PHYS 328
HOMEWORK # 5
Solutions

1. This first question is one of several that will employ Stirling' s approximation to obtain analytic expressions that will help us understand various thermodynamic systems. Here, we are asked to find the multiplicity function for a large Einstein solid in the low temperature limit, i.e., q << N (in other words, there are many more oscillators than there are packets of energy to allocate among them). We begin by writing :

$$\Omega(N, q) = \frac{(q+N-1)!}{q!(N-1)!} \approx \frac{(q+N)!}{q!N!} \quad \text{since } N-1 \sim N \text{ for large N}$$

Following the method shown on p. 63 of the text, we take the ln of Ω :

$$\ln\Omega(N, q) = \ln(q+N)! - \ln q! - \ln N!$$

Apply Stirling' s approximation :

$$\ln\Omega(N, q) \approx (q+N)\ln(q+N) - (q+N) - (q\ln q - q) - (N\ln N - N) =$$

$$(q + N)\ln(q + N) - q\ln q - N\ln N$$

Rewrite (q + N) ln (q + N) as ln [N (1 + q/N)] ≈ (q + N)[ln N + q/N] using the property that ln(1+x) ~ x for |x|<<1 and we obtain:

$$\ln\Omega(N, q) \approx q\ln N + N\ln N + \frac{q^2}{N} + q - q\ln q - N\ln N \approx q\ln(N/q) + q$$

In the last step, the q^2/N term becomes very small for q<<N. Thus, we have:

$$\ln\Omega(N, q) \approx q\ln(N/q) + q$$

Exponentiating both sides yields :

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

Note that this is the text' s equation 2.21, with N and q interchanged.

2.. This is another question that will give us the opportunity to use Stirling’s approximation to derive general results about various systems. In this case, we are told that both q and N are large (but we are not necessarily in either the high or low temperature limit). Let' s begin by writing the expression for the multiplicity of an Einstein solid of N oscillators with a total of q units of energy :

$$\Omega(N, q) = \frac{(q+N-1)!}{q!\,(N-1)!}$$

Now, recognize that we can write :

$$(N-1)! = \frac{N!}{N} \text{ and } (q+N-1)! = \frac{(q+N)!}{q+N}$$

Make these substitutions and we get :

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

Now, we make use of Stirling' s approximation in the form :

$$N! = N^N e^{-N} \sqrt{2\pi N}$$

and obtain :

$$\Omega(N, q) = \frac{(q+N)^{(q+N)}}{(q+N)} e^{-(q+N)} \sqrt{2\pi(q+N)} \cdot \frac{N}{q^q e^{-q} \sqrt{2\pi q}\; N^N e^{-N} \sqrt{2\pi N}} =$$

Notice that the exponential in the numerator cancels the exponentials in the denominator, and we can write

$$(q+N)^{(q+N)} = (q+N)^q (q+N)^N$$

Using these results, and rewriting terms :

$$\Omega(N, q) = \frac{(q+N)^q}{q^q} \frac{(q+N)^N}{N^N} \frac{\sqrt{2\pi(q+N)}}{(q+N)} \frac{N}{\sqrt{2\pi q}\;\sqrt{2\pi N}} =$$

$$\frac{\left(\frac{q+N}{q}\right)^q \left(\frac{q+N}{N}\right)^N}{\sqrt{2\pi q\,(q+N)/N}} \tag{1}$$

3. In the case of a two state paramagnet, the particle can have one of two possible states, up or down. I will use the notation of N and D to represent the total number of particles and the number that are oriented downward (it' s just easier for me to type "D" than use the text' s notation of the down arrow.

The multiplicity of a system of N particles is then :

$$\Omega(N, D) = \frac{N!}{D!\,(N-D)!}$$

We can follow the treatment of the text on p. 63 to take the ln of this expression and apply Stirling' s approximation :

$$\ln\Omega =$$
$$\ln N! - \ln D! - \ln(N-D)! \approx N \ln N - N - (D \ln D - D) - ((N-D)\ln(N-D) - (N-D))$$

$$= N \ln N - D \ln D - (N - D) \ln (N - D)$$

In the limit where D << N, we can write the last ln term as :

$$\ln (N - D) = \ln\left[N\left(1 - \frac{D}{N}\right)\right] \approx \ln N - \frac{D}{N}$$

Using this expression we get :

$$\ln \Omega \approx N \ln N - D \ln D - (N - D)\left(\ln N - \frac{D}{N}\right) = N \ln N - D \ln D - N \ln N + D + D \ln N - \frac{D^2}{N}$$

