PHYS4031 STATISTICAL MECHANICS Problem Set 3 Due: 12 October 2016 (Wednesday)
"T+2" = 14 October 2016 (Friday)

All problem sets should be handed in not later than 5pm on the due date. Drop your assignment in the PHYS4013 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.

3.0 *Reading Assignment*: We have established the theory for two ensembles: microcanonical (Ch.II-IV) and canonical ensembles (Ch.V-VI, and a later part on classical statistical mechanics (Ch.IX)). We set up these calculation schemes/methods in a general form so that they are applicable to interacting and non-interacting systems alike. In Ch.VI, we apply the canonical ensemble method and discuss the statistical physics of two-level systems, theory of paramagnetism, collection of oscillators and the heat capacity of insulating solids. These examples can be found in standard textbooks such as Mandl, Rossner, Yoshioka, and Bowley and Sanchez. Chemists also learn and use stat mech., as they need to understand a gas of diatomic or polyatomic molecules, where there are translation, vibrational (oscillators), and rotational motions. Statistical Mechanics is an important part of physical chemistry. For a good discussion on chemistry applications of stat mech, see "Physical Chemistry: A molecular approach" and "Statistical Mechanics" by D. McQuarrie.

Background for Problem Set 3 (See Ch.V and Ch.VI)

This Problem Set focuses on the Partition Function and how to make use of it. The partition function $Z(T,V,N)$ is **the** key quantity in the canonical ensemble theory. It first appeared as a normalization constant to the result that the probability $P(E_i)$ (or equivalently P_i) that a system is in a N-particle state of energy E_i when the system is in thermal equilibrium with a heat bath at a temperature T, i.e.,

$$P(E_i) \propto e^{-E_i/kT} \ .$$

It follows that the partition function is given by:

$$\begin{aligned} Z(T,V,N) &= \sum_{\text{all } N\text{-particle states } i} e^{-\beta E_i} && (1) \\ &= \sum_{\text{all } N\text{-particle levels } i} W(E_i,V,N)\, e^{-\beta E_i} && (2) \\ &= \int \mathcal{W}(E,V,N)\, e^{-\beta E} dE && (3) \end{aligned}$$

Equations (1) and (2) are completely general, i.e., they work for both interacting and non-interacting systems. In Eq. (1), the sum is over **all states**, i.e., when some states are of the same energy, we include them one by one into the sum. In Eq. (2), the sum is over **all levels**, i.e., over the different allowed values of energy (or energy levels) E_i and the factor $W(E_i,V,N)$ (the degeneracy) in the sum takes care of how many states there are at an energy E_i. Eq. (3) is also general and it takes the N-particle states as being continuously distributed in energy. Here $\mathcal{W}(E,V,N)dE$ is the number of N-particle states in the energy interval from E to $E+dE$. Once $Z(T,V,N)$ is obtained, other thermodynamic quantities can be calculated. Practically, this is all about the canonical ensemble theory.

3.1 **(Closely related SQ12.) Be very careful of what are being summed up in getting Z**

To apply Eq. (1) and Eq. (2) to get Z, it is important to understand what are being summed up. A way (not the cleverest way perhaps, but works) is to list clearly the N-particle states or levels together with degeneracy that are to be summed over. The list will **depend on** whether the particles are distinguishable particles, identical bosons or fermions, i.e., the quantum nature of the particles really matters! Here, you will explore this crucial point by yourself.

(See SQ12 for a similar exercise.) 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. **Find the partition function** Z for each of the following cases.

(a) Two **distinguishable particles**. By **listing out all the two-particle states** to be summed up in Eq. (1), **find** $Z_{distinct}$. Hence, **relate** your result to Eq. (2). In this case, **show** explicitly that

$Z_{distinct}$ can be factorized into a product of single-particle partition functions. **Point out** what the single-particle partition function is referring to.

(b) Two **identical fermions** (don't worry about spin, just impose the Pauli exclusion rule that says two identical fermions cannot occupy the same state). **Find** $Z_{fermion}$.

