Homework Assignment 4
PHYSICS 314 - THERMODYNAMICS & STATISTICAL PHYSICS (Spring 2018)
Due Friday, March 2nd, by noon, Noyce 1135

I cannot award full credit for work that I am unable to read or follow. For my benefit and for yours, please:
- *Write neatly*
- *Show and EXPLAIN all steps*
- *Make diagrams large and clearly-labeled*

You are welcome to collaborate with others on this assignment. However, the work you turn in should be your own. Please cite collaborators and outside sources. See the syllabus for details.

Regardless of the number of parts, all homework problems are weighted equally. Regardless of the number of questions, all homework assignments are weighted equally.

---

1) Derive the Sackur -Tetrode equation (Schroeder (2.49)) from the equation for the multiplicity of an ideal gas (Schroeder (2.40)). *Hint: Use techniques from HW3. Ignore the merely large $\sqrt{2\pi N}$ term in Stirling's approximation.*

Begin with Schroeder (2.40).

$$\Omega_N \approx \frac{1}{N!} \frac{V^N}{h^{3N}} \frac{\pi^{3N/2}}{(3N/2)!} (2mU)^{3N/2}$$

To calculate the entropy, first calculate the log of the multiplicity.

$$\ln \Omega_N \approx \ln \left[\frac{1}{N!} \frac{V^N}{h^{3N}} \frac{\pi^{3N/2}}{(3N/2)!} (2mU)^{3N/2} \right]$$

Use log rules for products and quotients.

$$\ln \Omega_N \approx \ln(V^N) + \ln(\pi^{3N/2}) + \ln((2mU)^{3N/2}) - \ln(N!) - \ln(h^{3N}) - \ln[(3N/2)!]$$

Use the log rule for exponents.

$$\ln \Omega_N \approx N\ln(V) + \frac{3N}{2}\ln(\pi) + \frac{3N}{2}\ln(2mU) - \ln(N!) - 3N\ln(h) - \ln[(3N/2)!]$$

Use Stirling's Approximation ignoring the large term for the factorial terms.
(Schroeder (2.16): $\ln(N!) \approx N\ln(N) - N$)

$$\ln \Omega_N \approx N\ln(V) + \frac{3N}{2}\ln(\pi) + \frac{3N}{2}\ln(2mU) - N\ln(N) + N - 3N\ln(h) - \frac{3N}{2}\ln(3N/2) + \frac{3N}{2}$$

Factor out the common N.

$$\ln \Omega_N \approx N\left[\ln(V) + \frac{3}{2}\ln(\pi) + \frac{3}{2}\ln(2mU) - \ln(N) + 1 - 3\ln(h) - \frac{3}{2}\ln(3N/2) + \frac{3}{2}\right]$$

Combine the terms without log.

$$\ln \Omega_N \approx N\left[\ln(V) + \frac{3}{2}\ln(\pi) + \frac{3}{2}\ln(2mU) - \ln(N) - 3\ln(h) - \frac{3}{2}\ln\left(\frac{3N}{2}\right) + \frac{5}{2}\right]$$

Use the log rule for exponents.

$$\ln \Omega_N \approx N\left[\ln(V) + \ln\left(\pi^{3/2}\right) + \ln\left[(2mU)^{3/2}\right] - \ln(N) - \ln(h^3) - \ln\left[\left(\frac{3N}{2}\right)^{3/2}\right] + \frac{5}{2}\right]$$

Use the log rule for sums and differences.

$$\ln \Omega_N \approx N\left[\ln\left[\frac{V(2\pi mU)^{3/2}}{Nh^3\left(\frac{3N}{2}\right)^{3/2}}\right] + \frac{5}{2}\right]$$

Examine the numerical factors in the log.

$$\frac{(2)^{3/2}}{\left(\frac{3}{2}\right)^{3/2}} = \left(\frac{4}{3}\right)^{3/2}$$

$$\ln \Omega_N \approx N\left[\ln\left[\frac{V(4\pi mU)^{3/2}}{Nh^3(3N)^{3/2}}\right] + \frac{5}{2}\right]$$

To match the form of the Sackur-Tetrode Equation, rewrite h^3 as $(h^2)^{3/2}$.

$$\ln \Omega_N \approx N\left[\ln\left[\frac{V(4\pi mU)^{3/2}}{N(3Nh^2)^{3/2}}\right] + \frac{5}{2}\right]$$

$$\ln \Omega_N \approx N\left[\ln\left[\frac{V}{N}\left(\frac{4\pi mU}{3Nh^2}\right)^{3/2}\right] + \frac{5}{2}\right]$$

Calculate the entropy. This is the Sackur-Tetrode Equation.

$$S = k\ln \Omega_N \approx Nk\left[\ln\left[\frac{V}{N}\left(\frac{4\pi mU}{3Nh^2}\right)^{3/2}\right] + \frac{5}{2}\right]$$

2)
   a) Use the Sackur-Tetrode equation to calculate the entropy of a mole of argon gas at room temperature and atmospheric pressure.

