Advanced Mathematical Techniques Exam II
Dr. Osborne 2014

The purpose of this exam is to assess your ability to analyze physical problems that either involve conservation of energy, experiments with probabilistic outcomes, the Boltzmann factor and equilibrium thermodynamics, and the energy contained in the electromagnetic field in thermal equilibrium with matter at a given temperature. There are 112 points available, but your total will be taken out of 100. DO NOT SPEND ALL WEEKEND ON THIS EXAM.

Ethics Statement: I, the undersigned, understand that I am able to use the book, my notes, the supplemental notes, fixed internet sites, computer algebra systems or calculators, and any other relevant fixed references on this take-home exam. I will cite any references used in this capacity in the body of my test work, and understand that I am expected to show the derivation of any formula that was not explicitly derived in class. Further, I understand that I am not allowed to use any living help, either in person, on the telephone, via e-mail, text messages, or any other mode of communication. If I am stuck on a problem, I understand that I can e-mail Dr. Osborne to ask for help and that he may or may not respond. I understand that any other help from living persons is strictly forbidden. I also understand that giving help to another person is as unethical as receiving help, and that both parties will receive a zero on this exam and appropriate school officials will be notified if it is discovered that students are in violation of this ethics statement. If I become aware that other students are in violation of this ethics statement, I will notify Dr. Osborne immediately via e-mail. While I am allowed to use fixed references for help on this exam, I understand that I still must show all of my work and cite references other than the book, the supplemental notes, or my own personal notes. Missing or incomplete work will result in a severe point penalty. I may use computer algebra systems such as Mathematica to check my work, but I must show how the answer was obtained ('Mathematica told me so' does *not* constitute work shown). I understand that numerical calculations do not require explanation *unless* a specific request is made in the problem to do it in a certain way). I hereby promise that all of the work associated with this exam is my own and I followed the rules outlined above, both in letter and in spirit.

Signed:_____ Date:_____

1. Suppose that the probability of being born on Monday is 20%, Tuesday through Thursday are 15%, Friday is 20%, Saturday is 10%, and Sunday is 5%. There are 20 people in a room, randomly distributed according to birthday.

    (a) Determine the expectation value of the number of people born on Friday and the standard deviation of this quantity. Quote your result as a number plus/minus an error, and include a confidence level for this result. Show all of your work; do not just quote a result from the notes. (4 pts)

    (b) Determine the expectation value of the product of the number of people born on Tuesday and the number of people born on Saturday. Then, determine the product of the expectation values of these quantities. Explain any difference between these two quantities. (3 pts)

    (c) Determine the probability that exactly 4 people are born on Monday, exactly 3 people are born on Tuesday, and no one is born on Sunday. (3 pts)

    (d) Your answer to part (c) contains several different situations associated with numbers of people born on the days not mentioned in that part. Determine the probability that the situation given in (c) is valid, along with

    (i)   3 people on Wednesday, Thursday, and Saturday. (3 pts)

    (ii)   3 people on Wednesday and Thursday, and 2 people on Saturday. (3 pts)

    (iii)   4 people on Wednesday, 3 people on Thursday, and 2 people on Saturday. (3 pts)

    Then, show that the sum of (i), (ii), and (iii) is less than your answer to part (c). (1 pt)

2. A 3 kg object moves in one dimension under the influence of a conservative force with potential energy $U(x) = 3x^4 - 4x^3 - 12x^2$. All quantities are understood to be given in SI units.

(a) Make a graph of this potential energy function. Indicate on your graph which values of x are associated with stable or unstable equilibria. Determine these values of x exactly. (3 pts)

(b) The object has a total energy of 2 J and initially is found to be moving left at $x = -1.3$ m. How fast is it initially moving? What are the minimum and maximum values of x it can attain? Give your answers to three digits. (2 pts)

(c) At what value of x will the object be moving the fastest under the conditions in part (b)? What is its maximum speed? (2 pts)

(d) Write an integral expression for the period of the object's motion under the conditions in part (b). Use the method shown in class, truncating your integral 0.01 meters from either turning point of the motion and including an approximation to the remaining contributions close to the turning points, to determine a numerical approximation to this period. Show your results on your graph. (3 pts)

