

PHYS 6107. Spring 2002.

HOMEWORK #3 Σ = 150 pts. + 35 bonus pts.

DUE: Apr. 2 by 6 p.m. (in Dr. Marchenkov's mail box)

The scope of this homework covers "Quantum Statistics, Part I". Problems 1 and 2 deal with simple quantum mechanical model systems. Problems 3 and 4 deal with fundamental properties of the Bose-Einstein, Fermi-Dirac and the quasi-classical Maxwell-Boltzmann statistics. Problem 5,6 and the bonus problems concentrate on the molecular degrees of freedom (translations, rotations and vibrations) that contribute to the specific heat and other properties of gases.

I. Quantum Statistics (150pts)

Problem I.1 (20 pts)

Find approximate expressions for the partition function $Z(T, L)$ for a single quantum-mechanical particle in an infinite one-dimensional square well of width L in the limits of high and low temperatures. Obtain the heat capacity c_L (1D equivalent of c_V) and the equation of state $f(T, p, L) = 0$ in these limits.

Problem I.2 (20 pts)

Compute the canonical partition function for a system consisting of:

1. $3N$ one-dimensional non-interacting quantum-mechanical harmonic oscillators.
2. N three-dimensional non-interacting quantum-mechanical harmonic oscillators.
3. Compare the results of parts 1. and 2.

Problem I.3 (35 pts)

1. Show that for an ideal gas of structureless fermions, the pressure is given by

$$\beta p = \frac{1}{\lambda^3} f_{5/2}(z),$$

where $z = \exp(\beta\mu)$, and $\lambda = \left(2\pi\beta\hbar^2/m\right)^{1/2}$, m is the mass of the particle, and

$$f_{5/2}(z) = \frac{4}{\sqrt{\pi}} \int_0^{\infty} dx x^2 \ln(1 + ze^{-x^2}) = \sum_{l=1}^{\infty} \frac{1}{l^{5/2}} (-1)^{l+1} z^l.$$

2. Show that the chemical potential is related to the average density,

$$\rho = \langle N \rangle / V \text{ by}$$

$$\rho \lambda^3 = f_{3/2}(z) = \sum_{l=1}^{\infty} \frac{1}{l^{3/2}} (-1)^{l+1} z^l.$$

3. Similarly, show that the energy $\langle E \rangle$ obeys the relation

$$\langle E \rangle = \frac{3}{2} p V.$$

4. Consider the *high temperature* and/or *low density* regime ($\rho \lambda^3 \ll 1$).

□ Show that

$$z = \rho \lambda^3 + \frac{1}{2\sqrt{2}} (\rho \lambda^3)^2 + \dots$$

□ Use this result together with the Fermi distribution for $\langle n_p \rangle$ to deduce the Maxwell-Boltzmann distribution

$$\langle n_p \rangle \approx \rho \lambda^3 e^{-\beta \varepsilon_p},$$

where p stands for the momentum and $\varepsilon_p = p^2 / 2m$.

□ Show that

$$\frac{\beta p}{\rho} = 1 + \frac{\rho \lambda^3}{(2)^{5/2}} + \dots$$

Why does a finite value of $\rho\lambda^3$ lead to deviations from the classical ideal gas law? Why should you expect the quantum deviations to vanish when $\rho\lambda^3 \rightarrow 0$?

5. Consider the *low temperature and/or high density* regime ($\rho\lambda^3 \gg 1$).
- Show that

$$\rho\lambda^3 = f_{3/2}(z) \approx (\ln z)^2 \frac{4}{3\sqrt{\pi}},$$

hence

$$z \approx e^{\beta\varepsilon_F},$$

where

$$\varepsilon_F = \frac{\hbar^2}{2m} (6\pi^2\rho)^{2/3}.$$

[Hint: use the integral representation of $f_{3/2}(z) = \frac{4}{\sqrt{\pi}} \int_0^\infty dx x^2 (1 + z^{-1}e^{x^2})^{-1}$.]

- Show that

$$p = \frac{2\varepsilon_F\rho}{5} \left[1 + O\left(\frac{T^2}{\varepsilon_F^2}\right) \right].$$

Hence the pressure does not vanish at $T = 0$! Why?

Problem I.4 (35 pts)

1. Prove that if the energy eigenvalues of a system can be expressed as a sum of independent contributions $E = E_A + E_B + E_C + \dots$ (e.g. electronic energy, vibrational energy, rotational energy, etc.) that the heat capacity can be written as $C = C_V^{(A)} + C_V^{(B)} + C_V^{(C)} + \dots$. In addition, show that the heat capacity is independent on the zero-point energy.

- Derive an expression for the electronic heat capacity assuming that there are only three significant electronic states and that they have energies and degeneracies given by $\{\varepsilon_0, g_0; \varepsilon_1, g_1; \varepsilon_2, g_2\}$
- Given that the energies required for electronic transitions correspond to roughly u.v. light (~ 50000 K), show how the calculated room temperature heat capacity of a diatomic molecule will change if the electronic degrees of freedom are totally neglected. What if the ground electronic state degeneracy is included but all the excited electronic states are neglected?

Problem I.5 (15 pts)

Compute the relative fluctuation $\frac{\Delta n_{\vec{k}}}{\langle n_{\vec{k}} \rangle}$ ($\Delta n_{\vec{k}} = \sqrt{\langle (n_{\vec{k}} - \langle n_{\vec{k}} \rangle)^2 \rangle}$)

in the occupation number of a given single-particle state for Bose-Einstein, Fermi-Dirac, and Maxwell-Boltzmann statistics.

Problem I.6 (25 pts)

At a given temperature, the difference between the specific heat of a diatomic ideal gas and a monatomic ideal gas is due in part to the rotational energy of the diatomic molecules. A rigid quantum rotator has energy levels $E_{rot}(l)$ with degeneracy $g(l)$ given by

$$E_{rot}(l) = l(l+1) \frac{\hbar^2}{2I}, \quad g(l) = 2l+1, \quad l = 0, 1, \dots$$

where I is the moment of inertia.

- Find the canonical partition sum of a gas of N non-interacting diatomic molecules.

2. Evaluate the specific heat of this gas at high temperatures, and at the lowest temperatures at which the rotational motion of the molecules makes a significant contribution.

II. Bonus Problem (35pts)

Problem II.1 (35 pts)

When a diatomic molecule vibrates, its moment of inertia depends to a small extent on the vibrational state. Consequently, the rotational and vibrational motions are not completely independent. Under suitable conditions, the spectrum of vibrational and rotational energies can be approximated as

$$E_{n,l} = \hbar\omega \left(n + \frac{1}{2} \right) + \frac{\hbar^2}{2I} l(l+1) + \alpha l(l+1) \left(n + \frac{1}{2} \right),$$

where the first two terms correspond to vibrational and rotational motion respectively, and the last term is a small correction that arises from the interdependence of vibrations and rotations. The various molecular constants

satisfy $\hbar\omega \gg \frac{\hbar^2}{2I} \gg \alpha$. For a gas of such molecules, compute the energy

for temperatures in the range $\hbar\omega > T > \frac{\hbar^2}{2I}$.