PHYS4031 STATISTICAL MECHANICS Problem Set 5 Due: 8 November 2016 (Tuesday)
"T+2" = 10 November 2016 (Thursday)

All problem sets should be handed in not later than 5pm on the due date. Drop your assignment in the PHYS4031 Box outside Rm.213. Work out the steps of the calculations in detail. While discussions with your classmates are encouraged, you should write up your answers independently.

MID-TERM EXAMINATION ANNOUNCEMENT - NOTE NEW VENUE!
Date: 5 November 2016 (Saturday)
Time: 10:00AM (2-hour exam)
Venue: LSK 304 (Lee Shau Kee Building)
Coverage: Everything from Ch.1 to Ch.9 Part 1 (inclusive), including materials discussed in class notes, lectures, sample questions, and problem sets.

5.0 *Reading Assignment*:

Read me: Part V (Ch.IX and Ch.X) of the course discusses two topics. The first one is about calculating the partition function in **classical statistical mechanics**, i.e., when summing over all N-particle states is replaced by integrating over phase space. The classical ideal gas, Langevin theory of paramagnetism, and classical oscillators are typical examples. A by-product is the Maxwell's distribution of molecular speeds. Applying classical stat mech to a **non-ideal gas** begins our short journey into **interacting systems**. Deviations from ideal gas behavior can formally be described by the virial coefficients. We derived the second virial coefficient, emphasizing that the repulsive part and the attractive part of the inter-particle interaction give qualitative different (different signs) contributions to B_2. The van der Waals equation of state, probably the most famous and useful equation in thermodynamics, is then derived. The vdW equation illustrates interesting features such as the jump in the volume in a first order phase transition, the power-law behavior near the critical point, and the law of corresponding states (same equation obeyed by different substances when reduced quantities are used). See SQ21 for an application of the van der Waals equation. This takes us naturally to an introduction to critical phenomena in Ch.X using ferromagnetism as the context. In Ch.X, we will discuss the ferromagnetic phenomenology, Ising model, mean field theory (MFT), critical phenomena as predicted by MFT, and Landau theory of continuous phase transitions.

References on the topics can be found in *Statistical Physics: An Introduction* by D. Yoshioka (Ch.7,8,9). Pathria's *Statistical Mechanics* Ch.9 and Ch.11 takes students from the undergraduate level to the graduate level on the topics. For students interested in learning more about phase transitions and critical phenomena, see M. Gitterman's *Phase Transitions: Modern Applications* and K. Christensen and N.R. Moloney's *Complexity and Criticality* (a master's degree level textbook).

Problems 5.1 and 5.2 are within the coverage of the mid-term exam. Try these before the mid-term exam.

5.1 **Density of Single-Particle States. (See Ch.VIII.)**

In getting $g(\epsilon)$, we emphasize that it is related to two things: Dimension of the problem AND the dispersion relation $\epsilon(k)$.

Although we have done some of these in class, but you ought to be able to do them independently. Let's consider a dispersion relation of single-particle states of the form

$$\epsilon(\mathbf{k}) = \mathcal{C}k^{\alpha} \tag{1}$$

where $k = |\mathbf{k}|$ is the magnitude of the wave vector and α is an exponent. The pre-factor $\mathcal{C}$ is a constant that makes sure that the left hand side has the units of an energy.

(a) For a 2D system (of area A), **derive** the density of (single-particle) states for non-interacting electrons (spin-1/2 particles).

(b) At the interface of two semiconductors (e.g. GaAlAs/GaAs interface), electrons are confined there. They cannot move into the bulk on either side, but only live in the 2D interface forming a so-called 2D electron gas. Taking these electrons to be non-interacting, apply the result in (a) and **get the density of states**. [This piece of information is needed to understand quantum Hall effect.] Hence, **write down two equations**, one for N (total number of electrons) and another for E (total energy) for this 2D electron gas by invoking the Fermi-Dirac distribution (recall physical meaning as discussed in Ch.VII).

(c) The electrons on graphene (single sheet of carbon) follow the dispersion relation

$$\epsilon = v\hbar k \; , \tag{2}$$

i.e., somehow they behave like massless fermions! Apply the result in (a) and **get the density of states** for the electrons on graphene (Nobel Physics Prize 2010).

5.2 **Bose 1924 work on Planck's black body radiation.** Why do we have Bose in the Bose-Einstein distribution and the name Bosons?

The story goes: Planck started the quantum era in 1900 by proposing his black-body radiation formula (better called thermal radiation formula), which he had some idea about oscillators. In 1905, Einstein used the idea of (only later formally called) photons in his photoelectric effect explanation and pointed out that $\epsilon = \hbar\omega$ for a photon. In his 1913 Bohr model of an atom, Bohr found that atomic spectral lines (photon comes out) come from transitions between two atomic energy levels and classical EM radiation theory does not work. Then it came the problem of whether one can derive Planck's formula based on Bohr's transition picture. In 1917, Einstein did the derivation and introduced his famous Einstein A and B coefficients, with the B coefficient indicating the process of stimulated emission for the first time (thus Einstein "invented" the idea for the development of laser). You had all these in your QM courses. This set the stage for Bose's work in 1924. Note that only in 1925-26 did Heisenberg, Born, Jordon, Kramers, Schrödinger, and Dirac wrote their papers on quantum mechanics.

