

Quiz 4 Solutions, Physics 176

March 28, 2011

The following solutions are far more detailed than what was needed to get full credit. But make the time to read through the details, it will help you understand physics and improve your problem solving abilities.

Problems That Require Writing

1. **(15 points)** Consider a small system whose volume and energy can not change. This system is in thermodynamic equilibrium with a reservoir in such a way that the system can exchange molecules of a certain type with the reservoir. The number N_s of molecules in the system (of the given type) therefore varies with the state s of the system. The reservoir has a fixed temperature T and a fixed chemical potential μ , and the system and reservoir together form a closed system so that the total number N of molecules of the given type is conserved.

Stating clearly your assumptions and approximations, derive an expression for the probability p_s for the small system to be in a particular state s that corresponds to the system having N_s particles. Your expression will look like an “exponential of something” over a quantity $\mathcal{Z}$ that is similar to a partition function.

Answer: You should have obtained the answer

$$p_s = \frac{e^{\beta\mu N_s}}{\sum_s e^{\beta\mu N_s}}, \quad (1)$$

for the probability p_s to observe the small system in a state s with N_s particles. To see this, observe that, given that the reservoir and small system form an isolated system, all microstates are equally likely and so the probability p_s will be proportional to the number of microstates available to the entire isolated system when the system has N_s particles and the reservoir has $N - N_s$ particles where $N_s \ll N$. But since we are asking for the probability for the system to be in a *particular* state s , all the available microstates come from the reservoir, i.e., we can assume

$$p_s = c \Omega_R(N - N_s), \quad (2)$$

where c is a constant of proportionality that will be determined by the condition that all the probabilities have to sum to one.

We can then follow step by step the discussion I gave in lecture (and in my lecture notes of March 15). The mathematics looks like this

$$p_s = c \Omega_R(N - N_s) \quad (3)$$

$$= c \exp \left[\frac{1}{k} S_R(N - N_s) \right] \quad (4)$$

$$\approx c \exp \left[\frac{1}{k} \left(S_R(N) + S'_R(N) \times (-N_s) + \text{h.o.t.s} \right) \right] \quad (5)$$

$$\approx \left[c e^{S_R(N)/k} \right] \exp \left[-\frac{1}{k} S'_R(N) N_s \right] \quad (6)$$

$$\approx \tilde{c} \exp \left[-\frac{1}{k} \left(\frac{-\mu}{T} \right) N_s \right] \quad (7)$$

$$\approx \tilde{c} e^{\beta\mu N_s}. \quad (8)$$

with the following justifications:

- (a) I expressed the multiplicity Ω_R in terms of the reservoir's entropy S_R via $S_R = k \ln \Omega_R$ or $\Omega_R = e^{S_R/k}$. The reason is that the entropy is what is more important physically since S , but not Ω , appears in the thermodynamic identity and it is S that can be computed from a knowledge of the heat capacity $C(T)$.
- (b) I then expanded the entropy in a Taylor series, $S_R(N - N_s) = S_R(N) + S'_R(N)(-N_s) + (1/2)S''_R(N)(-N_s)^2 + \dots$, about the value N in powers of the small quantity $(-N_s)$ and dropped all terms of second-order or higher in $-N_s$ as negligible. This is where one has to use the assumption that the system is small compared to the reservoir, the number of particles N_s associated with the system is always tiny compared to the number of particles $N - N_s \approx N$ in the reservoir.
- (c) I then used the given thermodynamic identity $dU = TdS - PdV + \mu dN$ with $dU = 0$ and $dV = 0$ to evaluate the derivative $S'_R(N) = (\partial S_R / \partial N)_{U,V} = -\mu/T$. This is where I used the assumption that the system can not change its energy U or its volume V .

To get full credit, you needed to show the above algebraic steps and mention some brief insights concerning why you were carrying out a particular step and what assumptions allowed you to carry out a particular step. It was especially important to justify Eq. (2), the key scientific insight that allows you to proceed with the math, by pointing out that, because the total system is isolated, the probability to observe some state of the total system (in which the system has N_s particles) is proportional to the number of accessible microstates.

The final step is to determine the constant $\tilde{c}$ by observing that all the probabilities Eq. (8) must sum to one:

$$1 = \sum_s p_s = \tilde{c} \sum_s e^{\beta \mu N_s}, \quad (9)$$

so

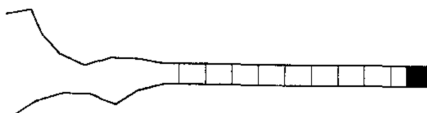
$$\tilde{c} = \frac{1}{\sum_s e^{\beta \mu N_s}} = \frac{1}{Z}, \quad (10)$$

which gives the stated answer Eq. (1).

