PHYS4031 STATISTICAL MECHANICS Problem Set 4 Due: 21 October 2016 (Friday)
"T+2" = 24 October 2016 (Monday)

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.

4.0 *Reading Assignment*:

Part III (Chapters V and VI) of our course discussed the **canonical ensemble** (formalism in Ch.V). The topic is covered in every reasonable textbook. We (You) also did the standard examples, including 2-level systems (defects, paramagnetism), harmonic oscillators (heat capacity of solids, vibrational levels in molecules), occupation of rotational levels in molecules, and classical ideal gas.

Chapter VI ends with a discussion on the point that evaluating the partition function $Z(T, V, N)$ is often not easy for quantum (Fermi and Bose) gases. It motivated us to go back to the microcanonical ensemble approach and call upon the concept of **the most probable distribution** (see Ch.III). **Part IV** (Chapters VII and VIII) has two short chapters handling non-interacting particles, in particular fermions and bosons. Using the microcanonical set up and finding the most probable distributions, together with the single-particle density of states, everything can be obtained. It provides a nice short-cut for doing all of undergraduate statistical physics. In Ch.VII, we apply the **Lagrange multipliers method** to derive the Fermi-Dirac and Bose-Einstein distributions (they emerge as the most probable distributions) and what these distribution really mean. A by-product is the Maxwell-Boltzmann distribution, which arises when the quantum nature of the particles can be ignored. The results tell us how to fill particles into single-particle states at an energy ϵ. How many states are there at an energy ϵ? This is the question answered in Ch.VIII on the **density of single-particle states** $g(\epsilon)$. Part IV gives the treatment in most introductory textbooks, e.g., the UK books by Guenault, Mandl, Trevana, the US book by Kerson Huang's *Introduction to Statistical Physics*, and all Chinese textbooks.

4.1 **Writing Z for Fermions and Bosons ain't easy - Problem 3.1 revisited.**

This is EXACTLY Problem 3.1, but you will re-do the problem here using the *occupation number* representation. You may consult the TA's solution to Problem Set 3. Here, the aim is to illustrate the discussion at the end of Ch.VI (Part 6) about the point that evaluating $Z(T, V, N)$ for a given fixed number of N fermions or bosons is often *inconvenient.*

Consider TWO PARTICLES which are to be placed in 5 single-particle states (i.e., assuming non-interacting particles). Two of these states have energy 0, two have energy ϵ, and one has energy 2ϵ.

The partition function Z is always given by

$$Z(T, V, N) = \sum_{\text{all } N\text{-particle states } i} e^{-\beta E_i} \; , \tag{1}$$

where the sum is over all N-particle states (here all 2-particle states) and E_i is the energy of the 2-particle state being summed up.

(a) The two particles are **Two identical fermions** (don't worry about spin, just impose the Pauli exclusion rule that says two identical fermions cannot occupy the same state).

(i) Let's label the five states by 1,2,3,4,5. Let n_1 be the number of particle in state number 1, n_2 particles in state number 2, and so on.
For fermions, $n_i = 0$ or 1 due to the Pauli exclusion rule. We also have $\sum_{i=1}^{5} n_i = 2$ as there are two particles in total. A list $\{n_1, n_2, n_3, n_4, n_5\}$ with $n_i = 0$ or 1 AND $\sum_{i=1}^{5} n_i = 2$ represents one possible 2-fermion state. [Pause: Understand this description?]
Make a table that gives the occupation numbers $\{n_1, n_2, n_3, n_4, n_5\}$ for all possible 2-fermion state. For each state, also give the corresponding energy E.

(ii) Hence apply Eq. (1) to **evaluate** $Z_{fermion}$ for two identical fermions.
[Remark: Now imagine we have exactly 10^{22} fermions and 10^{30} states. Writing down what to be summed up in Z is troublesome, if not impossible! This is exactly why we divert to look for the most probable distribution for fermions in Ch.VII and Ch.VIII.]

(b) The two particles are **Two identical bosons**.

(i) Now using the same occupation number representation for bosons. Now, n_i can be any integer (no Pauli rule). But we still have $\sum_{i=1}^{5} n_i = 2$ as there are two particles in total. A list $\{n_1, n_2, n_3, n_4, n_5\}$ with n_i being integers AND $\sum_{i=1}^{5} n_i = 2$ represents one possible 2-boson state. **Make a table** that gives the occupation numbers $\{n_1, n_2, n_3, n_4, n_5\}$ for all possible 2-boson state. For each state, also give the corresponding energy E.

