PHYS 328
HOMEWORK #5

Due : 27 Sept. 2012

1. Starting with the observation that the specific heat of water is 4.2 J/g/C (or 4200 J/kg/C), determine what fraction of the specific heat derives from quadratic forms of energy and the fraction due to hydrogen bonding. There are 12 degrees of freedom in a water molecule.

Solution : If only quadratic forms of energy contributed to the total energy of water, then the equipartition theorem suggests that the total energy of water could be expressed as :

$$U = \frac{1}{2} f\, N\, k\, T = 6\, N\, k\, T \quad \text{(since water has 12 degrees of freedom).}$$

Then, the specific heat of water would be :

$$C = \frac{dU}{dT} = 6\, N\, k.$$

For one molecule, the specific heat becomes 6 k (where k is Boltzmann' s constant).

Now, let' s use the observed value of water' s specific heat to determine the actual value/molecule. The molecular weight of water is 18 g, so that 1 gram represents 1/18 of a mole or :

$$6.02 \times 10^{23} \text{ molecules / mole} * \frac{1}{18} \text{ mole} = 3.34 \times 10^{22} \text{ molecules}$$

Then the specific heat per molecule is :

$$\frac{4.2 \text{ J}}{3.3 \times 10^{22} \text{ molecules}} =$$

1.27×10^{-22} J $= 9$ k when we write this in terms of the Boltzmann constant.

This last figure represents the actual value of the specific heat per molecule; when assuming only quadratic forms of energy, we computed a value of 6 k. Thus, the quadratic forms contribue 2/3 of the total specific heat, and hydrogen bonding accounts for 1/3 of it.

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2. Calculate the number of possible microstates for the cases shown in text problem 2.5, parts a) - e) inclusive. 2 pts each part.

Solution : For all parts, we will use :

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

a) $\Omega(3, 4) = \dfrac{6!}{4!\ \ 2!} = 15$

b) $\Omega(3, 5) = \dfrac{7!}{5!\ \ 2!} = 21$

c) $\Omega(3, 6) = \dfrac{8!}{6!\ \ 2!} = 28$

d) $\Omega(4, 2) = \dfrac{5!}{2!\ \ 3!} = 10$

e) $\Omega(4, 3) = \dfrac{6!}{3!\ \ 3!} = 20$

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3. Without doing any explicit calculations or making any reference to equation 2.9 in the text, determine the answers for text problem 2.5, parts f) and g). Explain your reasoning. 10 pts for the question.

Solution : In part f), there is one atom and the heat can be any integer value. There is only one possible microstate, namely, the microstate in which all the energy is in the one atom.

In part g), there is one unit of energy that can be distributed among N atoms. Since the one unit of energy could be in any of the atoms, there are N possible microstates available to this system.

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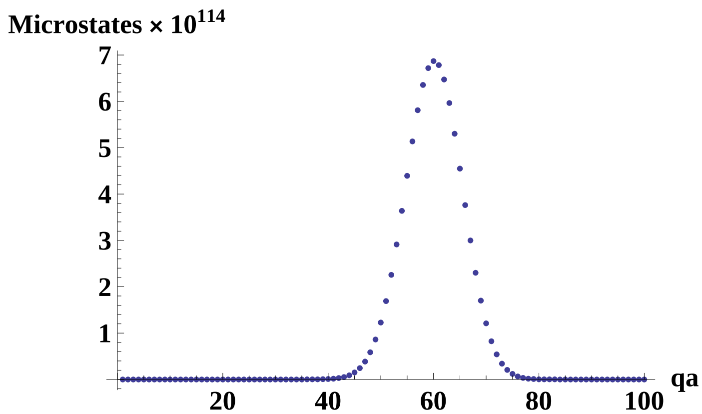
4. Consider a system A with 300 particles and a system B with 200 particles. The systems share a total of 100 units of energy. Write a *Mathematica* program that reproduces the plot on p. 59 of the text (you needn't worry about aesthetics such as shading and axis labels).

In[2]:=
```
Clear[microstatesa, microstatesb, microstates, na, nb, q]
na=300;nb=200;q=100;
microstatesa[qa_]:=(qa+na-1)!/(qa!(na-1)!)
microstatesb[qa_]:=(q-qa+nb-1)!/((q-qa)!(nb-1)!)
microstates[qa_]:=microstatesa[qa] microstatesb[qa]
ListPlot[Table[{qa,microstates[qa]/10^114},{qa,q}],PlotRange→All,AxesLabel→{qa,"Microstate
```

Out[7]=



In this program, I defined three functions to find the number of possible microstates for system A (microstatesa[qa]), system B (microstatesb[qa]), and the total number of microstates for the combined system (microstates[qa]). I wrote each one as a function of the energy in system A (qa), since the total energy q must equal the sum of qa and qb. The number of particles are represented by na and nb. We can use the program above to find the total number of microstates possible by summing microstates[qa] from qa = 0 to 100 :

```
totalstates = Sum[microstates[qa], {qa, 0, 100}] // N;
Print[
 "The total number of microstates available to the combined system = ", totalstates]
```

```
The total number of microstates available to the combined system = 9.26176 × 10^115
```

and this result agrees the number quoted in the text. Notice that we would also obtain this result by directly computing the total number of microstates for a system of 500 particles with 100 units of energy:

```
(500 + 100 - 1) ! / (100 ! (500 - 1) !) // N
```

```
9.26176 × 10^115
```

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5. For the system described in problem 4 above, write a short Mathematica program to determine the probability of finding all the energy in A; what is the probability of finding all the energy in B? Your graph above should show that the maximum probability occurs when $q_A = 60$. What is the probability of finding 60 units in system A? (Use *Mathematica* programs to solve all parts to the question; clearly define all the variables and functions you use in your programs).

