

## PHYS 813: Statistical Mechanics, Assignment 5

Due 4/09/09

1. Consider an extreme relativistic gas in a cubic box of volume  $V$ . The single-particle energy for such a gas is related to its momentum  $p$  by

$$\epsilon = pc$$

where  $c$  is the speed of light. Calculate the volume in the phase space available to  $N$  particles with the total energy smaller or equal  $E$ . The integration over momenta should produce the following type of integral

$$V_{3N} = \int \cdots \int_{0 \leq \sum_{i=1}^N r_i \leq R} (4\pi r_i^2 dr_i) = (8\pi R^3)^N / (3N)!$$

Calculate this integral (i.e., prove that the expression on the right hand side is the value of the integral) by a method similar to that used before to calculate the volume of the  $3N$  sphere, applying now as an auxiliary integral

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

Next, derive expressions for energy and entropy. Also, find the ratio of heat capacities and compare with the result obtained before.

2. The energy levels of an  $s$ -dimensional harmonic oscillator are given by

$$\epsilon_n = \left(n + \frac{s}{2}\right) \hbar \omega, \quad n = 0, 1, 2, \dots$$

Show first that the  $n$ th energy level has multiplicity  $(n + s - 1)! / [n!(s - 1)!]$ . Next, evaluate the partition function for  $N$  such oscillators fixed in space and use it to find the thermodynamic functions  $F$ ,  $S$ , and  $\mu$ . Compare your results with the corresponding system of  $sN$  one-dimensional harmonic oscillators.

3. Consider a classical gas of  $N$  particles interacting with each other at some temperature  $T$ . The Hamiltonian for the system is

$$H(q_1, q_2, \dots, q_{3N}, p_1, p_2, \dots, p_{3N}) \equiv H(q_i, p_i) = \sum \frac{p_i^2}{2m} + U(q_1, q_2, \dots, q_{3N})$$

The total interaction energy  $U(q_1, q_2, \dots, q_{3N}) \equiv U(q_i)$  is a function of all generalized coordinates  $q_i$  (in notation such that  $q_1 = x_1$ ,  $q_2 = y_1$ , etc.) and, analogously,  $p_i$  are generalized momenta.

- (a) Show that the entropy of the system is given by the expression

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

where  $\bar{V}$  is the so-called “free volume” defined as

$$\bar{V}^N = \int e^{[\bar{U} - U(q_i)]/kT} d^{3N}q$$

with  $\bar{U}$  being the average value of  $U$

$$\bar{U} = \frac{\int U(q_i) e^{-H(q_i, p_i)/kT} d^{3N}q d^{3N}p}{\int e^{-H(q_i, p_i)/kT} d^{3N}q d^{3N}p}.$$

(b) Interpret the free volume by computing it for hard spheres. Compare with the derivation of the van der Waals equation for this case.

4. Consider the same system as in the previous problem.

(a) The pair distribution function is defined as

$$g(\mathbf{r}_1, \mathbf{r}_2) = \frac{V^2(N-1) \int e^{-U(\mathbf{r}_1, \mathbf{r}_2, \dots)/kT} d^3\mathbf{r}_3 \dots d^3\mathbf{r}_N}{N \int e^{-U(\mathbf{r}_1, \mathbf{r}_2, \dots)/kT} d^3\mathbf{r}_1 \dots d^3\mathbf{r}_N}$$

where  $U(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$  is the same total interaction potential except that particle coordinates are now denoted by  $\mathbf{r}_i$ . Now assume that

$$U(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \sum_{i < j} u(\mathbf{r}_i - \mathbf{r}_j)$$

and that  $u$  depends only in the separation between particles

$$u(\mathbf{r}_i - \mathbf{r}_j) = u(|\mathbf{r}_i - \mathbf{r}_j|) = u(r_{ij}).$$

For atomic systems,  $u(r)$  is negligibly small for  $r$  larger than a few angstroms. Show that for a dilute gas

$$g(r) \approx e^{-u(r)/kT}.$$

(b) One can show that for an interacting gas that is not dilute

$$pV = NkT \left[ 1 - \frac{2\pi N}{3kTV} \int_0^\infty r^3 g(r) \frac{du(r)}{dr} dr \right].$$

Show that for a dilute gas (with  $u(r) \rightarrow 0$  faster than  $1/r^3$ ) this expression simplifies to

$$pV = NkT \left[ 1 + \frac{N}{V} B(T) \right]$$

where  $B(T)$  is the second virial coefficient

$$B(T) = -2\pi \int_0^\infty \left( e^{-u(r)/kT} - 1 \right) r^2 dr.$$

(c) What form will this result take for a gas of hard spheres of radius  $r_0$ ? For such spheres the pair potential is:

$$u(r) = \begin{cases} \infty & \text{for } r \leq 2r_0 \\ 0 & \text{otherwise.} \end{cases}$$

5. Consider an ideal-gas mixture of atoms  $A$ , atoms  $B$ , and molecules  $AB$ . Denote by  $n_X = N_X/V$  the concentration of species  $X$  (number density), where  $N_X$  is the number of particles  $X$  and  $V$  the volume. The system is mechanically isolated, kept at constant temperature, and does not exchange particles with its surroundings, but the numbers  $N_X$  can change according to the reaction  $A + B \rightleftharpoons AB$ . Show that in equilibrium

$$\frac{n_{AB}}{n_A n_B} = V \frac{f_{AB}}{f_A f_B} = K(T)$$

where  $f_X$  is the single-particle partition function and  $K$  depends only on temperature ( $K(T)$  is known as the equilibrium constant of the reaction). Recall that the partition function for the ideal gas is given by  $f = (2\pi mkT)^{3/2} V/h^3$  (but realize that  $f_X$  are of a more complicated form).

6. In statistical mechanics, one usually considers the states and energies of a total  $N$ -particle system. It is possible, however, to determine for noninteracting particles the probability of an individual particle to be in a given state. Assume  $N \gg 1$ .

(a) Consider a system of  $N$  quantum harmonic oscillators with total energy  $E$  in thermal equilibrium. What is the probability  $p_n$  that a particular oscillator is in the quantum state  $n$ ? Assume that  $n$  is much smaller than the number of quanta  $R$  available for distribution among the oscillators. Present your answer in terms of  $\bar{n} = R/N$ .

(b) Consider an ideal gas of  $N$  atoms with the total energy  $E$  in thermal equilibrium. Find, up to a proportionality constant, the probability of an individual atom to have energy in the range  $[\epsilon, \epsilon + d\epsilon]$ . Assume  $E \gg \epsilon$ . Express your answer as an exponential of  $\epsilon$ .

7. Consider a (nonideal) classical monoatomic gas of  $N$  atoms in volume  $V$  at temperature  $T$ . The atoms interact with each other via a pair potential  $u(R)$  only, where  $R$  is the distance between two atoms. The potential is of short-range character, so that at the density of the gas in question one can consider only one pair at a time in the partition function. Show that the entropy of the system can be written in a first approximation as

$$S = S_0 + N^2 A(T)/V$$

where  $S_0$  is the entropy of ideal gas. Find an explicit expression (in the form of an integral) for the coefficient  $A(T)$  in terms of  $u(R)$ . *Hint:* When analyzing the configurational part of the partition function, write  $e^{-u(R)/kT}$  as  $1 + f(R)$  and note that  $f(R)$  is nonzero only in a small region of space. Assume that  $\int_0^\infty f(R) R^2 dR \approx 0$ .