You might now enjoy taking a look at Section 7.1 of Schroeder, where he derives the more general case of the probability p_s for a small system to be in a state s that has an energy E_s and number of particles N_s , when the system can exchange energy *and* particles with a reservoir with constant temperature T and constant chemical potential μ . (Note that for an ideal gas, you can achieve a constant chemical potential for a fixed temperature by simply arranging experimentally for the pressure of the gas to be constant, see Eq. (3.63) on page 118 of Schroeder.) The resulting factor has the form $e^{-\beta(E_s - \mu N_s)} = e^{-\beta E_s} e^{\beta \mu N_s}$, which combines the Boltzmann factor with Eq. (8). For this more general case, the expression $e^{-\beta(E_s - \mu N_s)}$ is called the Gibbs factor rather than the Boltzmann factor, after Josiah Gibbs, one of the great theoretical pioneers of thermal physics who first studied this more general case.

Note: a few students used Schroeder's derivation and got the wrong sign in the exponent, $e^{-\beta \mu N_s}$, because, when using the thermodynamic identity for the reservoir, $dU_R = T_R dS - P_R dV + \mu_R dN_R$ in the form $dS_R = -\mu_R dN_R$, they forgot to switch from the reservoir differential dN_R to the system differential $dN = -dN_R$, with the minus sign arising from the conservation law for particles.

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



that has a maximum of N links. The chemistry of the links is such that each link can be closed with energy 0 or open with energy $\epsilon > 0$ (i.e., it takes energy ϵ to break a link and open it). The zipper can

unzip only from one side (say from the left as shown in the figure) and the n th link from the left can open only if all the links to the left of it $(1, 2, \dots, n-1)$ are already open. The N th link on the right is always closed.

- (a) **(4 points)** Using qualitative reasoning without mathematical calculation (but you need to explain your reasoning briefly), determine the average number of links $\langle n \rangle$ of the biomolecule in the limit of small temperatures T corresponding to $kT \ll \epsilon$.

Answer: $\langle n \rangle = N$ for $T = 0$.

We discussed and mathematically justified in class (see page 4 of my March 17 online lecture notes) the fact that, for a small system in equilibrium with a reservoir with constant temperature T , the probability p_1 for the system to be in its ground state approaches one, $p_1 \rightarrow 1$, as $T \rightarrow 0$. At the same time, the probability for the small system to be in any excited state goes to zero in the zero T limit, $p_s \rightarrow 0$ for $s > 1$.

Since breaking a link raises the energy of the zipper by ϵ , the lowest energy state of the biomolecule corresponds to no broken links, that is when there are N links and the zipper is completely closed (zipped). The corresponding ground state energy is 0.

You did not need to do any mathematics for this problem provided that you mentioned that $p_1 \rightarrow 1$ as $T \rightarrow 0$. But it did not hurt if you started with the Boltzmann factor $e^{-\beta E_s}$ and argued why this must be the case.

- (b) **(4 points)** Using qualitative reasoning without mathematical calculation (but you need to explain your reasoning briefly), determine the average number of links $\langle n \rangle$ in the limit of large temperatures T corresponding to $kT \gg \epsilon$.

Answer: $\langle n \rangle = (N + 1)/2 \approx N/2$.

We discussed and mathematically justified in class (see page 5 of my March 17 online lecture notes) the fact that, for a small system with a finite number K of energy levels and that is in equilibrium with a reservoir with constant temperature T , all energy levels become equally likely in the limit $T \rightarrow \infty$:

$$\lim_{T \rightarrow \infty} p_s = \lim_{T \rightarrow \infty} \frac{e^{-\beta E_s}}{Z} \rightarrow \frac{1}{K}. \quad (11)$$

For this zipper problem, there are N distinct energy levels: the zipper entirely zipped shut with total energy $E_1 = 0$ and $n = N$ links, the zipper closed except for one open link on the left for which $E_2 = \epsilon$ (this is the first excited state by analogy with a quantum problem) and there are $n = N - 1$ links, and so on until you get to the highest energy level $E_{N-1} = (N - 1)\epsilon$ for which the zipper is completely unzipped except for the N th link which is always closed, and so $n = 1$.

