PHYS4031 STATISTICAL MECHANICS Problem Set 2 Due: 30 September 2016 (Friday)
"T+2" buffer = 3 October 2016

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.

2.0 *Reading Assignment*: Chapters III and IV laid the foundation of statistical mechanics (the postulate and microcanonical ensemble). Two other ensemble theories will be developed based on these fundamentals. It is, therefore, important to understand Ch.III and IV completely and to do/see more examples. A list of golden standards include: the **classical ideal gas** (class work/notes), defect (**2-level**) problems (class notes, Problem 2.2), **harmonic oscillators** (Problems 1.6 and 2.6) and Einstein's solid (SQ1, Problem 1.6), and a polymer chain (Problem 2.3). Every student should be familiar with these standard examples and Ch.III and IV, before we move forward.

References on Ch.III and IV: Read class notes Chapters III and IV. For discussions on the fundamental concepts of Stat Mech similar to our Chapters III (and IV), see Rossner (Ch.2), Mandl (Ch.2), Bowley/Sanchez (Ch.3,4), Guenault (Ch.2), Trevena (Ch.2), Yoshioka (e-book, Ch.2). For a detailed discussion on microcanonical ensemble approach to the classical ideal gas, see Ch.5 of *Thermodynamics and Statistical Mechanics* by Greiner, Neise, and Stöcker. See book list for details.

2.1 *Marcostate, distributions, microstates, most probable and averaged distributions, thermodynamic limits.* **(Class notes Ch.III and SQ6.)**

Read Chapter III before working this out. In Ch.III, we considered a system of $N = 3$ distinguishable particles with 3 units of energy and found $W = 10$ microstates. Later, for $N = 6$ particles with 6 units of energy, $W = 462$ microstates. Here is your turn to count.

Statement of the problem. Let there be $N = 8$ distinguishable particles. Each of these particles has allowed **single-particle energy levels** (obtained, say, by solving the Schrödinger equation with the assumption that the particles are only weakly interacting and hence independent – thus, a single-particle Schrödinger equation suffices; but the details of how to obtain these states are not our concerns here! Some quantum person solved that for you!) labelled by $\epsilon_0 = 0$, $\epsilon_1 = \epsilon$, $\epsilon_2 = 2\epsilon$, $\epsilon_3 = 3\epsilon$, $\cdots$, $\epsilon_j = j\epsilon$, and so on. Thus, a particle can take on any integer units of energy.

Given that there are 8 units of energy, i.e., the total energy $E = 8\epsilon$. Thus, $N = 8$ and $E = 8\epsilon$ defined the **macrostate**. Note that the energy per particle is the same as the ($N = 3$, $E = 3\epsilon$) and ($N = 6$, $E = 6\epsilon$) cases that we discussed in Ch.III.

(a) The total number of accessible microstates is $W(E, N)$. These microstates fall into different distributions. **Identify** the possible *distributions* and the number of microstates for each of the distributions. **Find** the total number of accessible microstates $W(E, N)$ specified by $N = 8$ and $E = 8\epsilon$ macrostate? You may want to **list** them out as a table (e.g. see class notes for $N = 6$ and $E = 6\epsilon$ case).

(b) Based on the postulate of statistical mechanics, **what** is the probability of finding the system to be in one of these accessible microstates when the system is at equilibrium?

(c) **The average distribution.** Based on "every accessible microstate is equally probable", **find the average number of particles** in the levels ϵ_0, ϵ_1, $\cdots$, ϵ_7, ϵ_8, etc. This is called the **averaged distribution**. **Sketch** the averaged distribution, i.e., average number of particles at energy ϵ_n (y-axis) versus ϵ_n (x-axis).

Why is that the numbers are generally not integers? We don't have a fraction of a particle. **What does it mean then**? **Give an explanation** and try to make sense out of them.

We emphasized that the idea of equal *a priori* probabilities tells us a way **to do averages**. **Point out where** did you use the idea in getting the average distribution.

