Final Exam for Physics 176: Answers

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Note: with a few exceptions, the following answers are far more detailed than what were required to get full credit. The answers should help you realize that it is possible to understand and solve each problem rather thoroughly, using what you have learned over the semester.

Problems That Require Writing

Please write your answers to the following problems on extra blank sheets of paper, and make sure to write your name and the problem number at the top of each sheet. Unless otherwise stated, *you need to justify your answers to get full credit.*

1. **(6 points)** List six distinct criteria that a system has to satisfy to be in thermodynamic equilibrium. (No justification needed here.)

   Answer: I had not worded this problem carefully since what I had intended was for the class to give six *practical* criteria that an experimentalist or computational scientist could use to determine empirically whether a system was in thermodynamic equilibrium. Answers I had mind include:

   (a) All macroscopic properties of the system are time independent.

   (b) All parts of the system have the same temperature.

   (c) All parts of the system have the same pressure *unless* the system is in an external time-independent inhomogeneous field (say gravitational or electrical), in which case the pressure will vary spatially throughout the system. (Think about the isothermal exponential atmosphere discussed several times in Schroeder.)

   (d) All parts of the system have the same chemical potential. This criterion replaces the condition that the pressure is the same everywhere if the system is in an external time-independent spatially varying field like gravity.

   (e) There is no relative motion of one macroscopic part of the system with respect to another macroscopic part, i.e., the entire system moves or rotates rigidly. The time-independent isothermal flow of water through some pipe is not in thermodynamic equilibrium since the speed of the water is zero at the walls and finite in the center of the pipe, i.e. there is relative motion of the water.

   (f) All macroscopic properties of the system are independent of the history of the sample, for example how the system was warmed or cooled to its current temperature, or how an external magnetic field was increased or decreased to its current value.

   Note: This criterion is often the hardest to verify, in terms of time and effort. The idea here is that a system may be time-independent but also metastable in that the free energy (or entropy or Gibb's free energy) may be an extremum but not a global extremum. An example would be a supercooled fluid that has not yet transitioned to a solid phase.

   Students gave some other answers such as multiplicity or entropy being a maximum, or the free energy being a minimum. As this problem was worded, these are correct answers but they are more theoretical or conceptual in value since it is not easy to measure the multiplicity or free energy and plot it as a function of time and verify that it has reached an extremum.

   Other answers given included statements like "the system must be isolated", "energy must be conserved", "number of particles must be conserved", "the system must be in its most likely macrostate". Some of these statements are wrong, an equilibrium system does not have to be isolated but can exchange energy or particles with some reservoir in which case these are not conserved quantities. (Admittedly, the fluctuations around the mean values are of order $1/\sqrt{N}$ which is tiny for N of order Avogadro's number, but still conservation is not a requirement for equilibrium.)

Systems that can exchange energy with some reservoir do not have to be in their most likely macrostate, since it is the free energy $F = U - TS$ that needs to be minimized, and this now involves a trade-off of an entropy term $-TS$ (which when maximized by itself would give the largest multiplicity) and an energy term. At low temperatures, the $-TS$ term can be small compared to U and $F = U - TS \approx U$ is dominated by the effects of energy, which may have nothing to do with multiplicity.

2. **(8 points)** Draw a representative phase diagram (with horizontal axis the temperature T and vertical axis the pressure P) that includes all the features that are typically observed in the phase diagram of a pure substance like carbon dioxide. Make sure to label clearly all features and regions of your plot. (No justification needed here.)

Answer: You can look up phase diagrams in Schroeder or on the Internet to confirm your answer. You should have had at least eight items drawn and labeled:

(a) at least *three phase regions* representing solid, liquid, and gas phases, with the phases appearing in reasonable locations. Even better, point out the possibility for multiple phases of the same kind, e.g., water has numerous solid phases.

(b) at least *three phase lines*, which should have been labeled as sublimation or deposition (solid-gas), vaporisation or condensation (liquid-gas), and melting or freezing (solid-liquid). Some of you just labeled these phase lines with phrases like "solid-liquid phase line" which was a poor alternative compared to "melting-freezing".

(c) a *critical point* where the gas-liquid phase line ends.

Note: the solid-liquid phase line can not end at a critical point since there is no continuous way for the periodic order of a crystalline solid to change to the non-periodic disordered structure of a fluid.

By the way, it is possible for a physical system to have more than one critical point although I don't know if this has been found yet experimentally. For example, theoretical calculations show that some substances like liquid carbon can have two liquid phases, a high density phase and a low density phase. Both liquid phases can have their own critical point with respect to the gas phase.

(d) at least one *triple point*, where three phases can be in equilibrium simultaneously. The water phase diagram shown on the 176 homepage has *many* other triple points in addition to the gas-liquid-solid triple point. The table on the web page `http://www.lsbu.ac.uk/water/phase.html` in fact lists twelve other triple points that involve two solid phases in equilibrium with a liquid or third solid phase.

For you to think about:

(a) Using the Clausius-Clapeyron equation, can you explain why the slope of the liquid-gas phase line emerging from the triple point is always lower (less steep) than the slope of the solid-gas phase terminating at the triple point? This was a question I had considered asking on the final exam.

(b) Figures 5.11 and 5.12 of Schroeder (page 167) show the gas-solid sublimation phase line passing through the origin $T = P = 0$. Does this make sense: can a gas exist all the way down to absolute zero? What is the actual experimental behavior for different substances?

(c) Can there be quadruple or higher points for a pure substance, where more than three phases coexist?

3. Over the semester, you learned about two models for which many thermodynamic details can be worked out analytically, the Einstein solid and an ideal gas.

   (a) **(12 points)** In some detail (6 points worth each!), describe what *are* these two systems. Your discussion should state clearly what are the components of each system, and mention what assumptions, simplifications, and idealizations are made so that these models can be studied analytically.

   Answer: Many students did not do a good job explaining the basic facts and assumptions related to these two systems.

   Einstein solid: This is a model invented by Einstein to explain the temperature-dependence of the heat capacity of a solid, in particular why the heat capacity experimentally varied with temperature, in contradiction to the prediction of the equipartition theorem. Einstein assumed that the vibrations of N molecules in a crystal could be approximated as $3N$ independent and identical quantum mechanical harmonic oscillators, all with the same oscillator frequency f. The number $3N$ comes from the observation that a classical particle in a 3D lattice can vibrate in three independent directions (although not necessarily parallel to the Cartesian axes since not all periodic crystals have cubic symmetry), and each direction would correspond to one harmonic oscillator.

   As derived by a quantum mechanical calculation (discussed in the physics courses 143 and 211), each quantum harmonic oscillator has an infinite number of equally spaced energy levels $E = hf(1/2 + n)$ with n a non-negative integer. The Einstein solid can then be thought of as having a total amount of vibrational energy $q\epsilon = q(hf)$ (q some non-negative integer) that is distributed among the various quantum oscillators.

   The key assumptions that allow analytical progress are that the oscillators are independent, that the oscillators remain perfectly harmonic for arbitrarily large energies, and that they all have the same frequency. The Debye theory addresses some of these assumptions, e.g., allowing the frequencies to differ and allowing groups of atoms to move together (phonon excitations).

   Ideal gas: The opening paragraphs of the Wikipedia article "Ideal gas" provide the intended answer. In one sentence: the molecules of an ideal gas are treated as non-interacting point particles in random motion. Most students failed to take into account the many different kinds of ideal gases that we have discussed over the semester and talked only about the classical monoatomic ideal gas that we discussed the first two weeks of class. What I wanted you to mention at least briefly, was that we have discussed three kinds of ideal gases: classical (Maxwell-Boltzmann), and two quantum ideal gases that are described by Bose-Einstein statistics (photons and phonons) and Fermi-Dirac statistics (say electrons in a metal or nucleons in a nucleus). I especially wanted you to mention an ideal gas of diatomic molecules, for which we were able to calculate all qualitative and quantitative experimental details of the heat capacity (translational, rotational, and vibrational behaviors) by using the partition function method of Chapter 6.

