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Textbook: Silvio Salinas, *Introduction to Statistical Physics*  
Springer, 2001, ISBN 0-387-95119-9

**Do not forget to write your name and the homework number!**

**Each problem is worth 10 points.**

## Ch. 7 The Grand Canonical and Pressure Ensembles

**1. (a) Problem 7.2. Relativistic gas with  $\varepsilon = cp$ .**

Just calculate the grand partition function and the grand thermodynamic potential. You don't need to do the rest of the problem and use Eq. (7.71).

**(b) Problem 7.4.  $\langle(\Delta N)^2\rangle$  for the ideal gases.**

Do the problem for the ideal gases with both the quadratic dispersion  $\varepsilon = p^2/2m$  and the linear dispersion  $\varepsilon = cp$ .

**2. Problem 7.6. The chemical potential of the adsorbed gas.**

Assume that the adsorbed molecules have the binding energy to the surface  $-\epsilon_0$  relative to the unbound state. Assume that each adsorption center can be occupied by, at most, one molecule. Notice that the entropy for a similar problem was calculated in Problems 2.7 and 4.5.

## Ch. 8 The Ideal Quantum Gas

**3. Modified Problem 8.2. The entropies of the Fermi, Bose, and classical gases.**

*This formulation of the problem follows the book by Landau and Lifshitz "Statistical Physics, Part I", Secs. 40 and 55.*

Let us consider an element of the phase space, which has the following number of the quantum states

$$G_j = \frac{d^3r d^3p}{(2\pi\hbar)^3}. \quad (1)$$

We assume that the phase space element, on one hand, is big enough so that  $G_j \gg 1$ , and, on the other hand, is small enough, so that the quantum states in this element have approximately the same energy  $\varepsilon_j$ . (In the simplest case,  $\varepsilon_j = \mathbf{p}_j^2/2m$ , where  $\mathbf{p}_j$  is the momentum corresponding to this element.)

Suppose  $N_j$  identical particles occupy some of the states  $G_j$ . We wish to derive expressions for the corresponding multiplicity and entropy for the Fermi, Bose, and classical gases.

- (a) **Fermions.** Suppose the particles are identical fermions. Then, any of the  $G_j$  states can be occupied by, at most, one particle. The multiplicity in this case is equal to

$$\Omega_j = \frac{G_j!}{N_j!(G_j - N_j)!}. \quad (2)$$

This formula was already discussed in Problems 2.7 and 4.5 without mentioning fermions.

Using Eq. (2) and the Stirling formula, show that the entropy of the Fermi gas can be expressed as follows

$$S = \sum_j \ln \Omega_j = - \sum_j G_j [f_j \ln f_j + (1 - f_j) \ln(1 - f_j)] \quad (3)$$

$$= - \int \frac{d^3r d^3p}{(2\pi\hbar)^3} [f_{\mathbf{p}} \ln f_{\mathbf{p}} + (1 - f_{\mathbf{p}}) \ln(1 - f_{\mathbf{p}})]. \quad (4)$$

Here  $f_j = N_j/G_j = \langle n_j \rangle$  is the average occupation number of the quantum states in the phase-space element  $j$ . Eqs. (3) and (4) give a general expression for the entropy of the Fermi gas, where the occupation numbers may be out of statistical equilibrium.

Using the method of Lagrange multipliers, maximize the entropy (3) under the constraints of conserved number of particles and conserved energy

$$\sum_j N_j = \sum_j G_j f_j = N, \quad \sum_j \varepsilon_j N_j = \sum_j G_j \varepsilon_j f_j = E. \quad (5)$$

Keep in mind that the Lagrange multipliers enforcing the energy and number conservations are  $\beta = 1/T$  and  $\beta\mu$ , where  $\mu$  is the chemical potential. (You need to choose the signs of the Lagrange multipliers appropriately to agree with the standard conventions.) Show that the equilibrium occupation numbers (obtained from maximization of the entropy) are

$$f_j^{\text{eq}} = \langle n_j \rangle_{\text{eq}} = \frac{1}{e^{\beta(\varepsilon_j - \mu)} + 1}. \quad (6)$$

This is the famous Fermi-Dirac distribution function.