   First use the ideal gas law to go from volume and number of molecules to pressure and temperature.

$$PV = NkT \rightarrow \frac{V}{N} = \frac{kT}{P}$$

From the number of moles, we have the number of molecules.

$$1 \; mol \; \rightarrow N = N_A$$

The mass of an argon atom is about 40 amu. $1 \; amu \; \approx 1.66 \times 10^{-27} \; kg$

The energy can be calculated from the temperature using the equipartition theorem. Since it is monatomic, f = 3.

$$U = \frac{f}{2} NkT$$

Plug all of this into the Sackur-Tetrode equation.

$$S \approx Nk \left[\ln \left[\frac{V}{N} \left(\frac{4\pi mU}{3Nh^2} \right)^{3/2} \right] + \frac{5}{2} \right]$$

$$S \approx N_A k \left[\ln \left[\frac{kT}{P} \left(\frac{4\pi m_{Ar} \left(\frac{f}{2} N_A kT \right)}{3N_A h^2} \right)^{3/2} \right] + \frac{5}{2} \right]$$

$$S \approx N_A k \left[\ln \left[\frac{kT}{P} \left(\frac{4\pi m_{Ar} \left(\frac{f}{2} kT \right)}{3h^2} \right)^{3/2} \right] + \frac{5}{2} \right]$$

Plug in values using *T = 300 K* and *P = 1 atm = 10^5 N/m²*.

$$S \approx 6.02 \times 10^{23} \left(1.38 \times 10^{-23} \,{}^{J}/_{K} \right) \left[\ln \left[\frac{\left(1.38 \times 10^{-23} \,{}^{J}/_{K} \right)(300 \; K)}{10^5 \,{}^{N}/_{m^2}} \left(\frac{4\pi(40 \times 1.66 \times 10^{-27} \; kg) \left(\frac{3}{2}\left(1.38 \times 10^{-23}\,{}^{J}/_{K}\right)(300 \; K)\right)}{3(6.63 \times 10^{-34} \; J\,s)^2} \right)^{3/2} \right] + \frac{5}{2} \right]$$

$$S \approx 6.02 \times 10^{23} \left(1.38 \times 10^{-23} \,{}^{J}/_{K} \right) \left[\ln \left[4.14 \times 10^{-26} \; m^3 \left(\frac{4\pi(6.64 \times 10^{-26} \; kg)(6.21 \times 10^{-21} \; J)}{3(6.63 \times 10^{-34} \; J\,s)^2} \right)^{3/2} \right] + \frac{5}{2} \right]$$

$$S \approx 6.02 \times 10^{23} \left(1.38 \times 10^{-23} \,{}^{J}/_{K} \right) \left[\ln[1.02 \times 10^7 \,] + \frac{5}{2} \right]$$

$$S \approx 155 \,{}^{J}/_{K}$$

b) Is the entropy greater for a mole of argon or a mole of helium under the same conditions? (You do not have to calculate the entropy of the helium case.) If you use an equation in your explanation, be sure to also explain conceptually.

Helium has a mass of 4 amu compared to the 40 amu of argon. For a given energy, a smaller mass means a smaller momentum. Thus, the hypersphere in momentum space is smaller for He, and thus the multiplicity is lower. There are more accessible states in Ar, so the entropy is greater.

3) According to the Sackur-Tetrode equation, the entropy of a monatomic ideal gas can become negative when its temperature (and hence its energy) is sufficiently low. The Sackur-Tetrode equation must be invalid at very low temperatures.

a) Use the definition of entropy to explain why entropy must be non-negative for any accessible state.

The definition of entropy is $S = k \ln \Omega$. For any accessible state, there exists at least one microstate, and so the multiplicity is greater than or equal to one.

$$\Omega \geq 1 \quad \rightarrow \quad \ln \Omega \geq 0$$

The Boltzmann constant is positive. Entropy is the product of two non-negative numbers, and thus must be non-negative.

b) Suppose you start with a sample of helium at room temperature and atmospheric pressure, then lower the temperature holding the density fixed. For the purposes of this problem, assume that the helium remains a gas and does not liquefy. (*Note: This is not an accurate assumption.*) Find the temperature below which the Sackur-Tetrode equation predicts that S is negative.

Begin with the Sackur-Tetrode equation.

$$S \approx Nk \left[\ln \left[\frac{V}{N} \left(\frac{4\pi mU}{3Nh^2} \right)^{3/2} \right] + 5/2 \right]$$

The number of molecules and Boltzmann constant are positive, so the entropy will be negative when the term of brackets is negative.

$$\ln \left[\frac{V}{N} \left(\frac{4\pi mU}{3Nh^2} \right)^{3/2} \right] + 5/2 < 0$$

First find the energy, U, when this is true. Then convert to temperature, T, using the equipartition theorem.

$$\ln \left[\frac{V}{N} \left(\frac{4\pi mU}{3Nh^2} \right)^{3/2} \right] < -5/2$$

Exponentiate both sides.

$$\frac{V}{N}\left(\frac{4\pi mU}{3Nh^2}\right)^{3/2} < e^{-5/2}$$

Rearrange to isolate U. (All values are positive, so our inequality direction does not change.)

