

# J14 T.3

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See caltech 127 notes lecture 8 ([http://www.pmaweb.caltech.edu/mcc/Ph127/a/Lecture\\_8.pdf](http://www.pmaweb.caltech.edu/mcc/Ph127/a/Lecture_8.pdf)) for a good discussion of polymers.

## 1 A

The entropy is  $S(R, N) = k_B \ln(\Omega(R, N))$ . By the fundamental assumption of statistical mechanics, for an isolated system in equilibrium all accessible microstates are equally probable. Thus the number of states at a distance  $R$  is proportional to the probability at a distance  $R$ , so  $S = k_B \log(e^{-R^2/(2Nb^2)}) + \text{constant} = -k_B R^2/(2Nb^2) + \text{constant}$ .

## 2 B

There are two contributions to the free energy, one due to the free 'spring' energy stored due to the restoring force, and another due to the repulsive energy.

Spring energy:  $p = -T \frac{\partial S}{\partial V}$ , and multiplying each side by an area  $A$ , and using  $V = AL$ ,  $pA = F = -T \frac{\partial S}{\partial L}$  in general. Setting  $L = R$  gives  $F = Tk_B R/(Nb^2)$ . (Note: there should be a minus sign here, since the force is restoring. Cross has the same missing minus sign in his notes, I'm not sure what the issue is.) Thus the free 'spring' energy stored in a polymer of length  $R$  is the force times  $R/2$  (integrating  $FdR$ ), so  $F_s = Tk_B R^2/(2Nb^2)$ .

Repulsive energy: There is a clever solution Cross discusses. Suppose the repulsive energy is for any two units within a fixed distance  $d$  of each other, i.e. any two units within a volume  $d^3$ . The stored energy per polymer equals the number of polymers within a fixed distance  $d$  per polymer times the energy per polymer within a fixed distance  $d$ , which is  $\lambda \frac{N}{V} d^3$ . Note  $R^3 = V$ . Since there are  $N$  polymers, this stored energy is  $\frac{\lambda N^2 d^3}{R^3} = F_r$ .

$$\text{Free energy } F = F_s + F_r = \frac{\lambda N^2 d^3}{R^3} + Tk_B R^2/(2Nb^2)$$

### 2.1 Why no minus sign?

Curiously, I don't find a minus sign for the force. However, I know it has to be there - the polymer wants to be in the highest entropy state, which is where

$R = 0$  (meaning the separation of the ends of the polymer is zero), so it will feel an entropic force for it to get to this state. So what went wrong?

I see two fixes here. The first involves calculation of the free energy of an ideal polymer (ignoring the repulsive energy). Since there is no energy in the bonds,  $E = 0$ . So the free energy  $F$  (not to be confused with the force  $F$ ) equals just  $-TS$  which is  $\frac{k_B T R^2}{2N b^2}$  (plus a numerical constant). Using  $dF = -pdV - SdT$ , we have  $-\frac{\partial F}{\partial V} = p$ , which gives our original force (just with a minus sign, as desired).

The second fix involves deriving the formula for the force  $F$  from scratch, and using the first law of thermodynamics. From the first law of thermodynamics, we know that for a 1d system in equilibrium which can exchange energy and  $x$ -displacement with it's surroundings,  $dE = TdS - FdX$ , where  $F$  is defined as the outward force that the system exerts on it's surroundings. Also, from the chain rule we have  $dS = \frac{\partial S}{\partial E}dE + \frac{\partial S}{\partial X}dX = \frac{dE}{T} + \frac{\partial S}{\partial X}dX$ . Rearranging we get  $dE = TdS - T\frac{\partial S}{\partial X}dX$ . We see that this matches the first law of thermodynamics only if we define the force as  $F = T\frac{\partial S}{\partial X}$ . So my previous definition was off by a minus sign (as I suppose it had to have been). The key point is that my previous definition of  $p$  (with a minus sign) treats  $p$  as an inward force, not an outwards force.

### 3 C

Taking  $\frac{\partial F}{\partial R} = 0$ , we get  $R^5 \sim N^3$  or  $R \sim N^{0.6}$ . Note that this makes sense, since without the repulsive force we would have  $R \sim N^{0.5}$ , but here the radius grows faster due to the repulsive force.