Family name, Given name (Please print) **Student Number** **Tutorial Leader's Name**

PHY293F – STATISTICAL MECHANICS
DEPARTMENT OF PHYSICS, UNIVERSITY OF TORONTO

MIDTERM TEST #2 - SOLUTIONS
Thursday 19 November 2009 – 9:30-10:20 AM

PLEASE read carefully the following instructions.

AIDS ALLOWED: Equation sheet provided with test paper and a non-programmable calculator without text storage (Type 2 calculator).

Before starting, please **print** your name, tutorial group and student number **at the top of this page and on the cover of your answer booklet**.

This test has one cover sheet, two question pages and one equation sheet.

There are three questions on this midterm test. The value of each question is indicated next to the question part. The total number of points for the midterm is 35 points. *[Because of length, it was marked out of 30]*.

The test questions can be answered in any order. It is your responsibility to clearly indicate the question number (and part, where appropriate) for each of your answers.

Partial credit will be given for partially correct answers, so show any intermediate calculations that you do and write down, **in a clear fashion**, any relevant assumptions you are making along the way.

Do not separate the stapled sheets of the question paper. Hand in the question sheet with your exam booklet at the end of the test.

1. Please answer the following questions showing your reasoning as well as your final answer. To receive full marks for your answer, both your reasoning and your answer must be correct.

   To get full marks, both the work and the final answer needed to be shown clearly. Many people lost marks for not answering all of what the question asked for or for not using the information given in the question.

   a. Using both words and equations, define the terms partition function and Boltzmann factor. How are these related and what do they allow you to calculate about a system? [4 points]

   The Boltzmann factor for a particular state is equal to $e^{-E(s)/kT}$*. It is proportional to the probability of finding the system in this particular state.*

   The partition function, Z, is the sum of all of the Boltzmann factors for the system, $Z = \sum_s e^{-E(s)/kT}$*. It describes the available energies of the system at a given temperature.*

   The partition function is the normalization factor for the Boltzmann factor.

   Together, these can be used to calculate the absolute probabilities for finding the system in a particular state and the average values of thermodynamic properties such as total energy, E.

   b. At room temperature, the heat capacity at constant volume of one mole of water vapour is 25.27 J/K. How many degrees of freedom are active for gas-phase water at room temperature? Specify both number and type for each of these degrees of freedom. [3 points]

   Using the equipartion theorem (which applies at room temperature), the heat capacity can be used to calculate the number of degrees of freedom active in one mole of water vapour at room temperature:

$$\begin{aligned} C_V &= N\frac{1}{2}kf \\ &= \frac{1}{2}Rf \qquad \text{per mole.} \\ f &= \frac{2C_V}{R} = \frac{2\cdot 25.27\,\text{J/K/mole}}{8.31\,\text{J/K/mole}} \approx 6 \end{aligned}$$

   degrees of freedom.

   So, these degrees of freedom are:

   3 translations (smallest energy spacings)

   3 rotations (next smallest energy spacings – water is a triatomic molecule so it can rotate about all three molecular axes)

   Vibrations in water are not active at room temperature.

c. Derive the multiplicity of an Einstein solid for any large values of q and N without assuming that you are in the high or low temperature limit. Use (N-1)! = N!/ N and the more exact form of Stirling's approximation in your derivation. Simplify your answer so that there is only one term with exponent q and one term with exponent N (i.e. ...$(\ldots)^q(\ldots)^N\ldots$). Compare the relative sizes of all of the terms in your formula and briefly comment on whether any could be neglected. [5 points]

Starting from,

$$\begin{aligned}\Omega(q,N) &= \binom{q+N-1}{q} \\ &= \frac{(q+N-1)!}{q!(N-1)!} \\ &= \frac{(q+N)!}{(q+N)}\frac{N}{q!(N)!} \qquad \textit{using } (N-1)! = N!/N\end{aligned}$$

Then we apply the more exact form of Sterling's approximation (in this case, q and N are both large), to get:

$$\begin{aligned}\Omega(q,N) &= \frac{(q+N)^{q+N}e^{-(q+N)}\sqrt{2\pi(q+N)}}{(q+N)q^q e^{-q}\sqrt{2\pi q}}\cdot\frac{N}{N^N e^{-N}\sqrt{2\pi N}} \\ &= \frac{(q+N)^{q+N}\sqrt{N}}{q^q N^N\sqrt{(q+N)\cdot 2\pi q}} \\ &= \left(\frac{q+N}{q}\right)^q\left(\frac{q+N}{N}\right)^N\sqrt{\frac{N}{(q+N)\cdot 2\pi q}}.\end{aligned}$$

The terms in exponents of q and N are both very large. By comparison, the square root term is just large and could be neglected depending on the calculation to be done. Note: you cannot make any assumptions about the relative sizes of q and N here. It was stated that you were not in either the high or low temperature limit.

d. Briefly explain why the entropy of a system **should** be zero at zero temperature, $S(0)=0$. Give an example of a case where $S(0)$ is effectively non-zero and what this phenomenon is called [3 points].

At zero temperature, the multiplicity of your system should be Ω=1 because there is only one way to arrange the energy to have the lowest energy. Therefore, S(0) should be zero.

S(0) is effectively non-zero in cases where there can be different configurations with the same very low energy. In these cases, Ω>1. The example we talked about in class was water ice where there are multiple, equal-energy configurations for the hydrogen bonds in the water ice when it is a very low temperatures.

When S(0) is effectively non-zero, this is called residual entropy.

