PHYS4031 STATISTICAL MECHANICS

SAMPLE QUESTIONS FOR EXERCISE CLASSES in Week 6 (12 Oct 2016 Wednesday) and Week 7 (17 Oct 2016 Monday)

Reminder: Mid-Term Examination will be held on 5 November 2016 (Saturday) morning. Venue/Time to be confirmed.

You are encouraged to think about/work out the SQs before attending exercise class.
SQ14 - Energy scales in NMR/MRI (two level systems)
SQ15 - Typical numerical examples for diatomic molecules regarding fraction of molecules in vibrational states and rotational states
SQ16 - Could 2D solid exist? (And papers awarded 2016 Nobel Physics Prize)

SQ14 Two-level system and NMR/MRI energy scales.

We worked out in class that for magnetic moments due to spin-half ($J = 1/2$) electrons in a B-field, the single magnetic moment partition function

$$z = \exp\left(+\frac{\mu_B B}{kT}\right) + \exp\left(-\frac{\mu_B B}{kT}\right) \tag{1}$$

and the magnetization is given by

$$M = \mathcal{N}\mu_B \tanh\left(\frac{\mu_B B}{kT}\right) \tag{2}$$

where $\mathcal{N} = N/V$ is the number of ions/atoms per unit volume. Here, we see the competition between the magnetic interaction energy $\mu_B B$ with the thermal energy kT.

The results can also be applied to **nuclear spins**. It is helpful to get some sense on the numbers. After that, you will appreciate how technically demanding MRI is.

(Nuclear/Proton spins) Our body is full of water H_2O. All the electrons are bonded and the shells are full. Electrons do NOT play a role. Instead, there are plenty of protons because they are the nuclei of hydrogen atoms (e.g. in water). Proton is a spin-half particle. Proton is different from electron: It has its own g-factor given by $g = 5.5857$ and a much bigger mass. After doing a similar calculation for the two-level system of proton spins, the single-spin partition function is given by

$$z = \exp\left(+\frac{g\mu_N B}{2kT}\right) + \exp\left(-\frac{g\mu_N B}{2kT}\right) \tag{3}$$

where μ_N is the **nuclear magneton**, which is about 2000 times smaller than the Bohr magnetron μ_B. Let's say B is about 1 Tesla and $T = 310$ K (about your body temperature). Compare $g\mu_N B$ with $2kT$ and find their ratio. Hence, obtain the probabilities P_{lower} and P_{upper} for finding a proton moment to be in the lower energy state (aligned with B) and in the upper energy state (anti-aligned with B), respectively.

Remarks: See that P_{lower} is really not that much bigger than P_{upper}. Even so, physicists, engineers, applied mathematicians, and computer scientists worked out the ways to obtain images inside your body by applying a *non-uniform* B-field together with a radio frequency exciting pulse. Although the physics is not difficult, the engineering side is demanding. This is why it costs much to do a MRI scan. Sir Peter Mansfield, a physicist in training, was awarded the 2003 Nobel Prize in Physiology and Medicine for developing MRI techniques. Newer MRI machines in hospitals use a B-field of about 3 Tesla.

SQ15 Better (numerical) sense on Statistical Physics of Diatomic Molecules

For a gas of N diatomic molecules, a molecule carries kinetic energy due to CM translation motion, vibrational energy and rotational energy. The single-particle partition function factorizes into a part related to the transitional motion, z_{vib} that governs the physics due to vibrational states and z_{rot} that governs the physics due to rotational states. The CM (center-of-mass) motion gives the classical ideal gas behavior (see Problem 3.5). Here, let's get some numerical sense of the population of molecules in the vibrational and rotational levels.

(a) **Vibrational states.** The general 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 $\theta_{vib} = \hbar\omega/k \sim 10^3\ K$, and θ_{vib} is higher for molecules with light-mass atoms.

The picture of vibrational motion of a diatomic molecule is that of two balls connected by a spring. It is just oscillator physics. Thus, the key results of statistical physics of vibrational states are:

$$\begin{aligned} Z_{vib} &= z_{vib}^N & (4)\\ z_{vib} &= e^{-\beta\hbar\omega/2}\frac{1}{1-e^{-\beta\hbar\omega}} & (5)\\ C_{vib} &= Nk\left(\frac{\theta_{vib}}{T}\right)^2 \frac{e^{-\theta_{vib}/T}}{(1-e^{-\theta_{vib}/T})^2} & (6)\end{aligned}$$

Take nitrogen N_2 (gas) as an example. It is among the first few elements in the periodic table and thus a light mass. Therefore, $\theta_{vib} = 3374\ K$ is high for N_2. (i) Calculate the vibrational contribution to the molar heat capacity at 300 K. (ii) Calculate the vibrational contribution to the molar heat capacity at a higher temperature of 1000 K. Contrast the two cases.

