PHY5524
Problem Set 1: Solution

Problem 1

(a) If n is the number of segments which point up and L is the length of the rubber band, then

$$\frac{L}{a} = N - 2n \Rightarrow n = \frac{N}{2} - \frac{L}{2a} \tag{1}$$

The number of microstates corresponding to length L is then N choose n, i.e.

$$\#\text{ of microstates} = \begin{pmatrix} N \\ n \end{pmatrix} = \frac{N!}{(N-n)!n!} = \frac{N!}{\left(\frac{N}{2}+\frac{L}{2a}\right)!\left(\frac{N}{2}-\frac{L}{2a}\right)!} \tag{2}$$

From this, we find the entropy is

$$S = k_B \ln \frac{N!}{\left(\frac{N}{2}+\frac{L}{2a}\right)!\left(\frac{N}{2}-\frac{L}{2a}\right)!} \tag{3}$$

Or, since $E = -mgL$,

$$S(E,N) = k_B \ln \frac{N!}{\left(\frac{N}{2}-\frac{E}{2mga}\right)!\left(\frac{N}{2}+\frac{E}{2mga}\right)!} \tag{4}$$

(b) For $N \gg 1$, if we apply Stirling's approximation ($\ln N! = N\ln N - N + O(\ln N)$) we obtain

$$S \simeq k_B \left(N \ln N - \left(\frac{N}{2} + \frac{E}{2mga}\right) \ln \left(\frac{N}{2} + \frac{E}{2mga}\right) - \left(\frac{N}{2} - \frac{E}{2mga}\right) \ln \left(\frac{N}{2} - \frac{E}{2mga}\right) \right) \tag{5}$$

or, after simplifying things a bit,

$$S(E,N) = -k_B N \left(\left(\frac{1}{2} + \frac{E/N}{2mga}\right) \ln \left(\frac{1}{2} + \frac{E/N}{2mga}\right) + \left(\frac{1}{2} - \frac{E/N}{2mga}\right) \ln \left(\frac{1}{2} - \frac{E/N}{2mga}\right) \right) \tag{6}$$

(c) We can use the fact that $\left(\frac{\partial S}{\partial E}\right)_N = \frac{1}{T}$ to obtain

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_N = \frac{k_B}{2mga} \ln \frac{mga - E/N}{mga + E/N} \tag{7}$$

We can then solve for E by exponentiating both sides

$$e^{2mga/k_BT} = \frac{mga - E/N}{mga + E/N} \tag{8}$$

and doing a little algebra

$$(Nmga + E)e^{2mga/k_BT} = Nmga - E \tag{9}$$

$$E(1 + e^{2mga/k_BT}) = Nmga(1 - e^{2mga/k_BT}) \tag{10}$$

to obtain

$$E(N,T) = Nmga \frac{1 - e^{2mga/k_BT}}{1 + e^{2mga/k_BT}} = -Nmga \tanh \frac{mga}{k_BT} \tag{11}$$

(d) Since $E = -mgL$,

$$L = -\frac{E}{mg} = +Na \tanh \frac{mga}{k_BT} \tag{12}$$

Problem 2

We assume that $S = f(\Omega)$ where f is some universal function. If we have two systems with Ω_1 and Ω_2, then $S_{tot} = S_1 + S_2 = f(\Omega_1) + f(\Omega_2)$. At the same time, since the total number of microstates of the two systems taken together is $\Omega_{tot} = \Omega_1\Omega_2$, $S_{tot} = f(\Omega_1\Omega_2)$.

It follows that the function f must satisfy the following equation

$$f(\Omega_1\Omega_2) = f(\Omega_1) + f(\Omega_2) \tag{13}$$

for any Ω_1 and Ω_2. Clearly $f(\Omega) \propto \ln \Omega$ satisfies this equation, but is this the only solution? It's easy to prove that it is.

