Midterm Exam for Physics/ECE 176: Answers

Professor Greenside
Thursday, March 4, 2010

The following answers are far more detailed than what was necessary to get full credit for any given problem. I include the details with the hope that they will help you to understand the thermal physics better.

Problems That Require Writing

1. **(30 points)** The year is 2020 and you have been invited by one of your professor friends to be a guest speaker in her undergraduate thermal physics class. Using as a specific example one of the three key systems that you have studied so far this semester (Einstein solid, ideal gas, or paramagnet), discuss concisely what you would say to the class about how microstates, macrostates, multiplicity, and the second law of thermodynamics are related to one another: why does counting microstates have anything to do with thermodynamic equilibrium?

   Note: your goal is to show me that you understand the logical thread that ties various ideas together, in the context of a specific example. You don't need to write full sentences or give any mathematical derivations but you do need to state key definitions, assumptions, and mathematical expressions, and *especially* indicate through appropriate brief phrases the logic that connects the various concepts so that these future students understand what is going on.

   Answer: In your answer, I was looking for most of the following ideas, concepts, and equations. I have made bold certain words or phrases that were especially important to mention.

   (a) Thermal physics is concerned with macroscopic objects that consist of many parts. The object is **isolated** from the world so that its total energy U, volume V, and number of components N are **conserved**. Experiments then show that such isolated macroscopic objects eventually reach thermodynamic equilibrium, in which certain properties are uniform throughout the object (temperature, pressure, etc) and the properties are independent of how the object reached equilibrium.

   (b) The macroscopic object is characterized by certain macroscopic quantities such as U, V, and N, which defines the object's macroscopic state or **macrostate**. Many other properties could be used to characterize the object (color, geometric shape, heat capacity, resistivity, brittleness, sound speed, etc) but the most important parameters are ones for which some **conservation law** holds.

   (c) The macroscopic object may be further characterized by its microstates. A particular **microstate** is defined to be a list of all the states of each individual component that makes up the object at a particular time. For example, a microstate of an ideal gas would correspond to particular values of the position $\mathbf{x} = (x, y, z)$ and momentum $\mathbf{p} = (p_x, p_y, p_z)$ for each atom in the gas so the microstate involves a list of $6N$ numbers total if there are N atoms in the gas. For an Einstein solid with N quantum harmonic oscillators, a microstate would be a list of the N energy levels $(q_1, \ldots, q_N)$ occupied by each oscillator, which indicates how much energy is stored in each oscillator.

   An aside: the microstate of a system is difficult to define if the components interact with one another. For example, in a liquid, a given atom interacts via some potential energy with its nearby neighbors and so one can not describe the atom separately from its neighbors.

   (d) For a given description of the macroscopic object through values of U, V, and N, only certain microstates are compatible with those values. These are called the "accessible microstates" of the macroscopic object. For an Einstein solid, an accessible microstate would have $\sum_i q_i = q$, the sums of the energy q_i in each oscillator adds up to the fixed total amount of energy q.

   (e) The number of accessible microstates of a given macroscopic object is called the multiplicity of the object and is denoted by $\Omega = \Omega(U, N, V)$. It is an integer greater than or equal to one.

(f) An important fundamental hypothesis of thermal physics is that, **in thermodynamic equilibrium of an isolated macroscopic system, all accessible microstates are equally likely to be observed** if one were to measure the microstate of a system at any given time.

(g) This hypothesis has the very important consequence that some macroscopic states are much more likely to be observed than other macroscopic states, because some macroscopic states have many more accessible microstates. To see this, consider an Einstein solid that is divided into two equal weakly interacting macroscopic halves, with N oscillators in one piece and N oscillators in the other piece. A fixed total amount of energy q can now be divided macroscopically between the two halves, with q_A energy units going into half A and $q - q_A$ energy units going into half B. Because the two halves are weakly interacting (which is true for nearly all substances the class will ever need to consider), the multiplicity of the entire solid is approximately equal to the product of the multiplicities for each subsystem:

$$\Omega_{\rm AB} \approx \Omega_A(q_A)\,\Omega_B(q - q_A), \tag{1}$$

where I have assumed that the multiplicity of a subsystem depends only on the energy of that subsystem, at least over times short compared to some relaxation time like L^2/κ. But we learned earlier this semester, that in the high-temperature limit $q \gg N \gg 1$,

$$\Omega(N, q) \approx \left(\frac{eq}{N}\right)^N . \tag{2}$$

So in the high-temperature limit, Eq. (1) becomes

$$\Omega_{\rm total} \approx \left(\frac{e}{N}\right)^{2N} \left(q_A(q - q_A)\right)^N . \tag{3}$$

But we also learned earlier this semester that any function with a single global maximum, in particular the function $f(q_A) = q_A(q - q_A)$, raised to a high power acts like a very tall, very narrow Gaussian centered on the location of the maximum, here $q_A = q_B = q/2$ with energy equally distributed between the two halves, with a peak whose width is of order $1/\sqrt{N}$ where N is the number of components. The peak is exceedingly narrow if N is of order Avogadro's number. Since the probability of observing a particular macrostate with energy q_A in A is

$$p(q_A) = \frac{\Omega_{AB}(q_A)}{\Omega_{\rm total}}, \tag{4}$$

(this is the ratio of microstates compatible with q_A energy units in A over the total number of microstates), we conclude that, for N sufficiently large, only one macroscopic state is likely to be observed at any given time, the one corresponding to energy equally distributed between two equal halves.

Note: the above information is the most important collection of facts that I wanted to see in your answer to Problem 1. You needed to consider two weakly coupled systems of an isolated whole, and argue that the multiplicity for the entire system has an incredibly tall, incredibly sharp peak centered on the value that corresponds to equilibrium. You needed to mention that the width of the probability was of order $1/\sqrt{N}$ since that specifically tells you how unlikely it is to see anything but the equilibrium state: once the energy q_A deviates from the equilibrium value $q/2$ by about one part in 10^{10}, the probability is vanishing small to observe such a macroscopic state.

(h) The previous paragraph implies that the multiplicity of a macroscopic system will steadily increase over time until it reaches a maximum value corresponding to energy (or volume or particles if these two can vary) distributed in proportion to the size of each macroscopic system. In more detail, the number of microstates compatible with an equilibrium distribution of energy is so enormously greater than all the other accessible microstates, that the system will, with probability nearly one, change to a microstate that is consistent with equilibrium and then in the future switch only to other microstates consistent with equilibrium (say with $q/2$ amount of energy in subsystems A and in B).