At high enough temperatures, all energy states are equally likely so the thermal average $\langle n \rangle$ becomes just the arithmetic average of the possible values for n , which is the set of integers from 1 (the highest energy state, with just the N th link closed) to N (the lowest energy or ground state with all links closed). Since the average of a set of equally spaced numbers $1, 2, \dots, N$ in an interval $[a, b]$ starting from $a = 1$ and ending in $b = N$ lies at the middle $(a + b)/2$ of the set, we conclude that

$$\lim_{T \rightarrow \infty} \langle n \rangle = \frac{N + 1}{2}. \quad (12)$$

as mentioned above. If N is large (N is several billion for DNA!), $(N + 1)/2 \approx N/2$ so $N/2$ is an acceptable answer.

Alternatively, you could evaluate the average directly by observing that the thermal average

becomes the arithmetic average for sufficiently high temperatures:

$$\lim_{T \rightarrow \infty} \langle n \rangle = \frac{1}{N} \sum_s n_s \quad (13)$$

$$= \frac{1}{N} \times (1 + 2 + 3 + \dots + N) \quad (14)$$

$$= \frac{1}{N} \times \frac{N(N+1)}{2} \quad (15)$$

$$= \frac{N+1}{2}, \quad (16)$$

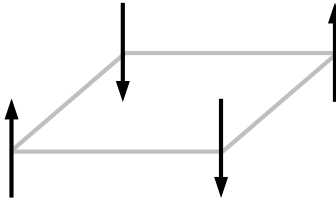
where I used the fact that the sum of the first N integers is $N(N+1)/2$.

And if you don't remember this last fact, at least remember the elegant insight of how to derive it. If S_N denotes the sum of the first N positive integers, we can write the sum twice, in increasing order and below it again in decreasing order, and then combined numbers in pairs like this:

$$\begin{aligned} 2S_N &= \begin{array}{ccccccc} 1 & + & 2 & + & \dots & + & N-1 & + & N \\ & + & N & + & N-1 & + & \dots & + & 2 & + & 1 \end{array} \\ &= (N+1) + (N+1) + \dots + (N+1) + (N+1) \\ &= N(N+1), \end{aligned} \quad (17)$$

which implies $S_N = N(N+1)/2$. (There is a story that, when Gauss was ten years old, his school teacher wanted to keep his class busy by asking the students to add all the integers from 1 to 100. Gauss gave the correct answer 5050 before the teacher was even able to finish writing the problem on the board, evidently by discovering on the spot, in his head, that the sum of the first N integers was $N(N+1)/2$.)

3. As a simple model of an antiferromagnet, consider four identical spin-1/2 magnetic dipoles that are placed at the vertices of a unit square:



If we consider dipole states perpendicular to the plane of the square, the state of each dipole can be described by a binary variable $s_i = \pm 1$ that has the value 1 if the dipole is up (say points in the $\hat{z}$ direction perpendicular to the square) and has the value -1 if the dipole points down. Assuming that only nearest neighbor dipoles interact and that successive vertices are labeled 1, 2, 3, and 4 as one goes around the square, quantum mechanics suggests the following form for the energy E of this system:

$$E(s_1, s_2, s_3, s_4) = J(s_1 s_2 + s_2 s_3 + s_3 s_4 + s_4 s_1). \quad (18)$$

The constant $J > 0$, which has units of energy, is called a “coupling constant” and measures how strongly one spin couples to its neighbor. A positive J favors antiparallel nearest neighbors.

- (a) **(10 points)** What are the different energy values E_n of this system and what are the corresponding degeneracies d_n of the distinct energy values?

Hint: there are $2^4 = 16$ possible states $\mathbf{s} = (s_1, s_2, s_3, s_4)$ since each dipole can be up or down. You can be efficient in determining all the distinct energy states by using two symmetries. First, the energy Eq. (18) does not change if all spin states are reversed, $(s_1, s_2, s_3, s_4) \rightarrow (-s_1, -s_2, -s_3, -s_4)$

since the energy depends only the relative orientation of neighboring spins. For example, a state $(1, 1, 1, 1)$ with all spins up has the same energy $E(1, 1, 1, 1) = 4J$ as a state with all spins down, $(-1, -1, -1, -1)$. Second, a cyclic permutation of the spin values such as $(s_1, s_2, s_3, s_4) \rightarrow (s_2, s_3, s_4, s_1)$ can't change the energy E since, again, it is only the relative orientation of neighboring dipoles that matters. So the four states $(1, 1, 1, -1)$, $(1, 1, -1, 1)$, $(1, -1, 1, 1)$, and $(-1, 1, 1, 1)$ must all have the same energy $E(1, 1, 1, -1) = 0$.

