Physics 176 Final Exam: Solutions

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The following answers are much more detailed and pedagogical than what was needed to get full credit for any given problem. My hope is that the answers will be insightful, help you to solve related problems, and perhaps help you to appreciate some of the thermal physics.

Problems That Require Writing

Please write your answers to the following problems on extra blank sheets of paper. Also 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. **(10 points)** Sketch qualitatively correct graphs of the Gibbs free energy $G = U - TS + PV$ versus temperature T for the three phases of water (ice, water, and steam) at atmospheric pressure. You should draw your three graphs on the *same* set of axes so that you can see how they imply which phase is stable at a given temperature. Also make sure to indicate where on your temperature axis $T = 0^\circ$ C and $T = 100^\circ$ C.

   Answer: This was Problem 5.30 on page 172 of Schroeder and should have been straightforward to solve if you had read Section 5.3 and had thought about the homework problems related to this section.

   Two important insights from pages 170-171 were that the qualitative behavior of the Gibbs free energy $G(T, P, N)$ as a function of temperature T or of pressure P could be understood from the relations

$$\left(\frac{\partial G}{\partial P}\right)_{T,N} = V, \tag{1}$$

   and

$$\left(\frac{\partial G}{\partial T}\right)_{P,N} = -S, \tag{2}$$

   which both follow from the thermodynamic identity for G:

$$dG = -SdT + VdP + \sum_i \mu_i dN_i. \tag{3}$$

   This identity in turn could be obtained from the given definition $G = U - TS + PV$ and the thermodynamic identity $dU = TdS - PdV$:

$$\begin{aligned} dG &= d(U - TS + PV) & (4)\\ &= dU - SdT - TdS + VdP + PdV & (5)\\ &= (TdS - PdV) - SdT - TdS + VdP + PdV. & (6) \end{aligned}$$

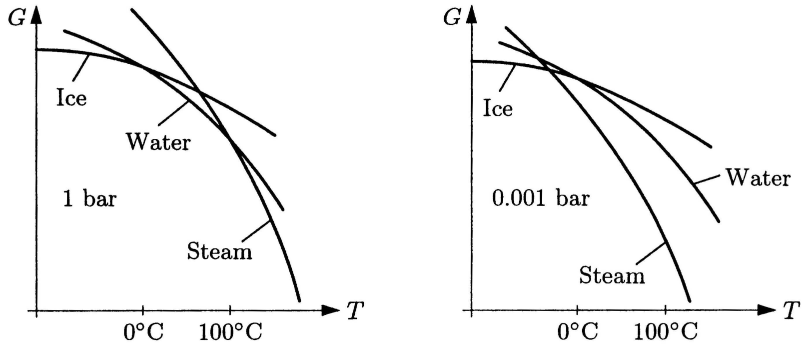
   Since you are being asked to plot G versus T for a fixed pressure of one atmosphere (and for a fixed number of particles N), Eq. (2) is the desired equation to get some insight. This equation implies the following, if one also uses some background knowledge that entropy generally increases with temperature, and also increases as phases change from solid to liquid to gas:

   (a) the slope of $G(T)$ for fixed pressure is always negative, i.e., $G(T)$ is a decreasing function of T.

   (b) the slope of $G(T)$ becomes more negative with increasing T since, generally, the entropy of a solid, a liquid, or a gas increases with temperature T. Thus not only does G decrease with increasing T, it has to decrease faster than a straight line and so have some curvature downward.

(c) finally, since generally $S_{\text{solid}} < S_{\text{liquid}} < S_{\text{gas}}$ for three different phases of the same substance, the slopes of the corresponding $G(T)$ curves must increase in steepness in going from solid to liquid to gas for a given temperature.

If we combined these observations with the fact that, for any given pressure, temperature, and number of particles the observed (stable) phase must have a lower Gibbs free energy than the unobserved (unstable) phases, one ends up with a qualitative figure like the following panel on the left (which I took from Schroeder's answer manual for the text):



The panel on the right is the similar diagram one would get for a constant pressure of 0.001 bar, which is below water's triple point in which case the liquid phase is not stable for any temperature value; see the water phase diagram, Figure 5.11, on page 167 of Schroeder, which shows that water's triple point occurs for $P \approx 0.006\,\text{bar}$.

Note that there is no discontinuous jump in the value of the Gibbs free energy G at the phase transitions at $T = 0^\circ$ C and at $T = 100^\circ$ C, although the slope dG/dT does jump discontinuously since one is switching to a different G-curve as the phase transition occurs. In contrast, recall from Problem 3.29 on page 113 of Schroeder how the entropy $S(T)$ increases discontinuously via a finite vertical jump as ice melts to water or water vaporizes into steam. This situation arises because one is adding latent heat to some phase (say ice melting to water) without changing the temperature, so $\Delta S = Q/T$ increases steadily with increasing Q, i.e., $S(T)$ increases vertically and so discontinuously during a phase transition. Once the initial phase is completely converted to the new phase, the entropy starts to increase monotonically again with increasing temperature.

There is a major qualification to this discussion: some phase transitions do not involve a finite jump in the entropy as some thermodynamic parameter is varied, instead the entropy varies continuously and its slope changes discontinuously at the transition (and then the Gibbs free energy would have a continuous first but discontinuous second derivative with respect to T at the phase transition). A transition that involves a latent heat and a finite jump in entropy (like the melting of ice into water) is called "first-order phase transition" while a transition for which the entropy varies continuously is called a "higher-order phase transition" with the order depending on how many derivatives of G are continuous at the transition. An example of a second-order phase transition would be the transition of a ferromagnet to an unmagnetized piece of iron as magnet's temperature is raised above a critical temperature $T_c \approx 1043\,\text{K}$ known as the Curie temperature; there is no latent heat during this phase transition.

A huge amount of interesting theory and experimental work was discovered in the context of understanding second-order phase transitions, try googling "critical phenomena" to get a sense of how big and influential this subject is. In particular, many features of second-order transitions have remarkable "universal" properties in that the properties do not depend on precise chemical or quantum details of the material, but only on the dimensionality of the medium (say 2D vs 3D) and on the symmetry of how the components are arranged inside the medium (for a 2D medium, a square lattice of atoms would have different critical properties than an hexagonal lattice of the same atoms).

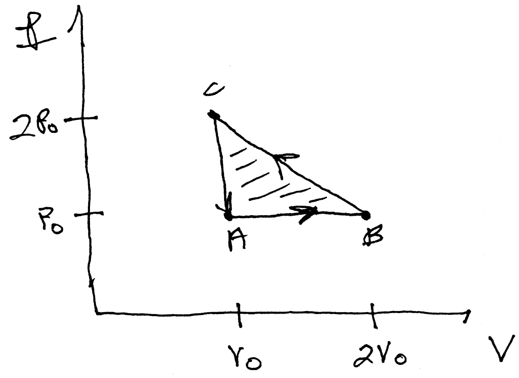
2. **(20 points)** Consider the following 3-step cyclic process $A \to B \to C \to A$ in the volume-pressure plane that characterizes an ideal monoatomic gas: the gas starts at point $A = (V_0, P_0)$ with initial temperature T_0, initial pressure P_0 and initial volume V_0. The gas then expands isobarically to point $B = (2V_0, P_0)$, is then compressed by following a straight line segment from point B to the point $C = (V_0, 2P_0)$, and finally the gas is brought back to the the point A by an isochoric process. After this cycle is carried out once, determine

   (a) the total change in energy ΔU of the gas;
   (b) the total heat Q added to the gas;
   (c) the total work W done on the gas;
   (d) the total change in temperature ΔT of the gas;
   (e) the total change in entropy ΔS of the gas.

   Assume that each step is carried out quasistatically (the gas and environment are always in thermodynamic equilibrium).

   Answer:

$$\Delta U = 0, \qquad Q = -(1/2)P_0V_0, \qquad W = (1/2)P_0V_0, \qquad \Delta T = 0, \qquad \Delta S_{\text{gas}} = 0. \tag{7}$$



With a little thinking before starting to calculate, one can find all the answers fairly quickly without computing the values of ΔU, W, and Q for each of the three steps:

(a) The internal energy[1] U of an ideal monoatomic gas is given by the equipartition theorem result $U = Nf(kT/2) = (3/2)NkT = (3/2)PV$ where I used the equation of state $PV = NkT$ for an ideal gas and the fact that the number of degrees of freedom $f = 3$ for an atom that has no internal structure that can rotate or vibrate. Expressing $U = (3/2)PV$ in terms of PV provides a useful way to calculate changes of energy between any two points in the volume-pressure parameter plane of an idea gas since

$$\Delta U = \frac{3}{2}\Delta(PV) = \frac{3}{2}\left(P_fV_f - P_iV_i\right), \tag{8}$$

where the subscripts f and i mean the "final" and "initial" points of some process of interest. Eq. (8) immediately implies that the energy change for any cyclic process that ends up at the same starting point must be zero. Noting that $U = (3/2)NkT$ implies

$$\Delta U = \frac{3}{2}Nk\,\Delta T, \tag{9}$$

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[1] Recall that U denotes the internal energy that can respond to heat and work, so does not include energy associated with the rest mass of particles or of electric and magnetic fields.

and so the temperature change caused by following any cycle back to some starting point must also be zero, $\Delta T = 0$.

More generally, since $1/T = (dS/dU)_{V,N}$ and since S and U are state variables, T must be a state variable and so must have a unique value at each point of an equilibrium system in the $V - P$ parameter plane, not just for a gas, and even if equipartition does not hold.

(b) After calculating the total energy change ΔU, the next easiest quantity to calculate is the work W done on the gas since we have the formula:

$$W = -\int_{V_i}^{V_f} P(V)\, dV, \tag{10}$$

which is useful if we know the pressure as a function of volume. For a cyclic process, Eq. (10) tells us that the total work done on the gas during some closed cycle is the area enclosed by the path in the PV plane that defines a cycle. The work is positive if the higher part of the cycle corresponds to a compression, negative otherwise. The work done during this three-step cycle is thus the positive area of the triangle in the figure

$$W = \frac{1}{2} P_0 V_0. \tag{11}$$

(c) After one has calculated ΔU and W, the heat transfer to the gas can be computed from conservation of energy:

$$Q = \Delta U - W = -W = -\frac{1}{2} P_0 V_0. \tag{12}$$

A negative value for Q means that heat is transferred from the gas to something in the environment, which in turn implies that at least once during the cycle, an object colder than the gas (although not necessarily colder than the starting temperature T_0) was brought in contact with the gas to extract the heat. When during the cycle this occurred requires finding the details for each step, which is interesting but again not necessary for this particular problem.

(d) We already determined that there is no change in temperature, $\Delta T = 0$, if there is no change in energy, $\Delta U = 0$, which is always the case for a cyclic process that ends up at the starting point.

(e) An important insight about thermodynamic variables like the energy U and entropy S is that these are so-called "state variables" that depend only on the state of the thermodynamic system (values of thermodynamic parameters like V, P, T, or μ) but not on how one arrived at that state. More precisely, some thermodynamic quantity is a state variable if its value does not depend on the path $P(V)$ in the PV parameter plane (or some other parameter space) that "brought" the system from some other set of conditions to the existing conditions.

In contrast, the heat Q added to a gas or the work W done on a gas are not state variables, their values can depend on the path $P(T)$ traced in the PT plane.

That the entropy S is a state variable was never clearly discussed in Schroeder (a minor but unfortunate weakness of this book) but should have been clear to you from looking at the Sackur-Tetrode equation for a monoatomic gas:

$$S(U,V,N) = Nk\left[\frac{5}{2} + \ln\left(\frac{V}{N}\left(\frac{4\pi m U}{3Nh^2}\right)^{3/2}\right)\right], \tag{13}$$

which depends only on the current values of the thermodynamic variables U, V, and N, not on the history of how one arrived at this state.

Given that S is a state variable, there is no calculation to make: if after a cycle, we end up with the same thermodynamic values, the entropy of the system must be the same and so $\Delta S = 0$.

Some students made an incorrect statement, that the entropy change would be the total heat Q added to the gas divided by the initial temperature T_0:

$$\Delta S = \frac{Q}{T_0} = -\frac{1}{2}\frac{P_0 V_0}{T_0}. \qquad \text{(this is wrong).} \tag{14}$$

One reason why this cannot be correct is that the gas does not have a constant temperature during the cycle, none of the three steps is isothermal.

