

6.6: Polymers

Basic concepts

Linear chain polymers are repeating structures with the chemical formula $(A)_x$, where A is the *formula unit* and x is the *degree of polymerization*. In many cases (polystyrene), $x \approx 10^5$ is not uncommon. For a very readable introduction to the subject, see P. G. de Gennes, *Scaling Concepts in Polymer Physics*.

Quite often a given polymer solution will contain a distribution of x values; this is known as *polydispersity*. Various preparation techniques, such as chromatography, can mitigate the degree of polydispersity. Another morphological feature of polymers is *branching*, in which the polymers do not form linear chains.

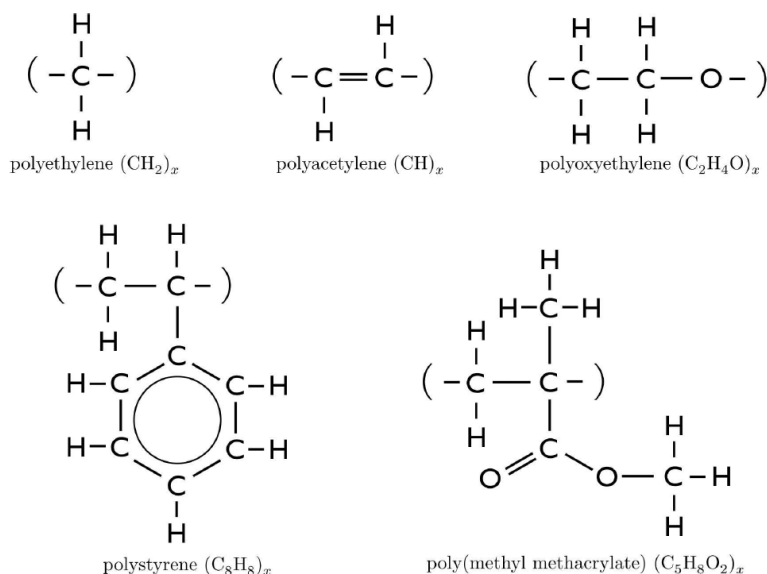


Figure 6.6.1: Some examples of linear chain polymers.

Polymers exhibit a *static flexibility* which can be understood as follows. Consider a long chain hydrocarbon with a $-C-C-C-$ backbone. The angle between successive $C-C$ bonds is fixed at $\theta \approx 68^\circ$, but the azimuthal angle φ can take one of three possible low-energy values, as shown in the right panel of Figure 6.6.2. Thus, the relative probabilities of *gauche* and *trans* orientations are

[Math Processing Error]

where $\Delta\varepsilon$ is the energy difference between *trans* and *gauche* configurations. This means that the polymer chain is in fact a *random coil* with a *persistence length*

[Math Processing Error]

where ℓ_0 is a microscopic length scale, roughly given by the length of a formula unit, which is approximately a few Ångstroms (see Figure 6.6.2). Let L be the total length of the polymer when it is stretched into a straight line. If $\ell_p > L$, the polymer is *rigid*. If $\ell_p \ll L$, the polymer is rigid on the length scale ℓ_p but flexible on longer scales. We have

$$\frac{\ell_p}{L} = \frac{1}{N} e^{\Delta\varepsilon/k_B T} \quad , \quad (6.6.3)$$

where we now use N (rather than x) for the degree of polymerization.

In the time domain, the polymer exhibits a *dynamical flexibility* on scales longer than a *persistence time*. The persistence time τ_p is the time required for a *trans-gauche* transition. The rate for such transitions is set by the energy barrier B separating *trans* from *gauche* configurations:

$$\tau_p = \tau_0 e^{B/k_B T} \quad (6.6.4)$$

where $\tau_0 \sim 10^{-11} \text{ s}$. On frequency scales $\omega \ll \tau_p^{-1}$ the polymer is dynamically flexible. If $\Delta\varepsilon \sim k_B T \ll B$ the polymer is flexible from a static point of view, but dynamically rigid. That is, there are many *gauche* orientations of successive carbon bonds which reflect a quenched disorder. The polymer then forms a frozen random coil, like a twisted coat hanger.