(d) Back to the result in (a). **Which distribution is the most probable distribution**? Let W_{mp} (or W_{max} in some books) be the number of microstates associated with the most probable distribution. **Evaluate** the ratio $\ln W_{mp}/\ln W$. This shows how representative the most probable distribution is. **Compare** this number with what we got for ($N = 3$,$E = 3\epsilon$) and ($N = 6$,$E = 6\epsilon$) (see class notes).

Important Take-Home Ideas:

- $*$ Convince yourself that for a constant E/N, $\ln W_{mp}$ becomes more and more representative of $\ln W$ when a system is scaled up. This is important because for macroscopic systems, N is huge (not 8, not 8888, but $\sim 10^{25}$ in a m^3 of air!). Strictly speaking, $S = k \ln W$ and we need $\ln W$ (total number of accessible microstates) to obtain the entropy S, but W is hard to find for a large system. If we can get $\ln W_{mp}$ instead (the number of microstates corresponding to the most probable distribution, which is an easier problem), then we have a very good approximation to $\ln W$, as long as $N \gg 1$, i.e., $S \approx k \ln W_{mp}$ and the approximation is very good!

  This idea gives a short-cut to get at the Bose-Einstein distribution, Fermi-Dirac distribution, and Maxwell-Boltzmann distribution - these are most probable distributions in systems consisting of non-interacting particles! The mathematical skill needed is the method of Lagrange undetermined multipliers. (See Ch.VII and Ch.VIII later)
- $*$ In PHYS4031, you take the longer path by first introducing the general **ensemble theories**, as they are good (i.e., generally applicable) even for systems consisting of *interacting* particles.

(e) **Thermodynamic limit** – The above discussion of scaling up E and N while keeping E/N a constant is related to a step of taking the thermodynamic limit. Below we illustrate the idea using N and V.

To illustrate the point that limits must be taken properly and carefully, consider the combination $NV/(N + V^2)$.

(i) Find

$$\lim_{N\to\infty} \lim_{V\to\infty} \frac{NV}{N + V^2}$$

(ii) Find

$$\lim_{V\to\infty} \lim_{N\to\infty} \frac{NV}{N + V^2}$$

Comment on the results in (i) and (ii).

(iii) However, the thermodynamic limit is not only $N \to \infty$ and it is not only $V \to \infty$. The proper thermodynamic limit is $N \to \infty$, $V \to \infty$, with N/V = finite. The physical meaning is that the number density, i.e., number per unit volume, is a constant (and finite). Take the thermodynamic limit of $NV/(N + V^2)$. Does the result depend on the order of taking the limits?

(f) Another important point in this problem is that when the system carries more energy, the number of microstates increases. Let's say for $N = 8$, the total energy is $E = 12\epsilon$. **Find** $W(N = 8, E = 12\epsilon)$. **Comment** on how $W(N, E)$ behaves as E increases. [Note: Here, each particle can take on any units of energy, i.e., the spectrum for a particle is unbounded. The behavior is quite different if the spectrum is bounded, as you will see in Problem 2.2.]

2.2 **Very important – Two-level Systems and features due to bounded single-particle energy spectrum.**

In Problem 1.6 (also 2.1), you worked out how M units of energy quanta ($\hbar\omega$) could be distributed among N distinguishable oscillators and each of them can take on $0, 1, 2, 3, \ldots$ units of energy. The important point is that the single-particle energy spectrum is unbounded, i.e., no ceiling on how much energy an oscillator can take. You then worked out the heat capacity $C(T)$.

There is another class of problems in which the **single-particle energy spectrum is bounded**, i.e., there is a ceiling. **The key point is to know that they exhibit qualitatively different behavior.**

Consider a system consisting of N independent (i.e., not interacting) particles with $N \gg 1$. Each particle can be in one of two energy levels $\epsilon_1 = 0$ (not excited) and $\epsilon_2 = \epsilon > 0$ (excited). [Many physical problems belong to this class. Consider magnetic moments (atoms may have magnetic moments) sitting at their equilibrium positions in a solid. When a magnetic field is applied, Zeeman splitting leads to a finite number of levels for each moment. For $J = 1/2$, we have two levels for each atom. Another example is the Schottky defect problem in solids where $\epsilon_1 = 0$ refers to an atom sitting in its crystalline (right) position and $\epsilon_2 = \epsilon$ is the excitation of an atom to a wrong position.]