Since D << N, the last term is negligible compared to D so may be omitted, and we get :

$$\ln \Omega \approx D \ln N - D \ln D + D = D \ln\left(\frac{N}{D}\right) + D$$

Exponentiating both sides to obtain an expression for Ω yields :

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

This is the same expression as derived in problem 1 with D substituted for q. In the paramagnet case, a particle can have only one of two orientations. In the case of a high temperature Einstein solid (which is not the case in problem 1), a particle can have many units of energy. When q << N, we approach a case where a few units of energy are spread among many particles, so we can frame this system as one in which a particle can have one of two states : either it has 1 unit of energy or more likely (since q << N) it has no units of energy. Not surprisingly, we obtain the same multiplicity.

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4. a) If there are 2 N units of energy, then there are 2 N + 1 macrostates. (0 energy in solid A, 1 unit of energy in A, ... all 2 N units in solid A). This may seem like a ridiculously easy question, you will see in part d) why it is asked explicitly.

b) We showed in problem 2 (see Eq. (1)) that we can express the multiplicity of an Einstein solid with large values of q and N as :

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

In our case, the total system has 2 N particles and 2 N units of energy. Setting both N and q in eq. (2) equal to 2 N, we get :

$$\Omega(2 N, 2 N) = \frac{\left(\frac{2 N+2 N}{2 N}\right)^{2 N} \left(\frac{2 N+2 N}{2 N}\right)^{2 N}}{\sqrt{2 \pi \cdot 2 N (2 N + 2 N) / 2 N}} = \frac{2^{2 N} \cdot 2^{2 N}}{\sqrt{8 \pi N}} = \frac{2^{4 N}}{\sqrt{8 \pi N}}$$

c) The multiplicity of the macrostate in which both A and B have N particles and N units of energy is :

$$\Omega_{\text{total}} = \Omega_A\,\Omega_B = \frac{\left(\frac{N+N}{N}\right)^N}{\sqrt{2\,\pi\,N\,(N+N)/N}} \cdot \frac{\left(\frac{N+N}{N}\right)^N}{\sqrt{2\,\pi\,N\,(N+N)/N}} = \left(\frac{2^N}{\sqrt{4\,\pi\,N}}\right)^2 = \frac{2^{4\,N}}{4\,\pi\,N}$$

where I use Eq. (2) for both solids, with q = N = N in both cases.

d) In part b) we computed the total number of microstates for the composite system. Since N is large, the sum of the microstates is the area under the curve of the probability distribution. In part c), we calculate the height of the peak of the distribution.

Now, we are being asked to approximate the peak of the distribution as a rectangle. Remember that as N grows large, the only states that have a meaninful probability of occurring are those near the peak (within roughly $1\big/\sqrt{N}$) of the peak, so we can set the area under the total curve to approximate the area of the rectangle around the peak and write:

$$\text{area of rectangle} = \text{area under curve} = \text{height of curve} \cdot \text{width of rectangle} \Rightarrow$$

$$\frac{2^{4\,N}}{\sqrt{8\,\pi\,N}} = \frac{2^{4\,N}}{4\,\pi\,N} \cdot \text{width of rectangle} \Rightarrow \text{width of rectangle} = \sqrt{2\,\pi\,N}\,.$$

This result is the width (measured in macrostates) of that part of the distribution that has a nonzero chance of occurring. Now, to answer the question of what fraction of states have any likelihood of being observed, we divide this result by the total number of macrostates in part a) :

$$\text{fraction of observable states} = \frac{\sqrt{2\,\pi\,N}}{2\,N+1} \text{ which goes as } \frac{1}{\sqrt{N}}$$

For N approaching Avogadro' s number, the fraction of observable states is tiny, on the order of 10^{-12}, underscoring again that when N is large, the only state we are likely to observe is the most probable state.

5. a) The most probable outcome is that there will be as many steps to the left as the right, so that your most probable final position will be where you started. We can use the mathematics developed in the text to determine the multiplicty of ways of obtaining as many steps to the left as to the right. If N is the total number of steps, we wish to calculate:

$$\Omega_{\max} = \frac{N!}{(N/2)!\,(N/2)!} \approx \frac{N^N\,e^{-N}\,\sqrt{2\,\pi\,N}}{\left((N/2)^{N/2}\,e^{-N/2}\,\sqrt{2\,\pi\,N/2}\right)^2} = \frac{N^N\,\sqrt{2\,\pi\,N}}{(N/2)^N\,(\pi\,N)} = 2^N\sqrt{\frac{2}{\pi\,N}}$$

This is the multiplicity of the macrostate in which there are as many steps to the left as to the right (in other words, the multiplicity of ways of ending up at your starting point). This results will be important in b).

b) By asking how far you expect to be at the end, we are really being asked to find the width of the probability distribution of possible final positions. In short, we will define where we ‘expect’ to end up in terms of the e-folding parameter for this distribution.