$$\left(\frac{4\pi mU}{3Nh^2}\right)^{3/2} < \frac{N}{V}e^{-5/2}$$

$$\frac{4\pi mU}{3Nh^2} < \left(\frac{N}{V}\right)^{2/3}\left(e^{-5/2}\right)^{2/3}$$

$$\frac{4\pi mU}{3Nh^2} < \left(\frac{N}{V}\right)^{2/3}e^{-5/3}$$

$$U < \left(\frac{N}{V}\right)^{2/3}e^{-5/3}\frac{3Nh^2}{4\pi m}$$

Use the equipartition theorem to rewrite $U = {}^f/_2 \, NkT$.

$$^f/_2\,NkT < \left(\frac{N}{V}\right)^{2/3}e^{-5/3}\frac{3Nh^2}{4\pi m}$$

$$fkT < \left(\frac{N}{V}\right)^{2/3}e^{-5/3}\frac{3h^2}{2\pi m}$$

$$T < \left(\frac{N}{V}\right)^{2/3}e^{-5/3}\frac{3h^2}{2\pi mfk}$$

The assumption is that the He remains a gas, so the number density can be written in terms of pressure and temperature using the ideal gas law. The assumption is also that the density stays constant, so room temperature and atmospheric pressure can be used for this density. $f = 3$ for a monatomic gas. The mass of He is 4 amu.

$$T < \left(\frac{N}{V}\right)^{2/3}e^{-5/3}\frac{3h^2}{2\pi mfk}$$

$$T < \left(\frac{P_{atm}}{kT_{room}}\right)^{2/3}e^{-5/3}\frac{3h^2}{2\pi mfk}$$

$$T < \left(\frac{10^5\,{}^N/_{m^2}}{\left(1.38\times10^{-23}\,{}^J/_K\right)(300\,K)}\right)^{2/3}e^{-5/3}\frac{3(6.63\times10^{-34}\,J\,s)^2}{2\pi(4\times1.66\times10^{-27}\,kg)3\left(1.38\times10^{-23}\,{}^J/_K\right)}$$

$$T < \left(\frac{10^5\,{}^N/_{m^2}}{\left(1.38\times10^{-23}\,{}^J/_K\right)(300\,K)}\right)^{2/3}e^{-5/3}\frac{(6.63\times10^{-34}\,J\,s)^2}{2\pi(4\times1.66\times10^{-27}\,kg)\left(1.38\times10^{-23}\,{}^J/_K\right)}$$

$$T < (2.42 \times 10^{25} \ m^{-3})^{2/3} e^{-5/3} (7.63 \times 10^{-19} \ K \ m^2)$$

$$T < (2.42 \times 10^{25} \ m^{-3})^{2/3} e^{-5/3} (7.63 \times 10^{-19} \ K \ m^2)$$

$$T < 0.01 \ K$$

The Sakur-Tetrode equation predicts negative entropies for $T < 0.01 \ K$.

4) For each of the following irreversible processes, explain in a sentence or two how you can tell that the total entropy of the Universe has increased.

The key is to look for processes that are irreversible or (equivalently) to look for processes that increase multiplicity.

a) Stirring salt into a pot of soup

When the salt is stirred, the sodium and chlorine ions that make up the salt are spread through a large volume of liquid. There are more possible arrangements of these dispersed ions than when they are rigidly arranged in a salt crystal. More arrangements leads to higher entropy. Some salt could be recovered by boiling off the soup, but the ions would still be more disordered.

b) Scrambling an egg

When an egg is scrambled, the molecules that make up the yolk are mixed with those that make up the white. The entropy of mixing increases the overall entropy. The cooking process also unfolds orderly proteins into disordered chains.

c) Humpty Dumpty (the nursery rhyme character) having a great fall

When Humpty Dumpty has a great fall and shatters into many pieces, there are many more possible arrangements of those pieces than when he was whole. Thus, the entropy is higher. The process must be irreversible because "All the king's horses and all the king's men couldn't put Humpty together again."

d) A wave hitting a sand castle

While there are many arrangements of sand that form a castle, there are many more possible arrangements after the wave hits and scatters the sand randomly. This increase in multiplicity leads to an increase in entropy.

e) Cutting down a tree

The process is irreversible; one cannot put the tree back up. Also, there are more possible arrangements of the tree broken apart and fallen than of the tree standing. Cutting down the tree also severs biological connections that cannot be reattached.

f) Burning gasoline in an automobile

When the gasoline burns, a smaller number of large hydrocarbon molecules are broken down into a larger number of smaller exhaust gas molecules. Chemical energy is also transferred into thermal energy, which is released into the environment. This excess energy increases the entropy of the environment as well.

5)

a) A particle of mass m is free to move in <u>one</u> dimension. Denote its position coordinates by x and its momentum by p. Suppose that this particle is confined within a box such that $0 \le x \le L$. Suppose that its energy is known to be between E and $E + dE$. Draw the classical position-momentum phase space of this particle. Be sure to indicate the regions of this phase space which are accessible to the particle. *Hint: This is similar to what we did in class with the hypersphere, except it is in 1-D.*

The plot will have x and y axes of x and p_x, respectively. The fact that the particle is restricted to a box means the allowed x values are limited from 0 to L.