(e) The object experiences a collision at $x = 2$ m that removes 32 Joules of its energy. It also changes direction as a result of this collision. Determine the magnitude of the object's change in momentum as a result of this collision. (2 pts)

(f) Write an integral expression for the new period of the object after the collision described in part (e). Use the method shown in class to evaluate this integral numerically, truncating 0.01 m from each turning point and including a correction to account for the motion near the turning points. Show these results on your graph. (4 pts)

(g) Suppose that, in a different experiment with the same mass and potential energy function, the object is found with a total energy of 0 J moving to the left at $x = 1$ m. What is its current speed? What is its maximum speed? What is the period of its motion? Explain your results *qualitatively*. (3 pts)

3. Consider a single atom moving around in a gas of identical atoms in thermal equilibrium at temperature T. At any given time, it will have a well-defined speed and will be moving in a well-defined direction. After moving for a little while in that direction, however, it will inevitably collide with another gas atom. This collision will change its velocity and possibly cause it to move back toward its starting point. The so-called *random walk*, or *Brownian motion*, problem asks us to determine how far our atom will get *on average* from its starting point in this situation. We will assume that, on average, our atom will move a distance equal to the *mean free path* ℓ between collisions.

(a) Determine the expectation value of the velocity and the square of the speed under the Maxwell-Boltzmann velocity distribution. (3 pts)

(b) The standard result associated with the random walk concerns how far the atom is from its starting point after n collisions. Note that each collision changes the velocity to a velocity that is randomly-determined according to the Maxwell-Boltzmann velocity distribution associated with temperature T. The atom will travel for a time of ℓ/v after each collision, where v is the speed the atom has after that collision. Its displacement right before a second collision is therefore given by

$$\Delta \mathbf{r} = \mathbf{v}_0 \frac{\ell}{v_0} + \mathbf{v}_1 \frac{\ell}{v_1} = \ell\left(\hat{\mathbf{v}}_0 + \hat{\mathbf{v}}_1\right).$$

Determine the expectation value of this displacement. (2 pts)

(c) Use the ideas expressed in part (b) to determine the expectation value of the *square* of the displacement the atom has from the origin right before a second collision. (3 pts)

(d) How far will the atom be from its starting place on average right before its nth collision? (4 pts)

(e) Our approach has assumed that we have knowledge of the number of collisions the atom has participated in. This is, of course, something we usually have no knowledge of at all. How can we modify this approach to determine how far, on average, an atom will have moved from its starting point after a known *time* t? Hint: break up the journey into pieces associated with how long it takes an atom to travel the mean free path ℓ. If it is moving so slowly that it cannot reach this distance after time t, then it has no collisions. If it is moving faster, it has more. Use this idea to set up nested integrals whose limits depend on the time t. Points are awarded here for thought and positive progress toward a solution rather than just the answer itself. (3 pts)

4. We have discussed in class the thermodynamics of a system containing a *fixed* number of particles, but you know that many physical situations allow the number of particles to change. In order to treat this possibility, we need to allow the total energy to be a function of the entropy, volume, and *particle number*:

$$dE = T \, dS - p \, dV + \mu \, dn \, .$$

The new state variable μ is called the *chemical potential*.

(a) Explain what the chemical potential *means* in terms of an increase in the number of particles. (3 pts)

(b) Suppose that a cell sits in a body where the sodium content is smaller than that found in the cell. Would you expect the chemical potential associated with sodium ions to be positive or negative? Explain why. (2 pts)

(c) Now that we have three terms in our differential expression, two state variables must be held constant in order to obtain a derivative. It is difficult to keep the chemical potential constant, so use Maxwell relations along with the standard rules of multivariable calculus in order to find a way to determine the following derivatives, explain how these quantities would be measured, and predict whether they would be positive or negative for ordinary materials... explain! (3 pts each)

(i) $\left(\dfrac{\partial p}{\partial S} \right)_{V,\mu}$.

(ii) $\left(\dfrac{\partial T}{\partial p} \right)_{S,\mu}$

(iii) $\left(\dfrac{\partial p}{\partial n} \right)_{V,\mu}$

5. The *partition function* plays an immense role in statistical mechanics. It is defined by

$$Z(\beta) \equiv \sum_{k=1}^{M} e^{-\beta \varepsilon_k} \, .$$

In this expression, ε_k represents the energy of the kth energy level and M represents the number of energy levels accessible to the system. The quantities β and ε_k play their usual roles, and we will take N as the total number of atoms, or *particles*, in the sample.