Solution : The probability of finding a macrostate with qa units of energy is :

$$\text{probability of macrostate with qa units of energy} = \frac{\Omega(\text{qa})}{\Omega(\text{all})}$$

where Ω (qa) is the number of ways we can get qa units of energy in system A, and Ω (all) is the total number of microstates available to the system (this is the number computed as totalstates in the problem above). Using our definitions from the previous problem, we have :

```
Clear[prob]
prob[qa_] := microstates[qa] / totalstates
```

The probability of finding all 100 units in system A is :

```
Print["The probability of finding 100 units of energy in A = ", prob[100] // N]
```

```
The probability of finding 100 units of energy in A = 1.81541 × 10^-20
```

And the probabilities for finding all the energy in B and 60 units in A :

```
Print["The probability of finding 100 units of energy in B = ", prob[0] // N]
Print["The probability of finding 60 units of energy in A = ", prob[60] // N]
```

```
The probability of finding 100 units of energy in B = 2.99313 × 10^-35
The probability of finding 60 units of energy in A = 0.0741361
```

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6. Problem 2.16 from the text. Use Stirling' s approximation even if your calculator can handle the factorials. You may use a calculator or Mathematica to check your results, but show your work and compute your values using Stirling' s approximation. 10 pts for part a), 5 pts for part b).

Solutions :

a) If we flip a coin 1000 times, then there are a total of 2^{1000} possible outcomes (microstates). The number of ways of getting exactly 500 heads is:

$$\Omega(500) = \frac{1000!}{500! \times 500!}$$

so the probabiility of getting exactly 500 heads is :

$$\text{prob}(500) = \frac{\Omega(500)}{2^{1000}}$$

Let' s use Stirling' s approximation to find the value of Ω (500). Since we are dealing with a large, but not very large number, we use Stirling in the form :

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

Applying this to (500) we get :

$$\Omega(500) = \frac{1000!}{500! \times 500!} \approx \frac{1000^{1000} e^{-1000} \sqrt{2\pi \cdot 1000}}{\left(500^{500}\right)^2 \left(e^{-500}\right)^2 \sqrt{2\pi \cdot 500} \sqrt{2\pi \cdot 500}} =$$

$$\frac{1000^{1000}\, e^{-1000}}{500^{1000}\, e^{-1000}\sqrt{2\pi\cdot 250}} = \frac{2^{1000}}{\sqrt{2\pi\cdot 250}}$$

The above expression is Ω (500), so the probability of obtaining exactly 500 heads is :

$$\text{prob}(500) = \left(\frac{2^{1000}}{\sqrt{2\pi\cdot 250}}\right) \Big/ 2^{1000} = \frac{1}{\sqrt{500\pi}} = 0.0252 = 2.52\,\%$$

b) The probability of obtaining exactly 600 heads is :

$$\text{prob}(600) =$$

$$\frac{\Omega(600)}{2^{1000}} = \frac{1000!}{600!\quad 400!}\, 2^{-1000} = \frac{1000^{1000}\, e^{-1000}\sqrt{2\pi\cdot 1000}}{600^{600}\, e^{-600}\, 400^{400}\, e^{-400}\sqrt{2\pi\cdot 600}\ \sqrt{2\pi\cdot 400}}\, 2^{-1000}$$

Notice that the exponential terms cancel; we can further write $1000^{1000} = 1000^{(600+400)} = 1000^{600}\, 1000^{400}$. Similarly, $2^{1000} = 2^{600}\, 2^{400}$, These expressions allow us to write prob(600) as:

$$\text{prob}(600) = \left(\frac{5}{6}\right)^{600}\left(\frac{5}{4}\right)^{400}\sqrt{\frac{5}{2400\,\pi}} = 4.63\times 10^{-11}$$

We compare the result obtained from Stirling' s Approximation with a direct calculation and see that Stirling’s approximation works quite well for N ~ 1000 :

```
(1000! / (600!  400!)) / 2^1000 // N
```

Out[1]= 4.63391×10^{-11}

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7. Text problem 2.17

Solution : Start with eq.2.18 from page 63 of the text :

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

In the low temperature limit, q << N, so we rewrite the ln (q + N) term as :

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

The last step uses the approximation you learned in your studies of Taylor series : $\ln(1+x) \approx x$ for $|x| << 1$. Substitute this into text eq. 2-18:

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

Since q << N, we can ignore the q^2/N term and get:

$$\ln\Omega = q\ln\left(\frac{N}{q}\right) + q$$

Exponentiate both sides :

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

Notice that this result has the same form of eq. 2.21 in the text with q and N interchanged.

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8. Text problem 2.18

Solution : In this problem, we are asked to verify an expression for the multiplicity of a system of oscillators. Since this is the general case, we cannot make any assumptions about the relative sizes of q and N, although we do assume they are both large enough to use Stirling' s approximation. We begin with the general expression for the multiplicity of an Einstein solid of N oscillators with a total of q units of energy :

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

Now, we follow the hint in the text and show that :

$$(q + N)! = (q + N)\,(q + N - 1)! \Rightarrow (q + N - 1)! = (q + N)! / q + N$$

Similarly, we can write (N - 1)! = N!/N. With these results, the multiplicity of the system becomes :

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

Expressing the factorials using Stirling' s approximation :

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

Notice that the exponential terms cancel. A little bit more algebra brings us to the desired form :

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