Introduction to Biopolymer Physics

Problem 2.2

Question

The size of a polymer chain R scales with the number of links N with the step length l according to a power law $R \sim N^\nu l$. Derive the value of the exponent ν for

a) A chain under theta conditions.

b) A swollen chain in a good solvent.

c) A compact, closely packed globule.

Solution

a) Under theta conditions the polymer chain can be modeled as an ideal chain, as attractive and repulsive forces between the monomers are balanced. The mean square end-to-end distance $\langle h^2 \rangle$ of an ideal chain is given by

$$\langle h^2 \rangle = N l^2. \tag{1}$$

The typical radius R of the ideal chain is on the same order of magnitude as the square root of the mean square end-to-end distance

$$R \simeq \sqrt{\langle h^2 \rangle} = N^{1/2} l. \tag{2}$$

In comparison with the power law $R \sim N^\nu l$ we get the exponent $\nu = 1/2$ for a chain under theta conditions.

b) In case of a swollen chain, we have to consider excluded volume effects, i.e. the repulsive interaction between two segments are close together spatially, but separated over a large distance along the contour. From eq. (2.41) we get the free energy $F_{rep,coil}$ of these repulsions

$$F_{rep,coil} \simeq kT \frac{BN^2}{R^3}, \tag{3}$$

here B is an excluded volume parameter, depending on thermodynamic properties and with the dimension of a volume. Increasing the polymer radius R decreases the repulsive interaction.

The swelling of the chain by the repulsive interactions is counterbalanced by the elastic force due to restriction in configurational degrees of freedom of the monomers with increasing radius. For the elastic free energy, we can take the ideal chain result from eq. (2.12)

$$F_{elas} \simeq kT \frac{R^2}{Nl^2}. \tag{4}$$

The equilibrium radius R of the polymer chain can be derived from minimization of the total free energy

$$\frac{\partial}{\partial R}\left(F_{rep,coil} + F_{elas}\right) = \frac{\partial}{\partial R}\left(\frac{BN^2}{R^3} + \frac{R^2}{Nl^2}\right) = 0. \tag{5}$$

The last equation leads to

$$R^5 \simeq BN^3 l^2, \tag{6}$$

which can be written as

$$R \simeq \left(B/l^3\right)^{1/5} N^{3/5} l. \tag{7}$$

As demanded the coefficient is dimensionless. So we get the exponent $\nu = 3/5$ for a swollen chain in a good solvent.

c) For a closely packed polymer the volume V is proportional to the number of links N

$$V \sim N. \tag{8}$$

In three dimensions the radius depends on the volume like

$$R \sim V^{1/3}. \tag{9}$$

Combining both relations leads to

$$R \sim N^{1/3}. \tag{10}$$

We get the exponent $\nu = 1/3$ for a closely packed polymer.