If we differentiate both sides of (13) w.r.t. Ω_2 while keeping Ω_1 fixed we obtain

$$\Omega_1 f'(\Omega_1\Omega_2) = f'(\Omega_2) \tag{14}$$

Since this equation must hold for all Ω_1 and Ω_2, it must hold when $\Omega_2 = 1$. So let's set $\Omega_2 = 1$ and let $k = f'(1)$. This implies that

$$f'(\Omega_1) = \frac{k}{\Omega_1} \tag{15}$$

Integrating this w.r.t. Ω_1 then yields

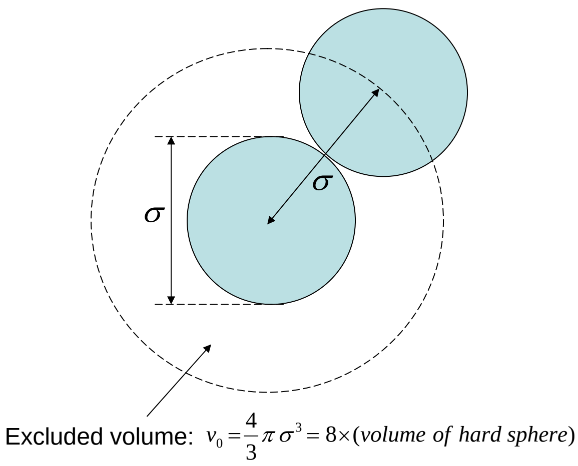
$$f(\Omega_1) = k \ln \Omega_1 + C \tag{16}$$

where C is an integration constant. Plugging this into the starting expression, we see that the integration constant C must equal 0. Thus we find that not only is $f(\Omega) = k \ln(\Omega)$ a solution to (13), it is the *only* solution.

Problem 3

In this problem we consider a classical gas of hard spheres with diameter σ. Each such hard sphere excludes a volume v_0 from each of the other hard spheres in the gas. (Note that since we are assuming that $Nv_0 << V$ we are in the *dilute* limit, so in calculating the excluded volume due to a given set of hard spheres, we can assume these spheres are well separated so each excludes the same volume v_0.)

The following figure makes it clear that v_0 is 8 times larger than the volume of a given hard sphere.



We expect the number of microstates for a given sphere to be proportional to the volume of space it can occupy. If the first sphere can occupy a volume V, then the second sphere occupies a volume $V - v_0$, the third a volume $V - 2v_0$, and so on. Thus we expect that the V dependence of Ω takes the following form

$$\Omega \propto V(V - v_0)(V - 2v_0)\cdots(V - (N-1)v_0) \tag{17}$$

We can then use the fact that

$$\left(\frac{\partial \ln \Omega}{\partial V}\right)_{E,N} = \frac{P}{k_B T} \tag{18}$$

to obtain

$$\frac{P}{k_B T} = \frac{\partial \ln \Omega}{\partial V} = \sum_{n=0}^{N-1} \frac{1}{V - n v_0} \tag{19}$$

Now, since we are assuming that $N v_0 << V$ we are justified in Taylor expanding each term in the sum on the right hand side to obtain

$$\frac{P}{k_B T} \simeq \sum_{n=0}^{N-1} \left(\frac{1}{V} + n \frac{v_0}{V^2}\right) \tag{20}$$

Using the fact that

$$\sum_{n=1}^{N-1} n = \frac{N(N-1)}{2} \tag{21}$$

we then have

$$\frac{P}{k_B T} \simeq \frac{N}{V} + \frac{N(N-1)}{2} \frac{v_0}{V^2} \tag{22}$$

$$= \frac{N}{V}\left(1 + \frac{N-1}{2} \frac{v_0}{V}\right) \tag{23}$$

$$\simeq \frac{N}{V - (N-1) v_0 / 2} \tag{24}$$

$$\simeq \frac{N}{V - N v_0 / 2}. \tag{25}$$

Since v_0 is eight times the volume of each hard sphere, $N v_0/2$ is *four* times the total volume taking up by the N spheres forming the gas. Our equation of state is then

$$P(V - b) = N k_B T \tag{26}$$

where b is four times the volume taking up the particles.