(ii) Hence apply Eq. (1) to **evaluate** Z_{boson} for two identical fermions.
[Remark: Now imagine we have 10^{22} bosons and 10^{30} states. Writing down what to be summed up in Z is troublesome, if not impossible! This is exactly the point why we divert to look for the most probable distribution for bosons in Ch.VII and Ch.VIII.]

There is yet another way out. Later in Ch.XI, we will develop the 3rd ensemble theory: The Gibbs distribution and Grand canonical ensemble for which the restriction $\sum_i n_i = N$ is relaxed. This will make life much easier for studying quantum gases.

4.2 **Statistical physics of gas of diatomic molecules. (Closely related to SQ15)**

Physics Background – This serves to remind you of the related physics. Consider a gas of N molecules (diatomic molecules for simplicity). The partition function is given by

$$\begin{aligned} Z &= Z_{trans} \times Z_{rot} \times Z_{vib} \\ &= \left(\frac{1}{N!}\, z_{trans}^N\right) z_{rot}^N\, z_{vib}^N, \end{aligned} \tag{2}$$

where the part of the translational motion $Z_{trans} = z_{trans}^N/N!$ is what **you worked out in Problem 3.5**. This part treats the motion of the center-of-mass of the molecules. For diatomic molecules, there are also **internal motions**, described by the rotational and vibrational states. Here, z_{rot} is the single-molecule rotational partition function and z_{vib} is the single-molecule vibrational partition function. The necessary quantum physics as covered in Applied QM (PHYS3022).

(a) *Vibrational states.* **(See SQ15)** The general physical sense is that *most molecules are in the vibrational ground state at room temperature.* It is because the typical vibrational energy scale given by $\hbar\omega$ is of the order of 0.1 eV and thus the vibrational temperature scale is $\theta_{vib} = \hbar\omega/k \sim 10^3\ K$. In addition, θ_{vib} is higher for molecules with light-mass atoms, as you would expect from $\omega \sim \sqrt{K/m}$ in a mass-spring system.

The key results of statistical physics of vibrational states are:

$$z_{vib} = e^{-\beta\hbar\omega/2}\frac{1}{1 - e^{-\beta\hbar\omega}} \tag{3}$$

$$C_{vib} = Nk\left(\frac{\theta_{vib}}{T}\right)^2 \frac{e^{-\theta_{vib}/T}}{(1 - e^{-\theta_{vib}/T})^2} \tag{4}$$

(i) Take the diatomic molecule HCl as an example. It has a light atom (hydrogen) and therefore the temperature scale $\theta_{vib} = 4227\ K$ set by the vibrational frequency is high. **Calculate the following quantities**: The vibrational contribution to the molar heat capacity at 300 K and at 2000 K; the fraction of molecules in the vibrational ground state ($n = 0$ state) and the fraction of molecules in all the excited states ($n > 0$ states altogether) at 300 K and at 2000 K.

(ii) Let's consider Cl_2, which differs from HCl only by replacing the light atom by another chlorine. The situation is quite different with $\theta_{vib} = 805\ K$. **Calculate the following quantities**: The vibrational contribution to the molar heat capacity at 300 K and 2000 K.

(iii) Consider $T = 900\ K$. **Calculate** the fractions of molecules in the $n = 0$ (vibrational ground state) and $n = 1, 2, 3, 4$ excited states one-by-one. **Sketch** the fractions as a function of n.

(b) *Rotational levels.* The key quantity of the statistical physics of rotational states is the rotational partition function

$$\begin{aligned} z_{rot} &= \sum_{J=0}^{\infty}\sum_{m_J=-J}^{+J} \exp\left(-\frac{J(J+1)\hbar^2}{2IkT}\right) \\ &= \sum_{J=0}^{\infty}(2J+1)\exp\left(-\frac{J(J+1)\hbar^2}{2IkT}\right) \end{aligned} \tag{5}$$

The general physical sense is that while molecules are mostly in the $n = 0$ vibrational ground state at room temperature, **most molecules are in excited rotational states**. It is because the typical rotational energy scale $\hbar^2/2I$ is of the order of 0.01 eV and thus the temperature scale $\theta_{rot} = \hbar^2/(2kI)$ is much less than room temperature. The room temperature thermal energy kT can excite molecules to higher rotational states. For example, HCl has $\theta_{rot} = 15\ K$.