(i) Thus if we define an entropy by $S = k \ln \Omega$, it will have the property that, for an isolated system such that U, V, and N are conserved, S will strictly increase over time until it reaches a maximum. (Further, by Eq. (1), the entropy will be additive over subsystems.) This explains the second law of thermodynamics in terms of microstates, conservation laws, and the fundamental postulate that all accessible microstates are equally likely.

2. A carbon nanotube is a remarkable straw-like molecule of carbon atoms that can be several millimeters long while having a tiny diameter of a few nanometers. Assume that $N \gg 1$ identical atoms with a fixed total energy U adsorb onto a nanotube of length L, such that the adsorbed atoms act as a one-dimensional ideal gas.

   (a) **(15 points)** Derive the Sackur-Tetrode equation for the entropy $S = S(U, L, N)$ of this one dimensional gas.

   Answer: This problem is a straightforward variation of what we discussed in class for a 3D gas and of two problems that you solved in a recent homework assignment regarding a 2D gas (see problems 2.26 and 3.39 of Schroeder). I will outline the key steps here and let you work out the algebra.

   The first step is to calculate the multiplicity $\Omega(U, L, N)$ of N adsorbed atoms on a 1d nanotube of length L with fixed total energy U. By analogy to how Schroeder derived Eq. (2.40) on page 71, we have:

$$\begin{aligned} \Omega_N &= \frac{1}{N!} L^N A_N\left(\sqrt{2mU}\right)\frac{1}{h^N} && (5) \\ &= \frac{1}{N!}\frac{L^N}{h^N}\frac{2\,\pi^{N/2}}{\Gamma(N/2)}\left(\sqrt{2mU}\right)^{N-1}. && (6) \end{aligned}$$

   The leading $1/N!$ factor comes from the assumption that the atoms are all identical particles, it decreases the multiplicity from the over-counting that arises if the particles are assumed to be distinct. The factor L^N comes from the fact that, for an ideal gas of non-interacting particles, each adsorbed atom independently has a number of distinct spatial positions proportional to L, the size of the space that the atoms move in. The factor $A_N(\sqrt{2mU})$ is the surface area of a N-dimensional hypersphere of radius $\sqrt{2mU}$ and arises from the fact that, on a one-dimensional nanotube, the N momenta p_1, p_2, $\ldots$, p_N of all the adatoms satisfies the condition that the kinetic energies of all the adatoms must add up to the fixed total energy U:

$$\frac{p_1^2}{2m} + \ldots + \frac{p_N^2}{2m} = U, \qquad (7)$$

   that is $p_1^2 + \ldots + p_N^2 = 2mU$, which defines the set of points on the surface of a N-dimensional hypersphere of radius $\sqrt{2mU}$. Finally the term $1/h^N$, where h is Planck's constant, is the crucial term required by quantum mechanics that converts the proportionality $\Omega \propto L^N A_N(\sqrt{2mU})$ to an exact integer count. (Each product of a length L with a momentum p must be divided by the smallest possible product $\Delta x \Delta p \approx h$ allowed by the uncertainty principle.)

   We next convert the multiplicity to an entropy. First, we observe that if $N \gg 1$, in Eq. (6) we can approximate $N - 1$ to be N, drop the 2 factor in Eq. (6) since it is a small number multiplying a very large number, and approximate $\Gamma(N/2) = (N/2 - 1)! \approx (N/2)!$. Thus

$$\Omega(L, N, U) \approx \frac{1}{N!}\frac{1}{(N/2)!}\frac{1}{h^N} L^N \pi^{N/2}(2mU)^{N/2} = \frac{1}{N!}\frac{1}{(N/2)!}\left[L\left(\frac{2\pi mU}{h^2}\right)^{1/2}\right]^N. \qquad (8)$$

   This is Eq. (2.40) on page 71 of Schroeder if we replace V with L and replace 3 everywhere with 1 (3D to 1D).

To get the one-dimensional Sackur-Tetrode equation, we use the definition $S = k\ln\Omega$ and apply Stirling's formula in the form $\ln(n!) \approx n\ln(n) - n$ to the two factorials in Eq. (8). We find:

$$\begin{aligned} S &= k\ln\Omega \quad &(9)\\ &= Nk\ln\left[L\left(\frac{2\pi mU}{h^2}\right)^{1/2}\right] - k\ln(N!) - k\ln[(N/2)!] \quad &(10)\\ &\approx Nk\ln\left[L\left(\frac{2\pi mU}{h^2}\right)^{1/2}\right] - Nk\ln(N) + Nk - \frac{Nk}{2}\ln\left(\frac{N}{2}\right) + \frac{Nk}{2} \quad &(11)\\ &= Nk\left[\frac{3}{2} + \ln\left(\frac{L}{N}\left(\frac{4\pi m}{h^2}\frac{U}{N}\right)^{1/2}\right)\right]. \quad &(12) \end{aligned}$$

The last line is the desired one-dimensional form of the Sackur-Tetrode equation. Note that the constant 3/2 changes to 4/2 in 2D and to 5/2 in 3D. I have also written Eq. (12) in a form that emphasizes the intensive ratios L/N and U/N.

(b) **(5 points)** Find the equation of state $P = P(T, L, N)$ for this one-dimensional gas.

Answer: In three dimensions, pressure has units of force per area. In two dimensions, pressure has units of force per length. In one dimension, pressure has units of force and the expression $-PdV$ for the work done on the gas related to compression or expansion becomes $-FdL$ where dL is some small distance over which the force F is applied. The thermodynamic identity for our nanotube should then be written as $dU = TdS - FdL$. For an isolated system for which energy is conserved, $dU = 0$, we obtain the following expression for the "pressure" F in terms of the entropy

$$F = T\left(\frac{\partial S}{\partial L}\right)_{U,N}. \quad (13)$$

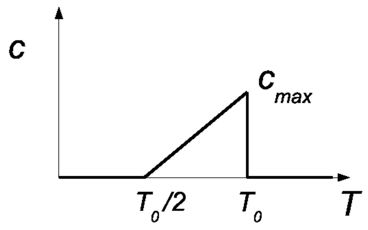
In the 1d Sackur-Tetrode equation Eq. (12), we see that $S = Nk\ln(L) + f(N,U)$ where f is some function of N and U but not of L. Eq. (13) then gives us

$$F = T\frac{\partial}{\partial L}\big(Nk\ln(L) + f(N,U)\big) = \frac{NkT}{L}. \quad (14)$$

This can be written in the form $FL = NkT$, which is the desired equation of state. Note how it has a form identical to the ideal gas law $PV = NkT$.