Bose was teaching in Dacca University in 1924 in India (now the city is called Dhaka in Bangladesh), quite unknown to the physics world. In 1924, he derived the Planck's formula in a new way. In modern statistical physics language, he was the first one to regard the problem as a **(Bose) gas of photons**. Photons hardly interact with each other and therefore it is an ideal (non-interacting) gas. Digesting Planck's formula, it says (Bose found) that **the number of photons** coming out in the range from ω to $\omega + d\omega$ from a cavity of volume V at equilibrium at a temperature T is given by

$$N(\omega)\, d\omega = \frac{V\omega^2}{\pi^2 c^3} \frac{1}{e^{\hbar\omega/kT} - 1}\, d\omega \; , \tag{3}$$

and Bose provided a proof that amounts to what we did in Ch.VII and Ch.VIII. The thermal radiation (Planck's) formula is about the energy flux, thus slightly different from Eq. (3).

(See SQ20) In SQ20, TA discussed how Eq. (3) comes about using oscillator physics.

The first factor $V\omega^2/\pi^2 c^3$ is simply $D(\omega)$, where $D(\omega)d\omega$ gives the number of EM modes in a 3D cavity with angular frequencies in the interval ω to $\omega + d\omega$. It is almost the same as the density of modes in the Debye model, which deals with elastic waves in a solid. The similarity comes from the same form $\omega \sim k$ of the dispersion relation.

(a) Bose then treated the statistics of photons as follows. There are energy levels $\epsilon_r = \hbar\omega_r$ consisting of g_r photon states (same as in Ch.VII). He found (observed) that he could get the second factor in Eq. (3) by finding the **most probable distribution** when there is NO RESTRICTION on the number of photons in a single phone state (in modern terms, photons are bosons) and under the constraint of constant energy **only**, but **without a constraint on the total number of photons**. Under these conditions, **show that** the most probable distribution is given by

$$\frac{n_r}{g_r} = \frac{1}{e^{\beta\epsilon_r} - 1} \; . \tag{4}$$

Digest the conditions before doing any derivation: It is IMPORTANT to note that the total number of photons is NOT fixed. There is no constraint on the total number. You only need one Lagrange multiplier for the constraint $\sum_r n_r \epsilon_r = E$.

[Bose treated photons with no restriction on number of photons per single photon state. Later, there are real matter particles that one can put as many of them in a single-particle state as one wishes. They are called Bosons!]

Comment/Make sense of/Explain why (they mean the same thing) on the following statement. "Photons follow the Bose-Einstein distribution but with the chemical potential $\mu = 0$."

(b) To see clearly (or looking at the problem from another angle) why we don't have a constraint for the total number of photons, note that the total number of photons regardless of energy (or frequency), i.e.,

$$N(T) = \int_0^\infty N(\omega) d\omega \tag{5}$$

with $N(\omega)$ given by Eq.(3). **Show that** $N(T)$ increases with temperature rapidly. You may need the the integral

$$\int_0^\infty \frac{x^2}{e^x - 1}\, dx = 2.404$$

Important physics: For photon gas, you see that N increases rapidly with T. That is to say, the number is NOT fixed. It should be contrasted with a gas of real matter particles (atoms in a gas or electrons in a metal). If you have 10^{23} electrons in 1 cm^3 of a metal at 300 K, you also have the same number in 400 K. Understand! In the photon case, we could also interpret the result as oscillator physics. Temperature works to increase the excitations of the oscillators (EM normal modes). Increasing the temperature gives more photons. (See SQ20).

(c) **Calculate the total energy emitted** $E(T)$ and **show** that it goes like T^4, which is the Stefan's law or Stefan-Boltzmann law. Hint: Start with

$$E = \int_0^\infty \hbar\omega N(\omega)\, d\omega \tag{6}$$

with $N(\omega)$ given by Eq.(1). You may need the integral

$$\int_0^\infty \frac{x^3}{e^x - 1}\, dx = \frac{\pi^4}{15}$$

You should have seen this result of $E(T) \propto T^4$ in secondary school physics.

Remarks: The expression in the integrand of Eq. (6) is very close to the Planck's thermal radiation formula. Looking closer, you may find a missing constant factor of $c/4$. It has to do with the definition in Planck's formula about the flux of energy. TA explained the $c/4$ factor in SQ20.

And the story continues... Bose wrote his paper in 1924. He sent the manuscript to Einstein, who was then a famous physicist, and asked Einstein to read the paper, helped arrange a translation to German and "communicate" it to a German physics journal (Z. Physik). Guess what? Einstein did all the things! He even added a comment at the end of the paper saying that the method Bose used should be of great importance even for real material particles (i.e., Bosons but now with $\mu \neq 0$). A year later, Einstein used the method and predicted a phenomenon of Bose gas at low temperature – called the Bose-Einstein condensation (BEC). BEC was experimentally realized in 1995 (70 years later). What a lovely story in the development of physics during its romantic period!

