Homework 5 (Due Tuesday, February 14th)

1. Consider a system that has Ω states; the probability of the system being in a particular state is $\mathcal{P}_i$. The entropy is defined as

$$S = -k \sum_{i=1}^{\Omega} \mathcal{P}_i \ln \mathcal{P}_i$$

Show that the entropy is maximum when $\mathcal{P}_i = 1/\Omega$ using the method of Lagrange multipliers to impose the condition that the probabilities sum to one.

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2. Write a program to explicitly count the number of states that satisfy the condition $n_x^2 + n_y^2 + n_z^2 \leq E^*$ where $n_i = 1, 2, \ldots$. This gives Σ, the number of states at or below the dimensionless energy $E^* = 8mL^2U/h^2$ for a quantum mechanical particle in a cubic box. Graph the number of states versus E^* (from $E^* = 1$ to 10^3) on a log-log scale.

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3. Demonstrate that the number of ways one can place M indistinguishable objects into N boxes is

$$\binom{M+N-1}{N-1} = \frac{(M+N-1)!}{(N-1)!M!}$$

The clearest and easiest way to formulate this demonstration is graphically rather than analytically.

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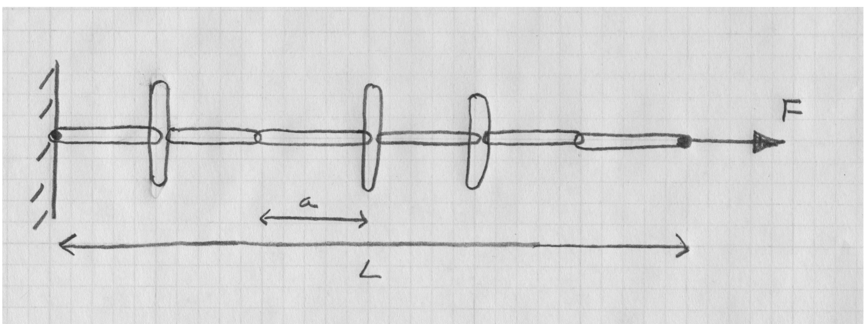
4. Consider a one-dimensional chain with $N \gg 1$ segments, as illustrated below. Let the length of each segment be a when the segment is horizontal and zero when the segment is vertical (these are the only two possible states for a segment). Call L the total length of the chain.

(a) Find the entropy of this system as a function of L. Hint: The number of combinations for choosing M objects out of N is $N!/[M!(N-M)!]$.

(b) Suppose that the chain is under a tension F at temperature T. Find $L(T, F)$. [Hints: $F = -dU/dL$ and you'll want to use Sterling's approximation]

(c) Show that at high temperature the length of the chain is linearly proportional to the tension (i.e., Hooke's law).



Solutions

1. To maximize S, we introduce the function

$$W = S - \alpha' \sum_i \mathcal{P}_i$$

where α' is a Lagrange multiplier. We seek to maximize W so we compute $\partial W/\partial \mathcal{P}_j$ and set the derivative to zero,

$$\begin{aligned}
\frac{\partial W}{\partial \mathcal{P}_j} &= \frac{\partial}{\partial \mathcal{P}_j}\left(-k\sum_i \mathcal{P}_i \ln \mathcal{P}_i - \alpha' \sum_i \mathcal{P}_i\right) \\
&= -\sum_i \frac{\partial}{\partial \mathcal{P}_j}\left(k\mathcal{P}_i \ln \mathcal{P}_i + \alpha' \mathcal{P}_i\right) \\
&= -\sum_i \left(k \ln \mathcal{P}_j + k + \alpha'\right)\delta_{ij} \\
&= -k(\ln \mathcal{P}_j + \alpha)
\end{aligned}$$

where $\alpha \equiv 1 + \alpha'/k$. Setting $\partial W/\partial \mathcal{P}_j = 0$ gives $\ln \mathcal{P}_j = -\alpha$ or $\mathcal{P}_j = e^{-\alpha}$ which means that $\mathcal{P}_j$ is a constant so

$$\sum_{i=1}^{\Omega} \mathcal{P}_i = (\mathcal{P}_i)\sum_{i=1}^{\Omega}(1) = (\mathcal{P}_i)(\Omega) = 1$$

which means that $\mathcal{P}_i = 1/\Omega$.