Answer: This is the first problem you have seen in the course where the microscopic objects, here four spin-1/2 magnetic dipoles, strongly interact with one another so that you can not treat each dipole as behaving independently from the other dipoles, say as you could for the molecules in an ideal gas, or for the quantum harmonic oscillators in an Einstein solid, or for the dipoles in a paramagnet. The analysis is straightforward here for this system of four spins, but becomes daunting for, say, ten spins with $2^{10} \approx 1,000$ states, and even more so for a macroscopic antiferromagnet with Avogadro number of spins; the assumption of independent objects makes a huge difference in the ability to solve a problem. Scientists have developed sophisticated and successful theoretical methods (such as Landau theory and renormalization group) and computational methods (such as the Monte Carlo method) for studying strongly interacting many-particle systems. I hope to mention some of these briefly toward the end of the semester.

Finding the energies and degeneracies does not take long if you follow the hints to use the inversion symmetry and cyclic permutation symmetry of this problem. The sixteen possible states correspond to three different energy levels with degeneracies of 2, 12, and 2 respectively:

energy E_n	degeneracy d_n	states
$4J$	2	$(1, 1, 1, 1), (-1, -1, -1, -1)$
0	12	$(1, 1, 1, -1), (1, 1, -1, 1), (1, -1, 1, 1), (-1, 1, 1, 1),$ $(-1, -1, -1, 1), (-1, -1, 1, -1), (-1, 1, -1, -1), (1, -1, -1, -1)$ $(1, 1, -1, -1), (1, -1, -1, 1), (-1, -1, 1, 1), (-1, 1, 1, -1)$
$-4J$	2	$(1, -1, 1, -1), (-1, 1, -1, 1)$

The ground state consists of alternating spins as one goes around the squares, and this indeed corresponds to the antiferromagnetic state of some magnetic substances, which can be thought of as a three-dimensional lattice of up spins overlapping spatially with a separate three-dimensional lattice of down spins. Although there is no net magnetic moment in an antiferromagnet, there is local magnetic order.

Note that the ground state here is degenerate with two distinct states having the same energy. This implies that the entropy of this little system at $T = 0$ will be $S = k \ln \Omega = k \ln 2 > 0$, in violation of the third law of thermodynamics which requires $S(T = 0) = 0$. Degenerate ground states occur rarely in real substances, often a macroscopic substance can lower its free energy by “breaking the symmetry” that leads to the degeneracy, say by the substance altering its volume or shape or surface structure.

Also, note that the degeneracies of the first and second excited states decrease substantially in the presence of even a tiny external magnetic field. For example, the states $(1, 1, 1, 1)$ and $(-1, -1, -1, -1)$ will have different energies in the presence of an external magnetic field $\mathbf{B} = B\hat{\mathbf{z}}$, in one case all the spins are aligned with $\mathbf{B}$, in the other case they are all antiparallel. You can work out the general case by generalizing Eq. (18) to include the energy of dipoles in an external magnetic field, which we assume is oriented perpendicular to the plane of the spins:

$$E(s_1, s_2, s_3, s_4) = J(s_1 s_2 + s_2 s_3 + s_3 s_4 + s_4 s_1) - \mu B(s_1 + s_2 + s_3 + s_4). \quad (19)$$

Can you work out the distinct energies E_n and their degeneracies d_n for a the case of a nonzero but weak magnetic field, for which $0 < \mu B \ll J$?

- (b) **(10 points)** Assuming that this small spin system is in thermodynamic equilibrium with a reservoir whose constant temperature is T , find a mathematical expression for the average energy $\langle E \rangle$

of this system as a function of temperature T , use your expression to sketch qualitatively the curve $\langle E \rangle$ versus T , and then sketch qualitatively how the heat capacity $C(T)$ for this system varies with temperature for $T \geq 0$. (Do not waste time differentiating $\langle E \rangle$ to get C .)

Answer: From the above table of energies E_n and degeneracies d_n , we find the partition function for this small antiferromagnetic system to be

$$Z = \sum_n d_n e^{-\beta E_n} \quad (20)$$

$$= 2e^{4\beta J} + 12e^0 + 2e^{-4\beta J} \quad (21)$$

$$= 2(6 + e^{4\beta J} + e^{-4\beta J}). \quad (22)$$

It is possible to go one more step and express Z in terms of a hyperbolic cosine

$$Z = 4(3 + \cosh(4\beta J)), \quad (23)$$

but, as you will see, it is easier to carry out the next few steps by using the form Eq. (22).