To find the limits on the p_x values, first consider the given restrictions on energy.

$$E \le E_{allowed} \le E + dE$$

Convert that to restrictions on momentum using the relationship between energy and momentum.

$$E \le \frac{p_{allowed}^2}{2m} \le E + dE$$

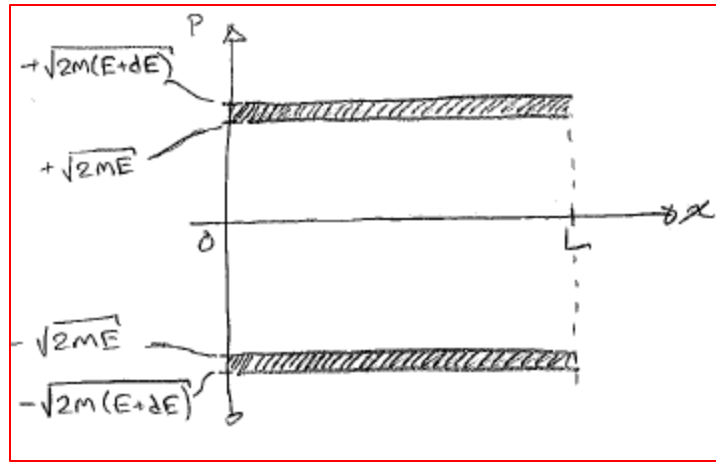Solve for $p_{allowed}$.

$$2mE \le p_{allowed}^2 \le 2m(E + dE)$$

Be sure to keep both roots. This gives us two regions of allowed momentum:

$$\sqrt{2mE} \le p_{allowed} \le \sqrt{2m(E + dE)}$$

and

$$\sqrt{2mE} \le -p_{allowed} \le \sqrt{2m(E + dE)} \quad \rightarrow \quad -\sqrt{2mE} \le p_{allowed} \le -\sqrt{2m(E + dE)}$$

Plot this result on x-p_x axes. The shaded regions are the allowed regions of phase space.

b) Now consider a system consisting of two weakly interacting particles, each of mass m, that are free to move in <u>one</u> dimension. Denote the respective position coordinates of the two particles by x_1 and x_2, and their respective momenta by p_1 and p_2. Both particles are confined within a box such that $0 \leq x_i \leq L$ for i=1,2. The *total* energy of the system is known to lie between E and E + dE. Instead of trying to draw a four-dimensional phase space, draw separately the part of phase space involving x_1 and x_2 (position-space), and that involving p_1 and p_2 (momentum-space). Indicate on these diagrams the regions of phase space accessible to the system.

The position-space plot will have x and y axes of x_1 and x_2, respectively. The fact that both particles are restricted to a box means the allowed x_1 values are limited from 0 to L. The same is true for x_2.

The allowed regions of position space thus make a square, as shown by the shaded region of the plot below.
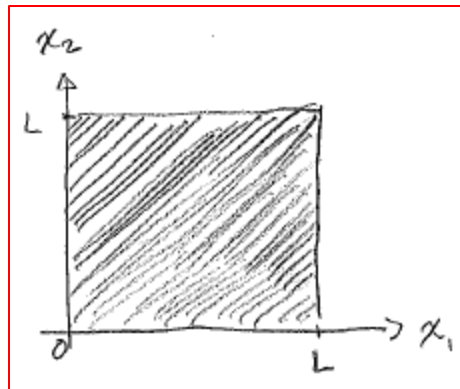
For momentum space, the two particles share the total energy of the system. Using the same energy and momentum relationship as in part a), connect the energy to momentum.

$$E_1 + E_2 = E_{total}$$

$$\frac{p_1{}^2}{2m} + \frac{p_2{}^2}{2m} = E_{total}$$

$$p_1{}^2 + p_2{}^2 = 2mE_{total}$$

The restrictions on energy are E and E + dE. These yield boundary conditions for the allowed region.
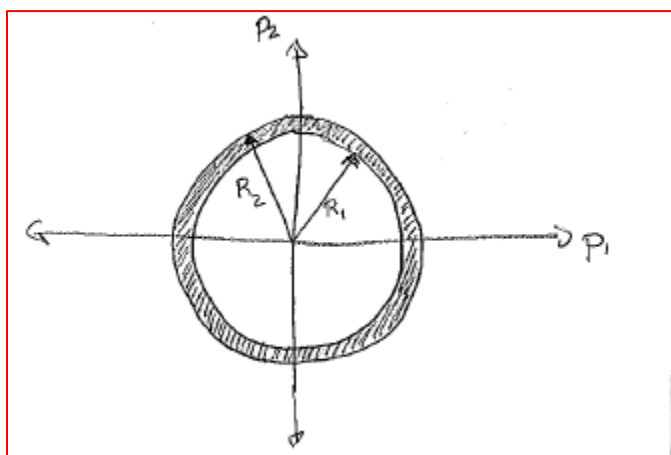$$p_1{}^2 + p_2{}^2 = 2mE$$

$$p_1{}^2 + p_2{}^2 = 2m(E + dE)$$

In momentum space, the x and y axes are p_1 and p_2. Thus, our restrictions are equations of circles. (Recall that $x^2 + y^2 = R^2$ is the equation of a circle with radius R.) **Thus, the boundaries are circles of radii** $R_1 = \sqrt{2mE}$ **and** $R_2 = \sqrt{2m(E + dE)}$.

The allowed regions of momentum space thus make a ring, as shown by the shaded region of the plot below.

