PHYS4031 STATISTICAL MECHANICS

SAMPLE QUESTIONS FOR DISCUSSION in WEEK 5 EXERCISE CLASSES (3,5 October 2016)

You may want to think about them before attending exercise class.
SQ11 - What negative temperatures are about? Revisiting two-level systems.
SQ12 - The Partition Function Z – The states to be summed over and the nature of the particles matters.
SQ13 - Dumb way to get Z for classical ideal gas, but it works!

SQ11 **"Negative Temperature?" Two-level systems revisited** (An extension of Problem 2.2)

This is **related to** the extra questions listed in **Problem 2.2** on two-level systems. As such, it is related to the physics of paramagnetism, Schottky defects problems (Ch.IV example) and interstitial defects (SQ10 on Frenkel defects), as they all fall into the class of problems in which the single-particle energy spectrum is **bounded**, i.e., there is a ceiling.

This SQ elaborates on the remark in Problem 2.2 about the situation where the total energy E requires $N_2 > N_1$. If we plug formulas and calculate the temperature, we will get a **negative temperature**.

Go back to Problem 2.2. After counting $W(E, N)$ one can then find $S(E, N)$, from which the temperature T is derived.

Physical sense: The result clearly show that the thermal energy kT competes with the energy interval ϵ between the two allowed energies for a particle. In this sense, when $kT \gg \epsilon$, the separation between the two levels can hardly be resolved in the scale of kT. Thus, the thermal energy could regard the two levels to be the same. The result will then be that *the two levels will approach the same population at high temperatures*, i.e. the most one can get by increasing the temperature is $N_1 \approx N_2$. In fact, N_2 is always slightly smaller than N_1. This is what equilibrium statistical mechanics tells us and **it is right**.

Mathematically speaking: After we get $S(E, N)$, formally the temperature is given by

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_N \tag{1}$$

Thus $1/T$ is the slope of the curve of $S(E)$.

TA: Formally, plot S/Nk as the y-axis and E/N as the x-axis. As discussed above, the range of $0 \leq E/N < \epsilon/2$ is the physical range. However, let's plot the graph for the range of $0 \leq E/N \leq \epsilon$. Using Eq. (1) as $1/T$ and tracing the slope of the curve, identify the region for positive temperatures and the region for "negative temperatures". Where is $T \to \infty$ and where is $T \to -\infty$? How about $T = 0$?

Physically, what does the range of negative temperature imply? Think about the two-level particles. In negative temperatures, more particles are in the higher energy state than the lower energy state, i.e. $N_2 > N_1$. This is what people called *population inversion* in laser physics. But to do that, we **cannot** rely on cranking up the temperature. We need to **pump** the laser system. The main point is - the system is actually **out-of-equilibrium**. In spin systems, a way to achieve population inversion (thus negative temperatures) is to apply a magnetic field. Zeeman effect (PHYS3022 Applied QM) puts more particles in the lower level (magnetic moment aligned with field) than the upper level (anti-aligned with field). After achieving equilibrium, one can **suddenly switch the direction of the field**. At that moment, the spins cannot respond instantaneously. So for the new field direction, more particles are in the upper level than lower level and thus population inversion. Of course, after some time (can be a few minutes) thermal equilibrium can again be achieved and more particles will then be in the lower energy state. At least for a while after the field switching, the spin system acts as if there is a negative temperature. Never mind about the fancy name "negative temperature". The main point is that such spin systems are the key to understand nuclear spin (and other spin) relaxation, which is important to NMR technique (using in hospitals) and even to quantum information processing (under development).

Interested students are referred to two papers separated by 60 years: (a) A classic 1951 paper: Purcell and Pound, *A nuclear spin system at negative temperature*, Physical Review **81**, 279 (1951); (Purcell was awarded the 1952 Nobel Physics Prize for his work on NMR) and (b) a more recent paper: Braun *et al.*, *Negative absolute temperature for motional degrees of freedom*, Science **339**, 52 (2013). It is about manipulating cold atoms to achieve negative temperatures. These papers are available by googling them via university sites. We paid for the subscriptions of these journals.