   (b) **(10 points)** With appropriate sketches showing axes and key graphical details clearly labeled, show how the normalized heat capacity $C_V/(Nk)$ varies with temperature for each of these two systems. Be particularly careful to draw the low- and high-temperature behaviors of $C_V/(Nk)$ correctly (e.g., if the curve approaches an axis, does it do so with a zero, finite, or infinite slope?). Where possible and as is appropriate, also indicate quantitative details on your plot, e.g., where room temperature ($T = 300\,\mathrm{K}$) lies on your plot, and the approximate values on the axes where there is some physically relevant change in behavior.

   Answer: What I was looking for was Figures 1.13 and 1.14 on page 30 of Schroeder's book and some comments about what was known about the functional dependence of the heat capacity in the limit $T \to 0$, e.g., that $C_V \approx c_1 T + c_3 T^3$ for a solid, that $C_V \approx (3/2)NkT$ for the low-temperature regime of a gas of diatomic molecules, in which case the rotational and vibrational internal degrees of freedom "freeze" out, but not the translational degrees of freedom, which can't freeze out if the particles do not interact with each other.

(c) **(6 points)** Give an example for each model of a prediction that is *incorrect* experimentally, and explain briefly the reason for the incorrect prediction.

Answer: The Einstein model gives the correct high-temperature result corresponding to equipartition, $C_V/(Nk) = 3$, but gives an incorrect analytical behavior for low temperature, that C_V has the functional form $(\epsilon/kT)^2 e^{-\epsilon/(kT)}$ as $T \to 0$. As I mentioned earlier in the semester, a function of the form $e^{-c/x}$ for $c > 0$ some constant is a non-analytic function as $x \to 0$ in that this function has a zero Taylor series around $x = 0$ (all the derivatives of this function are zero at $x = 0$). So while C_V for the Einstein model correctly goes to zero, as $T \to 0$, it does so as neither a polynomial nor an exponential. (It is not correct to say that $T^{-2}e^{-c/T}$ is exponential decay as $T \to 0$, exponential decay would be e^{-cT} as $T \to \infty$ for some constant c.) This behavior contradicts experiments which show that the specific heat behaves as T^3 over some range (due to phonons) and then switches to behaving as T at still lower temperatures (due to the electron gas).

Two students nicely pointed out something that Schroeder and I had not mentioned, that, since the Einstein solid can accept arbitrarily large amounts of energy (the integer q can be arbitrarily big), this model fails to undergo a phase transition to a liquid, gas, or plasma state at sufficiently high temperatures (large q values). This indeed severely contradicts experiment.

A simple and often useful rule for predicting at what temperature a solid will melt is something called the "Lindemann criterion", which simply states that when the root-mean-square displacement of an atom from its equilibrium position due to vibrations exceeds some fixed fraction of the interatomic distances (not that much, about 0.1), the solid will melt. This large amplitude motion of atoms away from their equilibrium positions causes strong deviations from a simple harmonic potential and so is difficult to calculate analytically, although not too bad to calculate using modern computer codes that can solve the Schrodinger equation for a three-dimensional solid.

We discussed the ideal gases in several different ways, using different tools such as kinetic theory (Chapter 1) and partition functions (end of Chapter 6). Kinetic theory was a classical theory (little balls moving around and colliding with walls) and so gives a wrong prediction that the specific heat $C_V/(Nk)$ should be independent of temperature with an equipartition value of $fk/2$ where f is the number of quadratic degrees of freedom ($f = 3$ for a monoatomic gas like He or $f = 7$ for a gas of diatomic molecules).

We later discussed ideal gases in terms of quantum energy levels of the molecules and of partition functions. This discussion eventually explained all experimental details of Figure 1.13 on page 30 of Schroeder, in which C_V increases with increasing temperature and has several plateaus corresponding to rotational and then vibrational degrees of freedom become "active" (or, as we know now, the ratio $E(s)/kT$ in the Boltzmann factor was becoming large).

But the idea gas completely gets wrong the existence of liquid and solid phases as the temperature is decreased. This is because such phase transitions fundamentally involve particle-particle interactions, which is precisely the detail that is ignored in an ideal gas.

4. **(6 points)** Estimate to one significant digit the height h in meters from which a penny at room temperature would have to fall so that the potential energy released, if delivered entirely to the penny, would raise the penny's temperature by one degree Kelvin.

Note: A penny has a mass of 2.5×10^{-3} kg and can be assumed to be pure zinc (it is actually 97.6% zinc coated with 2.4% copper). One mole of zinc has a mass of 6.5×10^{-2} kg.

Answer: Based on what you have learned in this course, a reasonable guess for the heat capacity C of zinc at room temperature would be the equipartition result $C = Nf(k/2) = 3Nk$ since many metals come close to the equipartition value at room temperature (look at Figure 1.14 of Schroeder, it is diamond that is anomalous with an unusually high Debye temperature). Alternatively, it is so difficult to calculate the specific heat from Debye's formula (a numerical approximation to an integral is necessary, see Eq. (7.117) of Schroeder on page 312), that you have to make some simplifying assumption and equipartition is the only one that is reasonable since you weren't given the Debye temperature for zinc.

Note: I used $f = 6$ for the number of degrees of freedom since atoms in a three-dimensional crystal can vibrate in three independent directions and each vibrational mode has two degrees of freedom corresponding to the kinetic energy and potential energy of an oscillator.

So this problem reduces to finding a height h such that $C_V = Q/\Delta T = mgh/\Delta T$ or

$$h = \frac{C_V\,\Delta T}{mg} = \frac{(3Nk)\,\Delta T}{mg} = \frac{3k\Delta T}{mg}\,N. \tag{1}$$

We can estimate the number N of Zn atoms in a penny from the given data as the number of moles of zinc times the number of atoms per mole (Avogadro's number N_A):

$$N = \frac{\text{mass } m \text{ of penny}}{\text{molar mass } M_{\text{zinc}} \text{ of zinc}} \times N_A\,\frac{\text{atoms}}{\text{mole}} \tag{2}$$

Combining Eqs. (1) and (2) yields a single expression containing all the data:

$$h = \frac{3k\Delta T}{mg} \times \left(\frac{mN_A}{M_{\text{zinc}}}\right) = \frac{3k\,\Delta T\,N_A}{g\,M_{\text{zinc}}}, \tag{3}$$

in which the mass m of the penny has divided out. (The above illustrates yet again why it is often better to simplify mathematically as much as possible *before* plugging in various numbers since you might find cancellations that reduce the amount of calculation, and make the calculation more accurate since there are fewer numbers to round). We can now substitute various numerical values and start to simplify:

$$\begin{aligned}
h &= \frac{3k\Delta T N_A}{g\,M_{\text{zinc}}} && (4)\\
&\approx \frac{3 \times \left(1.4 \times 10^{-23}\right) \times 1\,\text{K} \times \left(6.0 \times 10^{23}\right)}{10 \times (6.5 \times 10^{-2})} && (5)\\
&= \frac{3 \times 1.4 \times 6.0}{6.5} \times 10^{-23+23-1+2} && (6)\\
&\approx \frac{3 \times 1.5 \times 6.0}{5 \times 1.5} \times 10^{1} && (7)\\
&\approx \frac{18}{5} \times 10 = 36 \approx 40\,\text{m}, && (8)
\end{aligned}$$

to one significant digit. (I accepted 30 m and 50 m also for this problem, which is reasonable for some other choices of rounding; the answer to two digits turns out to be 39 m.) Others ways to approximate the combination of numbers in line (6) would be: round 1.4 down to 1 and round 6.5 down to 6 to get 3 (you want to round the 6.5 down to 6 in the denominator to increase the expression a little bit, which compensates for the decrease due to rounding 1.4 down to 1 in the numerator); replace 1.4×6 with 2.8×3 so the numerator $3 \cdot 1.4 \cdot 6.0 \approx 9 \times 2.8 \approx 27$. If we round 27 up to 30 we want to round 6.5 up to 7 (again so rounding errors compensate one another) and so $30/7 \approx 4$.