Once we have a mathematical expression Eq. (22) for the partition function, we can invoke the Boltzmann machinery to calculate the average energy:

$$\langle E \rangle = -\frac{1}{Z} \frac{\partial Z}{\partial \beta} \quad (24)$$

$$= -\frac{1}{2(6 + e^{4\beta J} + e^{-4\beta J})} \frac{\partial}{\partial \beta} [2(6 + e^{4\beta J} + e^{-4\beta J})] \quad (25)$$

$$= -4J \frac{(e^{4\beta J} - e^{-4\beta J})}{(6 + e^{4\beta J} + e^{-4\beta J})}. \quad (26)$$

As a general rule, when organizing symbols in some answer, it is helpful to pull the parameters together that provide the physical units of the quantity of interest. Here we are calculating the average energy $\langle E \rangle$ and so it is helpful to isolate the energy $4J$ in front of the expression, leaving a dimensionless ratio of expressions.

Note: after getting the correct energy levels E_n and their degeneracies d_n , some students incorrectly deduced that the probability for the system to have an energy value E_n was equal to $p_n = d_n/(\sum_n d_n)$, which was a serious error since this throws out the temperature dependence of the average energy. The probability is instead given by the Boltzmann factor and partition function:

$$p_n = \frac{d_n e^{-\beta E_n}}{Z} = \frac{d_n e^{-\beta E_n}}{\sum_n d_n e^{-\beta E_n}}. \quad (27)$$

To draw the qualitative curve $\langle E \rangle$ as a function of the dimensionless temperature $kT/(4J)$, we can first ask what are the limits of Eq. (26) as $T \rightarrow 0$ and $T \rightarrow \infty$ and guess that the curve changes smoothly and monotonically between those limits. From Problem 2 of this quiz (whose results you are allowed to use!), you actually know these limits without calculation just based on the energy levels and their degeneracies. For example, as $T \rightarrow 0$, the system must be in its ground state so $\langle E \rangle = -4J$ at $T = 0$. As $T \rightarrow \infty$, all states become equally likely and $\langle E \rangle$ approaches the arithmetic average (weighted by the degeneracies) of the energy levels:

$$\langle E \rangle \rightarrow \frac{1}{16} [2(-4J) + 12(0) + 2(4J)] = 0. \quad (28)$$

So you could expect $\langle E \rangle$ to increase from $-4J$ at $T = 0$ smoothly and monotonically to 0 at $T = \infty$. This leads to the qualitative curve given below and is actually sufficient to deduce the qualitative shape of the curve $C(T)$.

Although not necessary, we can check these insights by calculating the actual limits as $T \rightarrow 0$ and $T \rightarrow \infty$. Thus as T becomes small, $\beta = 1/(kT)$ becomes large, $4\beta J$ becomes large, and

$e^{4\beta J}$ becomes extremely large while $e^{-4\beta J}$ becomes extremely small. So in Eq. (26), for small enough T , we can ignore the 6 and term $e^{-4\beta J}$ as small compared to $e^{4\beta J}$. We therefore have:

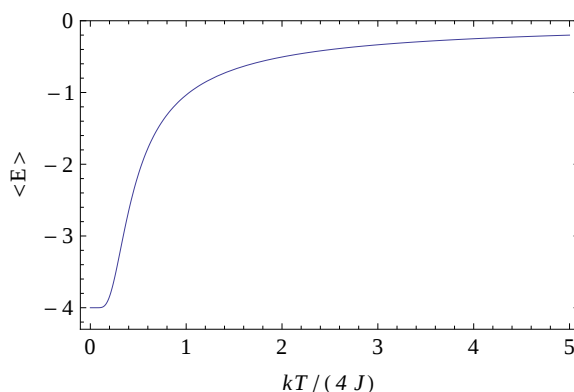
$$\lim_{T \rightarrow 0} \langle E \rangle = \lim_{T \rightarrow 0} -4J \frac{(e^{4\beta J} - e^{-4\beta J})}{(6 + e^{4\beta J} + e^{-4\beta J})} \approx \lim_{T \rightarrow 0} -4J \left(\frac{e^{4\beta J}}{e^{4\beta J}} \right) = -4J, \quad (29)$$

which is a negative number since you were told that the coupling constant J was positive.

