PHYS4031 STATISTICAL MECHANICS Problem Set 1 Due: 19 September 2016 (Monday) with "T+2" being 21 Sept 2015 (Wednesday)

Read me: *All problem sets should be handed in no later than 5pm on the due date for getting the full mark. Submit your work into the assignment box marked PHYS4031 outside the Year 1 Lab (outside Rm SC 213) on 2nd floor. To get a good training, work out the steps in detail. Discussions with your classmates are encouraged, but you should write up your answers independently. To learn Stat Mech effectively,* **keep a copy of the problem sets, your own answers and the TAs' suggested solutions as you proceed**. *Sample Questions in exercise classes before the due date are meant to give useful hints on selected homework questions. Problem Sets submitted after the due data but before the "T+2" date will get a 20% deduction.*

"Academic honesty declaration form" - If you have not signed one in class, you should attach a copy to your Problem Set 1. A blank form can be found in course webpage.

Problem Sets form an integrated part of PHYS4031. Some materials are introduced in problem sets, and you learn by working them out. This problem set deals with something that you should have learnt somewhere in the past (high school or other courses) and some math skills for stat. mech. **You should be able to start working on it immediately.**

Layout of Problems:
1.1 Gaussian Integrals and an application (classical ideal gas)
1.2 More on gaussian integrals
1.3 Introducing Gamma Function $\Gamma(n)$
1.4 Knowing the Stirling formula for $n!$
1.5 $n! = \Gamma(n+1)$ and what $0!$ and $\frac{1}{2}!$ are about
1.6 Your first stat mech calculation - Einstein's model of solids by microcanonical ensemble theory

1.0 *Reading Assignment:* (Don't need to hand in anything. But you should get into the habit of reading and reviewing regularly. This also gives some references on what we discussed.)

  (i) **Books!** Spend an hour in the University Library to browse through the books reserved under PHYS4031, as given on the book list. These books explain the same physics, but in different styles. There must be a few that fit your taste. Also take a look at the e-books (log on from university sites or use CUHK VPN). Try them out. They are good (and free).

  (ii) **Background and Math Skills!** For thermodynamics, I recommend *Equilibrium Thermodynamics* by C.J. Adkins (2 copies reserved in U. Library) and *Thermodynamics* by Fermi. For a review on ideas in counting (see Sample Question SQ1 for Week 1 exercise class) and probability, and other mathematical methods (partial derivatives and integrals) to come, the chapters in *The Chemistry Maths Book* by Erich Steiner (1 copy reserved) and in *Mathematical Methods for Physics and Engineering* by Riley, Hobson, and Bence (1 copy reserved) are useful. Steiner treated each topic in only a few pages with examples and exercises. It is perfect for learning the basics quickly.

1.1 *Mathematical Skills II – Gaussian Integrals.* Here are some integrals that you will use in PHYS4031.

  (a) Here is the most important integral. **Evaluate** the integral ($a > 0$)

$$\int_{-\infty}^{\infty} e^{-ax^2}\, dx \tag{1}$$

  Remark: You should have done this in normalizing the ground state wavefunction of a harmonic oscillator. You also used it in variational calculations in quantum mechanics.

  (b) Hence, apply the result to **evaluate** the following integrals (don't worry about the meaning of the symbols for the moment):

$$\int_{-\infty}^{\infty} e^{-\beta \frac{p_x^2}{2m}}\, dp_x \tag{2}$$

  and

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} e^{-\beta \frac{(p_x^2+p_y^2+p_z^2)}{2m}}\, dp_x dp_y dp_z \tag{3}$$

(c) Let's get a quick taste of Stat. Mech. Using the result in part (b), **write down** the answer to the following integral:

$$z(\beta, V) = \frac{1}{h^3}\left(\int_V dxdydz\right)\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} e^{-\beta\frac{(p_x^2+p_y^2+p_z^2)}{2m}} dp_x dp_y dp_z \tag{4}$$

where the integrals over x, y, z are meant to collectively go over a volume V. If p_x is a momentum and m is a mass, **what** should be the units of β?

Consider the function

$$Z(\beta, V, N) = \frac{[z(\beta, V)]^N}{N!} \tag{5}$$

with $z(\beta, V)$ given by Eq. (4). Let's define the pressure p as a derivative

$$p = \left(\frac{\partial}{\partial V}(\frac{1}{\beta}\ln Z)\right)_{\beta,N} . \tag{6}$$

Evaluate p and **give an expression** for pV. If $\beta = 1/kT$ with k being the Boltzmann constant, **what** does the answer refer to? **What** is the meaning of N?