So the penny has to fall about 40 m, a rather large height, before it has released enough potential energy to raise its temperature by one degree. This answer is independent of the mass of the penny since the heat capacity is an extensive quantity proportional to m and the energy released by gravity is also proportional to m. If you tried to calculate intermediate numbers like N, you would have missed the fact that the penny's mass is irrelevant.

Note: experimental data for zinc's heat capacity $C_V(T)$ as a function of temperature (which I found on the Internet) show that C_V has not quite reached the equipartition plateau at room temperature, but the error is of order ten percent which is fine for an estimate with one significant digit. The Debye temperature for zinc turns out to be 327 K (see the table in the Wiki article on the "Debye Model"), just above room temperature. Figure 7.29 on page 312 of Schroeder (which of course everyone in the class memorized in preparation for the exam) shows that the specific heat has essentially saturated to its equipartition value of $3Nk$ for $T \approx T_D$. Problem 7.52, which you did in the last homework assignment, also informed you that the specific heat has reached 95% of its equipartition value when $T = T_D$.

5. **(6 points)** A planet is orbiting a binary star system (two stars that are orbiting each other). The planet is a distance d_1 from star 1 and a distance d_2 from star 2. The surface temperatures of the two stars are T_1 and T_2 and their radii are r_1 and r_2, while the radius of the planet is R. Derive and write down an expression for the steady-state temperature T of the planet in terms of the data d_1, d_2, r_1, r_2, T_1, T_2, and R.

   Note: For this problem, assume that the planet is a perfect blackbody emitter of uniform surface temperature, that the distances d_i change so slowly over time that they can be assumed to be constant, and that one star does not block any light from the other star.

   Answer: If the two stars and planet are perfect blackbody emitters, we can describe their emission of thermal light by Stefan's law. If neither star blocks light from the other, the total power that the planet receives from the stars is simply the sum of the power contributed from each star separately. In equilibrium, the total power emitted by the planet has to equal this total power received (else the planet's temperature would increase or decrease over time). Equating the total power received by the planet to the total power radiated by the planet we find

$$\left(\frac{\pi R^2}{4\pi d_1^2}\right) \times \left(4\pi r_1^2\right) \cdot \sigma T_1^4 + \left(\frac{\pi R^2}{4\pi d_2^2}\right) \times \left(4\pi r_2^2\right) \cdot \sigma T_2^4 = \left(4\pi R^2\right) \sigma T^4. \tag{9}$$

   The ratios in parentheses are the fraction of the total power emitted by each star that is received by the planet, that is the cross-sectional area of the planet πR^2 compared to the surface area of a sphere of radius d_i. Simplifying the algebra gives the desired result, that the steady state temperature of the planet is

$$T = \frac{1}{\sqrt{2}} \left[\left(\frac{r_1}{d_1}\right)^2 T_1^4 + \left(\frac{r_2}{d_2}\right)^2 T_2^4 \right]^{1/4}. \tag{10}$$

   An interesting feature of this expression is that it does not depend on the radius of the planet, so little rocks, asteroids, moons, and planets will all reach the same steady state temperature if they are the same distance from the two stars.

   While it is an excellent approximation to assume that stars act as constant temperature blackbody emitters, this might not be a reasonable assumption for a planet. For example, a planet without an atmosphere (which helps to transport heat from the bright to dark side by convection) might not be rotating quickly, in which case different parts of the planet might have different temperatures. The planet might have an atmosphere which can reflect incoming light (decreasing the final temperature T, Venus has a particularly reflective atmosphere), it might have a shiny icy surface which also reflects light (say Pluto, which is essentially a big ball of ice), or the atmosphere might contain gases like water vapor and carbon dioxide that can absorb and then re-emit infrared light from the planet's surface (the greenhouse effect, which Venus shows can be a much bigger effect than reflection of light by the atmosphere).

   Note: in answering this question, some students drew a picture of the planet between the two stars. This was fine for getting an answer, but represents a highly unlikely situation, that a planet would form near the center of mass of a binary star system.

6. Consider a system that is in thermodynamic equilibrium and that can exchange energy and particles with a reservoir whose constant temperature is T and whose constant chemical potential is μ.

   (a) **(6 points)** Derive and write down a formula for the heat capacity C of this system in terms of the grand partition function $\mathcal{Z}$.

   Note: Only T, μ, the Boltzmann constant k, $\mathcal{Z}$, and some derivatives of $\mathcal{Z}$ should appear in your answer.

   Answer: There were two rather different ways to solve this problem, one is to ignore the internal structure of the grand partition function and just work with thermodynamic identities, the other is to ignore the thermodynamic identities and just work with the partition function. I show you both ways.

   First approach: The specific heat $C = dU/dT$ can be determined if the energy U of a system is known as a function of temperature. Given the information for this problem, we know that we are dealing with a system that is described by the grand free energy $\Phi(T, V, \mu)$ (also called the grand potential) since this is the potential that is related to the grand partition function $\mathcal{Z}$ via $\Phi = -kT\ln(\mathcal{Z})$. From the information given on the first page of the exam, we also know that $\Phi = U - T\,S - \mu\,N$ which means that

$$U = \Phi + T\,S + \mu\,N. \tag{11}$$

   Since Φ is already known in terms of $\mathcal{Z}$, we can answer this problem if we can figure out how to express the entropy S and number of particles N in terms of $\mathcal{Z}$. (We can leave T and μ alone since these are parameters that characterize the properties of the reservoir.) But the thermodynamic identity also given on the first page of the exam

$$d\Phi = -S\,dT - P\,dV - N\,d\mu, \tag{12}$$

   implies that

$$S = -\left(\frac{\partial\Phi}{\partial T}\right)_{V,\mu} \qquad \text{and} \qquad N = -\left(\frac{\partial\Phi}{\partial\mu}\right)_{T,V}, \tag{13}$$

   which tells us how to express S and N in terms of $\mathcal{Z}$. We therefore have

$$\begin{aligned}
C &= \frac{dU}{dT} && (14)\\
&= \frac{d}{dT}\left(\Phi + T\,S + \mu\,N\right) && (15)\\
&= \frac{d}{dT}\left(-kT\ln(\mathcal{Z}) - T\frac{\partial\Phi}{\partial T} - \mu\frac{\partial\Phi}{\partial\mu}\right) && (16)\\
&= \frac{d}{dT}\left(-kT\ln(\mathcal{Z}) + kT\frac{\partial[T\ln(\mathcal{Z})]}{\partial T} + kT\mu\frac{\partial\ln(\mathcal{Z})}{\partial\mu}\right). && (17)\\
&= \frac{d}{dT}\left(kT^2\frac{\partial\ln(\mathcal{Z})}{\partial T} + kT\mu\frac{\partial\ln(\mathcal{Z})}{\partial\mu}\right). && (18)
\end{aligned}$$

   Eq. (17) is already enough to answer the question to my satisfaction, it is straightforward but not necessary to differentiate everything insides the big parentheses with respect to temperature since it is clear that the resulting expression will just involve T, μ, and various derivatives of $\ln(Z)$, confirming that the specific heat can be expressed purely in terms of the grand partition function $\mathcal{Z}$ and of the thermodynamic variables T and μ. With a program like Mathematica that can symbolically differentiate expressions, it would likely be quicker and more accurate just to let Mathematica work out the derivative. But if the tension of not carrying out the temperature derivative is too much for you, you can differentiate to find

$$C/k = 2T\frac{\partial\ln(\mathcal{Z})}{\partial T} + \mu\frac{\partial\ln(\mathcal{Z})}{\partial\mu} + T^2\frac{\partial^2\ln(\mathcal{Z})}{\partial T^2} + T\mu\frac{\partial^2\ln(\mathcal{Z})}{\partial\mu\,\partial T}. \tag{19}$$

We see that two first-order partial derivatives and two second-order partial derivatives (one mixed) of $\ln(\mathcal{Z})$ are needed to calculate the specific heat C.

