Solution 9

Confining a Polymer in a Space with Low Dimensionality[1]

1. Within the Flory theory, in the case of a self-avoiding walk we can factorize the end-to-end distribution as
$$p(\vec{R}) = p_{FJC}(\vec{R})s(\vec{R})\,, \tag{1}$$
where
$$p_{FJC}(\vec{R}) = \left(\frac{3}{2\pi N b^2}\right) e^{-\frac{3\vec{R}^2}{2Nb^2}} \tag{2}$$
is the end-to-end vector distribution of the corresponding Freely Jointed Chain, and $s(\vec{R})$ is the so-called *survival probability*, i.e. the probability that the configuration considered is accepted (which in the Flory framework depends only on the end-to-end vector rather than to the whole set of bond vectors). Now, assuming the monomers to have spherical shape, the excluded volume is roughly b^3. Given a certain couple of monomers, within the Flory framework the probability of one being within the excluded volume of the other is roughly b^3/R^3. Since the number of couples to consider is order of N^2, we can conclude that the *rejecting probability* is roughly $N^2 b^3/R^3$. We thus obtain for the survival probability
$$s(\vec{R}) \sim 1 - N^2\frac{b^3}{R^3} = e^{\log\left(1-N^2\frac{b^3}{R^3}\right)} \simeq e^{-N^2\frac{b^3}{R^3}} \tag{3}$$
where we made use of the approximation $\log(1+x) \simeq x$, valid for small x[2]. We therefore conclude that
$$p(R) \propto e^{-\frac{3R^2}{2Nb^2} - N^2\frac{b^3}{R^3}} \tag{4}$$
Assuming the main contribution to the partition function (and thus to the free-energy) to come from the maximum value of the probability (which will then correspond to the average end-to-end distance), by minimizing the exponent we find for the average end-to-end distance the Flory result $R \sim bN^{3/5}$.

2. By following the same reasonment as before, in the two-dimensional case we have that for each couple the probability of one monomer to be within the excluded volume of the other one is roughly $b^3/(R^2 b) = b^2/R^2$. By following the same steps as before, we obtain that the quantity to maximize (apart from numerical coefficients) is
$$\frac{R^2}{Nb^2} + N^2\frac{b^2}{R^2} \tag{5}$$
By minimizing it, we easily obtain $R \sim bN^{3/4}$. Naturally, the N-dependence is stronger than before, since the confinement of the polymer gives a major role to the repulsion between monomers, with a consequent stretching of the chain.

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[1] M. Rubinstein and R. H. Colby, *Polymer Physics*, Oxford University Press.

[2] Since we are neglecting three-body interactions, we are implicitly assuming to be in a dilute enough solution, where it can be shown that $N^2\frac{b^3}{R^3} \ll 1$.

3. In the case of a one-dimensional chain, one trivially has that $R = Nb$, since the polymer has not space to go back and forth without self-overlapping. It is interesting to notice that even in this case Flory theory gives the correct result, since by repeating the same reasonment as before one has that the probability of one monomer to be within the excluded volume of the other one is roughly $b^3/(Rb^2) = b/R$, to which corresponds the following quantity to maximize:

   $$\frac{R^2}{Nb^2} + N^2 \frac{b}{R} \tag{6}$$

   which gives $R \sim bN$, as expected.

Confining a Polymer on a Space with Low Dimensionality (Scaling Approach)[3]

1. Let us start by considering the ideal chain case. Since we can assume that up to length scale h the statistics of the polymer is totally unaffected by the presence of the layers, we can imagine the chain as made of "blobs" of size h. If g is the number of monomers within each blob, we thus have $h \sim bg^{1/2} \Rightarrow g \sim (h/b)^2$. Therefore, the number of blobs n is given by $n = N/g \sim N(b/h)^2$. Now, at the blob level we have a two-dimensional ideal chain of blobs, so that its end-to-end distance follows random walk statistics. We thus have (the "renormalized" bond length is given by the size of a blob)

   $$R' \sim n^{\frac{1}{2}} h \sim N^{\frac{1}{2}} \frac{b}{h} h = N^{\frac{1}{2}} b \tag{7}$$

   which has the same N-dependence as in the case of the unperturbed chain.