6)
a) Start with the full expression for the multiplicity for the *large* Einstein solid (Schroeder (2.17)), and show that in the low-temperature limit, where $q \ll N$, the multiplicity is approximately equal to $\left(\frac{Ne}{q}\right)^q$.
    Hint: Ignore the merely large $\sqrt{2\pi N}$ term in Stirling's approximation.

Start with Schroeder (2.17).

$$\Omega \approx \frac{(q + N)!}{q!\, N!}$$

Examine the log of multiplicity.

$$\ln \Omega \approx \ln\left[\frac{(q + N)!}{q!\, N!}\right]$$

Use log rules for products and quotients.

$$\ln \Omega \approx \ln[(q + N)!] - \ln[q!] - \ln[N!]$$

Use Stirling's approximation in the form of Schroeder (2.16). $\ln[N!] \approx N \ln[N] - N$

$$\ln \Omega \approx (q + N) \ln[q + N] - (q + N) - [q \ln q - q] - [N \ln N - N]$$

$$\ln \Omega \approx (q + N) \ln[q + N] - q \ln q - N \ln N$$

Examine the first log term.

$$\ln[q + N] = \ln\left[N\left(1 + \frac{q}{N}\right)\right]$$

Rewrite using the log term for products.

$$\ln[q + N] = \ln[N] + \ln\left(1 + \frac{q}{N}\right)$$

Use the Taylor expansion approximation that $\ln(1 + x) \approx x$ for $x \ll 1$. $\frac{q}{N} \ll 1$ because this is the low-temperature limit.

$$\ln[q + N] \approx \ln N + \frac{q}{N}$$

Plug this back into the expression for the log of the multiplicity.

$$\ln \Omega \approx (q + N)\left[\ln N + \frac{q}{N}\right] - q \ln q - N \ln N$$

Distribute.

$$\ln \Omega \approx q \ln N + \frac{q^2}{N} + N \ln N + q - q \ln q - N \ln N$$

$$\ln \Omega \approx q \ln N + \frac{q^2}{N} + q - q \ln q$$

Combine the log terms using the difference log rule. Combine the other two terms.

$$\ln \Omega \approx q \ln\frac{N}{q} + q\left(\frac{q}{N} + 1\right)$$

In the low-temperature limit, $\frac{q}{N} \ll 1$, so the term in parentheses is approximately equal to one.

$$\ln \Omega \approx q \ln\frac{N}{q} + q$$

Use the log rule for multiplicative factors.

$$\ln \Omega \approx \ln\left(\frac{N}{q}\right)^q + q$$

Exponentiate to get back to multiplicity.

$$\Omega = e^{\ln \Omega} \approx e^{\left(\ln\left(\frac{N}{q}\right)^q + q\right)}$$

Split up the sum in the exponential into a product of two exponentials.

$$\Omega \approx e^{\ln\left(\frac{N}{q}\right)^q} e^q$$

$$\Omega \approx \left(\frac{N}{q}\right)^q e^q$$

$$\Omega \approx \left(\frac{Ne}{q}\right)^q$$

b) Starting with the multiplicity for an Einstein solid in the "low-temperature" limit from part a), find a formula for the temperature of an Einstein solid in the limit $q \ll N$. Solve for the energy as a function of temperature to obtain $U = N\epsilon e^{-\epsilon/kT}$ (where ϵ is the spacing between energy levels).

First calculate the entropy from the multiplicity in part a). Later differentiate to get temperature.

$$S = k \ln \Omega \approx k \ln \left(\frac{Ne}{q}\right)^q$$

Use log rules to bring the exponent out front and to break up the product and quotient.

$$S \approx kq[\ln N + \ln e - \ln q]$$

$$S \approx kq[\ln N - \ln q + 1]$$

Get entropy in terms of U to differentiate and get to temperature. q is the quantum of energy, and thus $U = q\epsilon$.

$$S \approx k \frac{U}{\epsilon} \left[\ln N - \ln \frac{U}{\epsilon} + 1\right]$$

Differentiate with respect to U to get temperature.

$$\frac{1}{T} = \frac{\partial S}{\partial U} = \frac{\partial}{\partial U}\left[k \frac{U}{\epsilon}\left[\ln N - \ln \frac{U}{\epsilon} + 1\right]\right]$$

$$\frac{1}{T} = \frac{k}{\epsilon} \frac{\partial}{\partial U}\left[U \left[\ln N - \ln \frac{U}{\epsilon} + 1\right]\right]$$

Differentiate using the product rule.

$$\frac{1}{T} = \frac{k}{\epsilon}\left[\ln N - \ln \frac{U}{\epsilon} - U\left(\frac{1}{U}\right) + 1\right]$$

$$\frac{1}{T} = \frac{k}{\epsilon}\left[\ln N - \ln\frac{U}{\epsilon} - 1 + 1\right]$$

$$\frac{1}{T} = \frac{k}{\epsilon}\left[\ln N - \ln\frac{U}{\epsilon}\right]$$

Combine the log terms using the difference log rule.

$$\frac{1}{T} = \frac{k}{\epsilon}\left[\ln\frac{N\epsilon}{U}\right]$$

Solve for U.

$$\frac{\epsilon}{kT} = \ln\frac{N\epsilon}{U}$$

Exponentiate both sides.

$$e^{\frac{\epsilon}{kT}} = e^{\ln\frac{N\epsilon}{U}}$$

$$e^{\frac{\epsilon}{kT}} = \frac{N\epsilon}{U}$$

$$U = N\epsilon e^{-\frac{\epsilon}{kT}}$$

7)

   a) Starting with the result from part b) of the previous problem, calculate the heat capacity of an Einstein solid in the low-temperature limit.