Second approach: Alternatively, we can solve the problem by just working with the grand partition function

$$\mathcal{Z} = \sum_s e^{-\beta[E(s)-\mu N(s)]}. \tag{20}$$

Again the specific heat $C = dU/dT$ can be deduced if we have an expression for the average energy U, which we get from $\mathcal{Z}$ via

$$\overline{E} = \sum_s E(s)\, p(s) = \sum_s E(s)\, \frac{e^{-\beta[E(s)-\mu N(s)]}}{\mathcal{Z}} = \frac{1}{\mathcal{Z}} \sum_s E(s)\, e^{-\beta[E(s)-\mu N(s)]}. \tag{21}$$

There is nothing we can differentiate $\mathcal{Z}$ with respect to that will produce just a coefficient of $E(S)$ in the sum as desired but we can notice that

$$-\frac{\partial \mathcal{Z}}{\partial \beta} = \sum_s (E(s) - \mu N(s))\, e^{-\beta[E(s)-\mu N(s)]}. \tag{22}$$

and that

$$\frac{1}{\beta}\frac{\partial \mathcal{Z}}{\partial \mu} = \sum_s N(s)\, e^{-\beta[E(s)-\mu N(s)]}, \tag{23}$$

which therefore implies

$$\overline{E} = \frac{\mu}{\beta}\, \frac{\partial \ln(\mathcal{Z})}{\partial \mu} - \frac{\partial \ln(\mathcal{Z})}{\partial \beta} = kT^2 \frac{\partial \ln(\mathcal{Z})}{\partial T} + kT\mu\, \frac{\partial \ln(\mathcal{Z})}{\partial \mu}. \tag{24}$$

This last equation, which is exactly the quantity being differentiated in Eq. (18) above, solves the problem since we again have $\overline{E}$ in terms of T, μ, and derivatives of $\mathcal{Z}$, and differentiating both sides with respect to T gives C in the requested form.

One student started from $S = -(\partial\Phi/\partial T)_{V,\mu}$ and observed that since $dS = dQ/T = (CdT)/T$, $C = T(dS/dT)$ and used this to deduce C in terms of $\ln(\mathcal{Z})$. Does this lead to a correct answer?

(b) **(4 points)** Describe briefly how to construct an experimentally feasible reservoir, and explain how (at least in principle) the values of μ and T can be varied independently for your reservoir. Such a reservoir would then allow you to study the properties of some system as a function of μ and T.

Answer: This is a question of the sort that I (and Schroeder) should have discussed more often over the semester: how does one actually make contact experimentally with various abstract concepts like entropy, temperature, chemical potential, and reservoirs? You have seen how the heat capacity plays a central role in the subject of thermal physics, it is easily measured and can be compared straightforwardly with theoretical predictions.

This problem was open ended and I was looking for just a few ideas for you to get full credit. One idea was that the reservoir had to be "big" compared to the system of interest and almost no one in the class addressed this point. This requires estimating the number of molecules in the system (easily done if you know the chemical constitution and mass of the system) and the magnitude of its energy U (again easily done if one is close to room temperature and one can use equipartition). Then any reservoir you plan to build should be ten or one hundred times greater in the number of molecules and in the amount of energy available. This way, small amounts of energy or particles that transfer between the reservoir and system will not alter the properties of the reservoir

A second idea I looked for was some way to stabilize the temperature of the reservoir. This could be done in many ways but they all end up involving a thermometer of some kind to monitor the temperature of the reservoir (a second thermometer for the system would be a good idea also) and one or more sources of heat, say resistive wires glued to the outside of the system, or water carrying pipes that are thermally attached to the reservoir. One can then maintain the temperature of the reservoir with some feedback circuit that adds or extracts heat from the reservoir if the temperature on the thermometer drifts from the desired temperature. This is simple in concept but complicated in practice. For example, adding heat to a reservoir will cause the temperature to increase locally near the heat source, and then one has to wait many relaxation times for the temperature to become spatially uniform and time independent at its new value. For this reason, an experimentalists might want to add fans or some other mechanism to the reservoir, to spread the heat rapidly throughout the reservoir. Otherwise, the temperature could slowly drift from one value to another during an experiment.

A third idea, perhaps the most important that I looked for, was any understanding of how to vary the chemical potential μ of a system and to explain why it is possible to vary μ independently of T. There is only one system that we have discussed this semester for which the chemical potential was easily calculated, namely the chemical potential of an ideal gas, as written on page 2 of the exam:

$$\mu_{\text{gas}} = -kT \ln\left(\frac{V\,Z_{\text{int}}}{NV_Q}\right) \tag{25}$$

$$= -kT \ln\left(\frac{1}{P}\left[\frac{kTZ_{\text{int}}}{V_Q}\right]\right), \tag{26}$$

where I used the ideal gas law $PV = NkT$ to express V/N in terms of kT/P. This last expression shows that the chemical potential of an ideal gas depends in a specific quantitative way on the pressure P of the gas and on the temperature T, via the potentially complicated expression TZ_{int}/V_Q. Eq. (25) shows that, for fixed temperature T, we can vary μ independently of T by varying the pressure P of an ideal gas.

So one quick answer to this problem is to build a reservoir out of an ideal gas which has many more moles of molecules than the system of interest. The reservoir is attached to some mechanical mechanism, say a release valve and high pressure tank of gas, that allows the pressure P to be varied over some range. (This requires in turn some device for measuring pressure, a pressure gauge or manometer.) For any change in pressure P, the temperature T could be varied independently by adding or removing heat from the reservoir.

7. **(6 points)** A long vertical cylindrical tube contains a pure substance at temperature T in a gravitational field with constant gravitational acceleration g. Below a certain height z_0 in the column (as measured from the bottom of the column), the substance is found to be in a solid phase, while above that height, the substance is in a liquid phase. When the temperature of the entire column is decreased a little bit to a new value $T - \Delta T$, the solid-liquid interface is observed to move upwards a small amount to a new value $z_0 + \Delta z$. Neglecting the thermal expansion of the solid and liquid, derive and write down an expression for the mass density ρ_l of the liquid phase in terms of: the mass density ρ_s of the solid phase, the latent heat L per mass of melting, the gravitational acceleration g, the absolute temperature T, the temperature change ΔT, and the change in height Δz.

Answer:

$$\rho_l \approx \rho_s \left(1 - \frac{L\Delta T}{gT\Delta z}\right). \tag{27}$$

That this problem involves coexisting liquid and solid phases and the fact that a latent heat L is given should have suggested to you to use the Clausius-Clapeyron equation in the form

$$\frac{dP}{dT} = \frac{L}{T\Delta V}. \tag{28}$$

We are told that when the temperature of the entire tube is decreased by a small amount to the new value $T - \Delta T_0$ (which immediately implies that $\Delta T_0 > 0$ must be a positive quantity), the interface between the solid and liquid rises a small amount to the level $z_0 + \Delta z_0$ (which tells us that Δz_0 is also a positive quantity). I have added a subscript zero here to distinguish these specific changes in quantities from generic symbolic changes ΔT and Δz.

Now if the solid-liquid interface rises, the pressure at the location of the interface must decrease since there is now a reduced amount of fluid sitting above the interface; this was perhaps the hardest scientific insight to determine for this problem. (In the extreme case that the interface rises to the very top of the tube, the pressure on the interface will simply be atmospheric pressure.) The decrease in pressure is given by subtracting out the pressure due to a cylinder of liquid of height Δz_0 and of density ρ_l that no longer occurs above the interface:

$$\Delta P_0 = -\rho_l \, g \, \Delta z_0, \tag{29}$$

and this is a negative number since $\Delta z_0 > 0$. Note how only the mass density ρ_l of the fluid enters since it is the amount of fluid lying above the interface that determines the pressure at the interface; the amount of solid phase below the interface has no effect on the pressure at the interface.