Note that we can pin down what temperature means for this 1d gas by calculating $1/T = dS/dU$ for S given by Eq. (12). As you should verify, this leads to the equipartition theorem $U = N(kT/2)$ with $f = 1$ since there is only one translational degree of freedom, which is along the axis of the nanotube.

3. **(10 points)** A ferromagnet at absolute zero has all of its $N \gg 1$ two-state (spin-1/2) magnetic moments aligned in parallel, with no external magnetic field present. The ferromagnet is then heated until its temperature exceeds its Curie temperature T_0, at which point the magnetization M of the magnet has decreased to zero. A crude model of how the heat capacity $C_V(T)$ of the ferromagnet depends on temperature is given by the following plot:



which corresponds to the mathematical expression

$$C_V(T) = \begin{cases} C_{\max}\,(2T/T_0\,-1)\,, & \text{for } T_0/2 \le T \le T_0 \\ 0, & \text{otherwise.} \end{cases} \tag{15}$$

By computing the entropy change of the ferromagnet from absolute zero to the Curie temperature in two different ways, determine the maximum value $C_{\max}$ of the heat capacity in terms of N and the Boltzmann constant k.

Answer: The two ways to calculate the entropy are first by integrating $C_V(T)/T$ over an appropriate temperature range, and second by calculating the change in multiplicity Ω of the ferromagnet as it changes from its ground state with $\Omega = 1$ to its high-temperature state for which there are equal numbers of up and down spins. Equating the two expressions then let's one deduce a value for $C_{\max}$, the maximum possible heat capacity.

Using the given expression Eq. (15) for $C_V(T)$, we find

$$\begin{aligned} \Delta S_1 &= \int_0^{T_0} \frac{C_V(T)}{T}\,dT && (16) \\ &= \int_{T_0/2}^{T_0} \frac{C_{\max}(2T/T_0-1)}{T}\,dT && (17) \\ &= C_{\max}\int_{T_0/2}^{T_0}\left(\frac{2}{T_0}-\frac{1}{T}\right)dT && (18) \\ &= C_{\max}\big(1-\ln(2)\big). && (19) \end{aligned}$$

The second way to compute the change in entropy of the ferromagnet involves calculating the change in multiplicity between the ground state at $T = 0$ and the non-magnetic state at $T = T_0$:

$$\Delta S_2 = S(T_0) - S(0) = S(T_0) = k\ln\Omega(T_0), \tag{20}$$

where I used the fact that the zero temperature entropy $S(0) = 0$ by the third law of thermodynamics. (Alternatively, $\Omega = \binom{N}{N} = 1$ in the ground state for which all spins are parallel, so $S(T=0) = k\ln\Omega = k\ln(1) = 0$.) We are told that the magnetization of the ferromagnet has become zero at $T = T_0$ and this corresponds to equal numbers of up and down spins, $N_\uparrow = N_\downarrow = N/2$ where N is the total number of two-state magnetic dipoles. Using Stirling's formula[1] in the form $n! \approx (n/e)^n$, the high-temperature multiplicity is then

$$\Omega(T_0) = \binom{N}{N/2} = \frac{N!}{[(N/2)!]^2} \approx \frac{(N/e)^N}{[((N/2)/e)^{N/2}]^2} = 2^N. \tag{21}$$

The prefactors of the form $\sqrt{2\pi n}$ in Stirling can be ignored since they are large numbers multiplying the very large number 2^N. Thus $S(T_0) = k\ln\Omega(T_0) \approx Nk\ln(2)$ and equating this to Eq. (19) gives us the desired answer

$$C_{\max} \approx \frac{\ln(2)}{1-\ln(2)}Nk, \tag{22}$$

which has a numerical value of about $2.3Nk$.

4. **(10 points)** For an ideal gas of diatomic nitrogen N_2, draw qualitatively but carefully the heat capacity $C_V(T)/(Nk)$ as a function of temperature T in kelvin. Label the horizontal axis with numerical values that indicate at approximately what temperatures various degrees of freedom start to increase

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[1] One could avoid using Stirling's formula by observing that the total number of microstates of N two-state magnetic dipoles is 2^N. But in equilibrium at $T = T_0$, the area under the incredibly narrow incredibly tall peak in $\Omega(N_\uparrow)$ is basically the area of the entire $\Omega(N)$ curve and so must be about 2^N. Stirling's formula confirms this argument is correct, it corresponds to neglecting large factors like $\sqrt{2\pi n}$ that multiply very large factors.

as the temperature increases, and indicate the corresponding numerical values of the heat capacity on the vertical axis. Also label what type of degree of freedom corresponds to the different regimes of your drawing.

Answer: Please refer to Figure 1.13 on page 30 of Schroeder which answers this question completely. We will not discuss much data during this course, but the few cases that we do discuss, especially curves that we compare with theory, are important and you should study and think about the data carefully so that you remember and appreciate key points. There will be future questions on the quizzes or final exam that will test whether you are familiar with some of the more important experimental plots.

5. **(10 points)** Calculate the leading-order low-temperature (small T) and high-temperature (large T) behaviors of the expression

$$\bar{n} = \frac{1}{e^{c/T} - 1} - \frac{N}{e^{Nc/T} - 1}, \tag{23}$$

and use your results to draw qualitatively how $\bar{n}$ varies with T from low to high temperatures. Here $N \gg 1$ is a large positive integer and $c > 0$ is a positive constant. This expression arises when trying to understand how a zipper-like DNA molecule self-assembles as a competition between energy and entropy; $\bar{n}$ is the average number of cross-links formed.

Answer: Let's work out the low-temperature and then high-temperature approximations to Eq. (23) and then figure out the overall shape of the curve $\bar{n}(T)$.