(a) Show that the expectation value of the energy of a single particle is given by $\langle \varepsilon \rangle = -\partial \ln Z(\beta)/\partial \beta$. (2 pts)

(b) Suppose that the energies of the states are given by $\varepsilon_k = k\varepsilon$, for whole numbers $k = 0, 1, 2, ..., M$. Determine the partition function in this situation, simplifying your result as much as possible, and find the expectation value of the energy. How does your result behave as T tends to zero and infinity? How would a negative temperature affect the system? What do these results *mean* qualitatively? (4 pts)

(c) Determine how the number of particles in states $k = 0, 1$, and 5 change as the temperature approaches zero and infinity and explain your results qualitatively. (3 pts)

(d) Determine how the number of particles in states $k = 0, 1$, and 5 change as the number of energy levels M increases from 5 to infinity at constant temperature. Explain your result qualitatively. (3 pts)

6. Consider a gas of N hydrogen fluoride molecules. Take the mass of hydrogen atoms as m and that of fluorine atoms as $19m$. The purpose of this problem is to flesh out the different ways in which these molecules use energy when they are in thermal equilibrium at a given temperature T.

(a) One way in which the molecules can use energy is by moving. Write the probability that a molecule will be found moving at a speed between v and $v + dv$. (2 pts)

(b) Determine the total amount of kinetic energy this gas requires in order to be in thermal equilibrium at temperature T. Give your answer as a multiple of $Nk_B T$. Hint: this is given by an integral over the expression you found in part (a), including also the energy associated with speed v. (3 pts)

(c) Another way these molecules can use energy is by rotating about their center of mass. This use of energy depends on the moment of inertia of the molecule about its center of mass. Given that the bond length (distance between the hydrogen and fluorine atoms in equilibrium) is 92 picometers and the mass m of a hydrogen atom is 1.67×10^{-27} kg, determine the moment of inertia of a HF molecule about its center of mass *in SI units*. Take the atoms as point masses and ignore the electrons' contribution to the moment of inertia. Hint: you first need to locate the center of mass… if you do not remember how to do this, then… there's the internet… ☺. (2 pts)

(d) The rotation energies of the molecules are *quantized* so they can only take values $\varepsilon_\ell = \ell(\ell+1)\hbar^2/2I$, where $\hbar = 10^{-34}$ J·s is Planck's constant divided by 2π, I is the moment of inertia found in part (c), and $\ell = 0, 1, 2, \ldots$ is a whole number. There are $2\ell+1$ states associated with energy ε_ℓ, so you should include the Boltzmann factor $e^{-\beta\varepsilon_\ell}$ $2\ell+1$ times. Write the number of molecules in rotation state ℓ when the gas is in thermal equilibrium at temperature T. You may leave an infinite series in your answer. (3 pts)

(e) Suppose that the temperature of the gas is 300 K, right above the boiling point at 292.5 K. Find the fraction of molecules in states associated with $\ell = 0, 1, 2$, and 5 up to three digits. (4 pts)

(f) Determine the total amount of rotational kinetic energy used by the molecules at 300 K. Give your answer as a multiple of $Nk_B T$ (with $T = 300$ K). (4 pts)

(g) Repeat parts (e) and (f) for a temperature of 2000 K. (4 pts)

(h) Repeat parts (e) and (f) for a temperature of 50 K (this is unphysical, of course, as the HF is firmly solid at this temperature, but… just go with it). (4 pts)

(i) Compare your answers to parts (f), (g), and (h), and explain what they mean about the *accessibility* of the rotation states. (2 pts)

(j) Molecules can also vibrate. The vibrational modes are also quantized, having energies of $n\hbar\omega_0$ where $\omega_0 = 12.4 \times 10^{13}$ Hz is the natural angular frequency of vibration and n is a whole number. Note that we are ignoring the so-called *zero-point energy*. Do you realistically expect an appreciable number of HF molecules to vibrate at 50 K? 300 K? 2000 K? Explain. (2 pts)

(k) The bond energy of HF is 568 kJ/mol. Compare this energy to that associated with vibration. What would you expect to happen to molecules of HF as the temperature increases to the point where vibration becomes common? (2 pts)