We can now invoke the Clausius-Clapeyron equation, to express the fact that the two phases coexist at a new location $(T - \Delta T_0, P + \Delta P_0)$ on the solid-liquid phase line. For the left side of the equation, we have

$$\frac{dP}{dT} \approx \frac{\Delta P}{\Delta T} \approx \frac{-\rho_l \, g \, \Delta z_0}{-\Delta T_0} = \frac{\rho_l \, g \Delta z_0}{\Delta T_0}, \tag{30}$$

which is a *positive* slope. That the slope is positive is consistent with the fact that the liquid is floating above the solid in the column, which is equivalent to saying that the change in volume per mass across the liquid-solid phase line $\Delta V = V_l - V_s > 0$. (So this problem does not apply to water and ice near water's triple point, for which the solid is less dense than the liquid and $dP/dT < 0$.)

The right side of the Clausius-Clapeyron equation can be written in terms of the densities of the solid and liquid phases like this:

$$\frac{L}{(T - \Delta T_0)\, \Delta V} = \frac{L}{(T - \Delta T_0)\, (V_l - V_s)} = \frac{L}{T - \Delta T_0} \frac{1}{\rho_l^{-1} - \rho_s^{-1}}. \tag{31}$$

The volume difference ΔV has to be $\rho_l^{-1} - \rho_s^{-1}$ and not $\rho_s^{-1} - \rho_l^{-1}$ to obtain a positive right side, to match the positive left side.

Equating the right-most term of Eq. (30) to the right-most term of Eq. (31), and carrying out some simple algebra leads to the intended answer:

$$\rho_l \approx \rho_s \left(1 - \frac{L \Delta T}{g(T - \Delta T) \Delta z} \right). \tag{32}$$

If ΔT is sufficiently small compared to the temperature T, we can simplify this further to get

$$\rho_l \approx \rho_s \left(1 - \frac{L \Delta T}{g T \Delta z} \right). \tag{33}$$

The minus sign on the right side makes physical sense: the fluid floats on top of the solid so $\rho_l < \rho_s$ which requires the sign in front of the positive quantity $L\Delta T / gT\Delta z$ be a minus sign. We also see that $L\Delta T/gT\Delta z$ can not be too big in magnitude, otherwise ρ_l will be a non-physical negative number.

8. **(6 points)** Long after studying thermal physics, a student has forgotten a crucial detail of the Debye theory of a solid, and has replaced the Bose-Einstein distribution with a Fermi-Dirac distribution like this:

$$U = \frac{3\pi}{2} \int_0^{n_{\rm max}} \frac{hc_s}{2L} \frac{n^3}{e^{hc_s n/(2LkT)} + 1} \, dn, \qquad n_{\rm max} = \left(\frac{6N}{\pi} \right)^{1/3}, \tag{34}$$

where the only error is a "+1" instead of a "-1" in the denominator of the integrand. By investigating the low- and high-temperature regimes of this fermion version of Debye's theory, explain how this error leads to a prediction that is inconsistent with experiment.

Answer: The high-temperature regime is in error, predicting a zero heat capacity, instead of the equipartition result $C/(Nk) = 3$.

As you learned in class and from reading Section 7.5 on the Debye theory of solids, a first step in studying how the energy U of a system depends on temperature is to change variables in Eq. (34) by setting

$$x = \frac{hc_s}{2LkT}\, n \qquad \Rightarrow \qquad dn = \frac{2LkT}{hc_s}\, dx \quad \text{and} \quad n_{\max} \to T_D/T. \tag{35}$$

You could then show that the integral in Eq. (34) becomes

$$U = \frac{9NkT^4}{T_D^3} \int_0^{T_D/T} \frac{x^3}{e^x + 1}\, dx. \tag{36}$$

This is exactly like the integral we discussed for the Debye theory (see Eq. (7.112) on page 310 of Schroeder) except the that -1 in the denominator for bosons has become a +1 for fermions.

Low-temperature regime $T \ll T_D$: We can now use Eq. (36) to study the low-temperature and high-temperature regimes the fermion version of the Debye theory. The low-temperature regime involves looking at the behavior as T becomes small, in which case the upper bound T_D/T of the integral in Eq. (36) approaches infinity and the value of the integral approaches some fixed number. In this case, $U \propto T^4$ and the heat capacity $C = dU/dT \propto T^3$. So the functional form of the specific heat for low temperatures, T^3, remains the same as for the correct Debye theory. One minor difference is that the numerical coefficient will be different by the ratio of the integrals

$$\int_0^\infty \frac{x^3}{e^x + 1}\, dx \Big/ \int_0^\infty \frac{x^3}{e^x - 1} \approx 0.87, \tag{37}$$

(which you could not deduce during the exam, I used Mathematica's function `NIntegrate` to estimate numerically both integrals), which is a small quantitative change. So the low-temperature regime seems to be experimentally reasonable.

High-temperature regime $T \gg T_D$: In this regime, the integral's upper bound in Eq. (36) becomes small, $T_D/T \ll 1$. All values of x that appear in the Eq. (36) are then small, in which case, to lowest-order, we can approximate the denominator as follows

$$e^x + 1 \approx (1 + x) + 1 \approx 2. \tag{38}$$

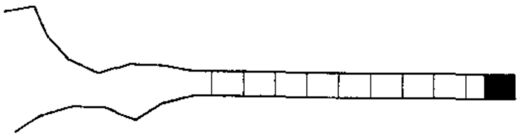
We thus have:

$$\int_0^{T_D/T} \frac{x^3}{e^x + 1}\, dx \approx \int_0^{T_D/T} \frac{x^3}{2}\, dx \approx \frac{1}{8} \left(\frac{T_D}{T} \right)^4. \tag{39}$$

Substituting this expression into Eq. (36), we see that the T^4 term cancels out and so the energy U is now independent of T. (In the Debye theory, the denominator instead becomes $e^x - 1 \approx (1+x) - 1 = x$, which causes $U \propto T$.) If $U \approx$ constant, then $C = dU/dT \approx 0$ at high temperatures, and this seriously disagrees with experiments since the experimental heat capacity approaches the equipartition result $C = 3Nk$ for sufficiently large temperatures. (You could also easily refine this calculation by using the approximation $x^3/(e^x+1) \approx x^3/(2+x) \approx (1/2)x^3(1-(1/2)x)$, which would give the leading two terms in approximating C at high temperatures, you reach the same conclusion that C now longer has the equipartition value $3Nk$.)

So using a fermion distribution in the Debye theory leads to an easily tested wrong prediction: the heat capacity decreases to zero for sufficiently large temperatures, instead of approaching the equipartition value $3Nk$.

9. A simple statistical physics model of the formation or unraveling of a long biomolecule like DNA as a function of temperature is a zipper



that has N links such that each link is closed with energy 0 or open with energy $\epsilon > 0$. The zipper can unzip only from one side (say from the left as shown above) and the nth link from the left can open only if all the links to the left of it $(1, 2, \ldots, n-1)$ are already open. The Nth link on the right is always closed.

(a) **(6 points)** By writing down an appropriate partition function for this zipper model, find an expression for the average number of open links $\overline{n}$.

Answer: When using a partition function to study some system, the first steps to take are to identify what are the distinct states of the system, what are the energies $E(s)$ of those states, and what are the degeneracies of the distinct states. For a zipper (biomolecule) with N links for which the Nth link is always closed, there are N distinct states: the state with $N-1$ links open and one link closed with energy $(N-1)\epsilon$, the state with $N-2$ links open and 2 links closed with energy $(N-2)\epsilon$, and so until you get to the fully closed state which has energy zero.