Let's consider a heavier molecule I_2 (iodine). It has $\theta_{vib} = 308\ K$. Calculate the fraction of molecules (equivalently the probability) in the vibrational ground state ($n = 0$ state) and a few low-lying excited states (e.g. $n = 1, 2, 3, 4$) at $T = 300\ K$. Sketch the fractions as a function of n.

(b) **Rotational levels.** The general sense is that while the molecules are largely 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 the room temperature. The room temperature thermal energy kT can excite molecules to higher rotational states.

The key quantity of the statistical physics of rotational states is the rotational partition function

$$\begin{aligned} z_{rot} &= \sum_{J=0}^{\infty}\sum_{m_J=-J}^{+J} \exp\left(-\frac{J(J+1)\hbar^2}{2IkT}\right) \\ &= \sum_{J=0}^{\infty}(2J+1)\exp\left(-\frac{J(J+1)\hbar^2}{2IkT}\right) & (7)\end{aligned}$$

Again, let's take nitrogen N_2 (gas) as an example. It has a tiny $\theta_{rot} = 2.88\ K$. Thus, room temperature T corresponds to the regime where $T \gg \theta_{rot}$. This allows us to turn the sum in Eq. (4) into an integral to evaluate (a classical limit of) z_{rot}. Hence, evaluate z_{rot} for N_2 at $T = 300\ K$. Using the result, find the fraction of molecules in the J-th rotational level for N_2 at 300 K and sketch the result as a function of J. Comment on the result in light of the shape of the envelope in the vibrational-rotational spectrum of molecules.

SQ16 Two-dimensional solids at finite temperatures?

This SQ is inspired by this year's Nobel Physics Prize. While the works that were awarded the prize are difficult to explain, they explored the unusual behavior for systems in two dimensions (2D). In particular, it was argued in the 1960's (Mermin-Wagner theorem) that 2D solids cannot survive at any finite temperature (it may exist at $T = 0$ though).

Here, the SQ illustrates the idea behind this statement in a hand-waving (rough) way. We discussed the statistical physics of one oscillator and found an expression for the energy. An estimate of the amplitude (or amplitude squared) of the oscillation can be made by (roughly): (i) P.E. equals K.E. on average for an oscillator, (ii) thus $m\omega^2\langle x^2\rangle$ is the energy. Thus,

$$\langle x^2\rangle \sim \frac{\hbar}{m\omega}\left(\frac{1}{e^{\hbar\omega/kT}-1}+\frac{1}{2}\right) \qquad (8)$$

Next, what Debye did correctly (and Einstein didn't) was to invoke the spread in normal mode frequencies (cross reference to phonon dispersion for those with solid state physics) in a solid. The key point here is that the angular frequencies extend from with cutoff Debye frequency ω_D (which is not important for our purpose) all the way down to zero frequency (this is important). For 3D, the distribution of frequencies $D_{3D}(\omega)d\omega \sim \omega^2$ (Debye model). For 2D, the dependence becomes $D_{2D}(\omega)d\omega \sim \omega$.

TA: Starting with an estimate of $\langle x^2 \rangle$ in 2D at finite temperature given by

$$\langle x^2 \rangle \sim \int \frac{\hbar}{m\omega} \frac{D_{2D}(\omega)}{e^{\hbar\omega/kT} - 1} \, d\omega \tag{9}$$

where the zero point energy term has been ignored, argue that the integral diverges due to the low frequency modes. Thus, the oscillating amplitude is so large at any $T \neq 0$ that an ordered solid could not exist.

Remarks: So a 2D solid that carries *long range order* could exist at $T = 0$ but could be destroyed by atomic vibrations (fluctuations) at any finite T. Immediately, there are follow-up questions: How does melting occur in 2D? [The theory of 2D melting is related to this year's Nobel prize.] Will there be other ordering (besides long-range order as in a solid) exist at low temperature in a 2D system? What is the nature of the state at low temperature? Will there be a finite temperature at which a low-temperature behavior (some kind of ordering) gives way to a disordered phase at high temperature?

The answer to these questions was first explored in a series of papers by Kosterlitz and Thouless in 1972-1974. Check out:

- J.M. Kosterlitz and D.J. Thouless, *Long range order and metastability in two dimensional solids and superfluids*, Journal of Physics C: Solid state Physics **5**, L124 (1972).
- J.M. Kosterlitz and D.J. Thouless, *Ordering, metastability and phase transitions in two-dimensional systems*, Journal of Physics C: Solid state Physics **6**, 1181 (1973).
- J.M. Kosterlitz, *The critical properties of the two-dimensional XY model*, Journal of Physics C: Solid State Physics **7**, 1046 (1974).

Thouless was awarded 1/2 of the 2016 Nobel Physics Prize. Kosterlitz was awarded 1/4 of the 2016 Nobel Physics Prize. The other 1/4 went to Haldane, whose works are too abstract for me to understand and appreciate in the mean time.