(c) Two **identical bosons**. **Find** Z_{boson}.

(d) Look at your results in (a)-(c). Some students thought that the Pauli exclusion rule applies to fermions only, and therefore $Z_{fermion} \neq Z_{distinct}$ is reasonable. But the Pauli exclusion rule does not apply to bosons and therefore it is **not too obvious** why Z_{boson} is different from $Z_{distinct}$. From your results, **explain why** Z_{boson} **and** $Z_{distinct}$ **are different**.

Intermission-what's next: The following two parts serve to illustrate why (sometimes) a correction factor $1/N!$ could turn the distinguishable particles result in part (a) into useful result for **indistinguishable but classical particles**. Part (e1) shows that **the correction factor does not always work**. Part (e2) shows that sometimes it works and why we have the idea of *classical particles*.

(e1) Many tried to **make a correction** to the counting of states for distinguishable particles and use the modified result for indistinguishable particles (and hopefully for bosons and fermions). A standard (and lazy) way is to introduce a factor $1/N!$ and thus $1/2! = 1/2$ to our two-particle problem. The idea is to *correct for the over-counting* in 2-particle states in the distinguishable case. **State** what "over-counting" refers to? **Examine whether** a factor 1/2 works in correcting $Z_{distinct}$ into Z_{boson} or $Z_{fermion}$? If not, **why not**?

(e2) Sometimes, the correction factor $1/N!$ actually works! Let's say we impose an additional condition that the two particles cannot occupy the same single-particle state into the counting in each of the three cases in (a)-(c). **Show** that the correction factor $1/2!$ works in correcting the over-counting of states in the distinguishable particle case.

Important remark: This is exactly the $1/N!$ that we included in the counting of states for the classical ideal gas problem (see microcanonical ensemble approach). "*Classical*" here means that we don't need to worry about the particles are bosons or fermions at all (as they will not occupy the same state anyway). This is the same physics behind the condition ($\lambda_{th} \ll (V/N)^{1/3} \approx$ particle-spacing) in the ideal gas argument. Thus, the correction factor $1/N!$ is also included in doing classical statistical mechanics within the canonical ensemble.

3.2 Two-level systems: Getting Z by Eq. (2). (See SQ13.)

In Problem 2.2, you did the problem of two-level systems in microcanonical ensemble. For N independent particles (distinguishable), each can be in one of two energy states $\epsilon_1 = 0$ (not excited) or $\epsilon_2 = \epsilon > 0$ (excited), you counted the number of microstates $W(E, N)$ for a given total energy E. The counting is easy to do by invoking the binomial coefficients.

Insert $W(E, N)$ (Problem 2.2) into Eq. (2) and **find** $Z(T, N)$ by summing over all allowed values of the total energy E. **Check against** class notes (Ch.VI Part 1) that it is the same Z that can be obtained by other ways.

Remark: From Z, then everything follows, as discussed in Ch.VI.

3.3 Estimating how much less oxygen at an altitude of 5000 m.

Without considering the variation of temperature with altitude, i.e., ignoring the fact that it is cooler the higher you go, **use** the Boltzmann factor to **explain** why there is less oxygen up on a mountain. **Estimate the percentage of oxygen left** at an altitude of 5000 m, when compared with the sea level.

Remark: In a very physics textbook manner, the problem can be stated as a huge column (cylinder) of oxygen with the same temperature T maintained throughout the column, and finding the distribution of the molecules as a function of the height. But this is too formal. The point is that most people will find it hard to breathe at such altitude without preparation and the help of equipment.

3.4 $J = 1$ case of the paramagnetic problem: three-level particles

The case of $J = 1/2$ paramagnetism is discussed in class. It is a realization of two-level systems. A simple review is that when there is no **external** magnetic field $\mathbf{B}_{ext}$, there are two degenerate states (i.e., with the same energy) for a magnetic moment. When $\mathbf{B}_{ext} = B_{ext}\hat{z}$, these states take on different energies. There is one state with the z-component of the magnetic moment $\mu_z = +\mu_B$, i.e., aligned along the external field direction with a lower energy of $-\mu_B B_{ext}$. Another state has the z-component of the magnetic moment $\mu_z = -\mu_B$, i.e., anti-aligned with the external field and thus has a higher energy of $+\mu_B B_{ext}$. It then follows that we have a compact equation for $\langle E \rangle$ and $\langle \mu_z \rangle$ and then the magnetization M.