   The volume of a solid is constant, so find the heat capacity at constant volume. Start with the definition of heat capacity, Schroeder (1.44).

$$C_V = \frac{\partial U}{\partial T}\bigg|_V$$

Plug in the expression for *U(T)* from problem 6 and differentiate.

$$C_V = \frac{\partial}{\partial T}\left[N\epsilon e^{-\frac{\epsilon}{kT}}\right]\bigg|_V$$

$$C_V = \left[N\epsilon e^{-\frac{\epsilon}{kT}}\right]\left(\frac{\epsilon}{kT^2}\right)$$

$$C_V = \frac{N\epsilon^2}{kT^2}e^{-\frac{\epsilon}{kT}}$$

   b) Now find the heat capacity in the <u>high</u>-temperature limit. *Hint: The equipartition theorem holds in the high-temperature limit. Leave your answer in terms of f.*

Begin with the same heat capacity equation.

$$C_V = \frac{\partial U}{\partial T}\bigg|_V$$

Plug in the expression for *U(T)* from the equipartition theorem.

$$C_V = \frac{\partial}{\partial T}\left[\frac{f}{2}NkT\right]\bigg|_V$$

Differentiate.

$$C_V = \frac{f}{2}Nk$$

c) On the same plot, sketch both the low-temperature limit (part a) and high-temperature limit (part b) expressions for heat capacity as a function of temperature. For the low-temperature limit, indicate the maximum value of C_V and the *T* value at which the maximum occurs.
(Note: Measurements of heat capacities of actual solids at low temperatures do not confirm the prediction that you make in this problem. We will develop a more accurate model of solids at low temperatures later this semester.)

I plotted the function from Wolfram Alpha. It is sketched below.

To find the maximum values, differentiate the expression from a) and set the derivative equal to zero. Differentiate using the product rule.

$$\frac{\partial}{\partial T}C_V = \frac{\partial}{\partial T}\left(\frac{N\epsilon^2}{kT^2}e^{-\frac{\epsilon}{kT}}\right)$$

$$\frac{\partial}{\partial T}C_V = \frac{N\epsilon^2}{k}\frac{\partial}{\partial T}\left(\frac{1}{T^2}e^{-\frac{\epsilon}{kT}}\right)$$

Differentiate using the product rule.

$$\frac{\partial}{\partial T}C_V = \frac{N\epsilon^2}{k}\left[\left(\frac{1}{T^2}e^{-\frac{\epsilon}{kT}}\frac{\epsilon}{kT^2}\right) + \left(e^{-\frac{\epsilon}{kT}}\frac{-2}{T^3}\right)\right]$$

$$\frac{\partial}{\partial T}C_V = \frac{N\epsilon^2}{k}e^{-\frac{\epsilon}{kT}}\left[\left(\frac{\epsilon}{kT^4}\right) - \left(\frac{2}{T^3}\right)\right]$$

Get a common denominator

$$\frac{\partial}{\partial T}C_V = \frac{N\epsilon^2}{k}e^{-\frac{\epsilon}{kT}}\left(\frac{\epsilon - 2kT}{kT^4}\right)$$

Set this equal to zero to find the maximum. The terms out front are only equal to zero at $T = \infty$. The maximum is found when the numerator of the term in the parentheses is equal to zero.