Let's consider a few ways of addressing this question.

A simple first way to approach this problem would be to cite the $1/\sqrt{N}$ behavior of the fractional spread of Gaussian distributions, and then argue in a trip of 10,000 steps, you would expect that your final position would be within $1/\sqrt{10,000}$ of 1/100th of the origin. In other words, you should expect your final position to be within 10,000/100 or 100 steps of the origin.

We can derive a much more detailed (and somewhat more precise) estimate of our expected range of final destinations by studying the behavior of the distribution near its peak. We know that we will likely have just about as many steps to the left as to the right, so we can define a parameter x, which measures the distance between the peak of the distribution and the number of steps taken to the right (we could equally well use steps to the left) as :

$$x = (R - N/2)$$

where R is number of steps to the right and N/2 is the peak of the distribution. Then, we can compute the multiplicity of obtaining R steps (and assume x << N/2) :

$$\Omega = \frac{N!}{\left(\frac{N}{2}+x\right)!\left(\frac{N}{2}-x\right)!}$$

Stirling' s Approximation gives us :

$$\Omega \approx \left(N^N e^{-N}\sqrt{2\pi N}\right) \Big/ \left((N/2+x)^{N/2+x} e^{-(N/2+x)} \sqrt{2\pi(N/2+x)}\ (N/2-x)^{N/2-x} e^{-(N/2-x)} \sqrt{2\pi(N/2-x)}\right)$$

Notice that the exponential terms in the numerator and denominator cancel to 1, leaving :

$$\frac{N^N\sqrt{2\pi N}}{\left(\frac{N}{2}+x\right)^{\frac{N}{2}+x}\sqrt{2\pi\left(\frac{N}{2}+x\right)}\left(\frac{N}{2}-x\right)^{\frac{N}{2}-x}\sqrt{2\pi\left(\frac{N}{2}-x\right)}}$$

We can rewrite the terms in the denominator to give us :

$$\frac{N^N\sqrt{2\pi N}}{\left(\frac{N}{2}+x\right)^{\frac{N}{2}}\left(\frac{N}{2}-x\right)^{\frac{N}{2}}\left(\frac{N}{2}+x\right)^{x}\left(\frac{N}{2}-x\right)^{-x}\sqrt{(2\pi)^2\left(\left(\frac{N}{2}\right)^2-x^2\right)}} =$$

$$\frac{N^N \sqrt{\frac{N}{2\pi}}}{\left[\left(\frac{N}{2}\right)^2 - x^2\right]^{\frac{N}{2}} \left(\frac{N}{2} + x\right)^x \left(\frac{N}{2} - x\right)^{-x} \sqrt{\left(\left(\frac{N}{2}\right)^2 - x^2\right)}}$$

Now, let' s work with the log of this expression for multiplicity :

$$\ln \Omega =$$

$$N \ln N + \ln \sqrt{\frac{N}{2\pi}} - \frac{N}{2} \ln\left[\left(\frac{N}{2}\right)^2 - x^2\right] - x \ln\left(\frac{N}{2} + x\right) - (-x) \ln\left(\frac{N}{2} - x\right) - \frac{1}{2} \ln\left(\left(\frac{N}{2}\right)^2 - x^2\right)$$

We will now focus on some of the expressions involving ln and use the fact that x << N to rewrite the expressions :

$$\ln\left[\left(\frac{N}{2}\right)^2 - x^2\right] = \ln\left[\left(\frac{N}{2}\right)^2 \left(1 - \left(\frac{2x}{N}\right)^2\right)\right] \approx 2 \ln\left(\frac{N}{2}\right) - \left(\frac{2x}{N}\right)^2$$

where I have made use of the approximation $\ln(1 + x) \approx x$ for $|x| << 1$. Using the same approximation allows us to write :

$$\ln\left(\frac{N}{2} \pm x\right) = \ln\left[\left(\frac{N}{2}\right)\left(1 \pm \frac{2x}{N}\right)\right] \approx \ln\left(\frac{N}{2}\right) \pm \frac{2x}{N}$$