Now, let's consider the $J = 1$ **or three-level case.** Now it is your turn to practice. To make it simple, the z-component of a magnetic dipole moment is assumed to take on $+\mu_B$, 0, and $-\mu_B$. The possible energies in the presence of an applied B_{ext} in the $+z$-direction are then $-\mu_B B_{ext}$, 0, and $+\mu_B B_{ext}$. The mathematics may not be as elegant/simple as the $J = 1/2$ case, but the physics will come out clearly.

(a) **Identify** which alignment of μ corresponds to which energy level.

(b) **Show** that $Z = z^N$, for N magnetic moments in a uniform B-field.

(c) **Calculate** the single-magnetic-moment partition function z. For this single-particle partition function, a "particle" refers to a magnetic moment.

(d) **Calculate** the average z-component of a magnetic moment $\langle \mu_z \rangle$, given that it is at equilibrium at a temperature T. You may either use physical reasoning or plug formula.

(e) **Write down** an expression for the magnetization M (defined as the magnetic moment per unit volume in electromagnetic theory), with $\mathcal{N} = N/V$ being the number of magnetic moments per unit volume. **Discuss** the physics in the two limits (what limits?). In particular, work out **how M depends on the temperature** in the limit of low applied field and high temperature and **relate** your result to the Curie's law.

3.5 **Z in Eq. (1) is also good for classical statistical mechanics. (See Problem 1.1(b)(c).)**

Equation (1) also works for classical statistical mechanics, i.e., when the discretized (or quantized) features can be ignored. The key point is, again, to express "summing over all N-particle states" correctly. Generally in classical physics, a state in an N-particle system is described by a point in the $6N$-dimensional phase space (Γ-space). Then summing over all states can be realized by integrating over the phase space. So, the expression for the partition function for **classical statistical mechanics** is

$$Z(T,V,N) = \frac{1}{N!}\underbrace{\frac{1}{h^{3N}}\int d^3x_1 \int d^3p_1 \cdots \int d^3x_N \int d^3p_N}_{\text{sum over all } N\text{-particle states}}\ e^{-\beta H(\{x,p\})} \tag{4}$$

where $H(\{x,p\})$ is the Hamiltonian of the N-particle system. Equation (4) is the starting point of all classical statistical mechanical calculations within the canonical ensemble. Non-ideal (real) classical gases and liquid state physics all start from here. The pre-factor $1/N!$ is introduced to take care of over-counting in situations where the particles are indistinguishable (see discussions in Problem 3.1(e)). For distinguishable classical particles, omit the $1/N!$ factor.

(a) Let's see that Eq. (4) works in a familiar case. Consider a monatomic ideal gas. There are N particles in a volume V. The Hamiltonian is then given by

$$H(\{x,p\}) = \sum_{i=1}^{N}\left(\frac{p_{i,x}^2}{2m} + \frac{p_{i,y}^2}{2m} + \frac{p_{i,z}^2}{2m}\right), \tag{5}$$

which is independent of the positions $\{x\}$. **Show** that

$$Z(T,V,N) = \frac{1}{N!}\,z^N \tag{6}$$

where z is a single-particle partition function. **Write down** a formal expression (as integrals) for z. Hence **evaluate** z (recall gaussian integrals) and hence **find** Z. (Hint: You did it in Problem 1.1.)

(b) **Obtain** the Helmholtz free energy by $F(T,V,N) = -kT\ln Z(T,V,N)$ and then **take derivatives to obtain** the entropy S, the pressure p and the chemical potential μ.