What if I had asked you to determine in addition the *total* change of entropy during this cycle, arising from the gas and environment? This would reduce to calculating the change of entropy of the environment since $\Delta S_{\rm gas} = 0$ for any cycle. But there is not enough information given in the problem to compute the entropy change to the environment, we would have to know whether various steps of the cycle were carried out reversibly or not and, if not, we would have to know some details of how heat was added or removed from the gas.

For example, one way to add or withdraw heat from the gas would be to put the gas in contact with a large constant temperature reservoir that has some arbitrary temperature T_R, in which case the entropy change of the environment would be $-Q_s/T_R$ where Q_s would be the heat that flows from the reservoir to the gas (and Q_s itself could be a negative quantity). Without specifying the value of T_R, you can't calculate the entropy change. Alternatively, you could add or withdraw heat from the gas by putting some finite size object with initial temperature T_o in contact with the gas. You would then have to know the heat capacity $C(T)$ as a function of temperature T for the finite object to compute its change in entropy.

So you can see why I didn't ask you to compute the total change in entropy (system plus world), the problem would have become much more detailed.

3. **(10 points)** Estimate to the nearest power of ten how many candy bars you would have to eat during a 24-hour period to supply the energy that you lose to the surrounding environment via blackbody radiation from your skin. To simplify this problem, assume that during this 24-hour period you are floating in outer space without clothes so that no heat is returned to your body by clothes, reflection, or by surrounding air, and assume that your skin is a perfect blackbody emitter (emissivity $e = 1$).

Note: a typical candy bar provides about 250 Calories, one Calorie is about 4,200 J, and the Stefan-Boltzmann constant has the value $\sigma \approx 6 \times 10^{-8}\,\mathrm{W/(m^2\,K^4)}$.

Answer: You would have to eat approximately 100 candy bars over a 24-hour period to supply the energy that you radiate by blackbody radiation to the surrounding vacuum.

Note: Eating this many candy bars over 24 hours should be possible, for example the 2009 world record by Joey Chesnut for eating hot dogs is 68 dogs in 10 minutes, which is close to eating 100 candy bars in volume. (It is a surprise to me that someone's stomach can contain such a large volume of food over such a short time without suffering harm.)

This problem was a straightforward application of the Stefan-Boltzmann radiation law: if an opaque body is in thermodynamic equilibrium with a uniform surface temperature T and has a surface area A, then the power $\mathcal{P}$ radiated by the body is given by

$$\mathcal{P} = A \times \sigma T^4, \tag{15}$$

where I have assumed a perfect emissivity of $e = 1$. Here σ is the Stefan-Boltzmann constant, which in turn implies that $\mathcal{P}$ has units of watts or J/s and that you want the area A in units of m^2. Part of the challenge of this problem was for you to estimate the temperature T and surface area A of your body, and for you to practice the skill of rounding numbers to make a quick insightful estimate.

As a science or engineering student, you should know some basic human scales in SI units, e.g., that a healthy person's body temperature is about 37° C (with variations of order two degrees), that a person's height is about 1.5-1.8 m (unless you are a Duke basketball player, for which 2 m would be about right), and that a typical adult weight is about say 70 kg (150 pounds). Your skin temperature is not quite the same as your internal temperature (your skin is somewhat cooler) but to one significant digit, 40° C would be fine. If you didn't know your body temperature in Celsius, you could still make a reasonable estimate by knowing that your body temperature is a bit warmer than room temperature, which is 20° C, and substantially colder than boiling water (100° C) which would lead to an estimate in the $30-50^\circ$ C range. Since what is needed in Eq. (15) is the absolute temperature, the corresponding range of absolute temperature would be $303-323\,\mathrm{K}$, which would be 300 K to one significant digit. So it really doesn't matter what body temperature you chose as long as it was close to room temperature and substantially less than boiling water.

Note: some students took the harder path of converting 98.6° Fahrenheit to Celsius and got the conversion wrong, ending up (in one case) with a body temperature of 200° C, which is just not physically reasonable. I think it was easier to use the fact that your body is a bit warmer than room temperature to get an estimate.

As to estimating their surface area, students took several reasonable approaches. One was to approximate their body as a cylinder of height about $h = 2\,\mathrm{m}$ and radius of about 0.3 m (the distance from the center of your neck to one of your shoulders is about a foot or 0.3 m) , which gives $A = (2\pi r)h \approx 4\,\mathrm{m}^2$, a bit on the high side but fine to the nearest power of ten. Other students approximated themselves as a thin rectangular box of height $h \approx 2\,\mathrm{m}$, width $w \approx 0.5\,\mathrm{m}$ and thickness $t \approx 0.1\,\mathrm{m}$ which gives an approximate area of $A = 2(hw + ht + wt) \approx 3\,\mathrm{m}^2$ to one significant digit. The Wikipedia page

`http://en.wikipedia.org/wiki/Body_surface_area#Normal_values`

gives $1.7\,\mathrm{m}^2 \approx 2\,\mathrm{m}^2$ as typical value for adults. Some students—these must be the ones who solve the New York Times Sunday crossword puzzle in under an hour—just stated that $A = 2\,\mathrm{m}^2$ without justification, in which case they lost some points since an essential part of this problem was practicing the skill of estimation.

With $T \approx 300\,K$ and $A \approx 2\,\mathrm{m}^2$ to one significant digit, we can substitute into Eq. (15) and get an order-of-magnitude estimate of the number of candy bars. Let's do the calculation two ways, first by rounding all numbers immediately to the nearest power of ten so that no arithmetic is needed, and second by rounding all numbers first to one significant digit and then retaining only one digit as various numbers are combined. The first approach leads to:

$$\begin{aligned}
\#\text{ of candy bars} &\approx \left[\left(A\,\sigma T^4\right) \times 1\text{ day}\right] \times \left[\frac{1\text{ candy bar}}{250\,\mathrm{Cal}} \times \frac{1\,\mathrm{Cal}}{4,200\,\mathrm{J}}\right] &(16)\\
&\approx \left[2\,\mathrm{m}^2 \cdot 6\times 10^{-8}\frac{\mathrm{W}}{\mathrm{m}^2\,\mathrm{K}^4} \cdot (300\,\mathrm{K})^4 \cdot \frac{20\,\mathrm{hrs}}{\mathrm{day}} \times \frac{60\,\mathrm{min}}{1\,\mathrm{hr}} \times \frac{60\,\mathrm{sec}}{1\,\mathrm{min}}\right] &(17)\\
&\qquad \times \frac{1\,\mathrm{bar}}{(3\times 10^2)\;(4\times 10^3\,\mathrm{J})} &\\
&\approx \left[1\,\mathrm{m}^2 \cdot 10^{-7} \cdot (100)^4\right] \times \left[10^1 \times 10^2 \times 10^2\right] \times \frac{1}{10^2 \times 10^3} &(18)\\
&\approx 10. &(19)
\end{aligned}$$

In line Eq. (16), the first bracket is the total energy in joules consumed over a day, the second bracket is the number of candy bars per joule.

In this calculation, note how I first collected *all* the numerical data together in line Eq. (17) although just retaining one significant digit[2]. It is actually important and significant that I did not try to calculate any intermediate numbers, such as the number of seconds in a day or the number of joules in a candy bar. These intermediate numbers are not needed for the answer and the chances for errors

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[2] In general, it is ambiguous how to round a number like 250 to one significant digit since it is halfway between 200 and 300. But in the context of this problem, it makes sense to round 250 Cal up to 300 Cal to compensate a little bit for rounding 4,200 J down to 4,000 J.

increase when I break a calculation into several pieces since it is easy to miss-copy a number from one place to another. Another reason for combining all data in one place is that it increases the opportunities to discover cancellations that reduce the amount of calculation, or to balance rounding[3] to give a more accurate final estimate.

After collecting all the numbers, I then replaced in line Eq. (18) each number in the previous line by the nearest power of ten, and only then did I start multiplying out numbers to get a final estimate. Note that by this approach, I did not have to multiply out any digits to get the answer, just add up powers of ten which is quick and easy. In replacing each number by the nearest power of ten, the most dangerous approximation was replacing 300^4 with 100^4 since the temperature is being raised to a fourth power so small changes get magnified. A better approximation would have been to note that $300^4 = (3 \times 100)^4 = 3^4\,10^8 = 9^2\,10^8 \approx 10^2\,10^8 = 10^{10}$, an estimate that is 100 times bigger than what I get if I round 300 to 100 right away and then compute 100^4.

If we repeat this calculation but retain one significant digit, we would start from Eq. (17) and get the following estimate:

$$\# \text{ of candy bars} \tag{20}$$

$$\approx \left[2\,\mathrm{m}^2 \cdot 6 \times 10^{-8} \frac{\mathrm{W}}{\mathrm{m}^2\,\mathrm{K}^4} \cdot (300\,\mathrm{K})^4 \times \frac{20\,\mathrm{hrs}}{\mathrm{day}} \times \frac{60\,\mathrm{min}}{1\,\mathrm{hr}} \times \frac{60\,\mathrm{sec}}{1\,\mathrm{min}}\right] \tag{21}$$

$$\times \frac{1 \text{ candy bar}}{3 \times 10^2 \cdot 4 \times 10^3\,\mathrm{J}}$$

$$\approx \frac{2 \times 6 \times 3^4 \times 2 \times 6 \times 6}{3 \times 4} \times 10^{-8+8+1+1+1-2-3} \tag{22}$$

$$\approx 2 \times 9^2 \times 6^2 \times 10^{-2} \tag{23}$$

$$\approx 2 \times 6^2 \approx 2 \times 40 = 80. \tag{24}$$

A calculation to two significant digits gives 84 candy bars, so 100 is indeed a good estimate to the nearest power of ten. I accepted 10 or 100 candy bars as reasonable estimates.

In obtaining line Eq. (23) from the previous line, I used the 4 in the denominator to cancel two of the 2's in the numerator, and I used the 3 in the denominator to divide into one of the factors of 6 in the numerator. I also approximated $9 \approx 10$ to replace $9^2 \approx 10^2$ to one significant digit.

I took points off if I saw that you wrote out some multiplications or divisions the long inefficient way, digit by digit, holding onto many significant digits. For example, some student fully multiplied out $24 \times 60 \times 60 = 86,400$ to get the approximate number of seconds in a day. This was a waste of valuable time and the multiplication provides more digits than was scientifically justified. (Because the surface area is known to only one significant digit, one only needs to retain one digit in all other quantities.) So round to one digit first, then calculate.

A conclusion of this problem is that, with a surface temperature of about 310 K, you have enough skin to radiate a lot of energy by blackbody radiation, about 1,000 watts. You don't have to eat 100 candy bars a day because you are surrounded by air which is close to your body temperature (so energy is returned to you from the environment), and because you wear clothes that reduce convection currents that would efficiently deplete you of energy (convection is much more efficient than thermal conduction in transporting heat). I will leave it to you as a challenge to see if clothes act like one of the heat blankets that we discussed in the context of Figure 7.25 on page 306 of Schroeder (greenhouse warming), and if this therefore plays a role in why clothes are useful.

4. **(15 points)** In one of the other universes of the multiverse, there is a particle (let's call it a mirron) that obeys the laws of quantum mechanics but unlike a boson or fermion, a mirron has the property

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[3] Another example of balanced rounding would be if I had a ratio 2.5/3.5 that I wanted to approximate to one significant digit. If I round the numerator up to 3 which would give me an overestimate, I would then want to round the denominator up also, to 4, which would help to compensate for the overestimate.

that, for any single-state quantum energy level ϵ, there can be 0, 1, or 2 mirrons in that energy level. Mirrons have the further properties that their total number is not conserved and that each mirron can exist in three distinct polarization states. If a finite volume V of mirrons is in thermodynamic equilibrium with temperature T and if mirrons interact weakly so that they form an ideal gas, determine the energy distribution function $\mathcal{D}(\epsilon)$ for mirrons (i.e., the amount of energy contributed by mirrons whose energies lie in the range $[\epsilon, \epsilon + d\epsilon]$). Determine also how the pressure P and heat capacity C_V of a mirron gas vary with the temperature T (your answers here will be simple powers of T).

Note: In a cubic box of volume $V = L^3$, the quantum states of this particle are labeled by positive integers n_x, n_y, and n_z, and the energy of a given mirron state is given by $\epsilon(n_x, n_y, n_z) = \epsilon(n) = \alpha n^2/L^2$ where $\alpha > 0$ is a constant, L is the size of the cubic box, and $n = \sqrt{n_x^2 + n_y^2 + n_z^2}$.