Because of the assumption that the *nth* link can open only if all the links to its left are already open, there is only way for $N-k$ links to be open and k links to be closed so the degeneracy of each energy state is 1. For many biomolecules like DNA, this assumption that the zipper can only open from the left is not accurate, for example DNA can open in multiple places simultaneously along its length, which is actually important for parallel processing of transcription sites (copying DNA regions into messenger RNA in preparation for creating a protein from a gene).

The partition function Z for the zipper is then

$$Z = \sum_s e^{-\beta E(s)} = 1 + e^{-\beta\epsilon} + e^{-\beta[2\epsilon]} + \ldots + e^{-\beta[(N-1)\epsilon]} = \frac{1 - e^{-\beta N\epsilon}}{1 - e^{-\beta\epsilon}}, \tag{40}$$

where I used the identity Eq. (12) given on page two of the exam, that sums the first $N-1$ terms of a geometric series. Since the energy of the zipper with n links open is simply $n\epsilon$, we can deduce the average number of links $\overline{n}$ from the average energy $\overline{E}$ as:

$$\overline{n} = \frac{\overline{E}}{\epsilon} = -\frac{1}{\epsilon}\frac{\partial \ln(Z)}{\partial\beta}. \tag{41}$$

Carrying out the derivative and simplifying gives the answer to part (a):

$$\overline{n} = \frac{1}{e^{\beta\epsilon} - 1} - \frac{N}{e^{N\beta\epsilon} - 1}. \tag{42}$$

Note: some students incorrectly assumed that this problem was somehow related to occupation of single-particle energy states, like that for Fermi-Dirac particles, since the links could be either open or closed. They then wrote $Z_N = Z_1^N$ and calculated Z_1 for a single particle occupying a link with energy 0 or ϵ. This approach does not work here since the links can only open in succession from the left. However, if each link could open or close independently of the other links, this problem would indeed reduce to a Fermi-Dirac problem of independent particles.

You can learn more about this zipper problem from the brief but readable paper "Phase Transition of a Molecular Zipper" by Charles Kittel, American Journal of Physics Volume 37, Number 9, pages 917-920. Experiments on synthetic double-stranded DNA segments show a surprising result:

the average number of open links $\overline{n}$ rises from 0 to $N/2$ over a very narrow range of temperature, i.e., the unfolding of a real molecular zipper acts like a phase transition where an abrupt change in the structure of the molecule occurs as T is varied. Making only a small change to this exam problem, namely let the degeneracy g of an open link be much greater than 1 (there is a lot more space for the atoms of an open link to move around in) and independent of the neighboring links. Eq. (42) becomes instead

$$\overline{n} = \frac{1}{(1/g)e^{\beta\epsilon} - 1} - \frac{N}{(1/g)^N e^{N\beta\epsilon} - 1}. \tag{43}$$

A numerical study of Eq. (43) shows that $\overline{n}$ does indeed undergo a transition over a narrow range of T from 1 to $N/2$ as T is varied. The asymmetric zipper problem turns out to be unexpectedly interesting since it is a one-dimensional problem that undergoes a phase transition for g sufficiently large.

(b) **(4 points)** Show that $\overline{n}$ becomes independent of N in the low-temperature limit and discuss the scientific meaning of this result.

Answer: In the limit of low temperature $T \to 0$, the parameter $\beta \to \infty$ becomes large and $e^{\beta\epsilon}$ becomes very large. In the denominators of Eq. (42), we can then neglect the 1 compared to the exponentials and find

$$\begin{aligned}\overline{n} &= \frac{1}{e^{\beta\epsilon} - 1} - \frac{N}{e^{N\beta\epsilon} - 1} && (44)\\ &\approx e^{-\beta\epsilon} - N e^{-N\beta\epsilon} && (45)\\ &\approx e^{-\beta\epsilon}. && (46)\end{aligned}$$

This last line follows for two reasons. First, in the term $Ne^{-N\beta\epsilon}$, the N coefficient is a large factor multiplying the reciprocal of a very large factor and so can be ignored, i.e.,

$$N\, e^{-\beta N\epsilon} \approx e^{-\beta N\epsilon} \qquad \text{for } N \gg 1. \tag{47}$$

Second, given that $\beta \gg 1/\epsilon$ implies that $e^{-\beta\epsilon} \ll 1$ is a very tiny number, then $e^{-N\beta\epsilon} = \left(e^{-\beta\epsilon}\right)^N \ll e^{-\beta\epsilon}$. So the second term in line (45) is negligible compared to the first and we have

$$\overline{n} \approx e^{-\beta\epsilon} \qquad \text{when } kT \ll \epsilon, \tag{48}$$

so the average number of open links is indeed independent of N, the total number of links.

This result is reasonable: at sufficiently low temperatures, the lowest energy state of the zipper will be favored and this is the state with all links closed, for which the energy does not depend on the length of the zipper. But the analytical result Eq. (44) is not obvious in that it tells us that the average number of links decays as $e^{-c/T}$ with decreasing temperature. This is the same non-analytic function that shows up many times in thermal physics: this is neither exponential decay nor polynomial decay, but rapid decay according to a function that does not have a Taylor series about its limit $T = 0$. (If you know some complex analysis, this function has an essential singularity at $T = 0$.)

What is the high-temperature limit for $\overline{n}$? From a question on the second midterm, we know that if a system has a finite number of energy states, then, for sufficiently high temperatures all states become equally likely and so we expect $\overline{n} \to N/2$ as $T \to \infty$. This is correct but I'll let you figure out how to deduce this directly from Eq. (42) when $\beta\epsilon \ll 1$. A hint is to use the approximation $e^x \approx 1 + x + \frac{1}{2}x^2$ to second-order accuracy.

10. **(8 points)** Experimentalists are able to create and study the properties of two-dimensional electron gases that float in a horizontal layer just above a liquid He surface. Consider such a gas of N electrons

at absolute zero that occupies a square planar region of area $A = L^2$. What is the quantum degeneracy pressure P (force per unit length) in terms of the gas's energy density U/A?

Note: You can start with the following expression for the total energy U of the electrons

$$U = 2 \iint \epsilon(n_x, n_y)\, dn_x\, dn_y, \tag{49}$$

and change to polar coordinates for which $n = \sqrt{n_x^2 + n_y^2}$ and $dn_x\, dn_y = n\, dn\, d\theta$. Also observe that $\epsilon_F = h^2 n_{\max}^2/(8mL^2)$ and $N = 2 \times$ (area of 1/4 circle of radius $n_{\max}$ in $\mathbf{n}$ space).

Answer: $P = U/A$

For a two-dimensional system in which areas rather than volumes vary, the thermodynamic identity $dF = -S\, dT - P\, dV + \mu\, dN$ becomes

$$dF = -S\, dT - P\, dA + \mu\, dN, \tag{50}$$

so that

$$P = -\left(\frac{\partial F}{\partial A}\right)_{T,N}, \tag{51}$$

where now the pressure P has units of force per length rather than force per area. (Think of a two-dimensional piston on a surface so that compressing a 2D gas involves sliding a linear boundary inwards, rather than the 2D area of a cylindrical piston.) At absolute zero $T = 0$, the free energy $F = U - TS = U$ is the same as the energy of the system so it suffices to calculate the total energy then differentiate with respect to area A. Following the suggestions given in the problem, we have

$$\begin{aligned} U &= 2 \iint \epsilon(n_x, n_y)\, dn_x\, dn_y & (52)\\ &= 2 \int_0^{\pi/2} \int_0^{n_{\max}} \frac{h^2 n^2}{8mL^2} \times n\, dn\, d\theta & (53)\\ &= \frac{\pi h^2}{32mL^2} n_{\max}^4. & (54) \end{aligned}$$

The maximum radius $n_{\max}$ in number space (n_x, n_y) is determined by requiring that the total number of energy states filled with electrons (two electrons per state, with up and down spins) is the number of particles N so

$$2 \times \left(\frac{1}{4} \times \pi n_{\max}^2\right) = N \quad \Rightarrow \quad n_{\max} = \left(\frac{2N}{\pi}\right)^{1/2}. \tag{55}$$

Combining Eq. (55) with Eq. (54) gives the energy in terms of N and A:

$$U = \frac{\pi h^2}{32mL^2} n_{\max}^4 = \frac{\pi h^2}{32mL^2} \times \left(\frac{2N}{\pi}\right)^2 = \frac{h^2 N^2}{8\pi m} \frac{1}{A}, \tag{56}$$

where I used the fact that $L^2 = A$ since we are considering a square domain. The answer $P = U/A$ then follows directly from Eq. (51), by differentiating Eq. (56) with respect to A with N fixed.