Next, **evaluate**

$$-\left(\frac{\partial}{\partial \beta}\ln Z\right)_{V,N} \tag{7}$$

and **what** does the answer refer to?

Remarks: You just derived some properties of an ideal gas by doing gaussian integrals! The quantity Z will be called the partition function and the calculation method in Eqs. (4)-(7) is referred to as the canonical ensemble theory. We will explain the formalism and the physics soon. With $\beta = 1/kT$, you will soon see that factors like $\exp(-p^2/2mkT)$ appear almost everywhere in statistical physics. You will need these integrals in many calculations to come.

1.2 *Mathematical Skills II: More on Gaussian Integrals*

(a) **Evaluate**

$$\int_{-\infty}^{\infty} x^2 e^{-ax^2} dx ,$$

which is an integral that you worked on in finding the uncertainty in position in harmonic oscillator ground state.

Consider again the integral

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} e^{-\beta\frac{(p_x^2+p_y^2+p_z^2)}{2m}} dp_x dp_y dp_z = \int e^{-\beta\frac{p^2}{2m}} d^3p .$$

The last form implies that the integral can also be **evaluated using the spherical coordinates**. **Do it and compare** result with 1.1(b).

(b) Hence, use the results to **evaluate** the following quantity (don't worry about the meaning of the symbols for the moment)

$$\frac{\int_{-\infty}^{\infty} \frac{p_x^2}{2m}\, e^{-\beta\frac{p_x^2}{2m}} dp_x}{\int_{-\infty}^{\infty} e^{-\beta\frac{p_x^2}{2m}} dp_x} .$$

The result is related to what you learned in high-school physics about the meaning of temperature!

Now, **evaluate**

$$\frac{\int_{-\infty}^{\infty} (\frac{1}{2}m\omega^2 x^2)\, e^{-\beta\frac{1}{2}m\omega^2 x^2} dx}{\int_{-\infty}^{\infty} e^{-\beta\frac{1}{2}m\omega^2 x^2} dx} .$$

Remarks: What you did up to there are the Gaussian Integrals – integrals that all physics students must know how to do! More importantly, please remember the answer to the first integral in 1.1(a). You will need it.

(c) A function of the form $\sim e^{-ax^2}$ is called a gaussian function because of the gaussian distribution function. Useful to quantum mechanics...it is often said that **the Fourier transform of a gaussian is another gaussian**. **Show it**.

[Hint: Starts with

$$\int_{-\infty}^{\infty} dx\, e^{kx} e^{-ax^2}$$

and evaluate it by completing a square and using previous result. Then, turn k into ik.]

1.3 *Mathematical Skills III - Meeting the Gamma Function* $\Gamma(n)$

(a) Let's continue with something related and eventually very useful. Define the integrals

$$I_n(a) \equiv \int_0^{\infty} x^n e^{-ax^2} dx,$$

where $a > 0$ and $n \geq 0$. **Note that the lower limit of the integral is ZERO.**

(i) **Write down** $I_0(a)$ (from your result above) and **find** $I_1(a)$.

(ii) Then one needs not evaluate other $I_n(a)$. Instead, $I_2(a)$, $I_4(a)$,… can be found by taking proper derivatives of $I_0(a)$ with respect to a. **Write down** a few of them (say three of them).

(iii) Similarly, **write down** a few $I_n(a)$ for odd n ($n = 3, 5, 7, ...$) by taking proper derivatives of $I_1(a)$.

(b) **Enters the Gamma Function** $\Gamma(n)$**.** Now make a change of variables $y = ax^2$ in $I_n(a)$ above and **show** that

$$I_n(a) = \frac{1}{2}\frac{1}{a^{(n+1)/2}}\Gamma(\frac{n+1}{2}),$$

where Γ is the Gamma Function (related to Euler) defined by

$$\boxed{\Gamma(n+1) \equiv \int_0^{\infty} x^n e^{-x}\, dx} \tag{8}$$

So, we have a compact form for $I_n(a)$, but we need to learn more about the Gamma Function. (More on Gamma Function in Problem 1.5.)