At low temperatures, $T < c$ is tiny and so $c/T > 1$ is a number much greater than one. Then $e^{c/T} \gg 1$ is an even bigger number and $e^{Nc/T} = \left(e^{c/T}\right)^N \gg e^{c/T}$ is an even bigger number. (If c/T is a "small number" in Schroeder's lingo of page 61, then $e^{c/T}$ will be a "large number".) For small temperatures, we therefore have

$$\begin{aligned}
\bar{n} &= \frac{1}{e^{c/T} - 1} - \frac{N}{e^{Nc/T} - 1} && (24)\\
&\approx \frac{1}{e^{c/T}} - \frac{N}{e^{Nc/T}} && (25)\\
&= e^{-c/T} - Ne^{-Nc/T} && (26)\\
&\approx e^{-c/T}. && (27)
\end{aligned}$$

Eq. (27) is the desired low-temperature leading-order behavior of $\bar{n}$. To get from line (24) to line (25), I ignored the 1's compared to the large numbers $e^{c/T}$ and $e^{Nc/T}$ in the denominators. To get from line (26) to line (27), I dropped $Ne^{-Nc/T}$ as a much smaller quantity since $(e^{-c/T})^N \ll e^{-c/T}$ if $e^{-c/T}$ is small and N is large. From your calculations of specific heats related to an Einstein solid which involved expressions of the form $e^{-\epsilon/(kT)}$ where $\epsilon = hf$ was the energy spacing between harmonic oscillator levels, you should recognize $e^{-c/T}$ as an expression that decays to zero rapidly[2] as $T \to 0$.

For large temperatures $T \gg c$, the ratio $c/T \ll 1$ is a small quantity and so we want to carry out a Taylor series of Eq. (23) about $c/T = 0$ to see what the leading order behavior is. As usual, it is too much work to calculate various derivatives $f^n(x)$ to get the coefficients in a Taylor series, instead we substitute and manipulate simpler Taylor series, which here would be the one based on the exponential:

$$e^x \approx 1 + x + \frac{1}{2}x^2 + O\left(x^3\right). \tag{28}$$

Since the wording of the problem is to determine the "leading-order" behavior, which means the first non-zero correction in the Taylor series of Eq. (23), we need to retain the first *three* terms in Eq. (28) since the lowest-order term (the one) gets killed by the subtraction in the denominators. Some students retained only the first two terms in Eq. (28) and found that the two terms canceled to give $\bar{n} = 0$ to

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[2] Note that it is wrong to say that the expression $e^{-c/T}$ decays exponentially rapidly to 0 since this expression does not depend exponentially on T.

order c/T, but that should have just warned them that they had to go to higher-order to find the first non-zero term.

Applying Eq. (28) to the two exponentials in Eq. (23), we find:

$$\begin{aligned}
\bar{n} &= \frac{1}{e^{c/T}-1} - \frac{N}{e^{Nc/T}-1} && (29)\\
&\approx \frac{1}{\left[1+c/T+\frac{1}{2}(c/T)^2\right]-1} + \frac{N}{\left[1+Nc/T+\frac{1}{2}(Nc/T)^2\right]-1} && (30)\\
&\approx \frac{T}{c}\left(\frac{1}{1+(1/2)(c/T)} - \frac{1}{1+(1/2)(Nc/T)}\right) && (31)\\
&\approx \frac{T}{c}\left(\left[1-\frac{1}{2}\frac{c}{T}\right] - \left[1-\frac{1}{2}\frac{Nc}{T}\right]\right) && (32)\\
&= \frac{N-1}{2} && (33)\\
&\approx \frac{N}{2}. && (34)
\end{aligned}$$

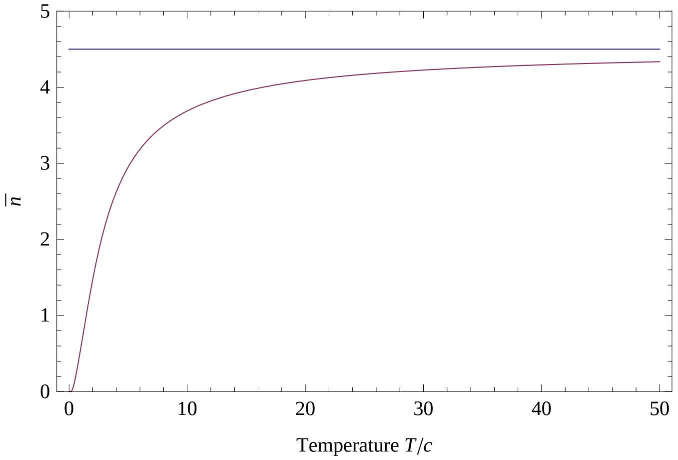
This first non-zero term is quite different from zero! On line (30), I approximated both exponentials with the Taylor expansion Eq. (28). Line (32) was obtained from the previous line by using the first two terms of the geometric series (which is the Taylor series for $1/(1+x)$)

$$\frac{1}{1+x} \approx 1-x \qquad \text{for } |x| \ll 1. \tag{35}$$

On line (34), I used the fact that $N \gg 1$ to drop the 1 compared to the N. We conclude that $\bar{n}(T)$ approaches a constant value $N/2$ as $T \to \infty$.

If we had extended the Taylor series Eq. (28) to include the third-order term $(1/6)x^3$, you would discover that Eq. (34) would have a $1/T$ correction added to $N/2$. This is similar to what you discovered in answering part (f) of Problem 3.25 on page 109 of Schroeder, except there the correction to the constant high-temperature value was quadratic in $1/T$.

The low-temperature behavior Eq. (26) and the high-temperature behavior (34) are sufficient to guess the overall qualitative form of the curve $\bar{n}(T)$: it is a function that increases rapidly from zero at $T = 0$ and then asymptotes to a horizontal plateau with value $N/2$, i.e., it looks qualitatively like the heat capacity $C(V)$ of an Einstein solid, being concave up and then becoming concave down. You can confirm the correctness of the above discussion with a Mathematica plot



