Stationary forms of polymer chains

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It is shown that in order to minimize its free energy long chain polymers can assume a helical form with a definite functional relationship between pitch and radius. Although entropic disorder will render its lifetime short and coherence length limited, in processes involving short times and/or distances this helical tendency could very well play a role.

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The shapes of long chain molecules at zero absolute temperature are governed largely by conformational requirements. At finite temperatures, we assume that the probability distribution (note that we concentrate on only one chain) takes the Rouse–Edwards form[1] and is composed of two parts, i.e. the entropy term and an effective interaction $V[\vec{r}(s) - \vec{r}(s')]$ among the monomers where s is the arc length parameter of the chain. The interaction V is an effective one because the solvent–monomer and solvent–solvent interactions have been taken into account in determining it. The probability that the chain assumes some spatial form $\vec{r} = \vec{r}(s)$ is therefore

$$P([\vec{r}]) \simeq \mathrm{e}[-\alpha \int \mathrm{d}s \left(\frac{\mathrm{d}\vec{r}}{\mathrm{d}s}\right)^2 - \beta \int \mathrm{d}s \int \mathrm{d}s' V[\vec{r}(s) - \vec{r}(s')]$$

where $\beta = 1/k_\mathrm{B}T$, k_B is Boltzmann's constant, T is temperature and V is assumed to be repulsive from now on. The first term in the exponent comes from the entropy due to the wriggling of the chain and α is a constant inversely proportional to the squared length of the Kuhn statistical segment (see page 11 in ref. 1) which is long enough so that the local detailed chemical structures do not matter. The shape $\vec{r}(s)$ satisfies

$$\frac{\mathrm{d}^2\vec{r}}{\mathrm{d}s^2} = \frac{\beta}{2\alpha} \int \mathrm{d}s' \nabla_{\vec{r}(s)} V[\vec{r}(s) - \vec{r}(s')] = \frac{\beta}{2\alpha} \int \mathrm{d}s' \frac{\vec{\Delta}(\vec{r}, \vec{r}')V'(|\Delta|)}{|\Delta(\vec{r}, \vec{r}')|} \tag{1}$$

where $\Delta(\vec{r}, \vec{r}')$ denotes $\vec{r}(s) - \vec{r}(s')$ and V is supposed to depend only on the absolute value of its argument. Assuming the chain to be infinite, it is immediately seen that a straight line $\vec{r} = \vec{g}s$ is always a solution, where $\vec{g}$ is a unit vector. A more general class of solution consists of helices. Choosing the axis of the helix as the z axis gives the following parametric form for a helix of pitch κ and radius r_0:

$$z = \kappa s \qquad x + iy = r_0 \, \mathrm{e}^{is}$$

where $\vec{r} = (x, y, z)$. On substitution into equation (1), it is seen that this shape is a solution, provided the equation

$$1 = -\frac{\beta}{\alpha} \int_{-\infty}^{\infty} \mathrm{d}\varepsilon \frac{V'\left[\sqrt{\kappa^2\varepsilon^2 + 4r_0^2 \sin^2\left(\frac{\varepsilon}{2}\right)}\right] \sin^2\left(\frac{\varepsilon}{2}\right)}{\sqrt{\kappa^2\varepsilon^2 + 4r_0^2 \sin^2\left(\frac{\varepsilon}{2}\right)}} \tag{2}$$

gives a real relation between κ and r_0. For example, for a repulsive potential of range much shorter than the pitch of the spiral, one may replace the sine function by its argument, and the equation is then

$$1 = -\frac{\beta}{2\alpha} \int_0^{\infty} \mathrm{d}\varepsilon \frac{\varepsilon V'(p\varepsilon)}{p} \tag{3}$$

where $p = \sqrt{\kappa^2 + r_0^2}$. For example, for an exponential potential $V(r) = V_0 \, \mathrm{e}^{-\lambda r}$ this gives $p^3 = \beta V_0 / 2\alpha\lambda$, or

$$\kappa^2 + r_0^2 = \left(\frac{2\lambda\beta V_0}{\alpha}\right)^{2/3} \tag{4}$$

Note that actual forms of the potential do not matter because if we redefine the dummy variable in equation (3) the integration becomes unitless and is just a constant.

Note that as the temperature goes to zero, κ and/or r_0 become large; presumably due to the repulsive force the model suggests that this chain tries to straighten out. At very high temperatures the repulsion is largely overcome, and both the radius and the pitch must be small, i.e. both curvature and torsion become large, as expected. Note also that no spiral solutions exist if V is purely attractive and is monotonically decreasing with distance. In a mixed case, such as short range repulsion and long range attraction, the issue cannot be decided without detailed calculation.

To see if these stationary states are in fact minima in the energy, we first determine which of the spirals gives minimum energy. For short-range potentials, equation (3) indicates that $\kappa^2 + r_0^2$ will be a constant. Therefore the entropic contribution to the exponent of the distribution function will not depend on the apportionment between r_0 and κ. The potential energy likewise depends only on that sum of squares if the potential is short-range. This

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means that the stationary state is very flat, with very little to choose between different helices of constant p given by equation (3). This argument fails for very low pitch helices because it depends on the force range being much smaller than the pitch.

Next, we write the equation determining the stability of the helix against arbitrary displacements. Writing $\vec{r} + \vec{\rho}$ for $\vec{r}$ and $\vec{\rho}$ small, we get the following linearized equation for ρ:

$$\vec{\rho}'' = A\left\{\frac{\int \mathrm{d}s'[\vec{\rho}(s) - \vec{\rho}(s')]V'(\Delta)}{\Delta} - \int \mathrm{d}s' \frac{\{[\vec{\rho}(s) - \vec{\rho}(s')]\cdot\vec{\Delta}\}(V' - V''\Delta)\vec{\Delta}}{\Delta^3}\right\} \tag{5}$$

where, as before, $\vec{\Delta} = \vec{r}(s) - \vec{r}(s')$ and Δ is the absolute value. The $\vec{r}$s are now the unperturbed coordinates of the helix. Finally, $A = \beta/2\alpha$, and the integrals extend from $-\infty$ to $+\infty$. Writing $\rho = \mathrm{e}^{ivs} \sum_n \rho_n \mathrm{e}^{ins}$, two equations for longitudinal and transverse components by equating equal powers of e^{is} can be obtained and used to determine v.

Because we are dealing with a one-dimensional object in this model, this does not mean that helical shapes have any kind of permanence. Also, the usual entropic considerations concerning one-dimensional disorder presumably mean that they have only finite lifetime and very limited coherence length. Nevertheless it is of interest to determine if there would be observable effects in processes involving short times and/or distances.

Reference

1 Doi, M. and Edwards, S. F. 'Theory of Polymer Dynamics', Oxford University Press, Oxford, 1986, sect. 4.1