1.4 *Mathematical Skills IV – Knowing the Stirling's formula.*

In statistical mechanics, we make frequent use of the **Stirling's formula** or Stirling's approximation. It comes from the fact that when we count, $n!$ for very large n often appears (e.g. $n = 10^{23}$ particles in a mole). Boltzmann told us to take a natural log, and thus we often encounter $\ln n!$ for large n. The Stirling formula says $ln\ n! = n\ ln\ n - n + O(ln\ n)$. The TA will show you how the Stirling formula comes out. Don't worry. For you, it is more important to get a sense of how well the formula works!

If you look at mathematical tables, you will find the following (scary) expression for $n!$

$$n! = \sqrt{2\pi n}\ n^n e^{-n}\left(1 + \frac{1}{12n} + \frac{1}{288n^2} - \frac{139}{51840n^3} + \cdots\right).$$

Take $n = 13$, rather arbitrarily, as an example.

(a) **Justify** that even for $n = 13$ (which is not-so-big), it is OK to keep only the term "1" in the brackets, e.g. evaluate the terms inside the parentheses and compare them to 1. The answer tells you that it is OK to use

$$n! \approx \sqrt{2\pi n}\ n^n e^{-n}. \tag{9}$$

Hence, **show** that

$$\ln n! \approx n \ \ln \ n - n + \frac{1}{2} \ln \ (2\pi n)$$

and **evaluate the three terms** on the right hand side one-by-one to get ln 13! and **compare** with exact value of ln 13!.

(b) Look at the last expression. Mathematically, the first two terms are of order n and the last term is of order $0(ln \ n)$. To get a sense of this statement: Compare 1000 with $\ln 1000$, and 10,000 with $\ln 10000$. Note that they differ by much! Keep this in mind. Hence, further **justify** that

$$\boxed{\ln n! \approx n \ln n - n} \tag{10}$$

is already a good approximation. **Remember this – it is the Stirling's approximation or Stirling's formula that we will use in our course**. **Show** that it can be written as

$$\boxed{n! \approx n^n e^{-n}} \tag{11}$$

which is also useful. [Note: If you are not convinced that the approximation is good, try $n = 130$ or 13000. These are just "tiny" numbers in stat mech. We treat systems with $N \sim 10^{20}$ (gas molecules in 1 cm^3 of air) or bigger (typical number of particles in a macroscopic system) in statistical mechanics. Thus the approximation in Eq. (10) and Eq. (11) is extremely accurate, so accurate that an estimation of the error becomes difficult to do!]

1.5 *Mathematical Skills V – Gamma Function* $\Gamma(n)$.

We need the Gamma Function in Stat. Mech. calculations when we discuss Fermi and Bose gases. The **Gamma function** is defined by

$$\Gamma(n+1) \equiv \int_0^\infty x^n e^{-x} \, dx. \tag{12}$$

Formally, it is defined for *all* values of n, although most of the time, integer and half-integer values of n are of interest to us.

(a) **Find** $\Gamma(1)$ and $\Gamma(1/2)$. [If you find the answer in earlier problems, just use it.]

(b) From the definition in Eq. (12), **show** that $\Gamma(n+1) = n\Gamma(n)$. [Hint: Try integration by parts.] Note that this relation is general, for any n.

This is nice! It says that using $\Gamma(1/2)$, you can get $\Gamma(n)$ for $n = 3/2, 5/2, 7/2, \ldots$, and using $\Gamma(1)$, you can get $\Gamma(n)$ for $n = 2, 3, 4, \ldots$. You only need to know $\Gamma(1)$ and $\Gamma(1/2)$ for all the other integer and half-integer Γ-functions.

(c) Hence **show** that $\Gamma(n+1) = n!$. And factorials are very useful in counting. Putting this result and the Γ-function together, we have

$$\boxed{n! = \Gamma(n+1) = \int_0^\infty x^n e^{-x} dx} \tag{13}$$

Eq. (13) formally relates $n!$ to the Gamma function. The nice feature is that we can talk about any $n!$, including $0!$, $\frac{1}{2}!$, and $\frac{5}{2}!$. **Evaluate them**. [Perhaps, 0! is something that you learned in high-school.]

See SQ3 in Week 2 Exercise Classes for a proof of the Stirling's Formula for $n!$ based on Eq. (13).