which I generated with the command

```
nn = 10. ;
Plot[
 1 / ( Exp[ 1 / T ]  -  1 )  -  nn / ( Exp[ nn / T ]  -  1 ) ,
 { T, 0, 5 nn } ,
 PlotRange -> { 0., nn/2. }
]
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where I have set $c = 1$ and $N = 10$. For N this small, I have to use the asymptote Eq. (33) and the curve indeed asymptotes to $(N-1)/2 = 4.5$.

6. **(10 points)** Two vessels of volume V_1 and V_2 each contain N atoms of the same ideal gas at the same pressure P but with temperatures of T_1 and T_2 respectively. In terms of the heat capacity C_p at constant pressure (which you can assume is constant) and the temperatures T_1 and T_2, calculate the change of entropy ΔS that arises when a tube connects the two vessels and thermodynamic equilibrium is attained. Determine also whether $\Delta S_{\rm total} \ge 0$ for your system.

   Answer: There are two ways to solve this problem. The more general and somewhat easier way is to use the formula

   $$\Delta S = \int_{T_1}^{T_2} \frac{C_P(T)}{T}\, dT, \tag{36}$$

   for the entropy change ΔS of any general system (solid, liquid, gas, etc) whose temperature changes while the external pressure is constant. The second way is to use the Sackur-Tetrode equation, which holds only for an ideal gas consisting of atoms (so there are no rotational or vibrational degrees of freedom). Both approaches lead to the answer Eq. (40) below.

   Let's try solving the problem first using Eq. (36). Since in equilibrium the temperature will be uniform throughout the combined vessels, a first step is to deduce the final equilibrium temperature T_f. From the ideal gas law $PV = NkT$, we have

   $$P(V_1 + V_2) = (2N)kT_f, \tag{37}$$

   since in the interconnected system, the total volume is $V_1 + V_2$ and the total number of particles is $2N$. The pressure will not change since it is already in equilibrium ($P_1 = P_2 = P$). So we have

   $$T_f = \frac{P(V_1+V_2)}{2Nk} = \frac{T_1+T_2}{2}, \tag{38}$$

   where I used

   $$T_1 = \frac{PV_1}{Nk} \qquad \text{and} \qquad T_2 = \frac{PV_2}{Nk}. \tag{39}$$

   That $T_f = (T_1 + T_2)/2$ could also be deduced from a heat capacity argument, energy conservation between the two vessels implies $C_P(T_f - T_1) = C_P(T_2 - T_f)$. Even more simply, since we are mixing two equal amounts of the same gas (both have N atoms), the final temperature must be the average of the two initial temperatures.

   By additivity of entropy (and assuming the two vessels together are thermally isolated so we don't have to worry about heat being exchanged with the surrounding environment), the total change in entropy will be the sum of the changes in entropy of each vessel, $\Delta S_{\rm total} = \Delta S_1 + \Delta S_2$. We can calculate this directly from the temperature change of the gas in each vessel:

$$\begin{aligned}
\Delta S_{\text{total}} &= \Delta S_1 + \Delta S_2 && (40)\\
&= \int_{T_1}^{T_f} \frac{C_P(T)}{T}\, dT + \int_{T_2}^{T_f} \frac{C_P(T)}{T}\, dT && (41)\\
&= C_P \ln\left(\frac{T_f}{T_1}\right) + C_P \ln\left(\frac{T_f}{T_2}\right) && (42)\\
&= C_P \ln\left(\frac{T_f^2}{T_1 T_2}\right) && (43)\\
&= C_p \ln\left[\frac{(T_1+T_2)^2}{4T_1T_2}\right]. && (44)
\end{aligned}$$

This last line, Eq. (44), is the desired answer[3]. In evaluating the integrals, I used the assumption that C_p is constant over the temperature range of interest, and I used the log identity $\ln(a) + \ln(b) = \ln(ab)$ to combine the two entropy expressions into a single log.

The expression Eq. (44) will be non-negative—a desired property of any total entropy expression—provided that the argument inside the log is greater than or equal to one:

$$\Delta S_{\text{total}} \geq 0 \quad \Leftrightarrow \quad \frac{(T_1+T_2)^2}{4T_1T_2} \geq 1. \tag{45}$$

But this last condition always holds[4] since it can be written in the form $(T_1 - T_2)^2 \geq 0$. So the total entropy change is always positive (the process of connecting the two vessels and waiting for equilibrium is irreversible) except when $T_1 = T_2$ in which case $\Delta S_{\text{total}} = 0$.

We can also solve this problem by using the Sackur-Tetrode equation

$$S = Nk\left(\frac{5}{2} + \ln\left[\frac{V}{N}\left(\frac{4\pi m}{3h^2}\frac{U}{N}\right)^{3/2}\right]\right), \tag{46}$$

which is the entropy of an ideal gas of N atoms[5] in a volume V with total energy U. By the equipartition theorem, the energy $U = Nf(kT/2)$ with $f = 3$ for atoms so the $U/N = 3kT/2$ term in Eq. (46) can be expressed in terms of T.

The total initial entropy S^i_{total} is the sum of the entropies of the gases in each vessel:

$$\begin{aligned}
S^i_{\text{total}} &= Nk\left(\frac{5}{2} + \ln\left[\frac{V_1}{N}\left(\frac{4\pi m}{3h^2}\frac{3kT_1}{2}\right)^{3/2}\right] + \frac{5}{2} + \ln\left[\frac{V_2}{N}\left(\frac{4\pi m}{3h^2}\frac{3kT_2}{2}\right)^{3/2}\right]\right) && (47)\\
&= Nk\left(5 + \ln\left[\frac{V_1V_2}{N^2}\left(\left[\frac{4\pi m}{3h^2}\frac{3k}{2}\right]^2 T_1T_2\right)^{3/2}\right]\right) && (48)
\end{aligned}$$

The final total entropy S^f_{total} corresponds to $2N$ molecules at temperature T_f in a total volume $V_1 + V_2$:

$$S^f_{\text{total}} = (2N)k\left(\frac{5}{2} + \ln\left[\frac{V_1+V_2}{2N}\left(\frac{4\pi m}{3h^2}\frac{3kT_f}{2}\right)^{3/2}\right]\right) \tag{49}$$

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[3] Alternatively, you can verify that Eq. (44) can also be written in terms of the volumes, $\Delta S = C_P \ln\left[(V_1+V_2)^2/(4V_1V_2)\right]$.

[4] The inequality $(T_1+T_2)^2/(4T_1T_2) \geq 1$ can also be written in the form $(T_1+T_2)/2 \geq \sqrt{T_1T_2}$, which is a simple case of the "arithmetic-geometric mean inequality", which states that the average of N numbers, $(1/N)\sum_1^N x_i$, is always greater than or equal to the geometric mean of the numbers, $(\Pi_1^N x_i)^{1/N}$, with equality if and only if all the numbers are equal.