(i) Evaluating z_{rot} is not easy. In SQ15, TA worked out the high-temperature limit of z_{rot}. It is often the useful limit. Here, we will look at the opposite *low-temperature* limit. Thinking like a physicist, the low temperature physics is dominated by the low-lying (meaning low energy) rotational states. Here, $\hbar^2/2I$ sets an energy scale for the problem. For $kT \ll \hbar^2/2I$, **show** that z_{rot} can be approximated to the lowest order as:

$$z_{rot} \approx 1 + 3e^{-\hbar^2/IkT}. \tag{6}$$

Hence, **find** the free energy (per mole), entropy, and heat capacity (due to rotational motion) in this temperature range. In particular, **point out** how the contribution to the entropy and heat capacity drops as T decreases.

(i') (Optional: NO bonus points) Work out part (i) to the next term in z_{rot} (in Eq. (5)) in the low temperature limit.

(ii) **(Closely related to SQ15)** Again, let's take HCl as an example. It has $\theta_{rot} = 15\ K$. Thus, room temperature T corresponds to the high-temperature regime where $T \gg \theta_{rot}$. This allows us to turn the sum in Eq. (5) into an integral to evaluate (a classical limit of) z_{rot}. Hence, **evaluate** z_{rot} for HCl at $T = 300\ K$. Using the result, **find the fraction** of molecules in the J-th rotational level for HCl at 300 K and **sketch the result** as a function of J. You have seen the HCl vibrational-rotational spectrum (see class note and Applied QM). In a few sentence, **explain the shape** of the envelopes in the vibrational-rotational spectrum as given in class notes.

4.3 **Statistical physics of oscillators and Heat capacity of insulating solids.**

Physics Background – There are N atoms in a 3D solid. Einstein assumed that there are $3N$ identical, distinguishable and independent oscillators, each with the same angular frequency ω_E. The heat capacity of Einstein's solid $C \to 0$ and $T \to 0$, in agreement with experimental data and as required by thermodynamics. Nice! However, the heat capacity drops to zero **too fast**. That was 1907. A few years later, Debye came in with his model of a distribution in the oscillators' frequencies and obtained $C \sim T^3 \to 0$ as $T \to 0$ in good agreement with experimental data.

Here, you will carry out the derivations that lead to Debye's result in 3D and 4D.

(a) **Debye model in 3D.** The starting point is the expression of the energy of a collection of oscillators:

$$\langle E \rangle = E_{GS} + \int D(\omega) \frac{\hbar\omega}{e^{\beta\hbar\omega} - 1}\, d\omega \tag{7}$$

where $D(\omega)d\omega$ being the number of oscillators (normal modes) with angular frequencies in the range ω to $\omega + d\omega$. The physics is that these are normal mode frequencies. In 3D Debye model of solids, $D(\omega)$ behaves as

$$D(\omega) = \mathcal{A}\omega^2 \tag{8}$$

where $\mathcal{A}$ is a constant to be determined. But this ω^2 dependence is followed only up to a cutoff frequency. It is because there are a total of $3N$ normal modes and no more. By integration $D(\omega)$ up to some cutoff frequency called ω_D (Debye frequency), **find an expression** for $\mathcal{A}$. Hence, **work out the steps/arguments** that lead to the conclusion that the second term in $\langle E \rangle$ goes like T^4 at low temperatures and hence give an expression of the heat capacity that goes like T^3. You may find the following integral useful:

$$\int_0^\infty \frac{x^3}{e^x - 1}\, dx = \int_0^\infty x^3 \left(\sum_{s=1}^{\infty} e^{-sx} \right) dx = 6 \sum_{s=1}^{\infty} \frac{1}{s^4} = \frac{\pi^4}{15}$$

[Remarks: You just filled in the details on the Debye model. Although we work on the problem of heat capacity of solids, the derivation and the result $\langle E \rangle \sim T^4$ are closely related to the Stefan-Boltzmann T^4 law in thermal radiation of a body at a temperature T.]

(b) **Debye model in 4D.** Let's start with Eq. (7) again. In 4D, we have

$$D(\omega) = \mathcal{B}\,\omega^3 \tag{9}$$

where $\mathcal{B}$ is a constant to be determined. **Carry out the same calculation as in (a)** and **find** the temperature dependence of the mean energy and heat capacity in 4D. You may leave an integral unattended (which is just a number after all) in the answer. Of course, you may also evaluate the integral.

4.4 **Physics of Ideal Bose gas using the most-probable distribution.** *DIY: Treating Ideal Bose Gas within microcanonical ensemble approach by the most probable distribution.*

In a separate Chapter on Ideal Bose Gas later after we develop the third ensemble theory (grand canonical ensemble), we will soon find that for an ideal (meaning: non-interacting) Bose gas, the quantity $\Omega = E - TS - \mu N$ is given by

$$\Omega_B = kT \sum_r \ln(1 - e^{-\beta(\epsilon_r - \mu)}) \ , \tag{10}$$

where the sum is over all single-particle states. The quantity Ω is called the **grand potential**.