$$\epsilon - 2kT = 0$$

$$2kT = \epsilon$$

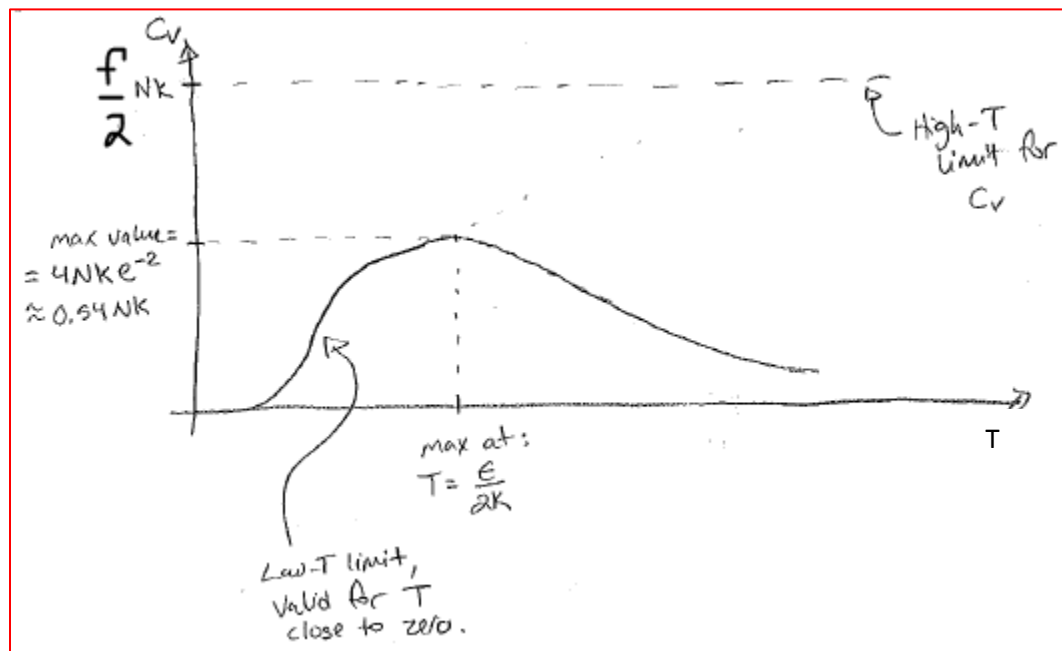$$T_{max} = \frac{\epsilon}{2k}$$

Plug in this temperature in to calculate the heat capacity maximum.

$$C_V(T_{max}) = \frac{N\epsilon^2}{kT_{max}^2} e^{-\frac{\epsilon}{kT_{max}}}$$

$$C_V(T_{max}) = \frac{N\epsilon^2}{k\left(\frac{\epsilon}{2k}\right)^2} e^{-\frac{\epsilon}{k\left(\frac{\epsilon}{2k}\right)}}$$

$$C_V(T_{max}) = 4Nke^{-2} \approx 0.54\,Nk$$

The exact relative height of the high-temperature limit depends on the value of f.

8) On HW 3 you found the following expression for the multiplicity of an Einstein solid containing N oscillators and q energy units.

$$\Omega \approx \frac{\left(\frac{q+N}{q}\right)^q \left(\frac{q+N}{N}\right)^N}{\sqrt{2\pi q \frac{q+N}{N}}}$$

a) Find an expression for the entropy of an Einstein solid as a function of N and q. *Hint: Use only the numerator of the formula for multiplicity. Explain why this is justified if both N and q are large.*

$$\Omega \approx \frac{\left(\frac{q+N}{q}\right)^q \left(\frac{q+N}{N}\right)^N}{\sqrt{2\pi q \frac{q+N}{N}}} \approx \left(\frac{q+N}{q}\right)^q \left(\frac{q+N}{N}\right)^N$$

This approximation is justified because if both N and q are large, then the numerator is very large, while the denominator is merely large. A very large number divided by a large number is essentially equal to the original very large number.

Now calculate entropy.

$$S = k \ln \Omega \approx k \ln \left[\left(\frac{q+N}{q}\right)^q \left(\frac{q+N}{N}\right)^N \right]$$

Simplify using the log rules for products.

$$S \approx k \left(\ln \left[\left(\frac{q+N}{q}\right)^q \right] + \ln \left[\left(\frac{q+N}{N}\right)^N \right] \right)$$

Simplify using the log rules for exponents.

$$S \approx k \left(q \ln \left[\frac{q+N}{q} \right] + N \ln \left[\frac{q+N}{N} \right] \right)$$

Simplify using the log rules for quotients.

$$S \approx k(q \ln[q+N] - q \ln q + N \ln[q+N] - N \ln N)$$

$$S \approx k[(q+N)\ln[q+N] - q \ln q - N \ln N]$$

b) Use the result of part a) to calculate the temperature of an Einstein solid as a function of its energy. (The energy is $U = q\epsilon$, where ϵ is the constant spacing between energy levels). Be sure to simplify your result as much as possible.

First rewrite the entropy expression from part a) replacing q with U.

$$S \approx k[(q+N)\ln[q+N] - q \ln q - N \ln N]$$

$$S \approx k \left[\left(\frac{U}{\epsilon} + N\right) \ln \left[\frac{U}{\epsilon} + N\right] - \frac{U}{\epsilon} \ln \frac{U}{\epsilon} - N \ln N \right]$$

Differentiate with respect to U to find temperature.

$$\frac{1}{T} = \frac{\partial S}{\partial U} \approx \frac{\partial}{\partial U} \left[k \left[\left(\frac{U}{\epsilon} + N\right) \ln \left[\frac{U}{\epsilon} + N\right] - \frac{U}{\epsilon} \ln \frac{U}{\epsilon} - N \ln N \right] \right]$$

$$\frac{1}{T} \approx k \left(\frac{\partial}{\partial U} \left[\left(\frac{U}{\epsilon} + N\right) \ln \left[\frac{U}{\epsilon} + N\right] \right] - \frac{\partial}{\partial U} \left[\frac{U}{\epsilon} \ln \frac{U}{\epsilon} \right] - \frac{\partial}{\partial U} [N \ln N] \right)$$

Use the product rule.

$$\frac{1}{T} \approx k \left(\left(\frac{1}{\epsilon} \ln \left[\frac{U}{\epsilon} + N \right] + \left(\frac{U}{\epsilon} + N \right) \frac{1}{\left(\frac{U}{\epsilon} + N \right)} \frac{1}{\epsilon} \right) - \left(\frac{1}{\epsilon} \ln \frac{U}{\epsilon} + \frac{U}{\epsilon} \frac{1}{U} \right) - 0 \right)$$

$$\frac{1}{T} \approx k \left(\frac{1}{\epsilon} \ln \left[\frac{U}{\epsilon} + N \right] + \frac{1}{\epsilon} - \frac{1}{\epsilon} \ln \frac{U}{\epsilon} - \frac{1}{\epsilon} \right)$$

$$\frac{1}{T} \approx k \left(\frac{1}{\epsilon} \ln \left[\frac{U}{\epsilon} + N \right] - \frac{1}{\epsilon} \ln \frac{U}{\epsilon} \right)$$