Answer: This problem has many similarities to what you learned about an equilibrium gas of photons, with the main difference being that you had to derive and use a number distribution $\overline{n}(\epsilon)$ that was different from the Fermi-Dirac, Bose-Einstein, and Boltzmann distributions.

A useful starting point for all quantum ideal gases (electrons, photons, phonons, mirrons) is to assume that the particles move freely and independently in a cubic volume, in which case it is easy to label each single-particle energy state by quantum numbers (n_x, n_y, n_z) that are positive integers. The total energy of the system is then given by a triple sum:

$$U = c_p \sum_{n_x} \sum_{n_y} \sum_{n_z} \epsilon(n_x, n_y, n_z)\, \overline{n}\left[\epsilon(n_x, n_y, n_z)\right], \tag{25}$$

where the coefficient c_p counts the number of independent polarizations (and also possibly the number of particle types if there is a degeneracy, such as matter and antimatter), $\epsilon(n_x, n_y, n_z)$ is the single particle energy level for given quantum numbers, and $\overline{n}(\epsilon)$ is the occupation number or average number of particles with energy ϵ.

Given Eq. (25), there were then three steps to carry out to answer this problem:

(a) Determine the occupation number $\overline{n}(\epsilon)$ for mirrons.

(b) Substitute your expression for $\overline{n}$ into Eq. (25) and evaluate the sum by changing to spherical coordinates in number space, $(n_x, n_y, n_z) \rightarrow (n, \theta, \phi)$.

(c) Change the integration variable to determine the temperature dependence of U.

To compute the occupation number $\overline{n}(\epsilon)$ for mirrons, we follow Schroeder's discussion in Chapter 7 and assume that a single energy level ϵ can be treated as a small physical system that is in thermodynamic equilibrium with all the other particles (mirrons) that constitute a reservoir with constant temperature T and constant chemical potential μ. Since the problem states that the number N of mirrons is not conserved, we conclude that the chemical potential is zero,

$$\mu = 0, \tag{26}$$

just as was the case for photons and phonons. (Recall that if particle number is not conserved, the mean number will keep changing until, in equilibrium, the free energy $F(N)$ reaches a minimum at which point $0 = \partial F/\partial N = \mu$.)

We are told that a given energy level can be occupied by up to two mirrons. The grand partition function for that energy level is then given by

$$\mathcal{Z} = \sum_s e^{-\beta(E_s - \mu N_s)} = 1 + e^{-\beta\epsilon} + e^{-2\beta\epsilon} = 1 + e^{-x} + e^{-2x}, \tag{27}$$

where $x = \beta\epsilon$. There are three terms since there are three possible mirron states for a single energy level: no occupation ($n_s = 0$, $E_s = 0$), one mirron ($n_s = 1$ and $E_s = \epsilon$), and two mirrons ($n_s = 2$ and $E_s = 2\epsilon$). The μN_s terms in the exponents all vanish since $\mu = 0$.

The occupation number is the average number $\overline{n}$ of particles for a given energy level, which we can compute from the partition function Eq. (27) via the relation

$$\overline{n} = -\frac{1}{\mathcal{Z}} \frac{\partial \mathcal{Z}}{\partial x}. \tag{28}$$

A straightforward calculation gives

$$\overline{n}(\epsilon) = \frac{e^{-\beta\epsilon} + 2e^{-2\beta\epsilon}}{1 + e^{-\beta\epsilon} + e^{-2\beta\epsilon}}. \tag{29}$$

Although not needed for the solution of this exam problem, it is good practice to figure out the qualitative shape of the curve $\overline{n}(\epsilon)$ as a function of energy. For a fixed finite temperature T, you can verify that $\overline{n}(0) = 1$ so the lowest energy state $\epsilon = 0$ always has an occupation of one. For the same fixed temperature, for large energies $\beta\epsilon \gg 1 \Rightarrow e^{-\beta\epsilon} \ll 1$ so $2e^{-2\beta\epsilon} = 2\left(e^{-\beta\epsilon}\right)^2 \ll e^{-\beta\epsilon}$ can be ignored in the numerator compared to $e^{-\beta\epsilon}$. In the denominator, both powers of $e^{-2\beta\epsilon}$ can be ignored compared to one. So $\overline{n} \propto e^{-\beta\epsilon}$ decays exponentially for large energies, which we could have guessed since all occupation numbers look like the Boltzmann distribution for large enough energies. It is less clear what happens for intermediate energies but you can verify that the derivative of Eq. (29) w.r.t. ϵ is always negative so the occupation number decreases monotonically from 1 and eventually decays exponentially, so roughly looks like exponential decay over its entire range.

Given the occupation number expression Eq. (29), we can substitute into Eq. (25) and proceed to calculate the energy U of an ideal gas of mirrons that is in thermodynamic equilibrium with temperature T. At a finite temperature, the sums in Eq. (25) each extend from 1 to ∞ since the number of particles is not conserved. We then have:

$$U = c_p \sum_{n_x} \sum_{n_y} \sum_{n_z} \epsilon(n_x, n_y, n_z)\, \overline{n}\left[\epsilon(n_x, n_y, n_z)\right] \tag{30}$$

$$= 3 \sum_{n_x=1}^{\infty} \sum_{n_y=1}^{\infty} \sum_{n_z=1}^{\infty} \frac{\alpha n^2}{L^2}\, \overline{n}\left(\frac{\alpha n^2}{L^2}\right) \tag{31}$$

$$= 3 \times \frac{1}{8}(4\pi) \times \int_0^{\infty} \frac{\alpha n^2}{L^2}\, \overline{n}\left(\frac{\alpha n^2}{L^2}\right) \times n^2\, dn \tag{32}$$

$$= \int_0^{\infty} \left[V \frac{3\pi}{4\,\alpha^{3/2}} \epsilon^{3/2} \frac{e^{-\beta\epsilon} + 2e^{-2\beta\epsilon}}{1 + e^{-\beta\epsilon} + e^{-2\beta\epsilon}} \right] d\epsilon. \tag{33}$$

Eq. (31) is obtained from the previous line by simple substitution of known expressions. Eq. (32) is obtained from Eq. (31) by changing to spherical coordinates and by observing that since the integrand doesn't depend on angles (it depends only on the "radius" n), the angular integrals must evaluate to 1/8 of the surface area 4π of a unit sphere. Eq. (33) is obtained from Eq. (32) by changing variables from n to energy ϵ:

$$\epsilon = \frac{\alpha}{L^2} n^2 \quad \Rightarrow \quad n = \frac{L}{\alpha^{1/2}} \epsilon^{1/2} \quad \Rightarrow \quad dn = \frac{L}{\alpha^{1/2}} \frac{1}{2} \epsilon^{-1/2}\, d\epsilon. \tag{34}$$

The final line Eq. (33) answers the question of what is the energy distribution of mirrons, it is the expression in brackets

$$\mathcal{D}(\epsilon) = V \frac{3\pi}{4\,\alpha^{3/2}} \epsilon^{3/2} \frac{e^{-\beta\epsilon} + 2e^{-2\beta\epsilon}}{1 + e^{-\beta\epsilon} + e^{-2\beta\epsilon}}. \tag{35}$$

You should compare this expression with Eqs. (7.83) and (7.84) on page 292 of Schroeder where the analogy should be clear. The 3/2 power of ϵ in Eq. (35) differs from the power of 3 for photons because mirrons have a different energy dependence, with $\epsilon \propto n^2$ like an electron, as opposed to $\epsilon \propto n$ as the case for photons and phonons.

Some students didn't appreciate that this problem involved quantum statistics and tried to deduce the energy distribution $\mathcal{D}(\epsilon)$ in analogy to how Schroeder derived the Maxwell speed distribution:

$$\mathcal{D}(\epsilon) \propto \text{probability of mirron to have energy } \epsilon \times \text{degeneracy of energy } \epsilon. \tag{36}$$

The wording in the problem where it said that up to two mirrons could occupy a given energy level was the giveaway that you had to use the ideas of Chapter 7 related to dense quantum ideal gases since once multiple particles can occupy an energy level, the approximation $Z_N \approx Z_1^N/N!$ fails.

The remaining parts of this problem are straightforward to obtain once the integral Eq. (33) is obtained. To get the temperature dependence of the energy U, all we have to do is change variables to a variable $x = \beta\epsilon$ that eliminates the presence of temperature (β) in the integral:

$$x = \beta\epsilon \quad \Rightarrow \quad \epsilon = \frac{1}{\beta}x = (kT)x \quad \Rightarrow \quad d\epsilon = \frac{dx}{\beta} = kT\,dx. \tag{37}$$

Eq. (33) then becomes

$$U = V\frac{3\pi}{4\,\alpha^{3/2}}\int_0^\infty (kTx)^{3/2}\,\overline{n}(x)\,(kT)dx \tag{38}$$

$$= V\frac{3\pi}{4\,\alpha^{3/2}}(kT)^{5/2} \times \int_0^\infty x^{3/2}\,\overline{n}(x)\,dx \tag{39}$$

where the integral over x is just some pure number; you should now appreciate that the functional form Eq. (29) does not affect the temperature dependence for particles whose number is not conserved. We thus conclude that

$$U \propto V\,T^{5/2}. \tag{40}$$

We now see that the pressure $P = -(\partial U/\partial V)_T$ has the same temperature dependence, $P \propto T^{5/2}$, and that the heat capacity $C_V = (dU/dT)_V \propto T^{3/2}$.

5. **(10 points total)** Consider a magnetic substance of volume V that responds to the presence of a magnetic field $\mathbf{B}$ of strength B *inside* the substance by becoming magnetized along the direction of $\mathbf{B}$ with a magnetization of magnitude M. In studying the thermodynamics of magnets, it turns out that a key variable is an auxiliary magnetic field $\mathcal{H}$ defined by

$$\mathcal{H} = \frac{1}{\mu_0}B - \frac{M}{V}, \tag{41}$$

where μ_0 is the vacuum permeability. It then turns out that the thermodynamic potential G_m that is minimized when the magnetic system is in thermodynamic equilibrium for constant temperature T and constant field $\mathcal{H}$ is a magnetic analog of the Gibbs free energy that satisfies the following thermodynamic identity:

$$dG_m = -S\,dT - \mu_0 M\,d\mathcal{H}. \tag{42}$$

(a) **(5 points)** Derive an analog of the Clausius-Clapeyron relation for the slope of a phase boundary in the $\mathcal{H} - T$ plane of this magnetic substance. You should write your equation in terms of the difference in entropy of the two phases.

Answer: I adapted this problem from Problems 5.17 and 5.47 on pages 160 and 179 respectively of Schroeder.

The Clausius-Clapeyron equation is an equation that relates the slope of a phase line at a certain point in some parameter plane (that characterizes a thermodynamic system) to thermodynamic properties of the phases on either side of the phase line. A point on the phase line is defined by where the chemical potential μ_1 of one phase is equal to the chemical potential μ_2 of the other phase. (Recall that a necessary condition for thermodynamic equilibrium is that the chemical potential of each particle type be the same for all macroscopic subsystems.) An expression for the slope of the phase line can be obtained by choosing two points on the phase line that are infinitesimally close to each, subtracting the conditions that the chemical potentials are equal at each of the two points, and then expanding the difference to lowest order in a Taylor series.

For example, assume that the two thermodynamic parameters that characterize some given system are α and β, which could be volume and pressure for a gas or here temperature T and magnetic field $\mathcal{H}$. The conditions for equilibrium of phase 1 with phase 2 at a point (α, β) and at an infinitesimally nearby point $(\alpha + \Delta\alpha, \beta + \Delta\beta)$ are:

$$\mu_1(\alpha, \beta) = \mu_2(\alpha, \beta), \tag{43}$$

$$\mu_1(\alpha + \Delta\alpha, \beta + \Delta\beta = \mu_2(\alpha + \Delta\alpha, \beta + \Delta\beta). \tag{44}$$

Subtracting the first equation from the second gives

$$\mu_1(\alpha + \Delta\alpha, \beta + \Delta\beta) - \mu_1(\alpha, \beta) = \mu_2(\alpha + \Delta\alpha, \beta + \Delta\beta) - \mu_2(\alpha, \beta). \tag{45}$$

Expanding each side to lowest (linear) order in a two-variable Taylor series in the small quantities $\Delta\alpha$ and $\Delta\beta$ then gives

$$\frac{\partial\mu_1}{\partial\alpha}\Delta\alpha + \frac{\partial\mu_1}{\partial\beta}\Delta\beta \approx \frac{\partial\mu_2}{\partial\alpha}\Delta\alpha + \frac{\partial\mu_2}{\partial\beta}\Delta\beta. \tag{46}$$

Solving for the ratio $\Delta\beta/\Delta\alpha$ and taking the limits $\Delta\alpha \to 0$ and $\Delta\beta \to 0$, we obtain an equation for the slope $d\beta/d\alpha$ at a given point (α, β) where two phases are in thermodynamic equilibrium:

$$\frac{d\beta}{d\alpha} = \frac{\frac{\partial\mu_1}{\partial\alpha} - \frac{\partial\mu_2}{\partial\alpha}}{\frac{\partial\mu_2}{\partial\beta} - \frac{\partial\mu_1}{\partial\beta}}. \tag{47}$$

Note how the indices 1 and 2 are reversed in the denominator compared to the numerator. Eq. (47) is the general form of the Clausius-Clapeyron equation.