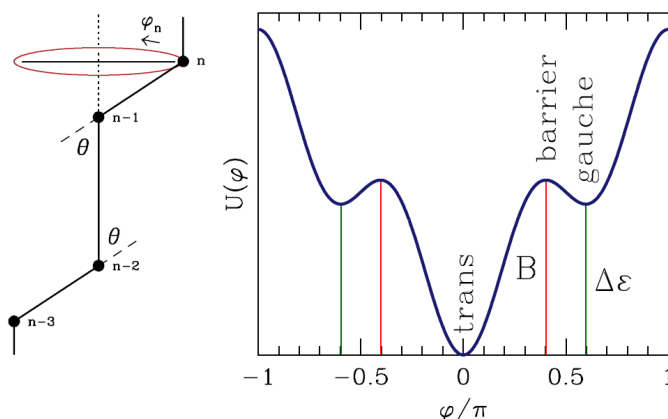


Figure 6.6.2: Left: *trans* and *gauche* orientations in carbon chains. Right: energy as a function of azimuthal angle φ . There are three low energy states: *trans* ($\varphi = 0$) and *gauche* ($\varphi = \pm\varphi_0$).

Polymers as random walks

A polymer can be modeled by a *self-avoiding random walk* (SAW). That is, on scales longer than ℓ_p , it twists about randomly in space subject to the constraint that it doesn't overlap itself. Before we consider the mathematics of SAWs, let's first recall some aspects of ordinary random walks which are not self-avoiding.

We'll simplify matters further by considering random walks on a hypercubic lattice of dimension d . Such a lattice has coordination number $2d$, there are $2d$ nearest neighbor separation vectors, given by $\delta = \pm a \hat{\mathbf{e}}_1, \pm a \hat{\mathbf{e}}_2, \dots, \pm a \hat{\mathbf{e}}_d$, where a is the lattice spacing. Consider now a random walk of N steps starting at the origin. After N steps the position is

$$\mathbf{R}_N = \sum_{j=1}^N \delta_j \quad (6.6.5)$$

where δ_j takes on one of $2d$ possible values. Now N is no longer the degree of polymerization, but something approximating L/ℓ_p , which is the number of persistence lengths in the chain. We assume each step is independent, hence $\langle \delta_j^\alpha \delta_j^\beta \rangle = (a^2/d) \delta_{jj'} \delta^{\alpha\beta}$ and $\langle \mathbf{R}_N^2 \rangle = Na^2$. The full distribution $P_N(\mathbf{R})$ is given by

$$\begin{aligned} P_N(\mathbf{R}) &= (2d)^{-N} \sum_{\delta_1} \dots \sum_{\delta_N} \delta_{\mathbf{R}, \sum_j \delta_j} \\ &= a^d \int \frac{dk_1}{2\pi} \dots \int \frac{dk_d}{2\pi} e^{-i\mathbf{k} \cdot \mathbf{R}} \left[\frac{1}{d} \sum_{\mu=1}^d \cos(k_\mu a) \right]^N \\ &= a^d \int \frac{d^d k}{(2\pi)^d} e^{-i\mathbf{k} \cdot \mathbf{R}} \exp \left[N \ln \left(1 - \frac{1}{2d} \mathbf{k}^2 a^2 + \dots \right) \right] \\ &\approx \left(\frac{a}{2d} \right)^d \int d^d k e^{-N \mathbf{k}^2 a^2 / 2d} e^{-i\mathbf{k} \cdot \mathbf{R}} = \left(\frac{d}{2\pi N} \right)^{d/2} e^{-d \mathbf{R}^2 / 2Na^2} \end{aligned}$$

This is a simple Gaussian, with width $\langle \mathbf{R}^2 \rangle = d \cdot (Na^2/d) = Na^2$, as we have already computed. The quantity \mathbf{R} defined here is the *end-to-end vector* of the chain. The RMS end-to-end distance is then $\langle \mathbf{R}^2 \rangle^{1/2} = \sqrt{Na} \equiv R_0$.