SQ12 **The Partition Function Z - Be very careful of what are being summed up!**

The partition function $Z(T,V,N)$ is **the most important quantity** in the canonical ensemble theory. It first appears as a humble normalization constant to the result that the probability $P(E_i)$ (or equivalently P_i) of finding a system to be in a N-particle state of energy E_i when the system is in thermal equilibrium with a heat bath at a temperature T, with

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

In normalizing $P(E_i)$, the partition function $Z(T,V,N)$ enters into the formulation.

There are very ways (of course all equivalent) of expressing Z. The partition function is given by:

$$Z(T,V,N) = \sum_{\text{all } N\text{-particle states } i} e^{-\beta E_i} \tag{2}$$

$$= \sum_{\text{all } N\text{-particle levels } i} W(E_i,V,N)\, e^{-\beta E_i} \tag{3}$$

$$= \int \mathcal{W}(E,V,N)\, e^{-\beta E} dE \tag{4}$$

The first sum is over **all states** in the N-particle system, i.e., for some states of the same energy, we include them *one by one* into the sum. The second sum is over **all energy levels**, i.e., over the allowed energy (values) levels E_i and use the factor $W(E_i,V,N)$ (it is the degeneracy) in the sum to take care of the number of states at that energy. The integral form treats the energies in continuous form by invoking $\mathcal{W}(E,V,N)dE$, which gives the number of states (N-particle states of course) in the energy interval between E to $E+dE$. Equations (2), (3), (4) are completely general, i.e., they work for both interacting and non-interacting systems. From $Z(T,V,N)$, other thermodynamic quantities can be calculated systematically (plugging formulas).

While Eqs. (2) and (3) are general, this SQ serves to illustrate that **the nature of particles, i.e., whether the particles are identical bosons or fermions, must be considered carefully** in getting the partition function Z. Here, we don't make any short cut. To apply these expressions, we list out all the states to be summed up. The list, as illustrated here, is dependent on the nature of the particles.

Consider the simplest "many-particle" case of **two particles**. They are non-interacting. The single-particle energy spectrum consists of 4 states. One of these states have energy 0, two has energy ϵ, and one has energy 2ϵ.

For each of the following cases, write down the partition function Z with special attention being paid to the 2-particle states summed over in getting Z.

(a) Let's start with two distinguishable, thus different, particles. Find Z using Eq.(2) and relate the answer to Eq.(3).

(b) Two identical fermions (don't need to worry about spin), by imposing the Pauli exclusion rule that the two fermions cannot occupy the same single-particle state.

(c) Two identical bosons.

(d) Many students thought that the Pauli exclusion rule applies to fermions only, and therefore it is reasonable for $Z_{fermion}$ to be different from $Z_{dinguish}$. But the Pauli exclusion rule does not apply to bosons and therefore it is **not too obvious** why Z_{boson} is different from $Z_{dinguish}$. TA should make the reason clear.

Important: Students should understand why these partition functions are different.

SQ13 **A dumb way of getting $Z(T,V,N)$ for classical ideal gas - but it works!**

Next, we play with Eq. (4) for a classical ideal gas. In SQ9, TA traced the "3/2" factors in the classical ideal gas calculation. In that calculation (done in class), we first found $W^{<}(E,V,N)$ and then obtained $\mathcal{W}(E,V,N)$. Now look at Eq. (4), it is exactly the $\mathcal{W}(E,V,N)$ that we need to evaluate $Z(T,V,N)$ for a classical ideal gas.

TA: Plug in $\mathcal{W}(E,V,N)$ and obtain $Z(T,V,N)$ and illustrate that the expected classical ideal gas features come out.

[Remark: This method looks stupid. For one thing, if we know $\mathcal{W}(E,V,N)$, we can use the microcaonical ensemble formulas. The point is: one can obtain Z in an easier way. You did it yourself in Problem 1.1(c).]