(a) Given ϵ_1 and ϵ_2, a macrostate can be described by E and N. To satisfy the given E and N, we need to put N_1 particles in level ϵ_1 and N_2 particles in level ϵ_2. **Find** N_1 and N_2, in terms of E, N, and ϵ.

(b) Counting comes in. The question is about dividing N objects into two groups of N_1 and N_2. **Find** the number of microstates $W(E, N)$. Hence **obtain an expression** for the entropy $S(E, N)$. **Simplify the expression** using the Stirling's formula, assuming N,N_1,$N_2 \gg 1$.

(c) **Derive an expression** for the temperature T, in terms of N_1 and N_2. Hence, obtain N_2/N_1 as a function of temperature and **sketch** the result.

(d) Next, turn the result to **obtain** $E(T)$. Hence, **obtain** the heat capacity by dE/dT and **sketch** $C(T)$.

Important remarks: The form of $C(T)$ is called the Schottky heat capacity. Contrast Schottky $C(T)$ (bounded spectrum) with that of a collection of oscillators (unbounded spectrum), as obtained in Problem 1.6. These are the TWO classes of $C(T)$ behavior in physics – they are fundamental different.

- With bounded spectrum, $C(T)$ goes up and down and shows a peak.
- There is also an unusual behavior in the (derived) "temperature" as a function of N_1/N_2. Could we have $N_2 > N_1$ for any positive temperature?
- What happens if we have $N_2 > N_1$?
- You may want to work out the more general answer in terms of ϵ_1 and ϵ_2.
- You may try 3-level, 4-level,... systems. They are just further examples of **bounded** single-particle levels.

2.3 *A model of polymer chain or rubber band - Microcanonical Ensemble.* The counting problem here is mathematically related to some other problems: two-level system (see Problem 2.2), paramagnetism (see class notes later), and random walk (Week 1 class work on gas molecules).

In applying Stat Mech to real systems, modelling plays an important role, i.e., we need to construct models that we can handle, e.g., counting the microstates, etc. Modelling is arts and science COMBINED! Here is a simple but non-trivial model of a polymer chain. This problem is taken from Chapter 6 of Yoshioka's *Statistical Physics* (e-book available via CU sites).

Physical Set up: Consider a one-dimensional chain consisting of N ($N \gg 1$) segments. Let a be the length of each segment. (A picture is that a segment is an arrow. The segments are joined together tail to head.) Each segment can either point to the right or to the left. Let L be the distance between the two end-points of the CHAIN. [Preview: The physics of polymers is very different from that of gases. The reason is that the physics is driven by **entropy**, instead of energy. Think about it – At temperature $T = 0$, S should be zero and thus there should only be one microstate. Which one? The one with the chain straightened out with the end-to-end distance being Na. But at higher temperature, then some folding may occur, i.e., the polymer chain (or your DNA, they aren't so different) may want to tangle up when one heats it up under tension. In fact rubber bands show this phenomenon – tangle up when it is heated, and thus giving out heat when it is stretched (since it wants to be cooler when stretched). In polymer science, the segments are called monomers.]

(a) For simplicity, we assume everything happens on a line. (Thus, you may think of the segments being going right or going left. A flavor of random walks enters.) So starting from the origin and with N segments, let the last segment end at a distance L (to the right, for simplicity). **Find the entropy** of a long chain as a function of the end-to-end distance L of the chain. [Hint: **Count** the number of ways of getting a particular vale of L and then use Boltzmann formula for S.]

(b) In the simplest model, one assumes that the joints between segments can move freely and the segments *do not* interact. There is NO bending energy and the internal energy E does not depend on L (it is just a constant, say zero). Instead of the $-pdV$ term for work done in a gas-and-piston system, we have a $\mathcal{F}dL$ term instead, where $\mathcal{F}$ is the *tension* and dL is an infinitesimal extension. Thus the thermodynamic identity becomes

$$dS = \frac{1}{T}dE - \frac{\mathcal{F}}{T}dL$$

From the entropy S, **find** the ratio "tension over temperature" $\mathcal{F}/\mathcal{T}$. Feel free to use the Stirling's formula. **Show** that

$$\frac{\mathcal{F}}{T} = \frac{k}{2a}\ln\left(\frac{N+\frac{L}{a}}{N-\frac{L}{a}}\right).$$

(c) Assuming $Na \gg L$, **show** that $L \sim \mathcal{F}/\mathcal{T}$. In words, the extension L is proportional to the tension $\mathcal{F}$ with a proportionality constant that goes like $1/T$. DONE! (See Remarks for the physics.)