The various derivatives $\partial\mu_i/\partial x$ where $i = 1, 2$ and $x = \alpha, \beta$ can be evaluated by using the thermodynamic identity for the Gibbs free energy G. For the given problem, we can choose $\alpha = T$, and $\beta = \mathcal{H}$. By dividing both sides of the given thermodynamic identity Eq. (42) by the number N of particles in a given phase, we obtain

$$d\mu_m = -s dT - \mu_0 m d\mathcal{H}, \tag{48}$$

where $\mu = G/N$ is the chemical potential, $s = S/N$ is the intensive entropy per particle in a given phase, and $m = M/N$ is the intensive magnetization per particle in a given phase. We thus see that

$$\frac{\partial\mu}{\partial\alpha} = \left(\frac{\partial\mu_m}{\partial T}\right)_{\mathcal{H}} = -s, \tag{49}$$

and similarly

$$\frac{\partial\mu}{\partial\beta} = \left(\frac{\partial\mu_m}{\partial\mathcal{H}}\right)_T = -\mu_0 m. \tag{50}$$

The Clausius-Clapeyron equation Eq. (47) for this magnetic system then becomes

$$\frac{d\mathcal{H}}{dT} = \frac{s_1 - s_2}{\mu_0\left(m_2 - m_1\right)}. \tag{51}$$

Note that Schroeder's discussion of the Clausius-Clapeyron equation on pages 172-173 is slightly flawed. Eq. (5.43) on page 172 is correct only if both phases have the same number of particles, which generally is not the case since one could have a little bit of ice in equilibrium with a large amount of water. Schroeder's Eq. (5.43) should be replaced by Eq. (43) above for the chemical potentials, which is the same as the Gibbs free energy per particle for each phase. I did not take off any points if you did not realize this subtlety and had written $d\mathcal{H}/dT = (S_1 - S_2)/[\mu_0(M_2 - M_1)]$ for your answer since I did address this point in class.

Most student followed Schroeder's discussion of Clausius-Clapeyron to get a quick answer: equate the differential change dG in the Gibbs energy for each phase:

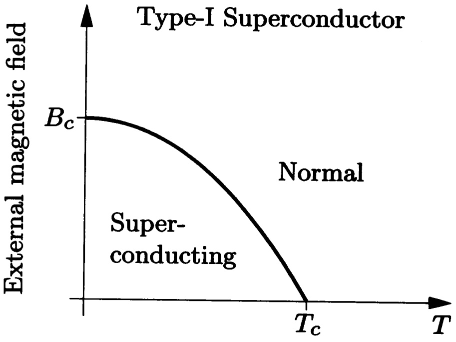
$$dG_1 = dG_2 \quad \Rightarrow \quad -S_1 dT - \mu_0 M_1 d\mathcal{H} = -S_2 dT - \mu_0 M_2 d\mathcal{H}, \tag{52}$$

to get

$$\frac{d\mathcal{H}}{dT} = \frac{S_2 - S_1}{\mu_0 \left(M_1 - M_2\right)}. \tag{53}$$

But again, this is strictly correct only for equal numbers of molecules in each phase and it is better to use Eq. (51) above.

(b) **(5 points)** When certain metals are cooled to a sufficiently low temperature in the presence of an external magnetic field, the metal can become a so-called type-I superconductor in which the resistance decreases enormously. (Superconducting wires are used in the magnets at the Large Hadron Collider and have been proposed for use in national power grids, to transport electricity over long distances without loss.) A representative phase diagram for a type-I superconductor is given by the following figure



In such a superconductor, surface currents flow in such a way so as to completely cancel the magnetic field inside (that is $B = 0$ but $\mathcal{H}$ is not zero in Eq. (41)). Given that the magnetization M of the metal is essentially zero in its normal state ("normal" means "non-superconducting"):

i. Use your magnetic version of the Clausius-Clapeyron equation to determine which phase has the greater entropy, superconducting or normal.

Answer: This problem should have been worded to ask instead "which phase has the greater entropy per particle $s = S/N$" since the entropy is extensive and its numerical value depends on the number of particles in a given phase. Or you could have interpreted the question as asking which phase has the greater entropy, assuming equal numbers of particles in each phase.

Let us arbitrarily label the normal phase to be 1 and the superconducting phase to be 2. The problem tells us that the magnetization per particle $m_1 = 0$ in the normal phase, and that the magnetic induction[4] $B = 0$ inside the superconducting phase (because of surface currents that flow without resistance and that generate a canceling magnetic field). If we set $B = 0$

---

[4] When one has a material substance (solid, liquid, gas) in the presence of an external magnetic field, it becomes subtle what one means by the magnetic field inside the substance, you cannot just insert a probe since a physical probe would alter the local atomic environment of the substance. It is traditional to call the magnetic field in the absence of the substance "the magnetic field" and to denote that field by the symbol $\mathcal{H}$. (A better phrase would have been "applied magnetic field", e.g., the field generated at the center of a solenoid.) The magnetic field at some location inside the substance is defined by averaging the microscopic magnetic field over some small macroscopic volume and is somewhat confusingly called by a different name, "the magnetic induction", and is denoted by the symbol $\mathbf{B}$. The magnetic field and magnetic induction are related to one another via the substance's local magnetization $\mathbf{M}$ by $\mathbf{B} = \mathcal{H} + \mu_0 \mathbf{M}$. For paramagnetic and ferromagnetic substances, $\mathbf{M}$ is parallel to $\mathcal{H}$ but points in the opposite direction for a diamagnetic substance, which is the case for a superconductor.

in Eq. (41), we find that in the superconducting phase, $\mathcal{H} = -M_2/V$ or $M_2 = -V\mathcal{H}$. The Clausius-Clapeyron equation Eq. (51) then becomes

$$\frac{d\mathcal{H}}{dT} = \frac{s_1 - s_2}{\mu_0([-v\mathcal{H}] - 0)}, \tag{54}$$

where $v = V/N$ is the volume per particle in a given phase. We can rewrite this as

$$s_1 - s_2 = -\mu_0 v \mathcal{H} \frac{d\mathcal{H}}{dT} \tag{55}$$

The given experimental curve shows that $d\mathcal{H}/dT$ is negative everywhere (I unfortunately did not clarify in this problem how the external magnetic field mentioned in the above figure was related to $\mathcal{H}$ and B) which implies that $s_1 - s_2 > 0$, so the normal phase has the greater entropy per particle.
The bigger picture here is that experiments give knowledge of the slope of phase lines. The Clausius-Clapeyron equation can then be used to deduce how some property changes upon crossing a phase line, e.g., does the entropy or magnetization increase or decrease.

ii. Determine what are the differences in entropy of the two phases at the two end points of the superconducting-normal phase line.

Answer: The differences in entropy are zero at both ends of the superconducting-normal phase line. This is an interesting result: although a phase line generally implies that something must change in crossing the line from one phase to another (e.g., typically the entropy jumps by a finite amount because of latent heat that has been added or removed), in certain situations typically corresponding to specific points on a phase line, certain quantities do not change across the phase line.
At the $T = 0$ end of the line (labeled B_c in the above figure), the third law of thermodynamics implies that the entropy of any phase must go to zero. So $S_1 = 0$ and $S_2 = 0$ for $T = 0$ and their difference vanishes.
At the $\mathcal{H} = 0$ end of the line labeled T_c in the above figure, the absence of an external field implies that the superconducting phase has no magnetization, just like the normal phase, and so there is no difference in entropy between the two phases.

6. **(15 points)** During the semester, we discussed how to calculate the fractional coverage θ of a surface that was in equilibrium with a surrounding ideal gas of identical atoms of mass m that had a fixed temperature T and fixed chemical potential μ. We first assumed that the surface resembled an egg carton with specific fixed locations where an atom could adsorb with binding energy $\epsilon_s < 0$. (The subscript s means "surface".) We then calculated the grand partition function $\mathcal{Z}$ for the surface, from which we were able to calculate the average number of occupied sites, which then gave the coverage.

Solve this problem again—calculate the surface particle density $n_s = N_s/A$ as a function of the external gas pressure P where N_s is the number of adatoms and A is the surface area—but now make a different assumption about the surface: instead of having specific binding sites like an egg carton, assume that the surface is perfectly smooth so that, once an atom adsorbs (again with a binding energy $\epsilon_s < 0$), the adatom can glide around as a free particle and all the adatoms together form a two-dimensional ideal gas in a finite surface area A.

Is your answer again a Langmuir isotherm, with $n_s \propto P/(P_0 + P)$ where P_0 is some constant? That is, does the behavior of surface coverage with pressure depend on whether adatoms bind in fixed locations or are free to move about?

Two hints: thermodynamic equilibrium between the two-dimensional surface gas and surrounding gas requires that their chemical potentials be equal, and the energy of an adatom can be written in the form $E = \epsilon + (p_x^2 + p_y^2)/(2m)$ (if we assume that the surface is the xy plane of some coordinate system).

Answer:

For some reason, this problem turned out to be exceptionally difficult for the class, few students had a sense of what to do. I took this into account when scaling the grades, so students were not penalized.

The goal of this problem was for you to explore a consequence of the fact that, for a macroscopic system to be in thermodynamic equilibrium, the chemical potential μ for a given kind of particle must have the same value in all macroscopic subsystems. Here there are two subsystems, a two-dimensional gas of adatoms that are bound to a surface, and a surrounding three-dimensional gas of the same kind of atoms. Equating the chemical potential of the surface gas to the chemical potential of the 3D gas gives an equation that allows one to relate the equilibrium particle density $n_s = N_S/A$ (analogous to the number density $n = N/V$ for a 3D gas) to the gas pressure P of the 3D gas.

Before getting into details and algebra, let's try to reason physically what the answer might be: should we expect a Langmuir isotherm? The problem gives no information about the size of the atoms or about how many atoms can fit on a surface. The implication is then that we should treat the atoms as point particles[5] that move about in a continuous finite area A so that an *infinite* number of atoms can occupy the finite surface area. Without an upper limit on the number N_s of surface atoms, there is no reason to expect N_s to saturate with increasing pressure P of the surrounding gas, which means that the surface density $n_s(P)$ as a function of pressure should not behave like a Langmuir isotherm, which does saturate with a maximum value for sufficiently large pressures.

We can try to be a bit bolder and try to guess the functional form of $n_s(P)$ as a function of P. Since $n_s = 0$ for $P = 0$, we would expect $n_s \propto P$ for small enough P. (That is, the first term n_s^0 in the Taylor series of $n_s(P) = n_s^0 + n_s^1 P + n_s^2 P^2 + \ldots$ about $P = 0$ must vanish if $n_s(0) = 0$, so the first nonzero term is likely proportional to P.) If the atoms have no size and there is no limit to the number of atoms we can pack into the area A, there is no reason for the functional form of n_s to change as P increases (there is no length or energy scale that would cause the physics to change as n_s increases). So we could guess that n_s might be proportional to P for all P, not just for small pressures.

The analysis below shows that this physical thinking is correct: $n_s \propto P$ for all pressure values and does not saturate like a Langmuir isotherm. This is not how the coverage behaves experimentally, which tells us that the assumption of point particles on a continuous surface is not physical. The egg-carton model that we discussed in class starts with the assumption of a finite number of binding sites, which automatically leads to saturation when all sites are occupied, and so is a more accurate model. And indeed, the surface coverage of many surfaces is accurately described by a Langmuir isotherm of the form $P/(P + P_0)$.

