

PHYSICS 112

Homework 4

Due in class, Tuesday, Feb. 7.

MIDTERM: The midterm will be in class on Thursday, Feb. 9, and will cover the material on the first three homework assignments (plus the Debye theory of specific heats). You should review the solutions for these as part of your preparation for the midterm. The midterm will be closed book but you can bring one sheet of your own notes.

NOTE: To do some of these questions you will need the result for the chemical potential of a classical ideal gas. We will derive this a little later in the course but for now I just quote the result. It is

$$\mu(T) = k_B T \ln(nV_Q), \quad (1)$$

where $n = N/V$ is the density of atoms and

$$V_Q = \left(\frac{2\pi\hbar^2}{mk_B T} \right)^{3/2}$$

is called the “quantum volume” (m is the mass of the atom). The physical significance of V_Q (which is written as $1/n_Q$ in the book) is as follows. Particles of momentum p have a de Broglie wavelength equal to $2\pi/k$ where k is given by $p = \hbar k$. Consider a particle whose kinetic energy is $k_B T$ (a typical value). The corresponding “thermal de Broglie” wavelength, λ_T is given by

$$\frac{1}{2m} \left(\frac{\hbar 2\pi}{\lambda_T} \right)^2 = k_B T,$$

or

$$\lambda_T = \sqrt{\pi} \sqrt{\frac{2\pi\hbar^2}{mk_B T}}. \quad (2)$$

Hence apart from the numerical factor of $\sqrt{\pi}$, the quantum volume is the cube of the thermal de Broglie wavelength. It will figure extensively in our discussion of the ideal gas (both classical and quantum) a little later in the course.

The combination nV_Q is therefore the cube of the ratio of the thermal de Broglie limit to the typical interparticle spacing (remember that n is the inverse of the volume per particle). It is therefore the average number of particles in a volume equal to V_Q .

A little later in the course we shall see that the **classical limit** is when

$$\lambda \equiv \exp(\beta\mu) \ll 1,$$

or equivalently μ is large and negative. From Eq. (1), we see that **for the ideal gas the classical limit can be expressed as**

$$nV_Q \ll 1. \quad (3)$$

In other words the **classical limit is when** the average number of particles per quantum volume is very much less than one, or in other words, **the typical interparticle spacing is much greater than the thermal de Broglie wavelength**. Since the thermal de Broglie wavelength is proportional to $T^{-1/2}$, see Eq. (2), the ideal gas is always classical at high enough temperature, but quantum effects become important at sufficiently low temperatures. Quantum effects start to be important when $\lambda \simeq 1$, or equivalently when $nV_Q \simeq 1$. Note that Eq. (1) is no longer valid at temperatures lower than this.

I emphasize that $\mu(T)$ and V_Q are *temperature dependent*.

1. **Heat capacity of photons and phonons.** (Left over from HW 3.)

Consider a solid with a Debye temperature equal to 100 K and with 10^{22} atoms cm^{-3} . Estimate the temperature at which the photon contribution to the heat capacity would equal to the phonon contribution at 1 K.

Note: Use the Debye approximation for the specific heat of the phonons. Note that $C \propto T^3$ for *both* photons and phonons because they have the same dispersion relation $\epsilon \equiv \hbar\omega = \hbar ck$, where c is the speed of the wave. However, the speed of light is much greater than the speed of sound in a solid, which accounts for your answer being different from 1K. In fact Eq. (46), (in Kittel and Kroemer, 2nd Ed.), which gives the phonon energy in the Debye theory at low T , is equivalent to the Stefan-Boltzmann law, Eq. (20). This can be seen by using the relation between the Debye temperature θ_D , and the sound speed and atomic density, given in Eq. (44). The expression for phonons is 1.5 times as big because, for each wavevector, there are three polarizations for sound (one longitudinal and two transverse) whereas light only has two polarizations (there is no longitudinally polarized light wave).

2. **Potential Energy in a Gravitational Field**

In class we will show that concentration of molecules in a gas in a gravitational field varies with height h according to

$$n(h) = n_0 \exp(-mgh/k_B T), \quad (4)$$

where g is the acceleration due to gravity, m is the mass of a molecule, and n_0 is the density at $h = 0$. Find the total heat capacity per atom.

Note: The main part of the question is to determine the average *potential* energy per atom. The average *kinetic* energy per atom you may take to be $(3/2)k_B T$ (which will be discussed in class). You will need to average from $h = 0$ (the bottom of the gas) to $h = \infty$.

3. **Grand Partition Function for a Two-Level System**

- (a) Consider a system which may be unoccupied with zero energy, or occupied by one particle in either of two states, one of energy 0 and the other of energy ϵ . Show that the grand partition function (Gibbs sum) for this system is

$$\mathcal{Z} = 1 + \lambda + \lambda \exp(-\beta\epsilon),$$

where

$$\lambda = \exp(\beta\mu)$$

is the “fugacity” (activity) and $\beta = 1/k_B T$.

Note: We assuming here that we cannot have two particles in the system at the same time.

