

that is, if the numbers n_i are generally 0, occasionally 1, and rarely greater than 1. Condition (3) in a way defines the *classical limit*. We must, however, remember that it is because of the application of the correction factor $1/N!$, which replaces (1) by (2), that our results agree with reality *at least* in the classical limit.

In Section 5.5 we shall demonstrate, in an independent manner, that the factor by which the number of microstates, as computed for the “labeled” molecules, be reduced so that the formalism of classical statistical mechanics becomes a true limit of the formalism of quantum statistical mechanics is indeed $N!$.

Problems

- 1.1. (a) Show that, for two *large* systems in thermal contact, the number $\Omega^{(0)}(E^{(0)}, E_1)$ of Section 1.2 can be expressed as a Gaussian in the variable E_1 . Determine the root-mean-square deviation of E_1 from the mean value \bar{E}_1 in terms of other quantities pertaining to the problem.
- (b) Make an explicit evaluation of the root-mean-square deviation of E_1 in the special case when the systems A_1 and A_2 are ideal classical gases.
- 1.2. Assuming that the entropy S and the statistical number Ω of a physical system are related through an arbitrary functional form

$$S = f(\Omega),$$

show that the additive character of S and the multiplicative character of Ω *necessarily* require that the function $f(\Omega)$ be of the form (1.2.6).

- 1.3. Two systems A and B , of identical composition, are brought together and allowed to exchange both energy and particles, keeping volumes V_A and V_B constant. Show that the minimum value of the quantity (dE_A/dN_A) is given by

$$\frac{\mu_A T_B - \mu_B T_A}{T_B - T_A},$$

where the μ 's and the T 's are the respective chemical potentials and temperatures.

- 1.4. In a classical gas of hard spheres (of diameter D), the spatial distribution of the particles is no longer uncorrelated. Roughly speaking, the presence of n particles in the system leaves only a volume $(V - n\nu_0)$ available for the $(n + 1)$ th particle; clearly, ν_0 would be proportional to D^3 . Assuming that $N\nu_0 \ll V$, determine the dependence of $\Omega(N, V, E)$ on V (compare to equation (1.4.1)) and show that, as a result of this, V in the ideal-gas law (1.4.3) gets replaced by $(V - b)$, where b is four times the actual volume occupied by the particles.
- 1.5. Read Appendix A and establish formulae (1.4.15) and (1.4.16). Estimate the importance of the linear term in these formulae, relative to the main term $(\pi/6)\epsilon^{*3/2}$, for an oxygen molecule confined to a cube of side 10 cm; take $\epsilon = 0.05$ eV.
- 1.6. A cylindrical vessel 1 m long and 0.1 m in diameter is filled with a monatomic gas at $P = 1$ atm and $T = 300$ K. The gas is heated by an electrical discharge, along the axis of the vessel, which releases an energy of 10^4 joules. What will the temperature of the gas be immediately after the discharge?
- 1.7. Study the statistical mechanics of an extreme relativistic gas characterized by the single-particle energy states

$$\epsilon(n_x, n_y, n_z) = \frac{hc}{2L} (n_x^2 + n_y^2 + n_z^2)^{1/2},$$

instead of (1.4.5), along the lines followed in Section 1.4. Show that the ratio C_P/C_V in this case is $4/3$, instead of $5/3$.

- 1.8. Consider a system of quasiparticles whose energy eigenvalues are given by

$$\epsilon(n) = nh\nu; \quad n = 0, 1, 2, \dots$$

Obtain an asymptotic expression for the number Ω of this system for a given number N of the quasiparticles and a given total energy E . Determine the temperature T of the system as a function of E/N and $h\nu$, and examine the situation for which $E/(Nh\nu) \gg 1$.

- 1.9. Making use of the fact that the entropy $S(N, V, E)$ of a thermodynamic system is an extensive quantity, show that

$$N \left(\frac{\partial S}{\partial N} \right)_{V,E} + V \left(\frac{\partial S}{\partial V} \right)_{N,E} + E \left(\frac{\partial S}{\partial E} \right)_{N,V} = S.$$

Note that this result implies that $(-N\mu + PV + E)/T = S$, that is, $N\mu = E + PV - TS$.

- 1.10. A mole of argon and a mole of helium are contained in vessels of equal volume. If argon is at 300 K, what should the temperature of helium be so that the two have the same entropy?
- 1.11. Four moles of nitrogen and one mole of oxygen at $P = 1$ atm and $T = 300$ K are mixed together to form air at the same pressure and temperature. Calculate the entropy of mixing per mole of the air formed.
- 1.12. Show that the various expressions for the entropy of mixing, derived in Section 1.5, satisfy the following relations:
- (a) For all N_1, V_1, N_2 , and V_2 ,

$$(\Delta S)_{1 \equiv 2} = \{(\Delta S) - (\Delta S)^*\} \geq 0,$$

the equality holding when and only when $N_1/V_1 = N_2/V_2$.

- (b) For a given value of $(N_1 + N_2)$,

$$(\Delta S)^* \leq (N_1 + N_2)k \ln 2,$$

the equality holding when and only when $N_1 = N_2$.