Substituting these expressions into our equation for $\ln \Omega$ gives :

$$\ln \Omega = N \ln N + \ln \sqrt{\frac{N}{2\pi}} - \frac{N}{2}\left(2 \ln\left(\frac{N}{2}\right) - \left(\frac{2x}{N}\right)^2\right) -$$

$$x \ln\left(\frac{N}{2}\right) - \frac{2x^2}{N} + x \ln\left(\frac{N}{2}\right) - \frac{2x^2}{N} - \frac{1}{2}\left(2 \ln\left(\frac{N}{2}\right) - \left(\frac{2x}{N}\right)^2\right) =$$

$$\color{blue}{N \ln N} + \color{red}{\ln \sqrt{\frac{N}{2\pi}}} \color{blue}{- N \ln\left(\frac{N}{2}\right)} \color{lime}{+ \frac{2x^2}{N}} \color{purple}{- x \ln\left(\frac{N}{2}\right)} \color{lime}{- \frac{2x^2}{N}} \color{purple}{+ x \ln\left(\frac{N}{2}\right)} \color{lime}{- \frac{2x^2}{N}} \color{red}{- \ln\left(\frac{N}{2}\right)} + \frac{2x^2}{N^2} \Rightarrow$$

$$\ln \Omega = N \ln 2 - \frac{2x^2}{N} + \ln \sqrt{\frac{2}{\pi N}} + \frac{2x^2}{N^2} \qquad (3)$$

The color coding in the penultimate expression shows which terms I combined to obtain the final expression for $\ln \Omega$. Since x << N, we can ignore the final term in eq. (3); exponentiating both sides we obtain finally :

$$\Omega = e^{N \ln 2 - 2 x^2/N + \ln \sqrt{2/\pi N}} = 2^N \sqrt{\frac{2}{\pi N}}\, e^{-2 x^2/N} = \Omega_{max}\, e^{-2 x^2/N} \tag{4}$$

We recover a by now familiar Gaussian distribution. It would be easy to think we are complete, but we are not quite there. Remember, that the parameter x is not displacement from the origin, but the number of steps to the right taken. So we now need to find an expression relating the parameter x to displacement from the origin.

In order for x to be non - zero, there must be an excess of steps to the right (or to the left). We can equate displacement from the origin to this parameter x by noting that the displacement from the origin will be :

$$\text{displacement} \equiv \Delta = (R - L)\, D$$

where R is the number of steps to the right, L the number of steps to the left, and D is the length of each step. (Clearly, if L = R, the displacement is zero). Recognizing that R + L = N, we can rewrite the displacement in terms of R and N :

$$\Delta = (R - (N - R))\, D = (2 R - N)\, D = 2 \left(R - \frac{N}{2}\right) D$$

If you look all the way back to the beginning of this problem, you will see that the term in parentheses is just our parameter x, so we can write :

$$\Delta = 2\, x\, D \Rightarrow x = \frac{\Delta}{2 D}$$

Use this expression for x in the Gaussian eq. (4) and we can express the multiplicity of macrostates in terms of the displacement from the origin :

$$\Omega = \Omega_{max}\, e^{-2 (\Delta/2 D)^2/N} = \Omega_{max}\, e^{-\Delta^2/2 N D^2}$$

We now have a Gaussian distribution describing the displacement from the origin and can ask how far from the origin we expect to travel in N steps. This is equivalent to asking what is the e - folding height of the distribution :

$$e^{-\Delta^2/2 N D^2} = e^{-1} \Rightarrow \frac{\Delta^2}{2 N D^2} = 1 \Rightarrow \Delta = \sqrt{2 N}\, D =$$

If we set D = 1 unit step, then our expected displacement after 10, 000 steps is approximately 141 steps from the origin.

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6. The probability of a molecule being in the leftmost 99 % of the vessel is 0.99. Therefore, the probability of finding N molecules in the leftmost portion is simply 0.99^N. If N is 100, then:

In[3]:= 0.99^{100}

Out[3]= 0.366032

and the rightside will be empty 3/8 of the time. For larger values of N :

In[5]:= $0.99^{10\,000}$

Out[5]= 2.24877×10^{-44}

In[6]:=
```
Clear[n]
n = 10^23;
0.99^n
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General::unfl : Underflow occurred in computation. ≫

Out[8]= Underflow[]

For 10, 000 molecules, the likelihood that 1 % of the volume is empty is ridiculously low. For an Avogadro' s number of molecules, we cannot easily compute it on Mathematica