Let's proceed with working out the details. The main challenge of this problem was to calculate the chemical potential μ_{2D} of a 2D ideal atomic gas with the wrinkle that the energy of a particle on the surface includes a binding energy $\epsilon_s < 0$ so

$$\epsilon_{2D} = \frac{p_x^2 + p_y^2}{2m} + \epsilon_s. \tag{56}$$

We then need to equate μ_{2D} to the chemical potential of an ideal three-dimensional gas with temperature T and pressure P:

$$\mu_{3D} = -kT \ln\left(\frac{VZ_{\rm int}}{NV_Q}\right) = kT \ln\left(\frac{P}{P_0}\right), \tag{57}$$

where

$$P_0 = \frac{kTZ_{\rm int}}{V_Q} = \frac{kTZ_{\rm int}}{(h/\sqrt{2\pi mkT})^3}. \tag{58}$$

Here $Z_{\rm int}$ is the partition function over internal energy states of a molecule and has the value 1 for an atom with no internal structure, N is the number of atoms in the gas phase, and $V_Q = L_Q^3 =$

---

[5] Throughout the semester, we have used a similar assumption about our ideal molecular gases: we have ignored the finite size of the molecules and so ignored the fact that, at large enough densities, the molecules must eventually be close enough to interact in which case the gas is no longer ideal and may condense to a liquid or solid. And indeed, the ideal gas law $PV = NkT$ implies that the number density $N/V = P/(kT) \propto P$ for all P which incorrectly does not saturate for large enough P.

$(h/\sqrt{2\pi mkT})^3$ is the quantum volume. You would know Eqs. (57) and (58) formula from your formula sheet or should be able to derive them from what you learned in Chapter 6.

There is a valuable insight here worth discussing: in using ideas from Chapter 6 (a "canonical ensemble") to calculate the chemical potential for the 2D gas and in equating that potential to that of the 3D gas Eq. (57), I am assuming that the number N of particles in the gas and the number of particles N_s on the surface are each constant. This is of course not the case, the number of atoms in the gas and on the surface fluctuate around their average equilibrium values as atoms leave the gas to bond to the surface, or break away from the surface to join the gas. (However, the total number of particles $N + N_s$ is conserved.) But if N and N_s are sufficiently large, the deviations of their values from their average values at any given moment are tiny—of order $1/\sqrt{N}$ or $1/\sqrt{N_s}$ respectively—so only a small error is made by assuming that the numbers are fixed.

More generally, for systems with sufficiently many components N, one can solve a given thermodynamic problem using the methods of Chapter 3 (a microcanonical ensemble with fixed total energy, total volume, and total number of particles), or by using the methods of Chapter 6 (a canonical ensemble, with fixed volume and total number of particles, but the energy fluctuates as the system exchanges energy with a reservoir), or by using the methods of Chapter 7 (a grand canonical ensemble such that energy and number of particles can vary). One has to get the same average values for E, N, and other macroscopic quantities in all three cases for N sufficiently large.

For example, in Chapter 3 we derived the entropy S of an atomic gas by deriving a formula for the gas's multiplicity $\Omega(N, V, U)$ under the assumption that the gas's energy U was constant. In Chapter 6, we later calculated the entropy of a gas of molecules (see Eq. (6.92) on page 255 of Schroeder) under the assumption that the gas was in contact with a thermal reservoir, so its energy was not constant. But we got the same formula—the Sackur-Tetrode equation Eq. (13) above—despite the different assumptions. What would not be the same are the statistical deviations from the average behaviors, but, again, those are negligibly small if an equilibrium system has enough particles.

For problems in which particle number can vary, it is often easier to use a Gibbs sum $\mathcal{Z}$ but the present problem is an example where it is more direct to assume constant particle numbers since we already know Eqs. (57) and (58). You did not need to realize this point to get the answer, and indeed one reason for my choosing this problem was to have you work through an example of solving a problem involving variable particle numbers by using methods in which the particle numbers were assumed constant.

So let's calculate the chemical potential $\mu_{2\mathrm{D}}$ for an ideal gas whose particles have energy states given by Eq. (56). Assuming that the N_s adatoms on the surface lie in a square area $A = L^2$ of side L, you learned during the semester (see pages 252-253 of Schroeder) that free particles in a square box have a quantized momentum vector given by

$$(p_x, p_y) = \frac{h}{2L}\,(n_x, n_y)\,, \tag{59}$$

and so a state s of the system is characterized by two quantum numbers n_x and n_y that are positive integers. The energy states Eq. (56) can then be written as

$$E_s = E(n_x, n_y) = \frac{p_x^2 + p_y^2}{2m} + \epsilon_s = \frac{h^2}{8mL^2}\left(n_x^2 + n_y^2\right) + \epsilon_s. \tag{60}$$

The single particle partition function Z_1 of the 2D gas is then given by the analog of the single particle partition function for the 3D ideal gas, see Eq. (6.82) on page 253 of Schroeder:

$$
\begin{aligned}
Z_1 &= \sum_s e^{-\beta E_s} && (61)\\
&= \sum_{n_x=1}^{\infty} \sum_{n_y=1}^{\infty} \exp\left[-\beta\left(\frac{h^2}{8mL^2}\left(n_x^2+n_y^2\right)+\epsilon_s\right)\right] && (62)\\
&= \sum_{n_x=1}^{\infty} \sum_{n_y=1}^{\infty} e^{-\beta h^2 n_x^2/(8mL^2)}\, e^{-\beta h^2 n_y^2/(8mL^2)}\, e^{-\beta\epsilon_s} && (63)\\
&= e^{-\beta\epsilon_s} \sum_{n_x=1}^{\infty} \sum_{n_y=1}^{\infty} e^{-\beta h^2 n_x^2/(8mL^2)}\, e^{-\beta h^2 n_y^2/(8mL^2)} && (64)\\
&= e^{-\beta\epsilon_s} \sum_{n_x=1}^{\infty} \left[e^{-\beta h^2 n_x^2/(8mL^2)} \sum_{n_y=1}^{\infty} e^{-\beta h^2 n_y^2/(8mL^2)} \right] && (65)\\
&= e^{-\beta\epsilon_s} \left(\sum_{n_x=1}^{\infty} e^{-\beta h^2 n_y^2/(8mL^2)} \right) \sum_{n_y=1}^{\infty} e^{-\beta h^2 n_x^2/(8mL^2)} && (66)\\
&\approx e^{-\beta\epsilon_s} \times \int_0^{\infty} e^{-\beta h^2 n_y^2/(8mL^2)}\, dn_y \times \int_0^{\infty} e^{-\beta h^2 n_x^2/(8mL^2)}\, dn_x && (67)\\
&= e^{-\beta\epsilon_s} \times \frac{L}{L_Q} \times \frac{L}{L_Q} && (68)\\
&= e^{-\beta\epsilon_s} \frac{A}{A_Q}. && (69)
\end{aligned}
$$

Here the area $A = L^2$ and the two-dimensional quantum area is $A_Q = L_Q^2 = (h/\sqrt{2\pi mkT})^2$. Now that we see the form of the answer, we perhaps could have guessed Eq. (69) from the 3D case $Z_1 = V Z_{\text{int}}/V_Q$ by making the substitutions $V \to A$, $V_Q \to A_Q$, and $Z_{\text{int}} \to e^{-\beta\epsilon_s}$.

Note that the double sum in Eq. (62) could alternatively be approximated by a double integral over the positive quadrant $n_x, n_y \geq 0$ and evaluated in polar coordinates (n, θ) involving the radial coordinate $n = \sqrt{n_x^2 + n_y^2}$. One would use the substitution $dn_x\, dn_y \to n\, dn\, d\theta$ and the θ integral would go from $\theta = 0$ to $\theta = \pi/2$.

We can also obtain the result Eq. (69) more quickly and easily by using a semiclassical approximation for a partition function that involves continuous classical variables like x and p (see Problem 6.51 on page 256 of Schroeder):

$$
Z_1 \approx \int \frac{d^2\mathbf{x}\, d^2\mathbf{p}}{h^2}\, e^{-\beta(\epsilon_0 + p^2/(2m))} \approx \frac{1}{h^2} \int_0^L dx \int_0^L dy \int_{-\infty}^{\infty} dp_x \int_{-\infty}^{\infty} dp_y\, e^{-\beta(\epsilon_0 + p^2/(2m))}, \tag{70}
$$

which you can verify also gives Eq. (69).

Once we know the single particle partition function Eq. (69), we compute the chemical potential $\mu_{2\text{D}}$ in terms of the partition function Z_N for the entire two-dimensional gas of N_s indistinguishable atoms:

$$
Z_{N_s} = \frac{1}{N_s!} \left(Z_1\right)^{N_s} \qquad \text{and} \qquad \mu_{2\text{D}} = \left(\frac{\partial F}{\partial N_s}\right)_{T,A} = -kT \left.\frac{\partial \ln(Z_N)}{\partial N_s}\right|_{T,A}. \tag{71}
$$

I leave you to use Stirling's formula $N_s! \approx N_s \ln(N_s) - N_s$ and show that

$$
\mu_{2\text{D}} = -kT \ln\left(\frac{A}{N_s A_Q} e^{-\beta\epsilon_s}\right). \tag{72}
$$

This is similar to the 3D formula Eq. (57) except for the exponential factor. Again, now that we see this answer, we could have bypassed the above algebra by using the analogous form of the 3D formula for μ and by realizing that the binding energy can be treated as an internal energy state.

The equilibrium state is determined by the condition $\mu_{\rm 2D} = \mu_{\rm 3D}$. Equating Eq. (72) to Eq. (57) and rewriting a little bit gives the answer to this exam problem:

$$n_s = \frac{N_s}{A} = \frac{P}{P_0}\frac{1}{A_Q}e^{-\beta\epsilon_s} = \left(\frac{L_Q}{kT}e^{-\beta\epsilon_s}\right)P, \tag{73}$$

the surface density is simply proportional to the surrounding gas pressure, and *not* proportional to a Langmuir isotherm $P/(P+P_c)$ that saturates with value 1 as $P \to \infty$. But we have learned more: the proportionality constant $(L_Q/(kT))e^{-\beta\epsilon_s} \propto T^{-3/2}e^{-\epsilon/(kT)}$ depends on temperature in an explicitly calculated way.

We could try to fix the lack of saturation by assuming that the adatoms have a finite size but this leads to a new difficulty, which is that when the spacing between adatoms becomes comparable to their size (high surface density), attractive interactions occur, the surface gas is no longer ideal, and we could expect condensation of the gas into a new phase, say liquid or solid. One could then try to use a van der Waals-like equation that takes into account the finite size of atoms and their interactions, and that includes a qualitative transition from a gas to liquid at high densities or low temperatures. Some of you might find this interesting to explore further on your own.

To wrap up the discussion for this problem, let me discuss briefly how we could solve this surface problem using the methods of Chapter 7, in which we take into account directly the fact that the number N_s of surface atoms can fluctuate. A useful insight here is that the Gibbs sum $\mathcal{Z}$ can be rewritten as a weighted sum that involves all the partition functions Z_N for N fixed particles, with N varying over all possible values:

$$\mathcal{Z} = \sum_s e^{-\beta(E_s-\mu N_s)} = \sum_s e^{\beta\mu N_s}e^{-\beta E_s} = \sum_{N=0}^{\infty} e^{\beta\mu N}\sum_n d_n e^{-\beta E_n(N)} = \sum_{N=0}^{\infty} e^{\beta\mu N} Z_N, \tag{74}$$

where the notation $E_n(N)$ denotes the nth energy level above the ground state for a system with N particles, and d_n is the degeneracy of that level. For indistinguishable particles, we know further that

$$Z_N \approx \frac{Z_1^N}{N!}. \tag{75}$$

which allows us to write Eq. (74) in terms of the single particle partition function Z_1:

$$\mathcal{Z} = \sum_{N=0}^{\infty} e^{\beta\mu N}\frac{Z_1^N}{N!} = \sum_{N=0}^{\infty}\frac{1}{N!}\left(e^{\beta\mu}Z_1\right)^N = \exp\left[e^{\beta\mu}Z_1\right], \tag{76}$$

which is a satisfyingly simple and concise form. We can now interpret the 3D gas as a reservoir of atoms with constant temperature T and constant chemical potential μ. The surface is the "small" system in equilibrium with this reservoir and exchanges energy and particles with this reservoir. The average number of particles $\overline{N_s}$ on the surface is given by the usual derivative of $\mathcal{Z}$, Eq. (76):

$$\overline{N_s} = kT\frac{\partial \ln(\mathcal{Z})}{\partial\mu} = kT\frac{\partial\left(e^{\beta\mu}Z_1\right)}{\partial\mu} = e^{\beta\mu}Z_1 = e^{\beta\mu}\times e^{-\beta\epsilon_s}\frac{A}{A_Q}. \tag{77}$$

This leads to the same answer we had before, Eq. (73), after we eliminate $e^{\beta\mu}$ in terms of the pressure P/P_0 via Eq. (57). This discussion basically justifies that it is ok to fix the number of particles in each subsystem and to equate their chemical potentials to get the same answer as what one would get by allowing particle numbers to vary. Note that this argument would fail for quantum gases because of the critical use of Eq. (75), which only holds for low-density high-temperature gases.

