf{P}$ of an ideal gas, consisting of molecules having a constant electric dipole moment $\mathbf{p}$ in a homogeneous external electric field $\mathbf{E}$ at temperature τ. What is the dielectric constant of this gas at small fields?

4.37   Two-Dipole Interaction (Princeton)

Two classical dipoles with dipole moments μ_1 and μ_2 are separated by a distance R so that only the orientation of the magnetic moments is free. They are in thermal equilibrium at a temperature τ. Compute the mean force $\langle \mathbf{f} \rangle$ between the dipoles for the high-temperature limit $\mu_1\mu_2/\tau R^3 \ll 1$. **Hint:** The potential energy of interaction of two dipoles is

$$U = \frac{\boldsymbol{\mu}_1 \cdot \boldsymbol{\mu}_2}{r^3} - 3\frac{(\boldsymbol{\mu}_1 \cdot \mathbf{r})(\boldsymbol{\mu}_2 \cdot \mathbf{r})}{r^5}$$

4.38   Entropy of Ideal Gas (Princeton)

A vessel of volume V_1 contains N molecules of an ideal gas held at temperature τ and pressure P_1. The energy of a molecule may be written in the form

$$E_k(p_x, p_y, p_z) = \frac{p_x^2}{2m} + \frac{p_y^2}{2m} + \frac{p_z^2}{2m} + \varepsilon_k$$

where ε_k denotes the energy levels corresponding to the internal states of the molecules of the gas.

a) Evaluate the free energy F. Explicitly display the dependence on the volume V_1.

Now consider another vessel, also at temperature τ, containing the same number of molecules of the identical gas held at pressure P_2.

b) Give an expression for the total entropy of the two gases in terms of P_1, P_2, τ, N.
c) The vessels are then connected to permit the gases to mix without doing work. Evaluate explicitly the change in entropy of the system. Check whether your answer makes sense by considering the special case $V_1 = V_2$ $(P_1 = P_2)$.

4.39   Chemical Potential of Ideal Gas (Stony Brook)

Derive the expression for the Gibbs free energy and chemical potential of N molecules of an ideal gas at temperature τ, pressure P, and volume V. Assume that all the molecules are in the electronic ground state with degeneracy g. At what temperature is this approximation valid?

4.40   Gas in Harmonic Well (Boston)

A classical system of N distinguishable noninteracting particles of mass m is placed in a three-dimensional harmonic well:

$$U(r) = \frac{x^2 + y^2 + z^2}{2V^{2/3}}$$

a) Find the partition function and the Helmholtz free energy.
b) Regarding V as an external parameter, find the thermodynamic force $\tilde{P}$ conjugate to this parameter, exerted by the system; find the equation of state and compare it to that of a gas in a container with rigid walls.
c) Find the entropy, internal energy, and total heat capacity at constant volume.

4.41   Ideal Gas in One-Dimensional Potential (Rutgers)

a) An ideal gas of particles, each of mass m at temperature τ, is subjected to an external force whose potential energy has the form

$$U(x) = Ax^n$$

with $0 \leq x \leq \infty$, $A > 0$, and $n > 0$. Find the average potential energy per particle.
b) What is the average potential energy per particle in a gas in a uniform gravitational field?

4.42   Equipartition Theorem (Columbia, Boston)

a) For a classical system with Hamiltonian

$$H(q_1 \cdots p_N) = \sum_{i=1}^{N} \frac{p_i^2}{2m_i} + \sum_{i=1}^{N} \frac{k_i}{2} q_i^2$$

at a temperature τ, show that

$$\frac{\langle p_i^2 \rangle}{2m_i} = \frac{\tau}{2} \qquad \frac{k_i}{2} \langle q_i^2 \rangle = \frac{\tau}{2}$$

b) Using the above, derive the law of Dulong and Petit for the heat capacity of a harmonic crystal.

c) For a more general Hamiltonian,

$$H(q_1 \cdots p_N) = \sum_{i=1}^{N} \frac{p_i^2}{2m_i} + U(q_1 \cdots q_N)$$

prove the generalized equipartition theorem:

$$\left\langle x_i \frac{\partial H}{\partial x_j} \right\rangle = \tau \delta_{ij}$$

where $x_1 = q_1, \ldots, x_N = q_N, x_{N+1} = p_1, \ldots x_{2N} = p_N$. You will need to use the fact that U is infinite at $q_i = \pm\infty$.

d) Consider a system of a large number of classical particles and assume a general dependence of the energy of each particle on the generalized coordinate or momentum component q given by $\varepsilon(q)$, where

$$\lim_{q \to \pm\infty} \varepsilon(q) = +\infty$$

Show that, in thermal equilibrium, the generalized equipartition theorem holds:

$$\left\langle q \frac{\partial \varepsilon(q)}{\partial q} \right\rangle = \tau$$

What conditions should be satisfied for $\varepsilon(q)$ to conform to the equipartition theorem?