A related figure of merit is the *radius of gyration*, R_g , defined by

$$R_g^2 = \frac{1}{N} \left\langle \sum_{n=1}^N (\mathbf{R}_n - \mathbf{R}_{CM})^2 \right\rangle \quad (6.6.6)$$

where $R_{CM} = \frac{1}{N} \sum_{j=1}^N \mathbf{R}_j$ is the center of mass position. A brief calculation yields

$$R_g^2 = (N + 3 - 4N^{-1}) a^2 \sim \frac{Na^2}{6} , \quad (6.6.7)$$

in all dimensions.

The total number of random walk configurations with end-to-end vector \mathbf{R} is then $(2d)^N P_N(\mathbf{R})$, so the entropy of a chain at fixed elongation is

$$S(\mathbf{R}, N) = k_B \ln \left[(2d)^N P_N(\mathbf{R}) \right] = S(0, N) - \frac{dk_B \mathbf{R}^2}{2Na^2} . \quad (6.6.8)$$

If we assume that the energy of the chain is conformation independent, then $E = E_0(N)$ and

$$F(\mathbf{R}, N) = F(0, N) + \frac{dk_B T \mathbf{R}^2}{2Na^2} . \quad (6.6.9)$$

In the presence of an external force \mathbf{F}_{ext} , the Gibbs free energy is the Legendre transform

$$G(\mathbf{F}_{ext}, N) = F(\mathbf{R}, N) - \mathbf{F}_{ext} \cdot \mathbf{R} , \quad (6.6.10)$$

and $\partial G / \partial \mathbf{R} = 0$ then gives the relation

$$\langle \mathbf{R}(\mathbf{F}_{ext}, N) \rangle = \frac{Na^2}{dk_B T} \mathbf{F}_{ext} . \quad (6.6.11)$$

This may be considered an equation of state for the polymer.

Following de Gennes, consider a chain with charges $\pm e$ at each end, placed in an external electric field of magnitude $E = 30,000 \text{ V/cm}$. Let $N = 10^4$, $a = 2 \text{ \AA}$, and $d = 3$. What is the elongation? From the above formula, we have

$$\frac{R}{R_0} = \frac{eER_0}{3k_B T} = 0.8 , \quad (6.6.12)$$

with $R_0 = \sqrt{Na} a$ as before.

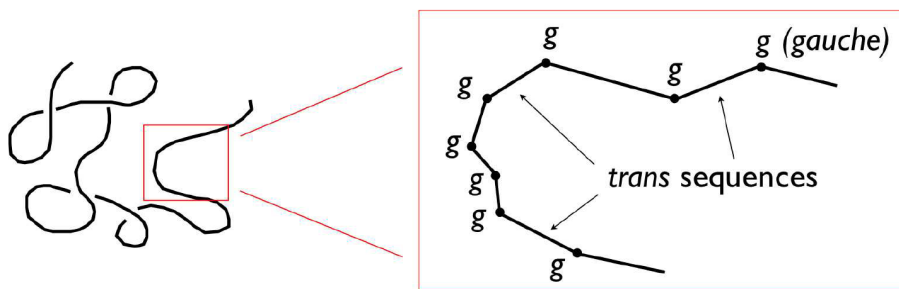


Figure 6.6.3: The polymer chain as a random coil.

Structure factor

We can also compute the structure factor,

$$\begin{aligned} S(\mathbf{k}) &= \frac{1}{N} \left\langle \sum_{m=1}^N \sum_{n=1}^N e^{i\mathbf{k} \cdot (\mathbf{R}_m - \mathbf{R}_n)} \right\rangle \\ &= 1 + \frac{2}{N} \sum_{m=1}^N \sum_{n=1}^{m-1} \left\langle e^{i\mathbf{k} \cdot (\mathbf{R}_m - \mathbf{R}_n)} \right\rangle \end{aligned}$$

For averages with respect to a Gaussian distribution,

$$\langle e^{i\mathbf{k} \cdot (\mathbf{R}_m - \mathbf{R}_n)} \rangle = \exp \left\{ -\frac{1}{2} \left\langle (\mathbf{k} \cdot (\mathbf{R}_m - \mathbf{R}_n))^2 \right\rangle \right\} . \quad (6.6.13)$$