1.6 *Einstein's model of Solid - Dividing energy among oscillators, Stirling formula, and doing derivatives.*

Let's put all we learn together and do a famous real stat mech problem. It is about the heat capacity of insulators. Each atom is on average sitting at its own location inside the solid. However, with given energy (or a finite temperature), the atoms vibrate about their equilibrium positions. Therefore, there are N oscillators corresponding to the N atoms. Let's say the oscillators are identical (same ω), as Einstein assumed in 1907. In addition to the ground state energy $N\hbar\omega/2$ that must be there, let's say there are $M\hbar\omega$ additional energy to be distributed among the N oscillators. Thus, the total energy is

$$E = M\hbar\omega + N\frac{\hbar\omega}{2}$$

(a) **(See SQ1) Count** the number of ways $W(M, N)$ of distributing M units of $\hbar\omega$ (energy) among N oscillators. Each oscillator can take on zero, one, two, three,... units of energy.

(b) In thermodynamics (see Ch.II), if we have $S(E, V, N)$ for a system, then all thermodynamic quantities can be found by taking partial derivatives. Statistical Mechanics was founded by Boltzmann's great insight. Boltzmann said $S = k \ln W$, where $W(E, V, N)$ is the total number of microstates that are compatible with the given (E, V, N). Thus, the resulting S is $S(E, V, N)$.

Let's apply it to the collection of oscillators. **Show** that formally, we could turn $W(M, N)$ into $W(E, N)$ as

$$W(E, N) = \frac{(\frac{E}{\hbar\omega} + \frac{N}{2} - 1)!}{(\frac{E}{\hbar\omega} - \frac{N}{2})!\,(N-1)!} \tag{14}$$

(b) Following Boltzmann's formula, **construct** the entropy

$$S(E, N) = k \ln W(E, N)\ . \tag{15}$$

Now the Stirling's formula in Problem 1.4 enters! Note that W is a number (no units) and k is the Boltzmann constant, and thus S has the right units of an entropy. Note that "1" is small compared with N.

(c) Recall

$$dS = \frac{1}{T}\,dE + \frac{p}{T}\,dV - \frac{\mu}{T}\,dN \tag{16}$$

What matters here is $S(E)$ in part (b). **Obtain an expression** for $1/T$ by taking a partial derivative. The answer is a function of E and N. Here T is the temperature and you have **derived the temperature** of the system.

(d) **Change the subject** of the formula in part (c) to **obtain** $E(T, N)$. Hence, **obtain an expression** for $C = \partial E/\partial T$. Obviously C is a heat capacity. [Remark: For the very careful students, this is formally C_V (heat capacity at constant volume). The physics is that the oscillators are the atoms vibrating about their equilibrium positions in a solid. For a solid, the expansion is so tiny that the heat capacity at constant pressure C_p is not much different from C_V, unlike in a gas.]

(e) From your answer in part (d), **describe the behavior** of C in the limit of $kT \gg \hbar\omega$ (high temperature behavior) and $kT \ll \hbar\omega$ (low temperature behavior). Hence, **make a sketch** of $C(T)$.

Read me - Historical and Physics Remarks: (a) You just did an important piece of physics. The high-temperature limit, quite boring if you inspect your result, is called the Dulong-Petit limit. It was known as early as 1819 – well before any microscopic physics was developed. But this cannot be right for all temperatures, as this would contradict the third law of thermodynamics (Why?). Einstein developed a theory in 1907 (after wrote up his papers on Brownian motion, photoelectric effect, and special relativity in 1905) that gives $C(T)$ a behavior consistent with thermodynamics, for the first time in history. He had in mind an insulator, with atoms sitting about their equilibrium positions and vibrating. That's why we started with dividing $M\hbar\omega$ of quanta of energies among N (atoms) oscillators. (b) In the Stat. Mech. calculation that you just did here, $W(E, N)$ is the number of microstates for the given macroscopic description (E, N). Boltzmann told us how to get the entropy $S(E, N)$ by $S = k \ln W$ (Eq. (15)), and thermodynamics told us how to get at the temperature T (Eq. (16)). (c) **This is the microcanonical ensemble calculation scheme.** The low-temperature behavior of $C(T)$ (different from Dulong-Petit behavior) is consistent with the third law – another important contribution of Einstein to physics (solid state physics that is)! However, it was soon found that the behavior was not quite right when compared with experimental data. Debye came in to help in 1912 (Debye model of solid) and got the right answer. You will study the detail in your solid state physics course. Debye received the 1938 Nobel Chemistry Prize.