Problems 5.3-5.5 are about the virial coefficients, real gases, van der Waals equation and its critical point

5.3 Ethane: Real gas and van der Waals gas (Closely related to SQ21)

Consider one mole of ethane at the temperature 400K confined to a volume 83.26 cm^3.

(a) Taking the van der Waals equation, i.e.,

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT\ , \tag{7}$$

where the parameters for ethane are $a = 5.5818$ dm^6 ·bar·mol^{-2} and $b = 0.065144$ dm^3·mol^{-1}, **calculate** the pressure.

(b) Taking the ideal gas law, **calculate** the pressure.

(c) **Comment** on the results in (a) and (b) in light of experimental value of the pressure being 400 bar.

[Remarks and Hint: Physics students tend to take symbols as symbols only. But we also need to handle real materials. In this question, the parameters a and b are given in their usual units as extracted experimentally. Hence, we need to be careful of units. It is a good habit to express the terms in consistent units. Here, it will be useful to first express the gas constant R into the right units for the problem.]

5.4 Critical temperature, volume, pressure of van der Waals equation of state.

In class notes, we took the short-cut in determining v_c, T_c and p_c in terms of a and b in the van der Waals equation of state. The van der Waals equation is cubic in v. At the critical point (C.P.), we enforce that the three roots are identical and hence the equation at C.P. should be of the form $(v-v_c)^3 = 0$, thus giving $v = v_c$ as required. Comparing this with the vdW equation gives v_c, T_c, p_c in terms of a and b in vdW equation (see Eq. (7)).

Here, you will work out the (same) results more formally.

(a) Looking at the pv isothermal lines, the critical point is the point of inflexion. Thus, the C.P. should correspond to where $\partial p/\partial v = 0$ and $\partial^2 p/\partial v^2 = 0$. Using these conditions, **derive** v_c, T_c, p_c in terms of a and b.

(b) Thus, measuring T_c, v_c, and p_c experimentally allows us to determine the parameters a and b in the van der Waals equation. Recall that a and b are related to the inter-particle interaction (attractive and repulsive parts), measuring the C.P. can tell us something microscopic! We have three measurable quantities and only two variables a and b to find. Usually, p_c and T_c are known more accurately. Hence, **express** a and b in terms of p_c and T_c.

Let's apply these relations to ethane again. Given that $T_c = 305.34\ K$ and $p_c = 48.714$ bar (or 48.077 atm), evaluate a and b for ethane.

(c) Universality or universal behavior is a big part of physics. Within the van der Waals equation, universal behavior is predicted when quantities are measured with reference to the critical point. For example, the reduced pressure is $p_R = p/p_c$, etc. **Show that** in terms of the reduced variables v_R, p_R and T_R, the van der Waals equation of state (Eq. (7)) says

$$\frac{pv}{RT} = \frac{v_R}{v_R - \frac{1}{3}} - \frac{9}{8 v_R T_R} \tag{8}$$

and hence pv/RT is some function $\mathcal{F}(v_R, T_R)$ that is unrelated to any material properties. [Remark: Now go to class notes and see a plot of pv/RT for many different gases as a function of v_R at various T_R and get a better sense of data collapse.]

5.5 About the second virial coefficient - Lennard-Jones (6-12) potential

(a) The second virial coefficient describes the leading term in the deviation from ideal gas behavior. We introduced it as

$$\frac{p}{kT} = \frac{N}{V} + B_2(T)\left(\frac{N}{V}\right)^2 + \cdots \tag{9}$$

Applying Eq. (9) to one mole and using the symbol v for the molar volume, **show** that Eq. (7) can be rewritten as

$$\frac{pv}{RT} = 1 + \overline{B}_2(T)\frac{1}{v} + \cdots \tag{10}$$

with $B_2(T)$ in Eq. (9) being related to $\overline{B}_2(T)$ in Eq. (10) by $\overline{B}_2(T) = N_A B_2(T)$.

(b) In class, we showed that $B_2(T)$ is related to an integral of the inter-particle potential energy function $U(r)$, i.e.,

$$B_2(T) = -2\pi \int_0^\infty [e^{-U(r)/kT} - 1] r^2 dr \tag{11}$$

Let's consider a model potential. The Lennard-Jones (or 6-12) potential is a popular inter-particle potential. In full, it has the form of

$$U(r) = \frac{c_{12}}{r^{12}} - \frac{c_6}{r^6} \tag{12}$$

The first term is the very steep repulsive part that two particles don't want to get too close to each other. The second term is a softer attractive part crucial for condensation. This full form is not easy to handle. So we model the repulsive "12"-part by a hard core and keep the "6"-part. This leads us to **consider a model potential** of a hard sphere plus a Lennard-Jones attractive part, i.e., $U(r) = \infty$ for $r < r_c$, and $U(r) = -c_6/r^6$ for $r > r_c$.

Evaluate B_2 in terms of c_6 and r_c. Hence, identify the expressions of a and b that go into the van der Waals equation of state (see class notes Ch.9 Part 3).