4.43   Diatomic Molecules in Two Dimensions (Columbia)

You have been transported to a two-dimensional world by an evil wizard who refuses to let you return to your beloved Columbia unless you can determine the thermodynamic properties for a rotating heteronuclear diatomic molecule constrained to move only in a plane (two dimensions). You may assume in what follows that the diatomic molecule does not undergo translational motion. Indeed, it only has rotational kinetic energy

about its center of mass. The quantized energy levels of a diatomic in two dimensions are

$$\varepsilon_J = hcBJ^2 \qquad J = 0, 1, 2, 3, \ldots$$

with degeneracies $g_J = 2$, for J not equal to zero, and $g_J = 1$ when $J = 0$. As usual, $B = h/8\pi^2 Ic$, where I is the moment of inertia.

Hint: For getting out of the wizard's evil clutches, treat all levels as having the same degeneracy and then... . Oh, no! He's got me, too!

a) Assuming $\tau \gg hcB$, derive the partition function Z_{rot} for an individual diatomic molecule in two dimensions.
b) Determine the thermodynamic energy E and heat capacity C_V in the limit, where $\tau \gg hcB$, for a set of indistinguishable, independent, heteronuclear diatomic molecules constrained to rotate in a plane. Compare these results to those for an ordinary diatomic rotor in three dimensions. Comment on the differences and discuss briefly in terms of the number of degrees of freedom required to describe the motion of a diatomic rotor confined to a plane.

4.44 Diatomic Molecules in Three Dimensions (Stony Brook, Michigan State)

Consider the free rotation of a diatomic molecule consisting of two atoms of mass m_1 and m_2, respectively, separated by a distance a. Assume that the molecule is rigid with center of mass fixed.

a) Starting from the kinetic energy ε_k, where

$$\varepsilon_k = \frac{1}{2} \sum_{i=1}^{2} m_i \left(\dot{x}_i^2 + \dot{y}_i^2 + \dot{z}_i^2 \right)$$

derive the kinetic energy of this system in spherical coordinates and show that

$$\varepsilon_k = \frac{1}{2} I \left(\dot{\theta}^2 + \dot{\varphi}^2 \sin^2\theta \right)$$

where I is the moment of inertia. Express I in terms of m_1, m_2, and a.
b) Derive the canonical conjugate momenta p_θ and p_φ. Express the Hamiltonian of this system in terms of p_θ, p_φ, θ, φ, and I.
c) The classical partition function is defined as

$$Z_{\text{cl}} = \frac{1}{\hbar^2} \int\limits_{-\infty}^{\infty} \int\limits_{-\infty}^{\infty} \int\limits_{0}^{2\pi} \int\limits_{0}^{\pi} e^{-H/\tau} \, d\theta \, d\varphi \, dp_\theta \, dp_\varphi$$

Calculate Z_{cl}. Calculate the heat capacity for a system of N molecules.

d) Assume now that the rotational motion of the molecule is described by quantum mechanics. Write the partition function in this case, taking into account the degeneracy of each state. Calculate the heat capacity of a system of N molecules in the limit of low and high temperatures and compare them to the classical result.

4.45   Two-Level System (Princeton)

Consider a system composed of a very large number N of distinguishable atoms at rest and mutually noninteracting, each of which has only two (nondegenerate) energy levels: 0, $\varepsilon > 0$. Let E/N be the mean energy per atom in the limit $N \to \infty$.

a) What is the maximum possible value of E/N if the system is not necessarily in thermodynamic equilibrium? What is the maximum attainable value of E/N if the system is in equilibrium (at positive temperature)?

b) For thermodynamic equilibrium compute the entropy per atom S/N as a function of E/N.