   In the case of a self-avoiding chain we can proceed in the same way, but the situation is a bit more complicated. In this case the size of a blob is given by $h \sim bg^{3/5}$, so that the number of monomers within a single blob is $g \sim (h/b)^{5/3}$ and the number of blobs is $n = N/g \sim N(b/h)^{5/3}$. As in the previous case, we now can consider the polymer as a two-dimensional self-avoiding chain of blobs. However, differently from the ideal case, for a self-avoiding walk the exponent changes with the dimension of the embedding space. In particular, for a 2-dimensional self-avoiding chain the exponent is given by 3/4. We thus have

   $$R' \sim n^{\frac{3}{4}} h \sim N^{\frac{3}{4}} \left(\frac{b}{h}\right)^{\frac{5}{4}} h = N^{\frac{3}{4}} b \left(\frac{b}{h}\right)^{\frac{1}{4}} \tag{8}$$

   which is larger (look at the dependence on N) with respect to the 3-dimensional case. This is expected, since by confining a self-avoiding polymer we expect the hard-core repulsion to play a stronger role than in the 3-D case, so that the chain results more stretched.

2. In the case of an ideal chain, proceeding as before we find that at the blob level we have a one-dimensional chain made of $n = N/g \sim N(b/h)^2$ blobs of size h. Such blobs will still be governed by a random-walk, so that we find again the same result as before.

   In the case of a self-avoiding polymer, we end up with a one-dimensional self-avoiding chain made of $n = N/g \sim N(b/h)^{5/3}$ blobs of size h. Since the blobs cannot interpenetrate, they can only be put in a row, so that we have

   $$R' \sim nh \sim N \left(\frac{b}{h}\right)^{\frac{5}{3}} h = Nb \left(\frac{b}{h}\right)^{\frac{2}{3}} \tag{9}$$

   As expected, in this case the N-dependence is even stronger than in the previous one.

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[3] M. Rubinstein and R. H. Colby, *Polymer Physics*, Oxford University Press.

Scaling Theory of a Chain under Tension

The work made by the force f to stretch the polymer up to a distance λ is simply given by $f\lambda$. At length scales lower than ξ, we expect the thermal energy to be much larger than the stretching one, i.e. $f\lambda \ll k_BT$, while at larger scales we expect $f\lambda \gg k_BT$. By definition, ξ is such that $f\xi \sim k_BT \Rightarrow \xi \sim k_BT/f$.

1. In the case of an ideal chain, by assuming the chain statistics to be unperturbed up to length scale ξ, we have $\xi \sim bg^{1/2} \Rightarrow g \sim (\xi/b)^2$. On the other hand, at larger length scales we expect the chain to be almost perfectly stretched, i.e. $R \sim n\xi$. Now, the number of blobs is simply given by $n = N/g \sim N(b/\xi)^2$, so that by substituting the scaling formula for ξ we finally find

   $$R \sim N \left(\frac{b}{\xi}\right)^2 \xi = N\frac{b^2}{\xi} \sim Nb^2 \frac{f_{\frac{1}{2}}}{k_BT} \tag{10}$$

   i.e.

   $$f_{\frac{1}{2}} \sim k_BTR\frac{1}{Nb^2} = k_BTR\frac{1}{(bN^{\frac{1}{2}})^2} = \frac{k_BT}{bN^{\frac{1}{2}}}\frac{R}{bN^{\frac{1}{2}}} \tag{11}$$

   which is the formula reported in the text.