- (b) Show that the average number of particles is given by

$$\langle n \rangle = \lambda \frac{1 + \exp(-\beta\epsilon)}{\mathcal{Z}}.$$

- (c) Show that the probability of the system being in the state with energy ϵ is

$$\frac{\lambda \exp(-\beta\epsilon)}{\mathcal{Z}}.$$

- (d) Determine the average energy of the system.

- (e) Allow for the possibility that the orbital at 0 and that at ϵ can be each occupied by a particle at the same time. Show that now

$$\mathcal{Z} = 1 + \lambda + \lambda \exp(-\beta\epsilon) + \lambda^2 \exp(-\beta\epsilon) = (1 + \lambda) [1 + \lambda \exp(-\beta\epsilon)] .$$

Note: Because \mathcal{Z} can be factored, we actually have two *independent* systems.

4. States of Positive and Negative Ionization

Consider a large number of hydrogen atoms fixed in space (so they are distinguishable). Suppose that they can each exist in one of four states

State	Number of electrons	Energy
Ground	1	$-\frac{1}{2}\Delta$
Positive ion	0	$-\frac{1}{2}\delta$
Negative ion	2	$\frac{1}{2}\delta$
Excited	1	$\frac{1}{2}\Delta$

Show that the condition that the average number of electrons is unity can be expressed as

$$\lambda^2 = \exp(\beta\delta) .$$

5. Carbon Monoxide Poisoning

In carbon monoxide poisoning a CO molecule replaces the O₂ absorbed on a hemoglobin (Hb) molecule in the blood. To illustrate this effect, consider a simplified model in which each absorption site on the Hb may be vacant (with energy zero), or occupied either by one molecule of O₂, in which case it has energy ϵ_A , or by one molecule of CO, in which case it has energy ϵ_B .

Let there be N Hb molecules in equilibrium with gaseous O₂ and CO. Let the activities (fugacities) be $\lambda(\text{O}_2) = 1 \times 10^{-5}$ and $\lambda(\text{CO}) = 1 \times 10^{-7}$ (i.e. the fugacity of CO is less than that of O₂ so the concentration of CO will be smaller than that of O₂). Also assume body temperature, $T = 37^\circ\text{C}$.

- (a) First assume that there is no CO (i.e. temporarily assume that $\lambda(\text{CO}) = 0$). Find the value of ϵ_A such that 90% of Hb sites are occupied by O₂.
Give your answer in eV per molecule, noting that $1 \text{ eV} = 1.6 \times 10^{-19} \text{ J}$ and $k_B = 1.38 \times 10^{-23} \text{ J K}^{-1}$.
- (b) Now admit the CO under the specified conditions. Find ϵ_B such that only 10% of the Hb sites are occupied by O₂.

Note: This question is taken from Kittel and Kroemer. Assuming that the resulting values for ϵ_A and ϵ_B are roughly correct, the reason why a relatively small concentration of CO will displace most of the O₂ from the Hb is that the binding energy of CO is more negative.

6. Concentration Fluctuations

- (a) Show that the mean number of particles can be expressed as

$$\langle N \rangle = \frac{k_B T}{\mathcal{Z}} \left(\frac{\partial \mathcal{Z}}{\partial \mu} \right)_{T, V} ,$$

where \mathcal{Z} is the grand partition function (Gibbs sum).

(b) Hence show that

$$\langle N^2 \rangle = \frac{(k_B T)^2}{\mathcal{Z}} \left(\frac{\partial^2 \mathcal{Z}}{\partial \mu^2} \right)_{T,V}.$$

(c) The mean square fluctuation of N from $\langle N \rangle$ is defined to be

$$\langle (\Delta N)^2 \rangle \equiv \langle (N - \langle N \rangle)^2 \rangle = \langle N^2 \rangle - 2\langle N \rangle^2 + \langle N \rangle^2 = \langle N^2 \rangle - \langle N \rangle^2.$$

From parts (a) and (b) this is given by

$$\langle (\Delta N)^2 \rangle = (k_B T)^2 \left[\frac{1}{\mathcal{Z}} \frac{\partial^2 \mathcal{Z}}{\partial \mu^2} - \frac{1}{\mathcal{Z}^2} \left(\frac{\partial \mathcal{Z}}{\partial \mu} \right)^2 \right]. \quad (5)$$

Show that Eq. (5) can be written as

$$\langle (\Delta N)^2 \rangle = k_B T \frac{\partial \langle N \rangle}{\partial \mu}.$$

This result shows that the mean square fluctuations in N are of order $\langle N \rangle$ itself. It follows that the typical deviation of N from the mean, which is the *root* mean square fluctuation, is of order $N^{1/2}$. Hence, if N is large, for example $N = 10^{22}$, the size of the number fluctuations relative to the mean, $N^{-1/2}$, is tiny (10^{-11} in this example) and so can be neglected for most purposes.

7. Ascent of Sap in Trees

Assume that water rises in trees in *vapor* form. Assume further that the air in the tree at ground level is saturated with water vapor (relative humidity is $r = 1$), and that at the level of the leaves the relative humidity is $r = 0.9$ (so the concentration of water vapor is 0.9 that at ground level). Assume that the temperature is 25°C . Find the maximum height to which water vapor can rise according to this model.

Hint: The variation of concentration with height is given in Eq. (4).

Note: For comparison, redwood trees grow up to a height of about 100 m.