As T becomes large, $4\beta J$ approaches zero and $e^{\pm 4\beta J} \rightarrow 1$. So we conclude that

$$\lim_{T \rightarrow \infty} \langle E \rangle = 0, \quad (30)$$

since the numerator $e^{4\beta J} - e^{-4\beta J} \rightarrow e^0 - e^{-0} = 1 - 1 = 0$ as $T \rightarrow \infty$. Thus a quick guess is that the average energy is always negative, and increases monotonically from $-4J$ at $T = 0$ to an asymptotic value of 0 for $T \rightarrow \infty$. The actual shape of the curve has this form:



which I obtained by executing this Mathematica code

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avgE = - 4 ( Exp[1/x] - Exp[-1/x] ) / ( 6 + Exp[1/x] - Exp[-1/x] ) ;

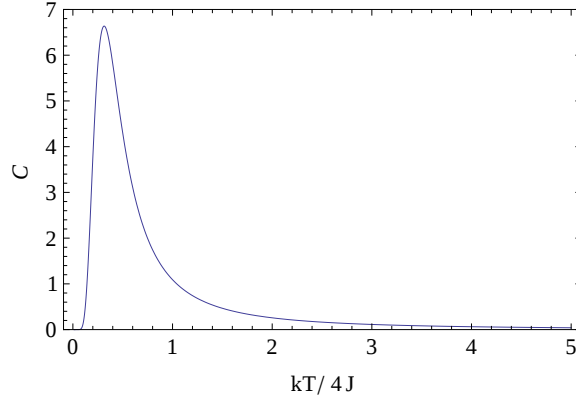
Plot[
  avgE ,
  { x, 0, 5 } ,
  PlotRange -> { -4.5, 0 } ,
  Frame -> True ,
  FrameLabel -> { "kT/4J", "<E>" } ,
  BaseStyle -> { FontSize -> 14 }
]
```

Any curve you drew that had roughly this shape was fine for getting credit.

If the average energy increases monotonically, the slope $d\langle E \rangle/dT$, which is the heat capacity, must be always positive. In addition to sketching the local slope of $\langle E \rangle$ versus T , we know two more facts:

- i. the heat capacity must go to zero as $T \rightarrow 0$ by the third law of thermodynamics,
- ii. C decays to zero as $1/T^2$ for large T , a general result that holds for any system that has a finite number of energy levels (see Problem 6 of Assignment 7, also Problem 6.18 on page 231 of Schroeder).

The result is that we expect a heat capacity curve $C(T)$ that is similar to that of a paramagnet. (In fact, once you have this insight, you can go back and improve your qualitative sketch of $\langle E \rangle$ versus T to be consistent with this insight.) The actual curve $C(T)$ looks like this



which you can obtain by substituting $\beta \rightarrow 1/(kT)$ in Eq. (26) to make the expression a function of T , then by differentiating (using Mathematica) the expression with respect to T . The peak again occurs when $kT/(4J)$ is of order one, the height of the peak is closer to 10 than 1, but that is because of the factor of 4 in the energy magnitude $4J$.

Because this small spin system is in equilibrium with a positive temperature reservoir, it is not possible for the system to have a negative temperature. But since this system does consist of a finite number of spins, an isolated version of this system, not in contact with a reservoir, would have an entropy S that reaches a maximum and then decreases as a function of energy U and so negative temperatures could occur.

We will learn soon how to calculate the entropy $S(T)$ of a small system in equilibrium with a reservoir. But for this particular problem, the entropy can be calculated directly for two simple cases. For $T = 0$, the multiplicity Ω is the degeneracy of the ground state so $S = k \ln 2$. For $T = \infty$, all sixteen states are equally likely and so equally accessible, which implies $\Omega = 16$ and so $S = k \ln(16) = k \ln(2^4) = 4k \ln(2)$, which is four times bigger than the zero temperature entropy.

The following equations may be useful:

$$S = k \ln \Omega, \quad dU = TdS - PdV + \mu dN. \quad (31)$$

$$\beta = \frac{1}{kT}, \quad p_s = \frac{e^{-\beta E_s}}{Z}, \quad Z = \sum_s e^{-\beta E_s} = \sum_n d_n e^{-\beta E_n}, \quad \langle E \rangle = \sum_s p_s E_s = -\frac{1}{Z} \frac{\partial Z}{\partial \beta}. \quad (32)$$