[5] If the wording of the problem had said "N molecules", we would not be able to use Sackur-Tetrode since that equation is based on the assumption of ignoring rotational and vibrational degrees of freedom. Can you pinpoint in the derivation of Sackur-Tetrode why this restriction was necessary?

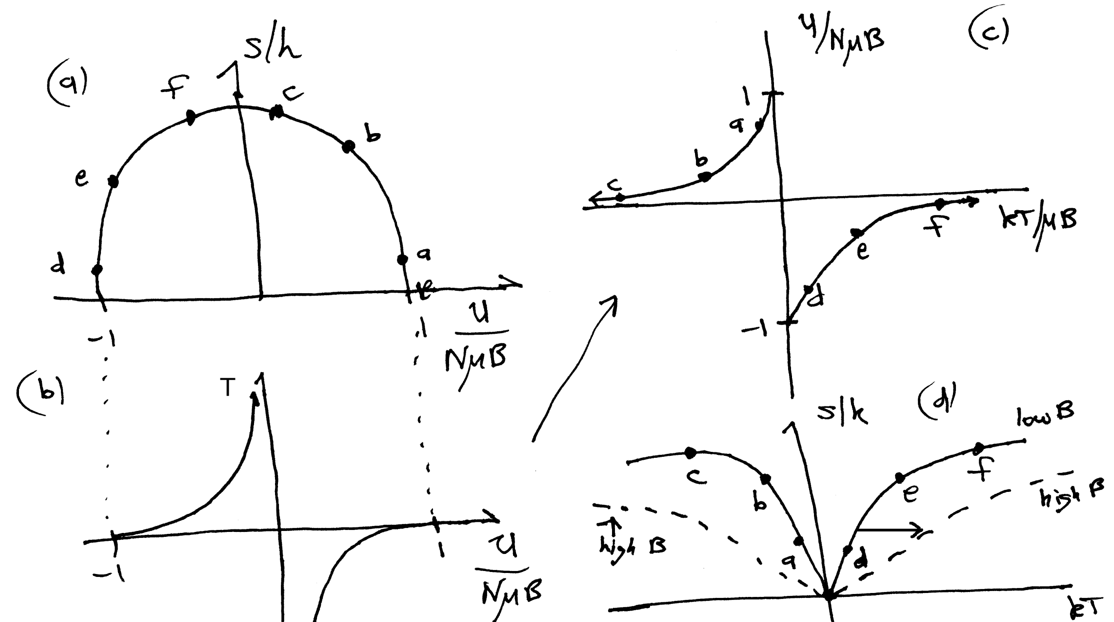
Using $2\ln(x) = \ln(x^2)$ on Eq. (49) and then subtracting Eq. (48) from Eq. (49) gives the total change in entropy ΔS_{total}:

$$\Delta S_{\text{total}} = S^f_{\text{total}} - S^i_{\text{total}} = Nk \ln \left[\frac{(V_1+V_2)^2}{4V_1V_2} \left(\frac{T_f^2}{T_1T_2} \right)^{3/2} \right]. \tag{50}$$

If we eliminate T_f, V_1, and V_2 in favor of T_1 and T_2 via Eqs. (38) and (39) and use the fact that, for a monoatomic gas, $C_P = C_V + Nk = (5/2)Nk$ (see Eq. (1.48) on page 30 of Schroeder), then we get the same expression as Eq. (44). (Please verify this for yourself.) That the two expressions agree for an ideal gas of atoms can be interpreted as confirmation of the correctness of Eq. (36), which was derived using only macroscopic thermodynamic definitions and arguments (for example, $dS = Q/T = (C_P(T)dT)/T$ and $dU = TdS - PdV$).

7. (a) **(6 points)** Starting with a qualitative plot of how the entropy $S(U, B)$ of a two-state paramagnet in a uniform magnetic field of strength B varies with energy U, deduce and then draw schematically for two different magnetic field strengths B_{low} and $B_{\text{high}} > B_{\text{low}}$ how the entropy $S(T)$ varies with temperature T over the range $-\infty < T < \infty$. Make sure to label your two entropy curves clearly, for low B and high B.

Answer: This question involved your ability to work out functional relations from qualitative drawings, a valuable skill since often in experimental or computational work, one does not have analytical formulas to work with or known analytical formulas might be too complicated to obtain intuition from. The flow of ideas is suggested in this figure:



Panel (a) shows what should be a familiar dependence of entropy S/k on energy $U/(N\mu B)$ for a paramagnet of N two-state magnetic dipoles. Just below panel (a), I have sketched in panel (b) how the temperature T varies with energy $U/(N\mu B)$ by taking several representative points on the entropy curve in (a) and looking at the reciprocal of the slopes at these points, $1/T = dS/dU$.

Rotating (b) counterclockwise about the origin by 90° and then rotating the curve 180° about the vertical axis gives us $U = U(T)$ as a function of T, as shown in panel (c). (This too should be familiar to you.)

To deduce how the entropy $S(T)$ varies with temperature, we choose several representative points on the curves in (c) which I have labeled a, b, ..., f. For a given point, say "a" corresponding to a slightly negative temperature, I look up the corresponding value of U (which is close to 1 on the $U/(N\mu B)$ axis) and then I go to panel (a) to see what value of S corresponds to this value of U; here S is positive and close to zero as shown by the point labeled "a" on the $S = S(U)$ curve. Repeating this for various representative points, we are led to panel (d), which shows qualitatively how the entropy $S = S(T)$ varies with temperature for a fixed external magnetic field. The entropy is zero at $T = 0$ (as we would expect from the third law of thermodynamics) and increases monotonically to the maximum value of $S_{\max} Nk\ln(2)$ which corresponds to the zero magnetization state, in which there are equal numbers of up and down spins. Although I didn't draw the curves accurately, S is an even function of temperature, $S(-T) = S(T)$ and so is symmetric for positive and negative temperatures. This is a consequence of $S = S(U)$ being an even function of energy, which in turn is a consequence of the binomial coefficient $\Omega = \binom{N}{N_\uparrow}$ being a symmetric function of $N_\uparrow$ about the point $N_\uparrow = N/2$.

The above sketch of $S(T)$ in panel (d) corresponds to a fixed magnetic field strength B. How does $S(T)$ change if B is increased to some larger value? There are two ways to figure this out. One is thinking physically: an increased magnetic field for a fixed temperature will align more magnetic dipoles parallel to the magnetic field, and this will decrease the entropy since there are then fewer microstates available and the multiplicity decreases. (In the extreme case of a nearly infinite magnetic field, all spins will be parallel to $\mathbf{B}$ and so $\Omega = 1$.) So $S(T)$ for larger B will be a curve similar to what we already drew but rising more slowly and so lying everywhere below the $S(T)$ curve. In panel (d), I have sketched the high-B entropy curve as dashed lines below the solid lines of the low-B curve.

A second way to figure out how $S(T)$ varies with B is to observe that all the quantities that characterize a paramagnet (energy U, magnetization M, heat capacity C, etc) depend on temperature through the expression $kT/(\mu B)$. If we write this as T/T_0 with $T_0 = (\mu/k)B$, we see that the magnetic field B defines a temperature scale T_0, this is the magnitude by which the temperature T has to change for something "interesting" to happen, e.g., for the magnetization to decrease substantially or for the entropy to rise substantially towards its maximum asymptotic value. Increasing the magnetic field B increases the temperature scale T_0 and so a larger value of T is now needed to achieve the same value of S that is observed for a smaller temperature value when B is smaller. This implies that a high-B entropy curve must lie below a low-B entropy curve since they are the same curves but one (the high-B curve) is stretched horizontally away from the origin compared to the low-B curve.

(b) **(4 points)** For a thermally isolated two-state paramagnet in the presence of a uniform magnetic field with strength B, discuss whether increasing B will increase, decrease, or leave unchanged the temperature of the paramagnet.