7. **(35 points total)** As a simple model of a so-called antiferromagnet, consider three identical spin-1/2 magnetic dipoles that are placed at the coordinates $(x, y) = (-1, 0)$, $(0, 0)$, and $(1, 0)$ of an xy Cartesian coordinate system. The entire system is immersed in a uniform magnetic field $\mathbf{B} = B\hat{y}$ of strength B that points in the positive y direction of the coordinate system. Unlike the dipoles of a paramagnet, these magnetic dipoles are so close to one other that adjacent spins interact (but spins further separated in space than nearest neighbor do not interact). If we describe the state of each dipole by a spin variable $s_i = \pm 1/2$ that has the value $+1/2$ if the spin is up (points in the $\hat{y}$ direction) and has the value $-1/2$ if the spin is down, the energy of a particular state of this system can be written in the form:

$$E(s_1, s_2, s_3) = J\,(s_1 s_2 + s_2 s_3) - 2\mu B\,(s_1 + s_2 + s_3)\,. \tag{78}$$

The constant $J > 0$ is called a "coupling constant" that measures how strongly one spin couples to its neighbor, and a positive J favors antiparallel nearest neighbors. The term $-2\mu B(s_1 + s_2 + s_3)$ is the one you have seen before in our discussion of a paramagnet.

(a) **(10 points)** Summarize in a table with several columns all the microstates of this system. For each microstate, give its energy for general values of J and B. Then list the degeneracy of each state for the case of zero external magnetic field $B = 0$, and separately for the case of a small external magnetic field such that $0 < B \ll J/\mu$ (nearest neighbor interactions are much stronger than the interaction of each spin with the external magnetic field).

Answer:

There are three spins that each have two possible states (up or down) so there are $2^3 = 8$ microstates all together. It is straightforward to evaluate the energy Eq. (78) for all eight states. For the general case $0 < B \ll J/\mu$, the different energy values (from lowest to highest) and their degeneracies are :

E	degeneracy	states
$-J/2 - \mu B$	1	↑↓↑
$-J/2 + \mu B$	1	↓↑↓
$-\mu B$	2	↓↑↑, ↑↑↓
μB	2	↓↓↑, ↑↓↓
$J/2 - 3\mu B$	1	↑↑↑
$J/2 + 3\mu B$	1	↓↓↓

The assumption $\mu B \ll J$ makes it easy to order the energy values without knowing the values of J and μ, and also ensures that there is not some accidental degeneracy that might arise because of a numerical coincidence, e.g. because $-J/2 - \mu B = J/2 - 3\mu B$ or $-J/2 + \mu B = -\mu B$. Note how reducing the number of spin pairs that are antiparallel raises the energy.

For the case $B = 0$, the energies (again from lowest to highest) and degeneracies become:

E	degeneracy	states
$-J/2$	2	↑↓↑, ↓↑↓
0	4	↓↑↑, ↑↓↓, ↑↑↓, ↓↓↑
$J/2$	2	↑↑↑, ↓↓↓

Note that in the absence of a magnetic field, the energy of any given microstate does not change if you reverse the directions of all the spins (up spins become down spins and vice versa) since it is the orientation of an external magnetic field that defines a specific sense of "up" versus "down" for the spins.

(b) **(10 points)** Assume now that this spin system is allowed to reach thermodynamic equilibrium by placing it contact with a thermal reservoir with constant temperature T. For each of the following three conditions, determine the values of the total internal energy U, the entropy S, and the magnetization $M = 2\mu(s_1 + s_2 + s_3)$ (so nine numbers in all).

i. $T = 0$ and $B = 0$.

Answer: The condition $T = 0$ (absolute zero) implies that this spin system must be in its lowest energy ground state. Looking at the above table for the case $B = 0$, we see that the ground state has energy $-J/2$ which is then the value of U. The ground state indeed is a small antiferromagnet, in which the spins alternate up-down-up or down-up-down. In a three-dimensional antiferromagnet, each up spin at a certain lattice point is typically surrounded by downspins at the nearest neighbor lattice sites.

The entropy $S = k \ln \Omega$ where the multiplicity Ω is the number of different microstates consistent with $U = -J/2$ which is $\Omega = 2$ so $S = k \ln 2$. Note that this system is an example for which the entropy $S \neq 0$ in the ground state. In practice, magnetic fields in the universe are never truly zero and an extremely small magnetic field would "break the symmetry" and favor one of the degenerate states over the other so that the entropy would really be zero at $T = 0$. (This is the situation in the next case below for which $T = 0$ and $0 < B \ll J/\mu$.) And even if there were no symmetry-breaking magnetic field, the degeneracy of the ground state of a macroscopic system is usually a small integer and so $S = k \ln \Omega$ is effectively zero (extremely tiny) compared to the entropy of a finite temperature system for which typically $S \propto N$ where N, the number of components in the system, may be of order Avogadro's number. So the flavor of the third law of thermodynamics still holds, the entropy becomes extremely tiny at sufficiently low temperatures.

Because there are two distinct ground states, there are two possible values for the magnetization, $\pm\mu$. A degenerate ground state is a situation you have not faced before. An acceptable answer was that the magnetization would be either μ or $-\mu$, or that the magnetization would be the average of the two possibilities, $\mu = 0$. A more accurate answer, but one that goes beyond the assumed knowledge for this course, is that the ground state would be some quantum superposition of the two possible ground states, and a measurement of the total magnetization in the $\hat{z}$ direction would yield either μ or $-\mu$ values randomly, with equal probability.

ii. $T = 0$ and $0 < B \ll J/\mu$.

Answer: Again $T = 0$ implies that the system must be in its ground state. Looking at the above table for the case $0 < B \ll J/\mu$,, the lowest energy state is now given by $U = -J/2 - \mu B$ which has a degeneracy $\Omega = 1$ so $S = 0$. The magnetization corresponds to the choice of spins $\uparrow\downarrow\uparrow$ for which $M = \mu$.

iii. $B = 0$ and $kT \gg J$.

Answer: From an earlier quiz problem, you figured out that, in the limit of high temperature, all the Boltzmann probabilities $e^{-\beta E_s}/Z$ become equal and equal to $1/N$ where N is the number of states. Further, in this limit, the average thermal energy $\overline{E}$ becomes the average of the energy values themselves. We conclude that, for $B = 0$,

$$U = \frac{1}{8}\left(2 \times \frac{J}{2} + 2 \times \frac{-J}{2} + 4 \times 0\right) = 0. \tag{79}$$

For sufficiently high temperatures, all states become equally likely so the multiplicity is $\Omega = 8$ and the entropy is $S = k \ln \Omega = k \ln 8 = 3k \ln 2$.
Just as the thermal energy becomes the average of the energy values, the thermal magnetization becomes the average of the possible magnetizations. But because of the spin symmetry that exists when with $B = 0$ (reversing all the spins doesn't change the energy), there is a negative magnetization of equal magnitude for each positive magnetization so the net high-T magnetization must be zero, $M = 0$.

(c) **(15 points)** For the case of zero external magnetic field ($B = 0$), deduce and sketch how the heat capacity $C(T)$ of this system varies with temperature for $T \geq 0$. Also calculate the approximate functional behavior of $C(T)$ for low temperatures ($kT/J \ll 1$) and for high temperatures ($kT/J \gg 1$).

Note: "approximate functional behavior" in some limit means carrying out some kind of Taylor series approximation to the lowest-order nontrivial term. You can also be efficient by avoiding an explicit calculation of $C(T)$ (which is a bit unwieldy). Instead, figure out qualitatively how the energy $E(T)$ varies with temperature and also deduce the functional forms of $E(T)$ for small and large T. You can then differentiate those limiting expressions of E to get the limiting behaviors of $C(T)$.

Answer: For $B = 0$, the energy levels you calculated in part (a) reduce to three distinct values: $E_1 = -J/2$ with degeneracy 2, $E_2 = 0$ with degeneracy 4, and $E_3 = J/2$ with degeneracy 2. The partition function Z for this three-spin system with $B = 0$ is therefore

$$\begin{aligned} Z &= 2e^{-\beta(-J/2)} + 4e^{-\beta(0)} + 2e^{-\beta(J/2)} && (80)\\ &= 4 + 2\left(e^{\beta J/2} + e^{-\beta J/2}\right) && (81)\\ &= 4 + 4\left(\frac{e^{\beta J/2} + e^{-\beta J/2}}{2}\right) && (82)\\ &= 4\left[1 + \cosh\left(\frac{\beta J}{2}\right)\right]. && (83)\end{aligned}$$

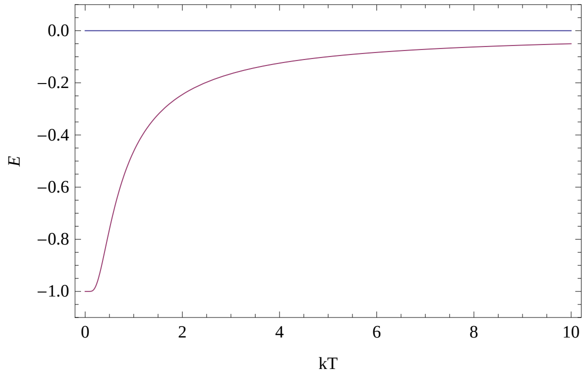
This is similar mathematically to the partition function $Z = 2\cosh(\beta\mu B)$ of a two-state paramagnet except for an additive constant. So you might guess correctly that the dependence of energy and heat capacity on temperature should be similar to a paramagnet.

Let's work out the details. The average energy of this system is given by the usual formula:

$$\overline{E} = -\frac{\partial \ln(Z)}{\partial \beta} = -\frac{J}{2}\left(\frac{\sinh(\beta J/2)}{1 + \cosh(\beta J/2)}\right) = -\frac{J}{2}\left(\frac{e^{\beta J/2} - e^{-\beta J/2}}{2 + e^{\beta J/2} + e^{-\beta J/2}}\right). \qquad (84)$$

As $T \to 0$, $\beta J/2$ becomes large, $e^{\beta J/2}$ becomes much larger than $e^{-\beta J/2} = 1/e^{\beta J/2}$ and much larger than 2. So the numerator $e^{\beta J/2} - e^{-\beta J/2}$ becomes dominated by $e^{\beta J/2}$, the denominator $2 + e^{\beta J/2} + e^{-\beta J/2}$ becomes dominated by the same term $e^{\beta J/2}$ so $\overline{E} \approx -J/2$, which we know is the ground state of this system for $B = 0$.

As $T \to \infty$, $\beta J/2$ becomes small and the numerator tends toward $e^0 - e^{-0} = 0$ so $\overline{E} \to 0$. From the general shapes of $\sinh(x)$ and $\cosh(x)$, we can also conclude that $\overline{E}$ must be increasing for increasing T. (One can just calculate $d\overline{E}/dT$ and verify that the derivative is always positive, so the energy is monotone increasing.) So we guess that $\overline{E}(T)$ is close to $-J/2$ for $T \approx 0$ and increases monotonically toward 0 as $T \to \infty$. Here is the actual shape of $\overline{E}$ versus kT according to Mathematica (with the choice $J = 2$):



The heat capacity $C(T) = d\overline{E}/dT$ is the local slope of this curve so must be zero close to $T = 0$, must be zero for large T, and must approach some maximum for intermediate T. Its form must indeed be similar to the heat capacity $C(T)$ of a paramagnet.

If you remembered an earlier homework problem, the heat capacity of any system whose energy levels E_s lie within a finite range must decay as $1/T^2$ for large T. This is a consequence of the relation

$$C_V = \frac{1}{kT^2}\sigma_E^2 = \frac{1}{kT^2}\left(\overline{E^2} - \left(\overline{E}\right)^2\right), \tag{85}$$

which was Problem 6.18 on page 231 of Schroeder. Our simple spin system definitely has a finite range of energy values since it has a finite set of energies and so we expect $C \propto 1/T^2$ for large T. Since $C(T = 0) = 0$ by the third law of thermodynamics, we again anticipate that the heat capacity of this small antiferromagnet must have the same qualitative shape as a paramagnet.

