# موال بای میشادی برای درس مکانیک آماری کارثناسی ارشد از فصل ۳

#### (Reference: Statistical Mechanics, Third Edition, R. K. Pathria)

- **3.6.** (a) Assuming that the total number of microstates accessible to a given statistical system is  $\Omega$ , show that the entropy of the system, as given by equation (3.3.13), is maximum when all  $\Omega$  states are equally likely to occur.
  - (b) If, on the other hand, we have an ensemble of systems sharing energy (with mean value  $\overline{E}$ ), then show that the entropy, as given by the same formal expression, is maximum when  $P_T \propto \exp(-\beta E_T)$ ,  $\beta$  being a constant to be determined by the given value of  $\overline{E}$ .
  - (c) Further, if we have an ensemble of systems sharing energy (with mean value  $\overline{E}$ ) and also sharing particles (with mean value  $\overline{N}$ ), then show that the entropy, given by a similar expression, is maximum when  $P_{r,s} \propto \exp(-\alpha N_r \beta E_s)$ ,  $\alpha$  and  $\beta$  being constants to be determined by the given values of  $\overline{N}$  and  $\overline{E}$ .
- **3.11.** Determine the work done on a gas and the amount of heat absorbed by it during a compression from volume  $V_1$  to volume  $V_2$ , following the law  $PV^n = \text{const.}$
- **3.12.** If the "free volume"  $\overline{V}$  of a classical system is defined by the equation

$$\overline{V}^N = \int e^{\{\overline{U} - U(\boldsymbol{q}_i)\}/kT} \prod_{i=1}^N d^3 q_i,$$

where  $\overline{U}$  is the average potential energy of the system and  $U(q_i)$  the actual potential energy as a function of the molecular configuration, then show that

$$S = Nk \left[ \ln \left\{ \frac{\overline{V}}{N} \left( \frac{2\pi mkT}{h^2} \right)^{3/2} \right\} + \frac{5}{2} \right].$$

In what sense is it justified to refer to the quantity  $\overline{V}$  as the "free volume" of the system? Substantiate your answer by considering a particular case — for example, the case of a hard sphere gas.

- **3.13.** (a) Evaluate the partition function and the major thermodynamic properties of an ideal gas consisting of  $N_1$  molecules of mass  $m_1$  and  $N_2$  molecules of mass  $m_2$ , confined to a space of volume V at temperature T. Assume that the molecules of a given kind are mutually indistinguishable, while those of one kind are distinguishable from those of the other kind.
  - (b) Compare your results with the ones pertaining to an ideal gas consisting of  $(N_1 + N_2)$  molecules, *all of one kind*, of mass m, such that  $m(N_1 + N_2) = m_1N_1 + m_2N_2$ .

# موال بای مینهادی برای درس مکانیک آماری کارثناسی ارشد از فصل ۳

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**3.15.** Show that the partition function  $Q_N(V,T)$  of an *extreme* relativistic gas consisting of N monatomic molecules with energy–momentum relationship  $\varepsilon = pc$ , c being the speed of light, is given by

$$Q_N(V,T) = \frac{1}{N!} \left\{ 8\pi V \left( \frac{kT}{hc} \right)^3 \right\}^N.$$

Study the thermodynamics of this system, checking in particular that

$$PV = \frac{1}{3}U$$
,  $U/N = 3kT$ , and  $\gamma = \frac{4}{3}$ .

Next, using the inversion formula (3.4.7), derive an expression for the density of states g(E) of this system.

**3.16.** Consider a system similar to the one in the preceding problem but consisting of 3*N* particles moving in one dimension. Show that the partition function in this case is given by

$$Q_{3N}(L,T) = \frac{1}{(3N)!} \left[ 2L \left( \frac{kT}{hc} \right) \right]^{3N},$$

*L* being the "length" of the space available. Compare the thermodynamics and the density of states of this system with the corresponding quantities obtained in the preceding problem.

**3.18.** Show that for a system in the canonical ensemble

$$\langle (\Delta E)^3 \rangle = k^2 \left\{ T^4 \left( \frac{\partial C_V}{\partial T} \right)_V + 2T^3 C_V \right\}.$$

Verify that for an ideal gas

$$\left\langle \left(\frac{\Delta E}{U}\right)^2 \right\rangle = \frac{2}{3N}$$
 and  $\left\langle \left(\frac{\Delta E}{U}\right)^3 \right\rangle = \frac{8}{9N^2}$ .