Remark 1: From (c), you showed that the polymer chain obeys the Hooke's law, i.e., $\mathcal{F} \propto L$, with the elasticity constant (or Young's modulus) being proportional to T. Note that the Hooke's law is rather general. It holds for a bar of copper and also for a piece of rubber (polymer). The point is that their origins are very different. The Hooke's law you found in rubber bands (polymer chains) here does not come from the inter-molecular forces (which are electrostatic in nature) as in ordinary solids, but instead from the **entropy**. Since $extension \sim (1/Young's\ modulus) \times tension$, the Young's modulus is proportional to T. Compared with copper (with Young's modulus $= 1.3 \times 10^5$ MPa), rubber has a much small ($\sim$ 1 to 3 MPa) Young's module. It makes sense, as a small Young's modulus means that one can easily deform it, e.g., one can elongate it to twice its length easily. These properties: Easily deformed by weak forces, Young's module $\sim T$, and shrinking when warmed (recall $T = 0$ for the longest chain length) are all observed properties of polymer chains. In a subject called **Soft Matter Physics**, the physics of polymers is a significant part. For a concise introduction to polymer physics, see *Introduction to Polymer Physics* by M. Doi.

Remark 2: The above problem can be mapped into other problems. For example, the net magnetic dipole moments of spin-1/2 particles in a magnetic field. This is just the two-level particles in Problem 2.2. What you considered as LLRLR... (L=left and R=right) now becomes DDUDU... (U = spin up and D = spin down). The length L becomes a net magnetic dipole moment. Instead of tension, we have the magnetic field. The behavior $\mathcal{F}/T$ in the above problem is related to the $\mathcal{B}/T$ behavior in the magnetization, which gives the $1/T$ behavior of the magnetic susceptibility $\chi(T) \sim 1/T$ in paramagnetism (known as Curie's law after Pierre Curie). We get this here from the microcanonical ensemble by mapping. This problem will be discussed later an example of the canonical ensemble theory.

2.4 *The factor of* $1/N!$ *and extensive quantities, as illustrated by the classical ideal gas.*

(a) When we did the classical ideal gas problem, we introduced a pre-factor $1/N!$ to take care of the indistinguishable nature of the particles. Let's say a "careless" mistake is made in omitting the factor $1/N!$ in front of the integrals. One is then led to the result $W(E, V, N; \Delta E)$ for the number of microstates in the energy interval between E and $E + \Delta E$ given by

$$W(E, V, N; \Delta E) = \left[V \left(\frac{2\pi m E}{h^2} \right)^{3/2} \right]^N \frac{1}{(\frac{3N}{2} - 1)!} \frac{\Delta E}{E} . \quad (1)$$

Applying $S = k \ln W$ to the above expression and ignoring terms that are small, **show that** one gets the following result

$$\mathcal{S}(E, V, N) = Nk \ln \left[V \left(\frac{4\pi m E}{3Nh^2} \right)^{3/2} \right] + \frac{3}{2} Nk . \quad (2)$$

Now you will see how "right" and how "wrong" this result is.

(i) **Derive** an expression for $1/T$ and **express** E in terms of kT.

(ii) **Derive** an expression for p/T and hence **express** pV in terms of kT.

(iii) Entropy should be an extensive quantity (see SQ4), i.e., $S(\lambda E, \lambda V, \lambda N) = \lambda S(E, V, N)$ when we scale the system by a factor λ. **Discuss the extensivity** of this expression for the entropy by scaling extensive quantities by a factor λ. **What's wrong**?

Part (a)(iii) thus serves to show the necessity of including the factor $1/N!$ in evaluating $W(E, V, N; \Delta E)$.