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2. Your graph should look something like Figure 1, which was produced by the MATLAB program below. Notice that the slope of the curve shows that the number of states goes as $(E^*)^{3/2}$.

```
% states2 - Program to count number of accessible states for
%          a particle in a box
clear; help states2; Nplot = 100;
Eplot = logspace(0,3,Nplot); % from 10^0 to 10^3
count = zeros(Nplot,1); for n=1:Nplot
  Es = Eplot(n);
  fprintf('Doing E = %g \n',Es);
  ijkMax = ceil(sqrt(Es));
  for i=0:ijkMax
   for j=0:ijkMax
    for k=0:ijkMax
      E = i^2 + j^2 + k^2;
      if(E <= Es)
        count(n) = count(n)+1;
      end
    end
   end
  end
end loglog(Eplot,count,'+'); xlabel('E^*');  ylabel('Number of states');
```

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3. The simplest way to understand the derivation is to consider a specific example. Suppose we take $M = 7$ objects to be placed into $N = 4$ boxes. First, make a sketch with $M + (N - 1)$ circles; in our example $M + (N - 1) = 10$ so

$$\circ\circ\circ\circ\circ\circ\circ\circ\circ\circ$$

Now select $N - 1$ circles and replace them with vertical bars, such as illustrated below,

$$\circ\circ|\circ\circ\circ|\circ|\circ$$

There were originally $M + (N - 1)$ circles from which we select $N - 1$; since the order in which they are selected does not matter, there are $\binom{M+(N-1)}{N-1}$ ways to select which circles become bars. Finally, draw a bar on each end, as shown,

$$|\circ\circ|\circ\circ\circ|\circ|\circ|$$

The bars represent the edges of the $N = 4$ boxes and the circles are the $M = 7$ objects placed in the boxes; in the above picture we have two objects in the first box, three in the next box and one object in each of the last two boxes. We already determined the possible number of ways to draw this picture so that is the number of ways to place the objects into the boxes.

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4. Call M the number of horizontal segments. The number of combinations for which there are M

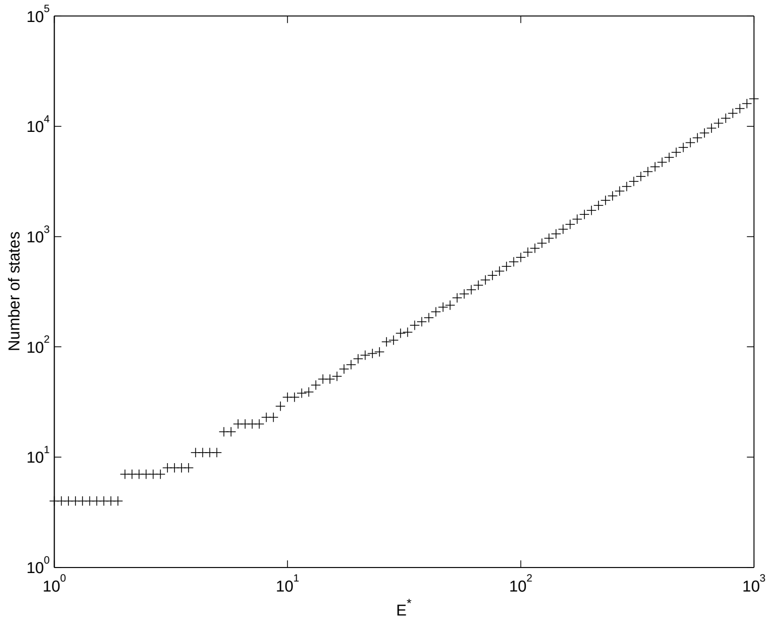

Figure 1: Number of states for a single particle in a box.

horizontal segments from a total of N segments is

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

so the entropy is

$$S = k \ln \Omega = k \ln N! - k \ln M! - k \ln(N-M)!$$

Using Sterling's approximation, $\ln x! \approx x \ln x - x$, this gives

$$S = kN \ln N - kM \ln M - k(N-M) \ln(N-M)$$

This may be written in terms of length since $M = L/a$ so

$$S = ka^{-1}[L_0 \ln L_0 - L \ln L - (L_0 - L) \ln(L_0 - L)]$$

where $L_0 = aN$ is the maximum length.

(b) We may write the temperature as

$$T = \frac{dE}{dS} = \frac{dE}{dL}\frac{dL}{dS}$$

Note that this system has only one extensive thermodynamic parameter since given S we know L and vice versa. From the result in part (a),

$$\frac{dS}{dL} = ka^{-1}[-\ln L + \ln(L_0 - L)] = \frac{k}{a} \ln \frac{L_0 - L}{L}$$

so

$$T = \frac{-aF}{k \ln \frac{L_0 - L}{L}}$$

or

$$L = \frac{L_0}{1 + e^{-aF/kT}}$$

Notice when $aF \gg kT$ the system's length is L_0 (i.e, fully stretched).

(c) In the high temperature limit, we may use the approximation

$$(1 + e^{-x})^{-1} \approx (1 + (1 - x))^{-1} = \frac{1}{2}(1 - x/2)^{-1} \approx \frac{1 + x/2}{2}$$

so

$$L \approx \frac{L_0}{2}\left(1 + \frac{aF}{2kT}\right)$$

Notice when $kT \gg aF$ the system's length is $\frac{1}{2}L_0$ as this is the most disordered state, with half of the segments in each configuration.