Solution 11

Scaling Theory of Excluded Volume Effects[1]

1. The basic idea is to compare the total excluded volume energy with the thermal one. If the size of a blob is ξ and the number of monomers it contains is n, we have:

   $$k_B T |v| \frac{n^2}{\xi^3} \sim k_B T \tag{1}$$

   At very small length scales, the monomers do not "see" each other, so that we expect ideal chain statistics to hold. Going to larger and larger length sizes, the left hand side of the previous formula gives a measure of the cumulated interaction energy due to excluded volume effects. Since ideal chain statistics holds, for a given length scale λ, the number g of monomers contained inside a blob of such size is given by $g \sim (\lambda/b)^2$. Thus, the interaction energy is given by

   $$k_B T |v| \frac{g^2}{\lambda^3} \sim k_B T |v| \frac{\lambda}{b^4} \tag{2}$$

   Thus, from the previous equation it is evident that the total excluded volume interaction energy increases with the length scale considered. The *thermal blob* will correspond to the size ξ such that eqn (1) holds. By assuming that this is the largest scale at which ideal chain statistics hold, we easily find that

   $$\xi \sim \frac{b^4}{|v|} \qquad n \sim \frac{b^6}{v^2} \tag{3}$$

   For larger length scales, we expect the blobs to follow the statistics dictated by the solvent. In the case of a good solvent, we thus expect $R \sim (N/n)^{3/5}\xi$, so that we find

   $$R \sim \left(\frac{N}{n}\right)^{\frac{3}{5}} \xi \sim \left(\frac{N}{\frac{b^6}{v^2}}\right)^{\frac{3}{5}} \frac{b^4}{v} = \frac{v^{\frac{6}{5}}}{b^{\frac{18}{5}}} \frac{b^4}{v} N^{\frac{3}{5}} = v^{\frac{1}{5}} b^{\frac{2}{5}} N^{\frac{3}{5}} \tag{4}$$

   which is exactly the formula (1) given in the text. Notice that in the case of an athermal solvent, $v \sim b^3$ and the previous formula gives $R \sim bN^{\frac{3}{5}}$.

   In the case of a poor solvent, we expect the blobs to collaps onto a globule. Since each blob has volume $\sim \xi^3$, the radius of the globule will be such that $R^3 \sim (N/n)\xi^3$, so that

   $$R \sim \xi \left(\frac{N}{n}\right)^{\frac{1}{3}} \sim \frac{b^4}{|v|} \left(\frac{N}{\frac{b^6}{v^2}}\right)^{\frac{1}{3}} = \frac{b^4}{|v|} \frac{|v|^{\frac{2}{3}}}{b^2} N^{\frac{1}{3}} = \frac{b^2}{|v|^{\frac{1}{3}}} N^{\frac{1}{3}} \tag{5}$$

   as in eqn (2) in the text. For a non-solvent, $v \sim -b^3$ and we are left with $R \sim bN^{\frac{1}{3}}$.

   It is interesting to note that for a θ-solvent ($v = 0$) the blob size diverges, i.e. the scaling theory predict that ideal chain statistics hold at all scales.

   The graph reports in log-log scale the expected behavior of the chain end-to-end distance according to the length scale we are looking at (given in abscissa by the number of monomers

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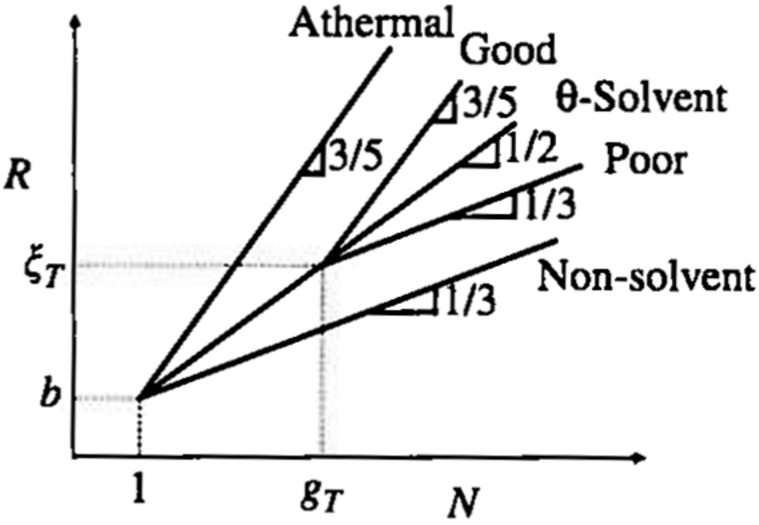
[1] M. Rubinstein and R. H. Colby, *Polymer Physics*, Oxford University Press.



of the portion of chain we are considering - note that the size of and number of monomers within a blob are indicated respectively as ξ_T and g_T). We note the transition corresponding to the size of a blob[2]. Note how the extreme cases of athermal and non- solvent do not show any transition, since in such cases the size of a blob reduces to that of a monomer (i.e. the "transition" is at the beginning of the line drawn). On the other hand, even the θ-solvent case does not show any transition, since in this case the size of a blob diverges, i.e. the transition would take place at infinite abscissa. Finally, for the good and poor solvents we observe an initial superposition to the line corresponding to the θ-solvent, followed by a region of different slope after the blob size has been reached.

2. First of all, we notice immediately that $v > 0$, as it has to be in the case of a good solvent. By blindly applying an hard-spheres-like picture, we would conclude that a DNA molecule in the solvent considered follows the statistics of a self-avoiding walk, i.e. $R \propto N^{3/5}$. However, this is not the case for the molecules under consideration. Indeed, substituting the numerical data in eqn (3), we immediately find that the size of a blob is order of 10 μm, which is larger than the contour length of the molecule itself. Thus, we conclude that ideal chain statistics is expected to hold in this case.

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[2] In real polymers the transition is actually smooth.