2. Starting with the multiplicity of a large Einstein solid in the low temperature limit, $\Omega = \left(\frac{eN}{q}\right)^q$ calculate the following parameters. The solid has N oscillators, q units of energy and ε is the size of an energy unit.

   a. Determine the entropy of this Einstein solid, in terms of N, U and ε. [3 points]

For the system given, the entropy is

$$\begin{aligned} S &= k \ln \Omega \\ &= kq\left[1 + \ln N - \ln q\right]. \end{aligned}$$

Using $q = \frac{U}{\varepsilon}$, *the entropy in terms of U,* ε *and N is*

$$\begin{aligned} S &= \frac{kU}{\varepsilon}\left[1 + \ln N - \ln U + \ln \varepsilon\right] \\ &= \frac{kU}{\varepsilon}\left[1 + \ln\left(\frac{N\varepsilon}{U}\right)\right]. \end{aligned}$$

   b. Find an expression for the total energy, U, as a function of temperature, T. [4 points]

To get the total energy, you start from

$$\frac{1}{T} = \frac{\partial S}{\partial U}.$$

Then, you get

$$\begin{aligned} \frac{1}{T} &= \frac{\partial}{\partial U}\left[\frac{kU}{\varepsilon}\left[\ln\left(\frac{N\varepsilon}{U}\right) + 1\right]\right] \\ &= \frac{k}{\varepsilon}\left[\ln\left(\frac{N\varepsilon}{U}\right) + 1\right] + \left(\frac{kU}{\varepsilon}\right)\left(-\frac{1}{U}\right) \\ &= \frac{k}{\varepsilon}\ln\left(\frac{N\varepsilon}{U}\right) \end{aligned}$$

and solve for total energy

$$\begin{aligned} \frac{\varepsilon}{kT} &= \ln\left(\frac{N\varepsilon}{U}\right) \\ e^{\varepsilon / kT} &= \frac{N\varepsilon}{U} \\ U &= N\varepsilon e^{-\varepsilon / kT}. \end{aligned}$$

c. What is the heat capacity at constant volume, C_V, for this system? Describe the behaviour of U and C_V as $T \rightarrow 0$. [3 points]

The heat capacity is

$$\begin{aligned} C_V &= \left(\frac{\partial U}{\partial T}\right)_V \\ &= \frac{\partial}{\partial T}\left(N\varepsilon e^{-\varepsilon/kT}\right) \\ &= N\varepsilon\left(\frac{\varepsilon}{kT^2}\right)e^{-\varepsilon/kT} \\ &= \left(\frac{N\varepsilon^2}{kT^2}\right)e^{-\varepsilon/kT}. \end{aligned}$$

As the temperature goes to zero, U goes to zero exponentially.

As the temperature goes to zero, C_V goes to zero exponentially because the exp($-\varepsilon/kT$) term dominates.

3. The magnetization of a two-state paramagnet is given by

$$M = N\mu \tanh\left(\frac{\mu B}{kT}\right).$$

The magnetization of a crystal of yttrium atoms (dipoles with nuclear spin=½) can be treated as a two-state paramagnet system using this equation. These yttrium atom dipoles have two energy states $-\mu B$ and $+\mu B$. For this system, the magnetic field strength is 0.5 T, μ is equal 5×10^{-8} eV/T and the temperature is 300 K.

a. Calculate the energy needed to flip the yttrium nuclear dipole from one state to the other. Which dipole state has the higher energy? [3 points]

The energy needed to flip the dipole from one state to the other is the difference in energy between the two spin states.

$$\begin{aligned} \varepsilon &= \varepsilon_{spin-down} - \varepsilon_{spin-up} \\ &= +\mu B - (-\mu B) \\ &= 2\mu B \\ &= 2 \cdot 5\text{x}10^{-8}\,\text{eV/T} \cdot 0.5\,\text{T} \\ &= 5\text{x}10^{-8}\,\text{eV}. \end{aligned}$$

The spin-down dipole state has the higher energy (+μB).

b. Determine the magnetization of the yttrium atom crystal per dipole, as *M*/*N*. Explain any simplifications you are able use to make your calculation easier. [3 points]

To determine if you can use a simplification, you need to calculate (μB/kT)

$$\frac{\mu B}{kT} = \frac{5\text{x}10^{-8}\,\text{eV/T}\cdot 0.5\,\text{T}}{8.6\text{x}10^{-5}\,\text{eV}\cdot 300\,\text{K}} = 9.7\text{x}10^{-7}$$

Since (μB/kT)<<1, we can approximate tanh(x)≈ x. So,

$$M = N\mu\left(\frac{\mu B}{kT}\right)$$

$$\frac{M}{N} = \frac{\mu^2 B}{kT} = 4.8\text{x}10^{-14}\,\text{eV/T}.$$

c. The magnetization of the crystal is related to the number of spin-up and spin-down dipoles. Write down a relation for *M* in terms of $N_\uparrow$ and $N_\downarrow$ and briefly explain where it came from. Use this expression to calculate the excess number of spin-up dipoles in the yttrium atom crystal. [4 points]

The magnetization of the crystal is $M = \mu\left(N_\uparrow - N_\downarrow\right)$*, the net spin of the crystal multiplied by the magnetic moment per dipole.*

To calculate the excess number of spin-up dipoles in the crystal, you need to solve for

$$\begin{aligned}\left(N_\uparrow - N_\downarrow\right) &= \frac{M}{\mu}\\ &= \left(\frac{\mu^2 B}{kT}.\frac{1}{\mu}\right)\\ &= \frac{\mu B}{kT} = 9.7\text{x}10^{-7}.\end{aligned}$$

The excess number of spin-up dipoles in the crystal is ~1 in 10^{6}*.*

This could also be solved by using the N/2±x method that we have used in other problems to solve for 2x – the excess number of spin-up dipoles in the crystal.