To complete this problem, let's work out the leading order behavior in the low- and high-temperature limits. Following my clue that the Taylor series of the derivative of a function $f'(x)$ is the derivative of the Taylor series of $f(x)$, it is easier to work out the low- and high-temperature behaviors for $\overline{E}$ from Eq. (84) and then differentiate those to get the leading behaviors of $C(T)$.

For the high temperature case, kT is large so $\beta J/2$ is small and we can get the leading nontrivial (non-constant) term from the Taylor series approximation for the exponential $e^x \approx 1 + x$. If we define $x = \beta J/2$, we have from Eq. (84):

$$\overline{E} \approx -\frac{J}{2}\left(\frac{(1+x)-(1-x)}{2+(1+x)+(1-x)}\right) \approx -\frac{J}{4}x \approx -\frac{J^2}{8}\frac{1}{kT} \propto -T^{-1}. \tag{86}$$

So the heat capacity $C = d\overline{E}/dT \propto T^{-2}$ at large temperatures, just as we argued above.

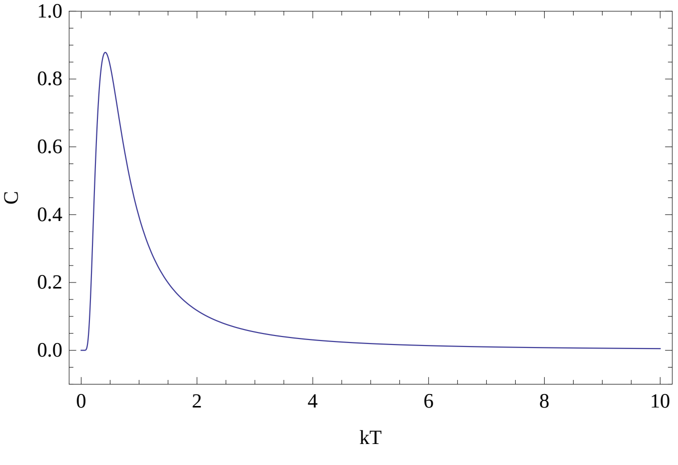
For the low temperature case, kT is small, $x = \beta J/2$ is large and we can *not* use a Taylor series approximation for e^x or for e^{-x} in an practical way since many terms would have to be included in the series. Instead, we recognize that x large implies that $y = e^{-x}$ is small so we Taylor expand in the small quantity y instead. Rewriting Eq. (84) in terms of y we find:

$$\overline{E} = -\frac{J}{2}\left(\frac{1-y^2}{1+2y+y^2}\right) \approx -\frac{J}{2}\left(\frac{1}{1+2y}\right) \approx -\frac{J}{2}(1-2y), \tag{87}$$

to the lowest nontrivial power in y. To get the second equality, I dropped the y^2 in the numerator $1 - y^2$ as being small compared to 1, and dropped the y^2 in the denominator $1 + 2y + y^2$ as being small compared to $1 + 2y$. I then used the approximation $1/(1 + u) \approx 1 - u$ with $u = -2y$. The corresponding behavior of the heat capacity for small T is obtained by differentiating Eq. (87) with respect to T. This gives:

$$C = \frac{d}{dT}\left[-\frac{J}{2}\left(1 - 2e^{-J/(2kT)}\right)\right] = \frac{J^2}{2}\frac{1}{T^2}e^{-J/(2kT)}. \tag{88}$$

The exponential term $e^{-J/(2kT)}$ decays to zero much faster than $1/T^2$ diverges as $T \to 0$ so Eq. (88) decays to zero rapidly (faster than any polynomial) as $T \to 0$. These insights can be compared with the actual functional form of $C(T)$ as obtained by differentiating Eq. (84) w.r.t. T and plotting with Mathematica:



This curve is consistent with the qualitative behavior of the slope of the $\overline{E}$ versus T plot above, and is indeed similar to the paramagnet heat capacity, see Figure 3.10 on page 103 of Schroeder.

True or False Questions (2 points each)

For each of the following statements, please circle **T** or **F** to indicate whether a given statement is true or false respectively.

1. **T / F** It is possible for the phase line separating a crystalline solid phase from a liquid phase in a temperature-pressure phase diagram to end abruptly in a critical point.

   Answer: F The phase line separating a solid from a liquid can *not* end at a critical point, which was mentioned briefly in Schroeder but not explained. The reason is that a critical point implies that one can continuously vary from one phase to another phase (say water to steam) by simply following a path in the temperature-pressure phase diagram that swings around the critical point. But there is no way to vary T and P so as to continuously change from a gas, which has no regular order in the locations of its atoms, to a crystalline solid, which has such order. So a critical point generally can't occur for a phase line separating any two phases that have different symmetries: gas-solid, liquid-solid, and even solid-solid phases if the two solid phases have different symmetries (say one phase has a face centered cubic lattice while another phase has a body centered cubic lattice).

2. **T / F** A system can be in thermodynamic equilibrium in the presence of a time-independent but spatially varying electric field.

   Answer: T This situation is no different than a a gaseous atmosphere being in thermodynamic equilibrium with a spatially varying gravitational field. For such a system, the condition that the pressure be the same everywhere for different subsystems is replaced by the condition that the chemical potential μ be the same everywhere. This typically implies that the pressure (and particle density) are spatially varying. This makes sense in that a local force induced by the electric field (say on a liquid dielectric in some non-planar capacitor) must be balanced by the local pressure so that there is no net force that would cause a time dependent bulk motion that would violate thermodynamic equilibrium, which requires time independence and no relative motion of subsystems.

3. **T / F** A gas of N identical particles is ideal if and only if the single particle partition function Z_1 satisfies $Z_1 \gg N$.

   Answer: F The single particle partition function Z_1 has the physical meaning of the approximate number of quantum levels that are within an energy distance kT of the ground state, i.e., it is the number of levels that are physically relevant for a system in thermodynamic equilibrium with temperature T. The condition $Z_1 \gg N$ implies that there are many more levels than particles, which is the same as saying it is unlikely that two or more particles can occupy the same energy level. This statement is not the same as saying that the particles don't interact with each other, which is the key assumption of an ideal gas. The statement $Z_1 \gg N$ is a necessary condition for the approximation $Z_N \approx Z_1^N/N!$ to hold.

4. **T / F** At a low temperature of $10^{-3}\,\mathrm{K}$, metals have a higher heat capacity than insulators.

   Answer: T Insulators have no free electrons and so their heat capacities are due mainly to phonons, which means $C \propto T^3$ at low temperatures. (At higher temperatures, the heat capacity eventually looks like the equipartition result $C = Nf(kT/2)$ with $f = 6$ and becomes independent of temperature.)

Metals have electrons and phonons, and their heat capacity has the form $C \approx c_1 T + c_3 T^3$. For sufficiently low temperatures, the T^3 term is ignorable compared to the linear term and a metal will have a higher heat capacity than an insulator. For a metal like copper, the phonon contribution to the heat capacity becomes less than the electron contribution around 5 K. At the much lower temperature of 10^{-3} K, the T^3 term is negligible than the T term and metals have a higher heat capacity than insulators.

5. **T / F** The root-mean-square variation $\Delta n(f)$ of the number of photons in an equilibrium photon gas that have frequency f (i.e., are in the energy level $\epsilon = hf$) is smaller than the average number $\overline{n}(f)$ of photons that have frequency f.

Answer: F This was a true-false question that required a calculation and so could not be answered just by qualitative reasoning or by background knowledge. The intent here was for you to realize that the Bose-Einstein and Fermi-Dirac distributions $\overline{n}(\epsilon)$ were obtained by calculating the average number of particles that occupy a particle energy level ϵ, based on a Gibbs sum (grand partition function):

$$\overline{n} = \frac{kT}{\mathcal{Z}} \frac{\partial \mathcal{Z}}{\partial \mu}. \tag{89}$$

Because this is an average number, the actual number can vary from moment to moment and so one can study the variations or fluctuations in $\overline{n}$ for a given energy level. For example, we can calculate the variance of the occupation number:

$$\sigma_n^2 = \overline{(n - \overline{n})^2} = \overline{n^2} - (\overline{n})^2 = \frac{(kT)^2}{\mathcal{Z}} \frac{\partial^2 \mathcal{Z}}{\partial \mu^2} - \left(\frac{kT}{\mathcal{Z}} \frac{\partial \mathcal{Z}}{\partial \mu} \right)^2. \tag{90}$$

So one has to plug and chug, and then think a little. A single photon energy level with energy ϵ can be occupied by zero photons with energy 0, by one photon with energy ϵ, by two photons with energy 2ϵ, etc. The corresponding partition function $\mathcal{Z}$ for a single photon level in equilibrium with a reservoir of temperature T is obtained by adding up a geometric series for energy levels 0, ϵ, 2ϵ, etc (see pages 267 and 289 of Schroeder):

$$\mathcal{Z} = 1 + e^{-\beta\epsilon} + e^{-\beta(2\epsilon)} + e^{-\beta(3\epsilon)} + \ldots = \frac{1}{1 - e^{-\beta\epsilon}}. \tag{91}$$

There are no terms $-\mu N_s$ in the exponents since the chemical potential $\mu = 0$ for a photon gas. This also means that we can't use Eq. (90) directly since there is no μ in Eq. (91) to differentiate with respect to. Instead, we can observe from Eq. (91) that

$$\sigma_n^2 = \overline{n^2} - (\overline{n})^2 = \frac{(kT)^2}{\mathcal{Z}} \frac{\partial^2 \mathcal{Z}}{\partial \epsilon^2} - \left(\frac{-kT}{\mathcal{Z}} \frac{\partial \mathcal{Z}}{\partial \epsilon} \right)^2. \tag{92}$$

Substituting Eq. (91) into Eq. (92) and evaluating the derivatives, we find the relative fluctuation squared to be:

$$\frac{\sigma_n^2}{\overline{n}^2} = 1 + \frac{1}{\overline{n}} = e^{\beta\epsilon}, \tag{93}$$

where I have used the fact that $\overline{n} = 1/(e^{\beta\epsilon} - 1)$, which is the Planck distribution. Eq. (93) is greater than one since the exponent $\beta\epsilon$ is positive. This result also implies that the relative fluctuation increases rapidly with photon energy for a fixed temperature.

So the variation σ_n in photon number for a given energy level is greater than the mean $\overline{n}$. This result has experimental consequences that allow one to test directly the hypothesis that photons are bosons and so tend to bunch together. Try googling the "Hanbury, Brown, and Twiss effect" which is a famous and originally controversial experiment that helped to establish that photon fluctuations had unusual statistics that could be explained by the assumption that they were bosons.

6. **T / F** In a temperature-pressure phase diagram, the solid-gas phase transition line always passes through the origin $P = T = 0$.

Answer: F The phase transition diagrams for water and CO_2 on page 167 of Schroeder were not drawn well: they suggest visually that the solid-gas phase line goes through the origin but the origin in these plots is not absolute zero but some finite temperature. With the exception of liquid helium below about 25 atmospheres of pressure, all substances solidify before reaching absolute zero.

Your knowledge of the He^4 phase diagram (from a homework problem, see Fig. 5.13 on page 168 of Schroeder)) also would be sufficient to determine that the answer is "false" since there the phase line involving a solid definitely does not go through the origin at $T = 0$.

7. **T / F** If three tiny holes are punched in the sides of a tall vertical enclosed cylinder near the cylinder's bottom, middle, and top, and if the cylinder contains an ideal gas in thermodynamic equilibrium, then the loss of gas by effusion will occur at the same rate for all three holes.

Answer: F If the gas inside the cylinder is in thermodynamic equilibrium, the temperature T is everywhere the same. This implies that the average molecular speed $\overline{v}$, which shows up in the effusion flux formula

$$\Phi = \frac{1}{4} n \overline{v}, \tag{94}$$

is the same everywhere and so is independent of height. But the particle density $n = N/V$ is not independent of height, it satisfies the "exponential atmosphere" law and decreases exponentially as $e^{-\beta m g z}$ where z is the height of the particle above the ground. So the rate of effusion is not the same at different heights: it is largest near the bottom of the cylinder (largest particle density) and smallest near the top, and the ratio of effusion rates is $e^{-\beta m g \Delta z}$ where Δz is the difference in height between two effusion holes.