Here, you will derive the result using the most probable distribution found in Ch.VIII for bosons together with the microcanonical ensemble (Ch.III). [Physics is physics – the same results emerge regardless of methods.] Let's see what we know. In Ch.VII, the Bose-Einsten distribution appears as the **most probable distribution** for bosons being put into single-particle states, using ideas in microcanonical ensemble and the method of Lagrange multipliers. In particular, we derived the number of microstates corresponding to the most probable distribution as

$$W_{BE}^{(mp)}(\{n_i\}) = \prod_i \frac{(g_i + n_i - 1)!}{n_i!(g_i - 1)!} \approx \prod_i \frac{(g_i + n_i)!}{n_i! g_i!} \tag{11}$$

and found that for bosons

$$\frac{n_i}{g_i} = \frac{1}{e^{(\epsilon_i - \mu)/kT} - 1} \ . \tag{12}$$

At this point, we can go back to $S = k \ln W$ (microcanonical ensemble) and work out the physics. You will DIY here for an ideal Bose gas using the (microcanonical ensemble) approach. You will obtain the grand potential Ω_B by manipulating the most probable distribution. Following the microcanonical ensemble approach, everything starts with $S = k \ln W$, which can be approximated by $S = k \ln W^{(mp)}$, where $W^{(mp)}$ is the number of microstates of the most probable distribution.

(a) Taking $\ln W \approx \ln W^{(mp)}$, i.e., the most probable distribution dominates the number of microstates and using $S_B \approx k \ln W_{BE}^{(mp)}$, **find an expression** for the entropy S_B for an ideal gas of bosons.

(b) Starting with the definition of the Helmholtz free energy F, **find an expression** for F_B.

(c) Hence, **show** that

$$\begin{aligned} \Omega_B &= kT \sum_i g_i \ln\left[1 - e^{-(\epsilon_i - \mu)/kT}\right] \\ &= kT \sum_r \ln\left[1 - e^{-(\epsilon_r - \mu)/kT}\right] , \end{aligned}$$

where the sum in the first line is over all cells i of single-particle states and the sum in the second line is over all single-particle states r. [Remark: This last result will be derived by the grand canonical ensemble approach later (see Ch.XII).]

[Remark: Given a situation (spatial dimension, dispersion relation), there is a single-particle density of states $g(\epsilon)$. The summations can then be turned into integrals using the single-particle density of states $g(\epsilon)$ as discussed in Ch. VIII, and the thermodynamics of a Bose gas can be studied. We will study it later.]

(d) Back to the definition of the grand potential $\Omega = E - TS - \mu N$. Recall Euler equation (what is it?) and **give an expression** for pV for an ideal Bose gas based on Eq. (10). Immediately, you will see that pV is different from that of a classical ideal gas for which $pV = NkT$.

4.5 Mathematical Skills VII – Method of Lagrange Undetermined Multipliers.

Recipe: For those who only want to know how to use the method.

Physical Sense of the problem: Let's consider a function $f(x, y, z)$ for a given domain of the arguments x, y, z. One can ask where is the maximum/minimum of f and what is its value at the maximum/minimum. Very often, we have an additional constraint which is represented by an equation $g(x, y, z) = 0$. The new question is: Where is the maximum/minimum of $f(x, y, z)$ **subject to** the constraint $g(x, y, z) = 0$? Obviously, it is different from just where f is a maximum/minimum with no constraint.

Here is the recipe.

Step 1. Set up the function

$$\mathcal{F} = f - \lambda\, g \tag{13}$$

where λ is an unknown (to be determined) *constant*.

Step 2. Take the partial derivative of h with respect to x, y, z and set each one equal to zero. That is to say, we have

$$\frac{\partial \mathcal{F}}{\partial x} = \frac{\partial f}{\partial x} - \lambda \frac{\partial g}{\partial x} = 0 \tag{14}$$

$$\frac{\partial \mathcal{F}}{\partial y} = \frac{\partial f}{\partial y} - \lambda \frac{\partial g}{\partial y} = 0 \tag{15}$$

$$\frac{\partial \mathcal{F}}{\partial z} = \frac{\partial f}{\partial z} - \lambda \frac{\partial g}{\partial z} = 0 \tag{16}$$

and

$$g(x, y, z) = 0 \tag{17}$$

Step 3. Equations (14)-(17) give *four equations* in *four unknowns*, x, y, z, and λ. Solving these equations will give the desired value (x_0, y_0, z_0) where f is a maximum/minimum subject to the constraint $g = 0$. Putting (x_0, y_0, z_0) back into the function f gives the value at the maximum/minimum. Done!