One lesson of this problem and of Chapter 7 in Schroeder is that the pressure for non-interacting particles is usually some constant of order one times the energy density of the system, e.g., this holds also for a gas of photons and of diatomic molecules.

Multiple Choice Questions (3 points each)

Circle the letter that best answers each of the following questions.

1. A system in thermodynamic equilibrium is quasistatically and adiabatically changed to some new equilibrium state. The thermodynamic quantity associated with this system that remains constant during this change is

   (a) energy U.
   (b) pressure P.
   (c) volume V.
   (d) entropy S.
   (e) chemical potential μ.

   Answer: (d) An adiabatic process is one in which heat does not flow into or out of the system. This implies that the entropy $S = Q/T$ of the system can not change, but all the other properties listed can change. For example, the chemical potential of an ideal depends on the pressure or density of the gas and so can in fact change during some process, even if the number of particles is conserved.

2. An object with constant heat capacity C_P and temperature T_1 is brought in contact with a thermal reservoir with constant temperature $T_2 \neq T_1$ until the object reaches equilibrium. The total change in entropy (of the object and reservoir) is then

   (a) $C_P \dfrac{T_2 - T_1}{T_2}$.
   (b) $C_P \left[\dfrac{T_2 - T_1}{T_1} - \dfrac{T_2 - T_1}{T_2} \right]$.
   (c) $C_P \ln\left(\dfrac{T_2}{T_1}\right)$.
   (d) $C_P \left[\ln\left(\dfrac{T_2}{T_1}\right) + 1 - \dfrac{T_1}{T_2} \right]$.
   (e) $C_P \left[\ln\left(\dfrac{T_2}{T_1}\right) - 1 + \dfrac{T_1}{T_2} \right]$.

   Answer: (e) Since entropy is an additive quantity for weakly interacting systems, the total entropy change is the sum of the change in entropy of the object and the change in entropy of the reservoir. The change in entropy of the object is given by:

$$\Delta S_{\text{object}} = \int_{T_1}^{T_2} \frac{C_P}{T}\, dT = C_P \ln\left(\frac{T_2}{T_1}\right). \tag{57}$$

   The entropy change in the reservoir is given by Q/T_2 where Q is the amount of heat transferred to the reservoir. Since an amount of heat

$$\int_{T_1}^{T_2} C_P(T)\, dT = C_P \left(T_2 - T_1\right), \tag{58}$$

   is needed to change the temperature of the object from T_1 to T_2, the negative of this amount is the heat that flows into the reservoir. We thus have

$$\Delta S_{\text{total}} = C_P \ln\left(\frac{T_2}{T_1}\right) + \frac{-C_P \left(T_2 - T_1\right)}{T_2}, \tag{59}$$

   which is answer (e).

3. If x is a small quantity so that $|x| \ll 1$, then the expression

$$\frac{1}{1+ax+bx^2} \tag{60}$$

can be approximated to second-order accuracy by the expression $1 + cx + dx^2$ provided that the coefficient d is

(a) b.

(b) $-b$.

(c) $-b-a^2$.

(d) $-b+a^2$.

(e) $-b+a^2+2ab$.

Answer: (d) If we let $\epsilon = ax+bx^2$ denote the small quantity being added to one in the denominator, we can use the first two terms of a geometric series in ϵ to find

$$\begin{aligned} \frac{1}{1+ax+bx^2} &= \frac{1}{1+\epsilon} && (61)\\ &\approx 1-\epsilon+\epsilon^2+\ldots && (62)\\ &= 1-\left(ax+bx^2\right)+\left(ax+bx^2\right)^2 && (63)\\ &\approx 1-ax-bx^2+a^2x^2+2abx^3+\ldots && (64)\\ &= 1-ax+(a^2-b)x^2+O(x^3). && (65)\end{aligned}$$

4. The multiplicity Ω of a one-dimensional ideal gas of N identical adsorbed particles of mass m moving freely about on a long carbon nanotube of length L is given by which of the following expressions:

(a) $\dfrac{L}{N!}\dfrac{A_1(\sqrt{2mU})}{h}$.

(b) $\dfrac{L^N}{N!}\dfrac{\left(A_1(\sqrt{2mU})\right)^N}{h^N}$.

(c) $\dfrac{L^N}{N!}\dfrac{A_{2N}(\sqrt{2mU})}{h^{2N}}$.

(d) $\dfrac{L^N}{N!}\dfrac{A_N(\sqrt{2mU})}{h^N}$

Note: The notation $A_d(r)$ denotes the surface area of a d-dimensional sphere of radius r.

Answer: (d) In Chapter 2, we saw that the multiplicity Ω for an ideal gas consisting of N non-interacting molecules in a volume V was proportional to the number of different ways that the location $\mathbf{x}$ of each molecule's center of mass could be varied, times the number of ways that the momentum $\mathbf{p}$ of each molecule's center of mass could be varied.

For a one-dimensional "volume" of length L, a particular molecule's location (given say by the values of a coordinate x along the length of the nanotube) can be anywhere inside that volume and so is proportional to L. For a gas of N independent molecules, each molecule's position can vary independently of the positions of the other molecules so $\Omega \propto L^N$ which rules out answer (a). The number of ways that the N momenta $\mathbf{p}_i = p_i\hat{\mathbf{x}}$ of all the molecules can be varied involves the number of ways that that the p_i can be varied independently when they are constrained by the conservation of total energy $\sum_i p_i^2/(2m) = U =$ constant or

$$p_1^2+p_2^2+\ldots+p_N^2 = 2mU. \tag{66}$$

The set of N points $(p_1, \ldots, p_N)$ that satisfy this equation is the set of points on the surface of a N-dimensional sphere of radius $\sqrt{2mU}$ and so the number of ways that the momenta coordinates can vary is proportional to $A_N(\sqrt{2mU})$. Thus $\Omega \propto L^N A_N(\sqrt{2mU})$ and the answer is (d). (The answer (b) is not correct since the momenta do not vary independently of one other, they are linked together by energy conservation.) Since the molecules are assumed to be identical, a $1/N!$ factor needs to be included in Ω since interchanging any two particles (which means exchanging their position *and* momentum vectors) yields the same state. The $1/h^N$ factor is needed to eliminate the proportionality and count the actual number of available states; the uncertainty principle $\Delta x \, \Delta p \geq h$ implies that, for each molecule, the two-dimensional space of positions x and momenta p is divided into cells of size $\Delta x \, \Delta p \approx h$.

Two related questions that I thought of asking on this exam:

(a) What is the partition function Z_N for N identical non-interacting monoatomic atoms that move freely along a one-dimensional nanotube?

This problem is actually easier than Multiple Choice 4 because energy is not conserved (the system is in contact with a heat reservoir with which it can exchange energy). For identical non-interacting particles, $Z_N = Z_1^N/N!$ where

$$Z_1 = \int_{-\infty}^{\infty} \int_0^L e^{-p^2/(2mkT)} \frac{dx \, dp}{h} = \frac{L \sqrt{2\pi mkT}}{h} = \frac{L}{\lambda_Q}. \tag{67}$$

(b) What is the multiplicity Ω of N identical non-interacting atoms that move about on the surface of a sphere of radius R? Answer: $\Omega \propto A_2(R)^N A_{2N}(\sqrt{2mU})$. Such particles are described by two-dimensional momentum vectors, and so $2N$ is the dimensionality of the momentum hypersphere.