2. In the case of a self-avoiding chain, we have to repeat the same argument as in the previous point, with the only difference that this time $\xi \sim bg^{3/5} \Rightarrow g \sim (\xi/b)^{5/3}$. It is then straightforward to show that in this case

   $$R \sim N \left(\frac{b}{\xi}\right)^{\frac{5}{3}} \xi = Nb^{\frac{5}{3}}\xi^{-\frac{2}{3}} \sim Nb^{\frac{5}{3}} \left(\frac{f_{\frac{3}{5}}}{k_BT}\right)^{\frac{2}{3}} \tag{12}$$

   so that

   $$f_{\frac{3}{5}} \sim k_BT \left(\frac{R}{Nb^{\frac{5}{3}}}\right)^{\frac{3}{2}} = k_BT \left(\frac{R}{(bN^{\frac{3}{5}})^{\frac{5}{3}}}\right)^{\frac{3}{2}} = \frac{k_BT}{bN^{\frac{3}{5}}} \left(\frac{R}{bN^{\frac{3}{5}}}\right)^{\frac{3}{2}} \tag{13}$$

   The slope 3/2 of this power-law is steeper than the linear relationship found for an ideal chain. This means that the *increase* of the force needed to mantain a certain end-to-end distance is faster for a self-avoiding chain. However, this does not mean that the force *per se* is larger. Indeed, if one computes the ratio of the forces with the same value of R, one easily finds that

   $$\frac{f_{\frac{3}{5}}}{f_{\frac{1}{2}}} \sim \left(\frac{R}{Nb}\right)^{\frac{1}{2}} < 1 \tag{14}$$

   Now, the previous calculation lacks of prefactors, but perfectly fits into the intuitively picture according to which it is easier to stretch a self-avoiding chain, since the hard-core repulsion "helps" us in pulling away the ends. Naturally, one expects that for larger values of R the repulsion has a less and less important role (since the monomers start not "seeing" each other), so that the two forces are expected to go to the same limiting value for $R \to Nb$[4].

3. In the case of general ν, we just have to repeat the calculation with $\xi \sim bg^\nu \Rightarrow g \sim (\xi/b)^{1/\nu}$. In this case

   $$R \sim Nb^{\frac{1}{\nu}} \left(\frac{f_\nu}{k_BT}\right)^{\frac{1-\nu}{\nu}} \tag{15}$$

   from which it is easily shown that

   $$f_\nu \sim \frac{k_BT}{bN^\nu} \left(\frac{R}{bN^\nu}\right)^{\frac{\nu}{1-\nu}} \tag{16}$$

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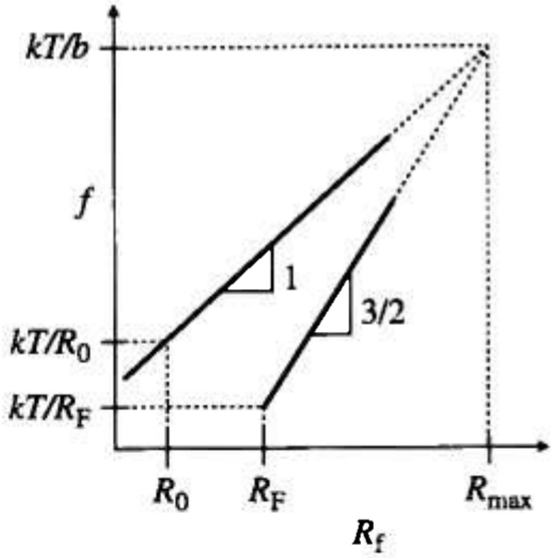
[4] Anyway, it is important to note at this point that the scaling theory completely fails at the high stretching regime, where the force actually diverges in the limit $R \to Nb$. Nonetheless, a comparison with more precise computations shows that in the limit of low forces the scaling theory gives the correct results.



In the figure the two formulas in eqns (11) and (13) are reported in log-log scale.

Now, as for the free-energy, by making use of the thermodynamic relation

$$f_\nu = \frac{\partial F_\nu}{\partial R} \tag{17}$$

we easily find

$$F_\nu \sim k_B T \left(\frac{R}{bN^\nu} \right)^{\frac{1}{1-\nu}} \tag{18}$$