Factor out the common $1/\epsilon$ term.

$$\frac{1}{T} \approx \frac{k}{\epsilon} \left(\ln \left[\frac{U}{\epsilon} + N \right] - \ln \frac{U}{\epsilon} \right)$$

Simplify using the log rule for differences.

$$\frac{1}{T} \approx \frac{k}{\epsilon} \ln \left[\frac{\frac{U}{\epsilon} + N}{\frac{U}{\epsilon}} \right]$$

$$\frac{1}{T} \approx \frac{k}{\epsilon} \ln \left[1 + \frac{N\epsilon}{U} \right]$$

c) Invert the relation you found in part b) to find the energy as a function of temperature, then differentiate to find a formula for the heat capacity.

Start with the answer from part b).

$$\frac{1}{T} \approx \frac{k}{\epsilon} \ln \left[1 + \frac{N\epsilon}{U} \right]$$

$$\frac{\epsilon}{kT} \approx \ln \left[1 + \frac{N\epsilon}{U} \right]$$

Exponentiate both sides.

$$e^{\frac{\epsilon}{kT}} \approx e^{\ln \left[1 + \frac{N\epsilon}{U} \right]}$$

$$e^{\frac{\epsilon}{kT}} \approx 1 + \frac{N\epsilon}{U}$$

Solve for U.

$$e^{\frac{\epsilon}{kT}} - 1 \approx \frac{N\epsilon}{U}$$

$$U \approx \frac{N\epsilon}{e^{\frac{\epsilon}{kT}} - 1}$$

Differentiate to find the heat capacity.

$$C_V \approx \left.\frac{\partial U}{\partial T}\right|_V$$

Plug in the expression for U.

$$C_V \approx \left.\frac{\partial}{\partial T}\left[\frac{N\epsilon}{e^{\frac{\epsilon}{kT}} - 1}\right]\right|_V$$

$$C_V \approx N\epsilon \left.\frac{\partial}{\partial T}\left[\frac{1}{e^{\frac{\epsilon}{kT}} - 1}\right]\right|_V$$

Differentiate (with u substitution).

$$C_V \approx N\epsilon \frac{-1}{\left(e^{\frac{\epsilon}{kT}} - 1\right)^2} \frac{-\epsilon}{kT^2} e^{\frac{\epsilon}{kT}}$$

$$C_V \approx \frac{N\epsilon^2}{kT^2} \frac{e^{\frac{\epsilon}{kT}}}{\left(e^{\frac{\epsilon}{kT}} - 1\right)^2}$$

d) Show that the heat capacity is $C = Nk$ in the limit $T \to \infty$. Is this the result you would expect for a 1-D oscillator? Explain. *Hint: When x is very small, $e^x \approx 1 + x$.*

As $T \to \infty$, $\frac{\epsilon}{kT}$ becomes very small. By the hint, $e^{\frac{\epsilon}{kT}} \approx 1 + \frac{\epsilon}{kT}$. Make this substitution in the expression for heat capacity.

$$C_V \approx \frac{N\epsilon^2}{kT^2} \frac{e^{\frac{\epsilon}{kT}}}{\left(e^{\frac{\epsilon}{kT}} - 1\right)^2}$$

$$C_V(T \to \infty) \approx \frac{N\epsilon^2}{kT^2} \frac{1 + \frac{\epsilon}{kT}}{\left(1 + \frac{\epsilon}{kT} - 1\right)^2}$$

$$C_V(T \to \infty) \approx \frac{N\epsilon^2}{kT^2} \frac{1 + \frac{\epsilon}{kT}}{\left(\frac{\epsilon}{kT}\right)^2}$$

Cancel common terms in numerator and denominator.

$$C_V(T \to \infty) \approx \frac{N}{k} \frac{1 + \frac{\epsilon}{kT}}{\left(\frac{1}{k}\right)^2}$$

$$C_V(T \to \infty) \approx Nk \left(1 + \frac{\epsilon}{kT}\right)$$

For very large T, the term in the parentheses is essentially equal to one.

$$C_V(T \to \infty) \approx Nk$$

This is what we expect from the equipartition theorem (which is true in the high-temperature limit) for a 1-D oscillator ($f = 2$).

$$C_V \approx \left.\frac{\partial U}{\partial T}\right|_V$$

$$C_V \approx \frac{\partial}{\partial T}\left[\frac{f}{2}NkT\right]$$

$$C_V \approx \frac{f}{2}Nk = \frac{2}{2}Nk$$

$$C_V \approx Nk$$

9) List *three* main ideas from this homework assignment. For example, you could write a few-sentence explanation of a concept, or list an equation and explain the variables and in what circumstances the equation applies.
The goal is for you to review and to reflect on the big picture. Think about what you might want to remember when you look back at this homework before the test. I hope that this will be useful for your studying. I am not looking for anything specific here; you will be graded on effort and completion.