Elasticity of a polymer chain

Consider the following one dimensional model of a "freely jointed" polymer chain. A chain is made of N linked segments, each of length l. In this one dimensional case, a chain is built by adding segments, each segment taking one of the two possible directions on the x axis ($\pm l$). Let R be the end to end distance (from the beginning of the first segment to the end of the last segment).

1. Justify that the number of configurations for any given R is

$$\Omega(R) = \frac{N!}{(\frac{N+n}{2})!(\frac{N-n}{2})!},$$

   with $R = nl$.

2. Obtain the entropy as a function of the end to end distance, $S = S(R)$, in the limit of a long chain ($N \gg 1$).

3. According to the Second Law of Thermodynamics. and given that the chain segments are non interacting, we have $TdS = fdR$, where f is the chain tension. Compute the tension f. Consider the limit of small extensions $R \ll nl$, and show that the chain obeys Hooke's Law. Obtain the spring constant, and discuss its dependence on the various parameters. Where is this force coming from ?

Ideal polymer chain. $d=1$

Barrat, p.25

Take $N = N_+ + N_-$ total steps. Let $n = N_+ - N_-$

so that the end to end distance is $R = n \cdot l$

for any configuration.

The number of configurations at R is: $\Omega(R) = \dfrac{N!}{N_+!\,N_-!}$ with $\begin{cases} n = N_+ - N_- \\ N = N_+ + N_- \end{cases}$

Try: $N_+ = \dfrac{N+n}{2}$ $\quad N_- = \dfrac{N-n}{2}$

$$N_+ + N_- = \frac{N+\cancel{n} + N-\cancel{n}}{2} = N \checkmark$$

$$N_+ - N_- = \frac{\cancel{N}+n - \cancel{N}+n}{2} = n \checkmark$$

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

If N is large:

$$\ln\left(\frac{N+n}{2}\right)! = \left(\frac{N+n}{2}\right)\ln\left(\frac{N+n}{2}\right) - \left(\frac{N+n}{2}\right)$$

$$\ln\left(\frac{N-n}{2}\right)! = \left(\frac{N-n}{2}\right)\ln\left(\frac{N-n}{2}\right) - \left(\frac{N-n}{2}\right)$$

$$\Rightarrow \ln\Omega(R) = N\ln N - \cancel{N} - \left(\frac{N+n}{2}\right)\ln\left(\frac{N+n}{2}\right) + \cancel{\left(\frac{N+n}{2}\right)}$$
$$- \left(\frac{N-n}{2}\right)\ln\left(\frac{N-n}{2}\right) + \cancel{\left(\frac{N-n}{2}\right)}$$

$$\ln\Omega(R) = N\ln N - \left(\frac{N+n}{2}\right)\ln\left(\frac{N}{2}\cdot\left(1+\frac{2n}{N}\right)\right)$$
$$- \left(\frac{N-n}{2}\right)\ln\left(\frac{N}{2}\left(1-\frac{2n}{N}\right)\right)$$

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

$\cancel{N\ln 2}$
$N\ln N - N\ln N + N\ln 2$

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

If $n/N \ll 1$

$$\ln\Omega(R) = N\ln 2 - \left(\frac{\cancel{N}+n}{2}\right)\frac{2n}{N} + \left(\frac{\cancel{N}-n}{2}\right)\left(\frac{2n}{N}\right)$$

$$= N\ln 2 - \frac{4n^2}{2N} \rightarrow \boxed{N\ln 2 - \frac{2n^2}{N} = \ln\Omega(R)}$$

Try computing force:

$$\frac{\partial\ln\Omega(R)}{\partial n} = -\frac{1}{2}\ln\left(1+\frac{2n}{N}\right) - \left(\frac{N+n}{2}\right)\frac{2/N}{1+2n/N}$$

$$+\frac{1}{2}\ln\left(1-\frac{2n}{N}\right) - \left(\frac{N-n}{2}\right)\frac{-2/N}{1-2n/N}$$

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

Simplify earlier:

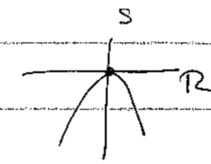
$$\ln\Omega(R) = N\ln N - \left(\frac{N+n}{2}\right)\ln\left(\frac{N+n}{2}\right) - \left(\frac{N-n}{2}\right)\ln\frac{N-n}{2}$$

$$\frac{\partial\ln\Omega}{\partial n} = -\frac{1}{2}\ln\frac{N+n}{2} - \left(\frac{N+n}{2}\right)\frac{1/2}{\left(\frac{N+n}{2}\right)} + \frac{1}{2}\ln\frac{N-n}{2}$$

$$- \left(\frac{N-n}{2}\right)\frac{(-1/2)}{\frac{N-n}{2}}$$

$$\frac{\partial \ln \Omega}{\partial n} = -\frac{1}{2}\ln\frac{N+n}{2} - \cancel{\frac{1}{2}} + \frac{1}{2}\ln\frac{N-n}{2} + \cancel{\frac{1}{2}}$$

$$= \frac{1}{2}\ln\frac{(N-n)/\cancel{2}}{(N+n)/\cancel{2}} = \frac{1}{2}\ln\frac{N-n}{N+n}$$



$$\frac{\partial \ln \Omega}{\partial n} = \frac{1}{2}\ln\left(\frac{1-n/N}{1+n/N}\right) = \frac{1}{2}\ln\frac{1-R/\ell N}{1+R/\ell N}$$

$$\frac{\partial \ln \Omega}{\partial R} = \frac{\partial \ln \Omega}{\partial n}\frac{\partial n}{\partial R} = \frac{\partial \ln \Omega}{\partial n}\frac{1}{\ell}$$

$$\Rightarrow \boxed{k_B\frac{\partial \ln \Omega}{\partial R} = \frac{k_B}{2\ell}\ln\frac{1-R/\ell N}{1+R/\ell N}} \quad (1.\overset{30}{\cancel{29}})$$

in Barrat except $\cancel{\partial}/\partial$ $(-T)$ favors S of F.

$$\left(F = E - TS \right)$$

Second Law: $TdS = dE + f \cdot dR$

We assume no interactions. Hence $f = T\dfrac{\partial S}{\partial R} = k_BT\dfrac{\partial \ln \Omega(R)}{\partial R}$

$$\Rightarrow \boxed{f = \frac{k_BT}{2\ell}\ln\frac{1-R/\ell N}{1+R/\ell N}}$$

Force "done" by the system. Barrat (1.30) is minus this force.

If $R \ll \ell N$ Then: $f = \dfrac{k_BT}{2\ell}\left(-\dfrac{R}{\ell N}\right) = -\dfrac{k_BT}{2N\ell^2}\cdot R$

It is a harmonic oscillator with constant $\boxed{\dfrac{k_BT}{2N\ell^2}}$ depends on temperature!