5. A ferromagnet at absolute zero has all of its $N \gg 1$ spin-1/2 magnetic moments aligned in parallel (even in the absence of an external magnetic field). The ferromagnet is then heated until its temperature exceeds its Curie temperature, at which point the magnetization is zero. The change in entropy ΔS of the ferromagnet is then approximately given by

(a) 0

(b) $2Nk$

(c) $2^N k$

(d) $k\ln(2)$

(e) $Nk\ln(2)$

Answer: (e) The entropy of the ferromagnet at absolute zero when all of its spins are aligned is $S = k \ln \Omega = k \ln(2)$. The multiplicity $\Omega = 2$ since, in the absence of an external magnetic field, the spins in a ferromagnet can all be parallel in two ways, all pointing along some given direction or all pointing in the opposite of some given direction.

The problem states that the magnetization of the magnet vanishes above the Curie temperature which means that there are equal numbers of up and down spins. (More accurately, on average there are equal numbers of up and down spins since, at high temperature, each spin will be switching from up to down randomly, independently of what the other spins are doing.) The multiplicity of this state is something you learned to calculate in the first third of the course (Chapter 2), namely the number of different ways one can choose $N_{\text{up}} = N/2$ up spins out of a total of N spins. The high-temperature zero-magnetization multiplicity can then be approximated as

$$\Omega = \binom{N}{N_{\text{up}}} \tag{68}$$

$$= \binom{N}{N/2} \tag{69}$$

$$= \frac{N!}{(N/2)!\,(N/2)!} \tag{70}$$

$$\approx \frac{\sqrt{2\pi N}\,(N/e)^N}{\left(\sqrt{2\pi(N/2)}\,[(N/2)/e]^{N/2}\right)^2} \tag{71}$$

$$\approx \left(\frac{\sqrt{2\pi N}}{\pi N}\right)\frac{N^N}{(N/2)^N} \tag{72}$$

$$\approx 2^N. \tag{73}$$

Here I first used Stirling's approximation for $N!$ and for $(N/2)!$, and then I dropped the factor in parentheses in Eq. (72) since it is "only" a big number that multiplies a very big number 2^N (if we assume that N is of order Avogadro's number). The corresponding entropy $S = k\ln\Omega = k\ln(2^N) = Nk\ln(2)$ so we finally find:

$$\Delta S \approx Nk\ln(2) - k\ln(2) \approx Nk\ln(2), \tag{74}$$

Note that this result is not exact, we did drop a multiplicative factor that was not important (line Eq. (72)), and we approximated $N-1$ as N. Eq. (74) based on the change in multiplicity could be tested experimentally via calorimetry, by estimating the entropy change $\Delta S = \int_0^{T_C} C_P(T)/T\,dT$ associated with heat capacity $C_P(T)$ of the ferromagnet.

6. The physicist Freeman Dyson has speculated about advanced civilizations that would harness the entire power of a star by surrounding it with an immense opaque shell that would trap all of the star's energy. Assume in the future that the human race disassembles the planet Venus (for which no one ever did find a good use) and uses its material to create a thin shell of thickness 100 meters that entirely surrounds the Sun, with a radius that is 1.1 times the radius of the Sun. After the Sun with its shell has reached a steady state, the difference ΔT_{S} between the the Sun's new surface temperature and previous surface temperature, and the difference ΔT_{E} between the Earth's new steady-state temperature and its previous temperature will satisfy

   (a) $\Delta T_{\text{S}} = 0$ and $\Delta T_{\text{E}} = 0$.
   (b) $\Delta T_{\text{S}} = 0$ and $\Delta T_{\text{E}} > 0$.
   (c) $\Delta T_{\text{S}} = 0$ and $\Delta T_{\text{E}} < 0$.
   (d) $\Delta T_{\text{S}} > 0$ and $\Delta T_{\text{E}} = 0$.
   (e) $\Delta T_{\text{S}} > 0$ and $\Delta T_{\text{E}} > 0$.
   (f) $\Delta T_{\text{S}} > 0$ and $\Delta T_{\text{E}} < 0$.

   Note: For the purpose of the problem, assume that difference in radius of the shell and Sun can be ignored, and that the Sun and shell are perfect blackbody thermal emitters. Through its fusion reactions, the Sun emits the same constant total power, whether or not it is covered with a shell.

   Answer: (d) This problem was a variation of the homework problem you solved recently, in which you calculated how an infrared opaque atmosphere caused the Earth's surface to increase in temperature beyond what an energy balance argument (power received from Sun versus power radiated into space) predicts.

   Here the insight is that the Sun, through its nuclear reactions, radiates a constant amount of power out into space. So if we surround the Sun with a shell and assume everything is in equilibrium so the temperature of the shell and the Sun's temperature have stopped changing, the shell has to transmit out into space the same amount of power as the Sun without the shell (otherwise the shell's temperature would continue to change as it absorbed more power from the Sun than it radiated out into space).

This observation implies two things: that the shell has to have the same temperature as the original surface temperature $T = 5,800\,K$ of the Sun (so that the total power emitted $4\pi R^2\,\sigma T^4$ out into space is unchanged) *and* that the temperature of the Earth will not change, $\Delta T_E = 0$, since it will be receiving the same amount of power from the shell as from the Sun. In fact, someone on Earth will not be able to tell that the Sun has been covered by a shell since the shell will be emitting exactly the same blackbody spectrum and power as the Sun itself. (However, a spectroscope would reveal that the Sun is covered by a shell since all kinds of spectral lines coming from partially excited atoms in the Sun's corona will not longer be present.)

Since the inner and outer surfaces of the shell are both blackbody emitters at the same temperature, the shell not only emits power out into space but also emits an equal amount of power back towards the Sun's surface. This implies that the Sun's surface will increase in temperature so $\Delta T_S > 0$ (so (d) is indeed the answer to this problem). In fact, the Sun's surface temperature has to increase just enough to provide the power transmitted out into space by the shell and the power transmitted by the shell back toward the Sun, which is twice the original power radiated by the Sun. Since the power radiated goes as T^4, to double the power radiated, the Sun's surface temperature would have to increase to $2^{1/4} \times 5,800 \approx 1.19 \times 5,800 = 6,900\,K$.

A few more comments:

(a) As stated, this problem makes no sense. All known materials vaporize at temperatures of 6,000 K, so an advanced civilization would not want to let a shell so close to the Sun reach thermodynamic equilibrium or, more obviously, would want to build the shell further from the Sun.

(b) It was important for this problem to assume that the shell had about the same radius as the Sun. If the shell were considerably bigger than the Sun, the fixed power emitted $4\pi R_{\text{shell}}^2\,\sigma T_{\text{shell}}^4$ would now correspond to a lower shell temperature (bigger R means smaller T for a fixed luminosity) and then the temperature of the Earth would decrease. I'll let you play with the numbers, to see how big the shell would have to be for its surface temperature to be a comfortable 300 K, at which point humans could live comfortably on the enormous interior surface (and one could rotate the entire shell so that people would feel an effective gravity toward the inside of the shell). I'll also let you play with the numbers to see if there is enough matter in our solar system to build such a large shell. (Venus in facts contains just enough matter to build a 100 m thick shell of radius $1.2R_{\text{Sun}}$.)

(c) You can learn more about Dyson spheres from the Wikipedia article "Dyson sphere". If you like science fiction, you might enjoy reading a 1970 novel by Larry Niven called "Ringworld" which concerns the discovery and exploration of a huge ring encircling a remote star, whose purpose is to trap some (but not all) of the energy of the star and to provide a huge amount of living space.