**3.20.** Show that, for a statistical system in which the interparticle potential energy  $u(\mathbf{r})$  is a homogeneous function (of degree n) of the particle coordinates, the *virial*  $\mathcal{V}$  is given by

$$\mathbf{v} = -3PV - nU$$

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and, hence, the mean kinetic energy K by

$$K = -\frac{1}{2}\mathcal{V} = \frac{1}{2}(3PV + nU) = \frac{1}{(n+2)}(3PV + nE);$$

here, U denotes the *mean potential energy* of the system while E = K + U. Note that this result holds not only for a classical system but for a quantum-mechanical one as well.

**3.24.** Show that in the relativistic case the equipartition theorem takes the form

$$\langle m_0 u^2 (1 - u^2/c^2)^{-1/2} \rangle = 3kT$$
,

where  $m_0$  is the rest mass of the particle and u its speed. Check that in the extreme relativistic case the mean thermal energy per particle is twice its value in the nonrelativistic case.

- **3.25.** Develop a *kinetic* argument to show that in a noninteracting system the average value of the quantity  $\sum_i p_i \dot{q}_i$  is precisely equal to 3PV. Hence show that, regardless of relativistic considerations, PV = NkT.
- 3.26. The energy eigenvalues of an s-dimensional harmonic oscillator can be written as

$$\varepsilon_i = (j + s/2)\hbar\omega; \quad j = 0, 1, 2, \dots$$

Show that the jth energy level has a multiplicity (j+s-1)!/j!(s-1)!. Evaluate the partition function, and the major thermodynamic properties, of a system of N such oscillators, and compare your results with a corresponding system of sN one-dimensional oscillators. Show, in particular, that the chemical potential  $\mu_s = s\mu_1$ .

**3.27.** Obtain an asymptotic expression for the quantity  $\ln g(E)$  for a system of N quantum-mechanical harmonic oscillators by using the inversion formula (3.4.7) and the partition function (3.8.15). Hence show that

$$\frac{S}{Nk} = \left(\frac{E}{N\hbar\omega} + \frac{1}{2}\right) \ln\left(\frac{E}{N\hbar\omega} + \frac{1}{2}\right) - \left(\frac{E}{N\hbar\omega} - \frac{1}{2}\right) \ln\left(\frac{E}{N\hbar\omega} - \frac{1}{2}\right).$$

[Hint: Employ the Darwin–Fowler method.]

3.29. The potential energy of a one-dimensional, anharmonic oscillator may be written as

$$V(q) = cq^2 - gq^3 - fq^4,$$

where c, g, and f are positive constants; quite generally, g and f may be assumed to be very small in value. Show that the leading contribution of anharmonic terms to the heat capacity of the

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oscillator, assumed classical, is given by

$$\frac{3}{2}k^2\left(\frac{f}{c^2} + \frac{5}{4}\frac{g^2}{c^3}\right)T$$

and, to the same order, the mean value of the position coordinate q is given by

$$\frac{3}{4} \frac{gkT}{c^2}$$

**3.30.** The energy levels of a quantum-mechanical, one-dimensional, *anharmonic* oscillator may be approximated as

$$\varepsilon_n = \left(n + \frac{1}{2}\right)\hbar\omega - x\left(n + \frac{1}{2}\right)^2\hbar\omega; \quad n = 0, 1, 2, \dots$$

The parameter x, usually  $\ll 1$ , represents the degree of anharmonicity. Show that, to the first order in x and the fourth order in  $u (\equiv \hbar \omega / kT)$ , the specific heat of a system of N such oscillators is given by

$$C = Nk \left[ \left( 1 - \frac{1}{12}u^2 + \frac{1}{240}u^4 \right) + 4x \left( \frac{1}{u} + \frac{1}{80}u^3 \right) \right].$$

Note that the correction term here *increases* with temperature.

**3.32.** The quantum states available to a given physical system are (i) a group of  $g_1$  equally likely states, with a common energy  $\varepsilon_1$  and (ii) a group of  $g_2$  equally likely states, with a common energy  $\varepsilon_2 > \varepsilon_1$ . Show that this entropy of the system is given by

$$S = -k[p_1 \ln(p_1/g_1) + p_2 \ln(p_2/g_2)],$$

where  $p_1$  and  $p_2$  are, respectively, the probabilities of the system being in a state belonging to group 1 or to group 2:  $p_1 + p_2 = 1$ .

(a) Assuming that the  $p_i$  are given by a canonical distribution, show that

$$S = k \left[ \ln g_1 + \ln\{1 + (g_2/g_1)e^{-x}\} + \frac{x}{1 + (g_1/g_2)e^x} \right],$$

where  $x = (\varepsilon_2 - \varepsilon_1)/kT$ , assumed positive. Compare the special case  $g_1 = g_2 = 1$  with that of the Fermi oscillator of the preceding problem.

- **(b)** Verify the foregoing expression for *S* by deriving it from the partition function of the system.
- (c) Check that at  $T \to 0$ ,  $S \to k \ln g_1$ . Interpret this result physically.