(b) Now with the factor of $1/N!$ in the calculation, we have (obtained in class and class notes)

$$S(E, V, N) = Nk \ln \left[\left(\frac{V}{N} \right) \left(\frac{4\pi m E}{3Nh^2} \right)^{3/2} \right] + \frac{5}{2} Nk \quad (3)$$

Check that this expression of the entropy is extensive.

Eq. (3) can be written in terms of the temperature by using $E = \frac{3}{2}NkT$ (classical ideal gas) as:

$$S(E,V,N) = Nk \ln \left[\left(\frac{V}{N}\right) \left(\frac{2\pi mkT}{h^2}\right)^{3/2} \right] + \frac{5}{2}Nk \,, \tag{4}$$

which is the famous Sackur-Tetrode equation. It is so accurate that it is being used to tabulate values of S cited in handbooks of physics and chemistry.

(c) **Entropy of Mixing**: Using the **wrong** result Eq. (2), which can be rewritten as:

$$\mathcal{S}(E,V,N) = Nk \ln \left[V \left(\frac{2\pi mkT}{h^2}\right)^{3/2} \right] + \frac{3}{2}Nk \,. \tag{5}$$

Consider an ideal gases. Initially, N_A atoms occupy the left hand side of a box of volume V_A and N_B atoms occupy the right hand side of a box of volume V_B. They are separated by a wall, but the two sides are at thermal and mechanical equilibrium. That is to say, they are just one ideal gas with an inserted partition into (N_A, V_A) one one side and (N_B, V_B) on another.

(i) Using Eq. (5), **write down** $S_{initial}$ when the gas is partitioned into two sides.
(ii) Now the partition is removed. Using Eq. (5), **write down** S_{final}.
(iii) Hence, **obtain** the change in entropy ΔS.
(iv) **Comment** on the correctness of the result in (iii) and **point out** what's wrong.

(d) **Entropy of mixing**: Using the **correct** result Eq. (4). Repeat part (c) and **find** ΔS when the partition is removed.

[Remarks: Part (c) is referred to the "Gibbs paradox". I avoided using the term because there is nothing mysterious, as you resolved it here.]

(e) Using the correct expression Eq. (3) in part (b), derive an expression for the chemical potential μ. **Show that it is negative for a classical ideal gas**. **Argue** that it should be a negative quantity based on the definition that

$$\mu = \left(\frac{\partial E}{\partial N}\right)_{S,V} \tag{6}$$

Hint: Pay attention to the condition of "constant entropy", and thus it requires the constant number of microstates be kept constant when one more particle is added to a system. How can one achieve this in a classical gas?

[Remarks: Here, you should see the familiar equations of states for an ideal gas also come out in part (a), even if S is slightly wrong. Of course, the correct expression for S in part (b) also gives the same results. Why is it? Equation (4) is the Sackur-Tetrode equation. Another remark is that in doing stat mech calculations, one often can get the correct answer simply using a number related to $W(E,V,N;\Delta E)$ but not $W(E,V,N;\Delta E)$ itself. For example, you may try to get S by $S = k\ln W^{<}(E,V,N)$ and see what it will lead to. How about $S = k\ln[\mathcal{W}(E,V,N)\cdot E]$? Try them! No bonus though.]

2.5 *The factor $1/h$ for every $dx\,dp$ in getting $W^{<}(E,V,N)$ for classical ideal gas.*

This problem serves to convey the necessity of including a factor of $1/h$ for every $dx\,dp$ in the integrals in doing **classical stat mech** calculations (see, e.g., classical ideal gas calculation).

(a) In the ideal gas problem, we introduced $1/h^{3N}$ and thus a factor of $1/h$ for every $dx\,dp$. To get a sense of the factor $1/h$, quantum mechanics is obviously useful, as the Planck constant h is a signature of quantum physics.

Ignoring interaction between the gas atoms, the simplest QM problem emerges – the particle-in-a-big-box problem. Consider a 1D infinite potential well (box) of length L. As a test of your QM, **write down** the energy and wavefunction for the ground state, 1st excited state, 2nd excited state, and $(n-1)$-th excited state.