(c) **Check that** the Helmholtz free energy so obtained is an extensive quantity. **What if** we left out the factor $1/N!$ in obtaining Z?

[Remark: The results should look very familiar – the standard ideal gas results. See, you just re-do the classical ideal gas problem yourself using the canonical ensemble method! Now you can compare which ensemble is more convenient, for this particular problem.]

3.6 **A first taste of Interacting Systems – Exact partition function of the one dimensional Ising model of interacting spins/moments.**

We stress that Eq. (1) is generally valid. Up to now, all the problems are related to non-interacting systems. **Equation (1) also works for interacting systems**. However, very seldom can we calculate Z exactly for an interacting system. Here is one of the very few examples. It is called the one-dimensional (1D) **Ising model**.

1D Ising Model: In words, let's consider a very long linear chain (say along x-axis) of N (with $N \gg 1$) magnetic moments. For simplicity, each moment can either point up ($+z$ direction) or down ($-z$ direction). Each magnetic moment can only **interact** with its two nearest neighboring moments (left and right). There are two possibilities. If two neighboring moments are pointing in the same direction (aligned), then the interaction energy is lower with a value of J. If two neighboring moments are pointing in opposite directions (anti-aligned), then the interaction energy is higher with a value of $-J$. This is the Ising model described in words. Of course, it can be expressed in terms of a Hamiltonian. But I intentionally do not give you the Hamiltonian. Note that if $J < 0$, then aligned neighboring moments is preferred. If this preference is obeyed by all nearest neighboring moments, we have global alignment with all moments pointing in the same direction, thus it is a ferromagnetic case. Therefore, $J < 0$ for ferromagnetic interaction. Making $J > 0$ will lead to anti-ferromagnetic interaction.

(a) **Show that** the partition function Z of the system can be exactly evaluated to be

$$Z = 2^N \cosh^{N-1}\left(\frac{J}{kT}\right) . \tag{7}$$

[**If you need help, follow the hints:** It will be useful to introduce N_p and N_a for the **numbers of neighboring pairs** with parallel moments and anti-parallel moments, respectively. These numbers are not independent. Find an equation that governs the sum of these numbers. Then, consider what is the energy of a state for a given N_p (and thus given N_a) and count how many such states are there. Knowing the number of states of a certain energy, one can evaluate Z exactly. Thus, this constitutes a clever move to consider bonds/links instead of sites.]

About Ising model: The Ising model is the simplest model of ferromagnetism. As such, it is the most important model for studying second order phase transitions. It first appeared in a paper by Ising in 1925 and he studied it in his thesis without solving it! (He just gave the model and became well known!) His thesis was supervised by Lenz (of the Lenz Law). There had been much effort on solving the Ising model in 2D and 3D and in various lattices. The problem attracted many famous physicists, including Kramers, Wannier, Onsager, CN Yang, T.D. Lee, Jaynes (information theory and large deviation theory), and Fisher. Lee and Yang (1952) pointed out a theorem related to the zeros of the partition function for the Ising model. Ising model in 2D square lattice can be solved exactly (with rather difficult mathematics and required someone like C.N. Yang to work it out). In 3D, it cannot be solved exactly but very detailed numerical simulations have been done. Those interested are referred to the chapter in Kerson Huang's *Statistical Mechanics*.

(b) The thermodynamics follows from Z. **Find** the Helmholtz free energy F and the entropy S. **Sketch** how the entropy S/Nk depends on the temperature kT/J. **Discuss** the high-temperature limit of the entropy. Hence, **find** the mean energy E by $E = F + TS$ and the heat capacity. **Sketch** the heat capacity C/Nk as a function of the temperature kT/J.

[Remarks: Inspecting F and its derivatives at some temperature (Curie's temperature) for signature of a phase transition, it was found that the Ising model in 1D does not show a (disorder to aligned) transition at any finite temperature. Disappointing though, but here at least you worked out an exact partition function and its consequences for an interacting system. In 2D and 3D, there is a transition between a ferromagnetic phase and a paramagnetic phase.]