- 1.13. If the two gases considered in the mixing process of Section 1.5 were initially at different temperatures, say T_1 and T_2 , what would the entropy of mixing be in that case? Would the contribution arising from this cause depend on whether the two gases were different or identical?
- 1.14. Show that for an ideal gas composed of monatomic molecules the entropy change, between any two temperatures, when the pressure is kept constant is $5/3$ times the corresponding entropy change when the volume is kept constant. Verify this result *numerically* by calculating the actual values of $(\Delta S)_P$ and $(\Delta S)_V$ per mole of an ideal gas whose temperature is raised from 300 K to 400 K.
- 1.15. We have seen that the (P, V) -relationship during a reversible adiabatic process in an ideal gas is governed by the exponent γ , such that

$$PV^\gamma = \text{const.}$$

Consider a mixture of two ideal gases, with mole fractions f_1 and f_2 and respective exponents γ_1 and γ_2 . Show that the *effective* exponent γ for the mixture is given by

$$\frac{1}{\gamma - 1} = \frac{f_1}{\gamma_1 - 1} + \frac{f_2}{\gamma_2 - 1}.$$

- 1.16. Establish thermodynamically the formulae

$$V \left(\frac{\partial P}{\partial T} \right)_\mu = S \quad \text{and} \quad V \left(\frac{\partial P}{\partial \mu} \right)_T = N.$$

Express the pressure P of an ideal classical gas in terms of the variables μ and T , and verify the above formulae.

(or from the states of polarization of the vibrational modes); this requires a multiplication of both expressions (4) and (5) by a factor of 2, leaving the conversion factor h^3 unchanged.

Problems

2.1. Show that the volume element

$$d\omega = \prod_{i=1}^{3N} (dq_i dp_i)$$

of the phase space remains *invariant* under a canonical transformation of the (generalized) coordinates (q, p) to any other set of (generalized) coordinates (Q, P) .

[Hint: Before considering the most general transformation of this kind, which is referred to as a *contact* transformation, it may be helpful to consider a *point* transformation — one in which the new coordinates Q_i and the old coordinates q_i transform only among themselves.]

- 2.2. (a) Verify *explicitly* the invariance of the volume element $d\omega$ of the phase space of a single particle under transformation from the Cartesian coordinates (x, y, z, p_x, p_y, p_z) to the spherical polar coordinates $(r, \theta, \phi, p_r, p_\theta, p_\phi)$.
- (b) The foregoing result seems to contradict the intuitive notion of “equal weights for equal solid angles,” because the factor $\sin \theta$ is invisible in the expression for $d\omega$. Show that if we average out any physical quantity, whose dependence on p_θ and p_ϕ comes only through the kinetic energy of the particle, then as a result of integration over these variables we do indeed recover the factor $\sin \theta$ to appear with the subelement $(d\theta d\phi)$.
- 2.3. Starting with the line of zero energy and working in the (two-dimensional) phase space of a classical rotator, draw lines of constant energy that divide phase space into cells of “volume” h . Calculate the energies of these states and compare them with the energy eigenvalues of the corresponding quantum-mechanical rotator.
- 2.4. By evaluating the “volume” of the relevant region of its phase space, show that the number of microstates available to a rigid rotator with angular momentum $\leq M$ is $(M/h)^2$. Hence determine the number of microstates that may be associated with the quantized angular momentum $M_j = \sqrt{j(j+1)}\hbar$, where $j = 0, 1, 2, \dots$ or $\frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \dots$. Interpret the result physically.
[Hint: It simplifies to consider motion in the variables θ and ϕ , with $M^2 = p_\theta^2 + (p_\phi/\sin \theta)^2$.]
- 2.5. Consider a particle of energy E moving in a one-dimensional potential well $V(q)$, such that

$$m\hbar \left| \frac{dV}{dq} \right| \ll \{m(E - V)\}^{3/2}.$$

Show that the allowed values of the momentum p of the particle are such that

$$\oint p dq = \left(n + \frac{1}{2}\right)h,$$

where n is an integer.

- 2.6. The generalized coordinates of a simple pendulum are the angular displacement θ and the angular momentum $m l^2 \dot{\theta}$. Study, both mathematically and graphically, the nature of the corresponding trajectories in the phase space of the system, and show that the area A enclosed by a trajectory is equal to the product of the total energy E and the time period τ of the pendulum.
- 2.7. Derive (i) an *asymptotic* expression for the number of ways in which a given energy E can be distributed among a set of N one-dimensional harmonic oscillators, the energy eigenvalues of the oscillators being $(n + \frac{1}{2})\hbar\omega$; $n = 0, 1, 2, \dots$, and (ii) the corresponding expression for the “volume” of the relevant region of the phase space of this system. Establish the correspondence between the two results, showing that the conversion factor ω_0 is precisely h^N .

2.8. Following the method of Appendix C, replacing equation (C.4) by the integral

$$\int_0^{\infty} e^{-r} r^2 dr = 2,$$

show that

$$V_{3N} = \int \dots \int \prod_{i=1}^N (4\pi r_i^2 dr_i) = (8\pi R^3)^N / (3N)!.$$

$0 \leq \sum_{i=1}^N r_i \leq R$

Using this result, compute the “volume” of the relevant region of the phase space of an extreme relativistic gas ($\varepsilon = pc$) of N particles moving in three dimensions. Hence, derive expressions for the various thermodynamic properties of this system and compare your results with those of Problem 1.7.

2.9. (a) Solve the integral

$$\int \dots \int_{0 \leq \sum_{i=1}^{3N} |x_i| \leq R} (dx_1 \dots dx_{3N})$$

and use it to determine the “volume” of the relevant region of the phase space of an extreme relativistic gas ($\varepsilon = pc$) of $3N$ particles moving in one dimension. Determine, as well, the number of ways of distributing a given energy E among this system of particles and show that, asymptotically, $\omega_0 = h^{3N}$.

(b) Compare the thermodynamics of this system with that of the system considered in Problem 2.8.