(b) Let's consider the ground state. **Identify the range** of of x-space that the particle can be found. For the momentum, **show** that $p = \hbar k$ is quantized and it can take on two possible values, corresponding to going to the left and one going to the right (i.e., one positive and one negative value).

(c) Let's display the answer to (b) in the **phase space**. It is a two-dimensional space (for a 1D problem) with the x-axis being the position (thus with a range) and the y-axis being the momentum p that ranges from negative values to positive values. **Marking the momentum values** on the phase space and considering the **range of positions**, **show** that the ground state "occupies" a phase space of area h. The moral of the story: a quantum state (ground state in this example) occupies h of phase space.

(d) Now consider the first excited state in a similar way. **Show** that an area of $2h$ of phase space is occupied by two allowed states (ground and 1st excited states). Similarly, **find the area of phase space** in which there are three allowed states.

(e) **Generalize** your discussion to the $(n-1)$-th excited state. Hence, **show** that **each** allowed state (energy eigenstate) occupies an area of h of phase space. This is the reason of having a factor $1/h$ for every $\int\int dxdp$.
[Remark: Although the quantum signature h gets in, we are still working on the classical ideal gas. It is "classical" in the sense that we don't need to consider the nature of the particles, i.e., whether they are identical fermions (where Pauli exclusion principle applies) or bosons (no Pauli exclusion principle). It is because the gas is dilute and at high temperature that two particles do not get close to the same single-particle state.]

2.6 *Classical Statistical Mechanics (Microcanonical Ensemble for a Collection of Distinguishable Oscillators).*

Introduction: (1) In Problem 1.6, you did the correct calculation of a collection of oscillators. By correct we mean that you took into account of the quantized energy spectrum of each oscillator. (2) In class, we did the classical ideal gas. Here is your turn to apply the techniques in the classical ideal gas calculation to a collection of **distinguishable classical oscillators**. By classical we mean that the quantized nature of the energy levels in an oscillator is ignored.

To build up your maturity in doing physics problem, I will NOT break this problem down into parts. Instead, I will let you work out the problems, compare results with Problem 1.6, and discover what you will get when you start with a classical approach at the very beginning. Hints will be given.

Consider a collection of N distinguishable (1D) oscillators. In classical mechanics, the Hamiltonian of each oscillator is

$$h(p,x) = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 x^2 \ .$$

The total Hamiltonian is given by summing over all N oscillators. [Thus, we have one more term in oscillator when compared with free particle.]

Approaching the stat mech problem classically, you may start with the following expressions for **the number of microstates with energy less than or equal to a given energy** E,

$$W^{<}(E,N) = \frac{1}{h^N} \underbrace{\int dp_1 \int dp_2 \cdots \int dp_N \int dx_1 \int dx_2 \cdots \int dx_N}_{\sum_{i=1}^{N}(\frac{p_i^2}{2m}+\frac{1}{2}m\omega x_i^2)\leq E} \ .$$

There is no $1/N!$ here because the oscillators are distinguishable (by their locations). The question is: **Obtain** all results and **discuss** the physics.

Hints: You may want to follow this path. Digest what the math expression means; evaluate $W^{<}(E,N)$ (volume of high dimensional sphere?); obtain $W(E,V;\Delta E)$; evaluate the entropy $S(E,N)$; evaluate the temperature; turn the result into $E(T,N)$; and then obtain the heat capacity $C(T)$. At the end, you will see a rather boring result for $C(T)$ when compared with what you got in Problem 1.6. It is this boring result that Einstein didn't like and eventually introduced his Einstein's model.

Remarks - Classical versus Quantum Oscillators. At this point, compare result with Problem 1.6. Note that in Problem 1.6, we take into account the quantum discrete nature of oscillator energies $(n+\frac{1}{2})\hbar\omega$ from the very beginning. The result there is more general, i.e., applicable to situations when quantum effect is important (what does it mean) and also to situations when quantum effect is not important. In this problem, the quantum nature of oscillator is completely ignored. It is educational to point out (discover) when the result here and Problem 1.6 agree as well as when they do not agree.

Problem 1.6 and this problem form an additional appendix to Chapter IV.