By the way, a similar answer holds for fluid flow but with quantitatively different behavior than effusion. If you fill a container with water, and punch three holes (say the width of a nail) near the bottom, middle, and top of a wall of the container, then the water will jet out the furthest at the bottom and least at the top. (Try this, say with a milk carton filled with water.) You can calculate quantitatively how far the jets go: when a small parcel of fluid of volume ΔV and mass M descends a distance Δz from the top of the fluid and reaches a hole, the parcel releases an amount of potential energy $Mg\Delta z$. This potential energy is converted into kinetic energy as the parcel flows out of the hole:

$$\frac{1}{2} M v^2 = M g \Delta z, \tag{95}$$

where $M = \rho \Delta V$ and ρ is the mass density of water. The speed v is the horizontal speed of the fluid just as it leaves the container. The mass ΔM of water that flows through a hole of area A in time Δt is $\rho(Av\Delta T)$ so the fluid mass flux is $\Delta M/(A\,\Delta T) = \rho v \propto \sqrt{\Delta z}$. So the ratio of fluxes for a fluid varies much less strongly, as the square root of the difference in heights of the holes, rather than as an exponential of the height difference.

8. **T / F** If two identical blocks of metal are welded to form a single larger metal block, the Fermi energy E_F will now be larger.

Answer: F The formula for the Fermi energy of a metal

$$\epsilon_F = \frac{\hbar^2}{8m} \left(\frac{3N}{\pi V} \right)^{2/3}, \tag{96}$$

depends on the intensive number density N/V so is an intensive quantity itself. Since welding two identical blocks together doubles N and doubles V, the Fermi energy does not change.

9. **T / F** The chemical potential μ of an ideal gas is zero if and only if the particles that make up the gas have zero mass.

Answer: F It is true that massless particles (photons, phonons) have a zero chemical potential since particle number is not conserved. But it is possible for massive particles to also have a zero chemical potential if the kinetic energy of the particles exceeds their rest mass energies mc^2 in which case particle number is also not conserved (particles can be created or destroyed during high-energy collisions). This point was never explicitly made by Schroeder but was mentioned in some of the problems in the section on blackbody radiation, e.g., Problem 7.48 on page 298 on a neutrino gas and Problem 7.49 on electron-positron pair creation in the hot early universe.

10. **T / F** When a star supernovas and most of its mass collapses into a black hole (which is then characterized by just its mass M, charge Q, and angular momentum $\mathbf{\Omega}$), the entropy of the hole is much less than the entropy of the original star.

Answer: F This was a "did you remember" true-false based on an earlier homework problem, Problem 2.42 on page 83, in which you estimated the entropy of a one-solar-mass black hole and found remarkably that it was of order 10^{20} times the entropy of a corresponding star with the same mass. So although black holes are almost completely empty (all matter in a black hole gets crushed to an extremely dense region near the center of the hole), the entropy is enormous. The intuitive reason is that a black hole obliterates all knowledge of the matter that falls inside (only the mass and charge of a black hole can be measured from outside the event horizon) so its entropy must exceed the entropy of any type of matter or particles that were used to make the black hole.

11. **T / F** For N of order Avogadro's number, $\ln[(N!)!] \approx N! \ln(N)$.

Answer: T Using Stirling's formula in the logarithmic form $\ln(M!) \approx M \ln(M) - M$, we have:

$$\begin{aligned}
\ln[(N!)!] &\approx N! \ln(N!) - N! && (97)\\
&\approx N![N\ln(N) - N] - N! && (98)\\
&= NN! \ln(N) - (N+1)N! && (99)\\
&\approx (N+1)!\,(\ln(N) - 1) && (100)\\
&\approx N!(\ln(N) - 1). && (101)
\end{aligned}$$

Here I have used the fact that $N+1 \approx N$ for $N \gg 1$ so $NN! \approx (N+1)!$, and I used the fact that $(N+1)! = (N+1)N! \approx N!$ since $N+1$ is a large number multiplying a very large number $N!$.

For $N \approx 10^{23}$, $\ln(N) \approx 23\ln(10) \approx 23 \times 2.3 \approx 50$ so $\ln(N) - 1 \approx \ln(N)$ and we have approximately $\ln[(N!)!] \approx N! \ln(N)$. So the statement is true.

A variation of this problem would have been to work out a low-order approximation to $\ln\ln[(N!)!)]$, which would have required using in addition the approximation $\ln(1+x) \approx x$ for x sufficiently small. Then

$$\begin{aligned}
\ln\ln[(N!)!] &\approx \ln[N!(\ln(N) - 1)] && (102)\\
&= \ln(N!) + \ln[\ln(N) - 1] && (103)\\
&= \ln(N!) + \ln\ln(N) + \ln\left(1 - \frac{1}{\ln(N)}\right) && (104)\\
&\approx \ln(N!) + \ln\ln(N) - \frac{1}{\ln(N)} && (105)\\
&\approx N\ln(N) - N - \frac{1}{\ln(N)} + \ln\ln(N). && (106)
\end{aligned}$$

12. **T / F** For an equilibrium low-density ideal gas that consists of N identical molecules, the single-particle partition function Z_1 is an extensive variable.

Answer: T From the expression on page 254 in Section 6.7 of Schroeder

$$Z_1 = \frac{V Z_{\rm int}}{V_Q}, \tag{107}$$

we conclude that Z_1 is an extensive quantity since $Z_1 \propto V$ and $Z_{\rm int} = Z_{\rm int}(T)$ and $V_Q = V_Q(T)$ are functions only of T and so are intensive variables.

This could also be deduced more generally from thermodynamic considerations. We know that the free energy $F = U - TS$ is an extensive quantity (since U and S are extensive), we know that $F = -kT \ln(Z_N)$, and for a low-density high-temperature gas, $Z_N \approx Z_1^N/N!$. Combining these ideas and using Stirling's formula, we find that

$$F = -NkT \ln\left(1 + \frac{Z_1}{N}\right). \tag{108}$$

Because of the overall N factor, Eq. (108) will be extensive only if Z_1/N is intensive, which in turn implies that Z_1 must be extensive since N is extensive.

13. **T / F** In a universe with ten spatial dimensions (a possibility suggested by string theory), the heat capacity C_V of an equilibrium ideal gas consisting of N identical atoms with temperature T has the same value $(3/2)Nk$ that the same gas would have in our three dimensional universe.

Answer: F The equipartition theorem says that the heat capacity $C_V = Nf(kT/2)$ where f is the number of degrees of freedom. For an atom, f is the number of independent coordinates needed to locate the atom's of center of mass. In our three-dimensional universe, $f = 3$ while in a 10-dimensional universe, $f = 10$ in which case the heat capacity is about $10/3 \approx 3$ times larger.

14. **T / F** The temperature dependence of the pressure of a photon gas does not depend on whether the gas is three-dimensional or two-dimensional.

Answer: F The pressure of an ideal gas is given by the derivative of energy U with respect to volume V with constant temperature

$$P = -\left(\frac{\partial U}{\partial V}\right)_T \tag{109}$$

and so has the same temperature dependence as the energy U itself. The energy is given by an expression similar to Eq. (30) above. For three dimensions, we have

$$U = 2 \sum_{n_x=1}^{\infty} \sum_{n_y=1}^{\infty} \sum_{n_z=1}^{\infty} \frac{hcn}{2L} \frac{1}{e^{\beta hcn/(2L)} - 1} \tag{110}$$

$$U \approx 2 \int_0^\infty dn_x \int_0^\infty dn_y \int_0^\infty dn_z \, \frac{hcn}{2L} \frac{1}{e^{\beta hcn/(2L)} - 1} \tag{111}$$

$$\approx \left(\frac{1}{8} \times 4\pi\right) \int_0^\infty dn \, n^2 \, \frac{hcn}{L} \frac{1}{e^{\beta hcn/(2L)} - 1} \tag{112}$$

$$= V \frac{8\pi (kT)^4}{(hc)^3} \int_0^\infty \frac{x^3 \, dx}{e^x - 1}. \tag{113}$$

Here I switched from Cartesian to spherical coordinates, $(n_x, n_y, n_z) \to (n, \theta, \phi)$ and recognized that, since the integrand does not depend on the spherical angles, the angular integrals evaluate to 1/8 the area of a unit sphere. I also changed variables from quantum number n to the dimensionless energy $x = \beta\epsilon = \beta hcn/(2L)$. We conclude that in 3D, U and so P are both proportional to T^4.

In two dimensions, we have two summations instead of three and the analogous calculation becomes:

$$\begin{aligned} U &= 2\sum_{n_x=1}^{\infty}\sum_{n_y=1}^{\infty}\frac{hcn}{2L}\frac{1}{e^{\beta hcn/(2L)}-1} && (114)\\ &= 2\int_0^{\infty}dn_x\int_0^{\infty}dn_y\,\frac{hcn}{2L}\frac{1}{e^{\beta hcn/(2L)}-1} && (115)\\ &\approx \left(\frac{1}{4}\times 2\pi\right)\int_0^{\infty}dn\,n\,\frac{hcn}{L}\frac{1}{e^{\beta hcn/(2L)}-1} && (116)\\ &= V\frac{8\pi(kT)^3}{(hc)^3}\int_0^{\infty}\frac{x^3\,dx}{e^x-1}. && (117)\end{aligned}$$

Here I changed Cartesian to cylindrical coordinates, $(n_x, n_y) \to (n, \theta)$ and $dn_x\,dn_y \to n\,dn\,d\theta$. The angular integral now goes over 1/4 the circumference of a unit circle so gives $\pi/2$. The change in dimensionality causes the n^2 factor in 3D to change to n in 2D (see line Eq. (116) above) and this directly changes the temperature scaling when we change variables from $n \to x = \beta\epsilon = \beta hcn/(2L)$. So the temperature dependence definitely depends on the spatial dimensionality.

It is not too hard to work out the general case, using what you learned when we discussed the surface area of a hyperdimensional sphere. In N spatial dimensions, Eq. (110) will involve N summations which will be approximated by N integrals. The change from Cartesian to "hyperdimensional spherical" coordinates, $(n_1, n_2, \ldots, n_N) \to (n, \theta_1, \ldots, \theta_{N-1})$, will cause the substitution $dn_1\,dn_2\,\ldots\,dn_N \to n^{N-1}f(\theta_1, \ldots, \theta_{N-1})\,dn\,d\theta_1\,\ldots\,d\theta_{N-1}$ for the infinitesimal volume, i.e., the integrand is multiplied by the radial power n^{N-1} and by a complicated bunch of sines and cosines. Since the the integrand just depends on the length n of the quantum state vector, the $N-1$ angular integrals evaluate to some multiplicative constant ($1/2^N$ times the surface area of a N-dimensional unit sphere) that does not affect the temperature scaling. The remaining radial integral has the form

$$U \propto \int_0^{\infty}dn\,n^{N-1}\,\frac{hcn}{L}\frac{1}{e^{\beta hcn/(2L)}-1}. \qquad (118)$$

Changing variables $n \to x = \beta\epsilon = \beta hcn/(2L)$ then reveals a T^{N+1} temperature dependence, which reduces correctly to the 2D and 3D cases.

We conclude that the temperature scaling of the photon energy density and pressure does depend on the spatial dimension.

15. **T / F** There are 130 distinct ways to place three identical bosons in ten degenerate energy levels.

Answer: F The number of distinct ways includes $\binom{10}{3} = 120$ ways to place three bosons in three distinct energy levels, $10 \times 9 = 90$ ways to place two bosons in one energy level and the third boson in some different level, and $\binom{10}{1} = 10$ ways to place all three bosons in the same energy level. The total number of ways is $120 + 90 + 10 = 220$. In this case, nearly half the energy levels have multiple occupations so the approximation $Z_N \approx (1/N!)Z_1^N$ will strongly fail.

16. **T / F** The equilibrium temperature of the Earth due to absorption of sunlight and blackbody emission depends on the radius of the Earth.

Answer: F The equilibrium temperature T_E of the Earth is determined by balancing the amount of blackbody radiation received from the Sun (of radius R_S, distance from Earth d_S, and absolute temperature T_S) by the blackbody radiation emitted by an Earth of radius R_E. This balance takes the mathematical form

$$\left(4\pi R_E^2\right)\sigma\,T_E^4 = \left(\frac{\pi R_E^2}{4\pi d_S^2}\right)\left(4\pi R_S^2\right)\sigma\,T_S^4, \qquad (119)$$

where I have assumed that the Earth and Sun have uniform surface temperatures and both are perfect blackbody emitters. The radius R_E of the Earth cancels from both sides to the answer is false, the equilibrium temperature of the Earth does not depend on the size of the Earth.