Answer: The temperature of the isolated paramagnet *increases* when B is increased. This is a consequence of the low-B and high-B entropy curves of panel (d) in the above figure. A thermally isolated paramagnet can not exchange heat with the outside world, i.e., its entropy is constant (since $dS = Q/T$), just like the case of an adiabatic change of an ideal gas. Increasing the magnetic field strength B then corresponds to starting on a low-B entropy curve and moving horizontally (constant S) to the right until one reaches a point on a high-B entropy curve. This is illustrated by the small horizontal arrow that I drew in panel (d), and you can see that the temperature indeed increases.

This is an important scientific insight that is often used in the opposite direction: decreasing the external magnetic field of a thermally isolated paramagnet will decrease the temperature of the paramagnet, and then bringing the cold paramagnet in contact with some other substance (say liquid helium) will decrease the temperature of that substance, i.e., we can use varying magnetic fields and a paramagnet as a refrigerator. This is, in fact, one of the important strategies that scientists and engineers have invented to cool substances to temperatures of order a millikelvin. You can read more about this on pages 144-146 of Schroeder, who describes "magnetic cooling" with several other strategies for reaching low temperatures. Look particularly at Figure 4.14 on page 146 of Schroeder, which illustrates the two keys steps used multiple times in magnetic cooling: increase the magnetic field while paramagnet is in thermal contact with a constant T reservoir (so you don't raise the temperature of the paramagnet as you increase B), then decrease the magnetic field of the thermally isolated paramagnet to decrease its temperature.

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** To the nearest power of ten, the entropy of a mole of Belgian chocolate molecules is approximately 10 J/K.

   Answer: T From Problem 2.36 on page 79 of Schroeder, which you did as one of your homework problems, you learned that the entropy of any object consisting of N components is approximately $S \approx Nk$. (Please confirm this result for the Einstein solid and ideal gas.) Since a mole consists of $N \approx 6.0 \times 10^{23}$ molecules and $k \approx 1.4 \times 10^{-23}$ J/K (each to two significant digits), a mole of Belgian chocolate molecules has an entropy of about

   $$S \approx Nk \approx (6 \times 10^{23}) \times (1.4 \times 10^{-23} \approx 10\,\mathrm{J/K}. \tag{51}$$

   Since chocolate has a complicated molecular structure (actually, chocolate consists of many different complicated molecules), it is convenient to be able to make a rough guess like this.

2. **T / F** $C_V(\text{steam}) > C_V(\text{water})$.

   Answer: F That $C_V(\text{steam}) < C_V(\text{water})$ is a fact that you were told and had to use in one of your homework problems, when you were asked to draw qualitatively but carefully the entropy $S(T)$ as a function as ice warmed up and melted into water, and the water warmed up and vaporized into steam.

3. **T / F** The heat capacity $C_{\text{Einstein}}(T)$ of an Einstein solid accurately describes the shape of the heat capacity $C_V(T)$ of an ideal gas of diatomic molecules in the regime for which vibrational degrees of freedom are freezing out (decreasing) as the temperature of the gas is decreased.

   Answer: T An ideal gas of diatomic molecules is essentially a perfect Einstein "solid": it consists of N non-interacting identical quantum harmonic oscillators (at least if the temperature is not too high, remember the homework problem about the Morse potential?) with each molecule corresponding to one oscillator. So the expression for the specific heat $C_V(T)$ that you calculated and plotted in Problem 3.25 on page 108 of Schroeder (and that is given in Eq. (7.103) on page 307 of Schroeder and plotted in Figure 7.29 on page 312) quantitatively and usefully describes the high-temperature regime of Figure 1.13, where the vibrational degrees of freedom are freezing out as T decreases.

   Somewhat ironically, a gas of diatomic molecules is much better described as an Einstein solid than a real solid since the latter involves many oscillators with different frequencies and the oscillators interact. We will learn how to correct the Einstein model when we discuss the Debye theory of Section 7.5 in Schroeder.

4. **T / F** If an ideal gas is compressed isothermally and then expanded adiabatically back to its original volume, the final pressure will be greater than the initial pressure.

Answer: F Please refer to Figure 1.12 on page 25 of Schroeder which pretty much answers this question: if you follow the curve labeled T_f to the left starting with initial volume V_i (an isothermal compression) and finishing at volume V_f, and if you then follow the adiabatic process labeled "Adiabat" from V_f to the right until you return to $V = V_i$ (an adiabatic expansion), you necessarily end up with a lower pressure.

The reason is that, during an adiabatic compression, the temperature of the gas increases. (If you don't remember the math on page 25, you should remember the fire piston demo I showed you in class or how a diesel engine works). This means that a curve $P(V)$ in the PV plane that corresponds to an adiabatic process must cross from a high-temperature isothermal hyperbola to a lower temperature isothermal hyperbola during an expansion as shown in Figure 1.12.

The same geometric picture shows without any calculation that it takes more work to compress a gas adiabatically than isothermally: starting from the initial volume V_i in Figure 1.12, the adiabat always lies above the isothermal hyperbola that grows out of the same initial point (V_i, P_i).