Remarks: The steps can be readily generalized to a function f with more variables and/or subject to several constraints $g_1 = 0$, $g_2 = 0$, etc. The point is: Following the procedure and there are always the right number of equations to solve for the unknowns.

Starting here is Problem 4.5

In Statistical Mechanics, we have the concept of the most probable distribution (the one that carries the largest number of microstates). In fact, the most probably distributions are the famous Fermi-Dirac distribution for fermions and Bose-Einstein distribution for bosons. The mathematical technique involved is called the **Lagrange undetermined multipliers method**. The method is part of earlier mathematics or mathematical methods course. We consider the simpler case of a function of two variables and one constraint. The bare minimum here is that you know how to use the method. Better still, you understand why the method works.

(a) Let $f(x, y) = ax + by$. We want to find the extremum of $f(x, y)$ under the constraint that $x^2 + y^2 = g(x, y) = 1$. For a **high school student**, s/he will do it as follows. **Solve the problem following the following steps.** (i) Solve y in terms of x using the constraint, (ii) then substitute $y(x)$ into f and (iii) look for extremum by $df(x, y(x))/dx = 0$. **Find both the extremal values of f and the corresponding x and y.** This method should work well. [It is also useful to think about the problem geometrically. To plot $f(x, y)$, you need a 3D plot. Thus, $f(x, y)$ looks like a piece of hanging cloth. Then the constraint defines a particular contour for which you want to find the extremum.]

(b) For an **undergraduate**, s/he will use the Lagrange's Method of undetermined multipliers (or in short, the method of Lagrange multipliers). We want to find the extremum of $f(x, y) = ax + by$ under the constraint $g(x, y) \equiv x^2 + y^2 = 1 \equiv c$. Here c means a constant. [Remark: One can also regard the constraint as another function $\overline{g}(x, y) = x^2 + y^2 - 1 = 0$.] **Set up two equations** by introducing a multiplier λ (one multiplier here because there is only one constraint):

$$\frac{\partial f}{\partial x_i} - \lambda \frac{\partial g}{\partial x_i} = 0$$

where $x_i = x$ and y. **Solve** for $x(\lambda)$ and $y(\lambda)$. To determine the "undetermined multiplier", use the constraint $g(x(\lambda), y(\lambda)) = 1$ and **solve** for λ. At this point, you have the values of $x(\lambda)$ and $y(\lambda)$ that give extremal value of f. **Compare** results with (a). They should come out to be the same, of course.

(c) Now think about what have been done in (a) and (b). Why do the two procedures give the same results? What is the difference between the two ways?

Let's use the **high school way again** but formally, i.e., without specifying the explicit form of $f(x, y)$ and $g(x, y) = c$. Solving $g(x, y) = c$ formally gives us a function $y = h(x, c)$. Imposing $df(x, h(x, c))/dx = 0$ gives one equation, in which there is a term dh/dx that we need to know. **Work out the equation.** [Hint: Use chain rule.] (This is what you did in (a).)

Next, we write the constraint $c = g(x, y)$ as $c = g(x, h(x, c))$. The latter is just the trivial equation $c = c$. Using the fact that $dc/dx = 0$, since c is a constant, to **obtain an expression** for dh/dx.

By substituting dh/dx into the former equation, **show** that the resulting equation is:

$$\frac{\partial f}{\partial x} - \frac{\partial g/\partial x}{\partial g/\partial y}\frac{\partial f}{\partial y} = 0.$$

This is the condition for extremum.

(d) Now, let's use the **undergraduate way** again. We introduce a Lagrange multiplier λ and try to find the extremum of the combined function $f(x, y) - \lambda g(x, y)$. Take derivatives with respect to x to get one equation, and with respect to y to get another equation. Now, eliminate λ from these two equations to **show that the resulting equation is the one you have in (c)**. [Remark: You have proven the validity of the method of Lagrange multipliers for the case of functions of two variables. (Remark:) **Students** may want to repeat parts (c) and (d) for functions of arbitrary number of variables and more constraints.]

References:

See Riley, Hobson, and Bence, *Mathematical Methods for Physics and Engineering* (2nd edition) (Cambridge Univ. Press), p.170-176
Steiner, *The Chemistry Maths Book* (Oxford Univ. Press), p.194-198.