4.46   Zipper (Boston)

A zipper has N links; each link has a state in which it is closed with energy 0 and a state in which it is open with energy ε. We require that the zipper only unzip from one side (say from the left) and that the link can only open if all links to the left of it $(1, 2, \ldots, n-1)$ are already open. (This model is sometimes used for DNA molecules.)

a) Find the partition function.

b) Find the average number of open links $\langle n \rangle$ and show that for low temperatures $\tau \ll \varepsilon$, $\langle n \rangle$ is independent of N.

4.47   Hanging Chain (Boston)

The upper end of a hanging chain is fixed while the lower end is attached to a mass M. The (massless) links of the chain are ellipses with major axes $l + a$ and minor axes $l - a$, and can place themselves only with either the major axis or the minor axis vertical. Figure P.4.47 shows a four-link chain in which the major axes of the first and fourth links and the minor axes of

the second and third links are vertical. Assume that the chain has N links and is in thermal equilibrium at temperature τ.

   a) Find the partition function.
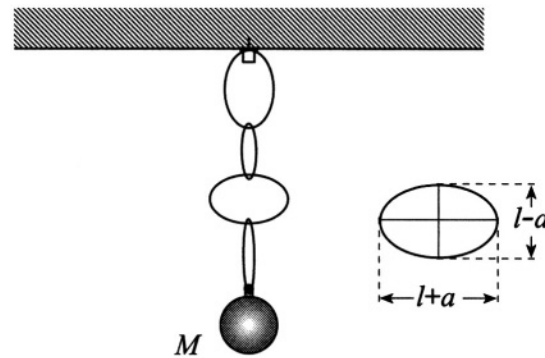   b) Find the average length of the chain.

Figure P.4.47

4.48 Molecular Chain (MIT, Princeton, Colorado)

Consider a one-dimensional chain consisting of N molecules which exist in two configurations, α, β, with corresponding energies ε_α, ε_β, and lengths a and b. The chain is subject to a tensile force f.
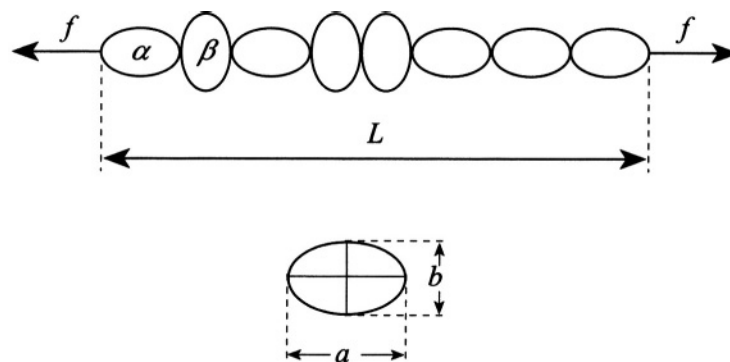

Figure P.4.48

a) Write the partition function Z_N for the system.
b) Calculate the average length $\langle L \rangle$ as a function of f and the temperature τ.
c) Assume that $\varepsilon_\alpha > \varepsilon_\beta$ and $a > b$. Estimate the average length $\langle L \rangle$ in the absence of the tensile force $f = 0$ as a function of temperature. What are the high- and low-temperature limits, and what is the characteristic temperature at which the changeover between the two limits occurs?
d) Calculate the linear response function

$$\chi = \left(\frac{\partial \langle L \rangle}{\partial f} \right)_{f=0}$$

Produce a general argument to show that $\chi > 0$

Nonideal Gas

4.49   Heat Capacities (Princeton)

Consider a gas with arbitrary equation of state $P = f(\tau, V)$, at a temperature τ, $\tau < \tau_{\mathrm{cr}}$, where τ_{cr} is a critical temperature of this gas.

a) Calculate $C_P - C_V$ for this gas in terms of f. Does $C_P - C_V$ always have the same sign?
b) Using the result of (a), calculate $C_P - C_V$ for one mole of a van der Waals gas.

4.50   Return of Heat Capacities (Michigan)

In a certain range of temperature τ and pressure p, the specific volume v of a substance is described by the equation

$$v(\tau, P) = v_1 \exp \left(\frac{\tau}{\tau_1} - \frac{P}{P_1} \right)$$

where v_1, τ_1, P_1 are positive constants. From this information, determine (insofar as possible) as a function of temperature and pressure the following quantities:

a) $c_p - c_v$
b) c_p
c) c_v