5. **T / F** For a two-state paramagnet in a uniform external magnetic field $\mathbf{B}$, all the magnetic dipoles are antiparallel to the direction of the magnetic field in the limit $T \to \infty$.

Answer: F By Curie's law for paramagnets which we discussed in class and which you read about in Schroeder (see page 105), the magnetization $M \propto 1/T$ for sufficiently large temperatures T, i.e., $M \to 0$ as $T \to \infty$. But $M \propto N_\uparrow - N_\downarrow$ so $M \to 0$ implies $N_\uparrow = N_\downarrow = N/2$ in the limit of high temperatures. So the magnetic dipoles are equally likely to be up or down at high temperatures, and it is not the case that the dipoles all assume the highest possible energy state of being antiparallel to the magnetic field as $T \to \infty$.

If you didn't remember Curie's law or think of using it, you could also deduce that $M \to 0$ as $T \to \infty$ from the qualitative drawing of how $U(T)$ depends on T for a paramagnet, since for a two-state paramagnet, $M = -U/B$. See also Figure 3.10b on page 103 of Schroeder, which plots $M(T)$ versus T, you can see that $M \to 0$ as $T \to \infty$.

6. **T / F** The ratio W/Q of work produced to heat added is 2/7 for an ideal gas of diatomic N_2 that undergoes an isobaric expansion close to room temperature.

Answer: T An isobaric expansion is a constant pressure expansion. Assume the constant pressure is P_0 and the gas expands from some initial volume V_1 to some final volume $V_2 > V_1$. The work W done on the gas is given by

$$W = -\int_{V_1}^{V_2} P(V)\, dV = -P_0 \int_{V_1}^{V_2} dV = -P_0(V_2 - V_1), \tag{52}$$

and so the work done by the gas on the environment is the negative of this and is the positive quantity $P_o(V_2 - V_1)$. As usual, we determine the heat that flows into the gas by energy conservation $Q = \Delta U - W$. By the equipartition theorem $U = Nf(kT/2)$ where $f = 5$ for a diatomic nitrogen at room temperature[6], the change in energy $\Delta U = (f/2)\Delta(NkT) = (f/2)\Delta(PV) = (f/2)P_0(V_2 - V_1)$. Using Eq. (52), the heat Q that flows into the gas is then

$$Q = \Delta U - W = \left[\frac{f}{2} P_0(V_2 - V_1)\right] - \left[-P_0(V_2 - V_1)\right] = \left(1 + \frac{f}{2}\right) P_0(V_2 - V_1). \tag{53}$$

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[6] Remember that, for many diatomic molecules including nitrogen, the vibrational degrees of freedom have frozen out for temperatures close to room temperature so $f = 5$, not $f = 7$.

This leads to the result

$$\frac{|W|}{Q} = \frac{P_0(V_2 - V_1)}{Q} = \frac{1}{1 + f/2} = \frac{2}{2 + f} = \frac{2}{7}, \tag{54}$$

so the claim is true. Note how by taking the ratio $|W|/Q$, we get a result that is independent of the values of P_0, V_1, and V_2. Note also that a ratio of 2/7 is not particularly impressive. You should be able to verify quickly that an isothermal expansion has a ratio $|W|/Q = 1$, so isothermal expansions produce more work for a given amount of heat.

7. **T / F** The surface area $A_d(1)$ of a d-dimensional hypersphere with unit radius is a decreasing function of d for sufficiently large d.

Answer: T From the formula for $A_d(r)$ that we used in our discussion of the multiplicity of an idea gas of atoms and that you of course wrote down on your one page of notes, we know that (for $r = 1$):

$$A_d(1) = \frac{2\,\pi^{d/2}}{\Gamma\left(\frac{d}{2}\right)}. \tag{55}$$

But, as I showed during one lecture, we also know that $\Gamma(x)$ can be accurately approximated by Stirling's formula for a large enough argument x:

$$\Gamma\left(\frac{d}{2}\right) = \left(\frac{d}{2} - 1\right)! \approx \left(\frac{d}{2}\right)! \approx \sqrt{2\pi(d/2)}\left(\frac{d/2}{e}\right)^{d/2}, \tag{56}$$

where I used $d/2 - 1 \approx d/2$ for d sufficiently big. Combining Eqs. (55) and (56), we find

$$A_d(1) \approx \frac{2}{\sqrt{\pi d}}\left(\frac{2\pi e}{d}\right)^{d/2}. \tag{57}$$

For d large, the factor $2/\sqrt{\pi d}$ is a small number (the reciprocal of a large number) multiplying a very small number (the reciprocal of a very large number) and so can be ignored compared to the very small number. So $A_d(1) \propto 1/(d/(2\pi e))^{d/2}$ and is in fact a rapidly decreasing function of d for sufficiently large d.

Since $2\pi e \approx 20$, from Eq. (57) we can guess that $A_d(1)$ might actually increase to some maximum before it starts to decrease since initially $2\pi e/d$ is greater than one. Plotting Eq. (55) with Mathematica confirms this: $A_d(1)$ increases to a maximum value of about 30 around $d = 7$ before decreasing monotonically and rapidly for all larger d.

8. **T / F** The expression $S = S(U, V) = S_0\,U^{3/4}V^{1/4}$ (where S_0 is a positive constant) is not a physically reasonable functional form for the entropy of some substance.

Answer: F This expression *is* a physically reasonable ansatz for the entropy of a system. In fact, later this semester we will discover this functional form when calculating the entropy of a gas of photons.

To determine whether S is physically reasonable, we want to check that

(a) S is an increasing function of U for $U \geq 0$, which is the case for most systems except paramagnet-like spin systems whose components do not have any kinetic energy and for which the energy U is bounded from above. Since $S \propto U^{3/4}$, S indeed increases with U so this checks.

(b) S is a first-order homogeneous function of the extensive variables U, V, and N, which is a necessary condition for S to be additive over weakly interacting subsystems. If we make the substitution $(U, V) \to (\lambda U, \lambda V)$, then $(\lambda U)^{3/4}(\lambda V)^{1/4} = \lambda U^{3/4}V^{1/4}$ so S is a linear homogeneous function, and this checks.

(c) Finally, we want to see whether S is consistent with the third law of thermodynamics, that $S \to 0$ as $T \to 0$. As usual, we determine T by $1/T = (dS/dU)_V \propto U^{-1/4}$ so $U \propto T^4$ and $S \propto U^{3/4} \propto (T^4)^{3/4} \propto T^3$ so the third law is indeed satisfied.