- (b) **Bosons.** Now suppose the particles are identical bosons. Then, any of the  $G_j$  states can be occupied by any number of particles. The multiplicity in this case is equal to

$$\Omega_j = \frac{(G_j + N_j - 1)!}{N_j!(G_j - 1)!}. \quad (7)$$

This formula was derived in Eqs. (2.13) and (4.32). The latter formula was derived for  $N$  quantum oscillators having  $M$  quanta of excitations. Now we associate each quantum of excitation with a Bose particle, such as a photon or a phonon. So,  $M$  represents the number of bosons ( $N_j$ ), and  $N$  the number of states that can be occupied by the bosons ( $G_j$ ). The index  $j$  may represent the frequency of oscillators, if we have a collection of oscillators with different frequencies  $\omega_j$ .

Using Eq. (7) and the Stirling formula, show that the entropy of the Bose gas can be expressed as follows

$$S = \sum_j \ln \Omega_j = \sum_j G_j [(1 + f_j) \ln(1 + f_j) - f_j \ln f_j] \quad (8)$$

$$= \int \frac{d^3r d^3p}{(2\pi\hbar)^3} [(1 + f_{\mathbf{p}}) \ln(1 + f_{\mathbf{p}}) - f_{\mathbf{p}} \ln f_{\mathbf{p}}]. \quad (9)$$

Here  $f_j = N_j/G_j = \langle n_j \rangle$  is the average occupation number of the quantum states in the phase-space element  $j$ . Eqs. (8) and (9) give a general expression for the entropy of the Bose gas, where the occupation numbers may be out of statistical equilibrium.

Using the method of Lagrange multipliers, maximize the entropy (8) under the constraints (5). Show that the equilibrium occupation numbers (obtained from maximization of the entropy) are

$$f_j^{\text{eq}} = \langle n_j \rangle_{\text{eq}} = \frac{1}{e^{\beta(\varepsilon_j - \mu)} - 1}. \quad (10)$$

This is the famous Bose-Einstein distribution function.

- (c) **Classical.** Now let us consider the case where the occupation numbers are very small  $f_j = N_j/G_j \ll 1$ . Show that Eqs. (3) and (8) give the classical Boltzmann expression for the entropy

$$S = \sum_j \ln \Omega_j = - \sum_j G_j f_j \ln(f_j/e) = - \int \frac{d^3r d^3p}{(2\pi\hbar)^3} f_{\mathbf{p}} \ln(f_{\mathbf{p}}/e), \quad (11)$$

where  $e$  is the base of the natural logarithm.

Argue that the multiplicity of the classical gas can be written as

$$\Omega_j = \frac{G_j^{N_j}}{N_j!}. \quad (12)$$

Indeed, the occupied states can be selected in  $G_j^{N_j}$  possible ways, and the result should be divided by  $N_j!$  for identical particles. Because the occupation number is very low  $N_j/G_j \ll 1$ , the probability of occupying the same state more than once is exceedingly small, so the Fermi or Bose statistics do not matter in this case. Show that Eq. (11) can be derived from Eq. (12).

From Eqs. (6) and (10), show that the equilibrium occupation numbers in the classical case  $f_j \ll 1$  are given by the exponential function:

$$f_j^{\text{eq}} = \langle n_j \rangle_{\text{eq}} = e^{-\beta(\varepsilon_j - \mu)}. \quad (13)$$

This is the Boltzmann-Gibbs distribution function.

**4. Problem 8.3.  $PV = (2/3)U$  or  $PV = (1/3)U$ .**

Show that the equation of state  $PV = (2/3)U$  applies for the ideal gas with the quadratic dispersion  $\varepsilon = p^2/2m$  and the equation of state  $PV = (1/3)U$  for the linear dispersion  $\varepsilon = cp$ . Consider the cases of the Fermi, Bose, and classical statistics.

Hint: Use Eq. (8.41), where  $\Phi$  can be expressed using Eq. (8.38). Replace summation in Eq. (8.38) by integration over the 3D phase space and then integrate by parts.

*The statement in the textbook, that  $PV = (2/3)U$  applies to the relativistic gas with the linear dispersion  $\varepsilon = cp$ , is clearly a mistake. It seems that this misconception is also perpetuated in Problem 3.4. With  $u = 3Pv$  and  $P = \alpha T^4$ , Problem 3.4 would have meaningfully described a gas of photons (see Problem 4 of HW 3). However, the unphysical combination  $u = (3/2)Pv$  and  $P = \alpha v T^4$  presented in the textbook produces the horribly complicated results shown in the solution of Problem 3.4 online.*

**5. Problem 8.5. Adsorbed 2D gas in equilibrium with the 3D gas.**

When two gases (2D and 3D) can exchange particles, their chemical potentials are equal in equilibrium.