Now for $m > n$ we have $\mathbf{R}_m - \mathbf{R}_n = \sum_{j=n+1}^m \delta_j$, and therefore

$$\langle (\mathbf{k} \cdot (\mathbf{R}_m - \mathbf{R}_n))^2 \rangle = \sum_{j=n+1}^m \langle (\mathbf{k} \cdot \delta_j)^2 \rangle = \frac{1}{d} (m - n) \mathbf{k}^2 a^2, \quad (6.6.14)$$

since $\langle \delta_j^\alpha \delta_{j'}^\beta \rangle = (a^2/d) \delta_{jj'} \delta^{\alpha\beta}$. We then have

$$\begin{aligned} S(\mathbf{k}) &= 1 + \frac{2}{N} \sum_{m=1}^N \sum_{n=1}^{m-1} e^{-(m-n) \mathbf{k}^2 a^2 / 2d} \\ &= \frac{N (e^{2\mu_k} - 1) - 2 e^{\mu_k} (1 - e^{-N\mu_k})}{N (e^{\mu_k} - 1)^2}, \end{aligned} \quad (6.6.15)$$

where $\mu_k = \mathbf{k}^2 a^2 / 2d$. In the limit where $N \rightarrow \infty$ and $a \rightarrow 0$ with $Na^2 = R_0^2$ constant, the structure factor has a *scaling form*, $S(\mathbf{k}) = N f(N\mu_k) = (R_0/a) f(k^2 R_0^2 / 2d)$, where

$$f(x) = \frac{2}{x^2} (e^{-x} - 1 + x) = 1 - \frac{x}{3} + \frac{x^2}{12} + \dots \quad (6.6.16)$$

Rouse model

Consider next a polymer chain subjected to stochastic forcing. We model the chain as a collection of mass points connected by springs, with a potential energy $U = \frac{1}{2} k \sum_n (\mathbf{x}_{n+1} - \mathbf{x}_n)^2$. This reproduces the distribution of Equation ??? if we take the spring constant to be $k = 3k_B T / a^2$ and set the equilibrium length of each spring to zero. The equations of motion are then

$$M \ddot{\mathbf{x}}_n + \gamma \dot{\mathbf{x}}_n = -k (2\mathbf{x}_n - \mathbf{x}_{n-1} - \mathbf{x}_{n+1}) + \mathbf{f}_n(t), \quad (6.6.17)$$

where $n \in \{1, \dots, N\}$ and $\{\mathbf{f}_n^\mu(t)\}$ a set of Gaussian white noise forcings, each with zero mean, and

$$\langle \mathbf{f}_n^\mu(t) \mathbf{f}_{n'}^\nu(t') \rangle = 2\gamma k_B T \delta_{nn'} \delta^{\mu\nu} \delta(t - t'). \quad (6.6.18)$$

We define $\mathbf{x}_0 \equiv \mathbf{x}_1$ and $\mathbf{x}_{N+1} \equiv \mathbf{x}_N$ so that the end mass points $n = 1$ and $n = N$ experience a restoring force from only one neighbor. We assume the chain is overdamped and set $M \rightarrow 0$. We then have

$$\gamma \dot{\mathbf{x}}_n = -k \sum_{n'=1}^N A_{nn'} \mathbf{x}_{n'} + \mathbf{f}_n(t), \quad (6.6.19)$$

where

$$A = \begin{pmatrix} 1 & -1 & 0 & 0 & \dots & 0 \\ -1 & 2 & -1 & 0 & \dots & 0 \\ 0 & -1 & 2 & -1 & \dots & 0 \\ 0 & 0 & -1 & \ddots & \dots & \vdots \\ \vdots & & & \ddots & \ddots & 2 & -1 \\ 0 & \dots & \dots & 0 & -1 & 1 \end{pmatrix}. \quad (6.6.20)$$

The matrix A is real and symmetric. Its eigenfunctions are labeled $\psi_j(n)$, with $j \in \{0, \dots, N-1\}$:

$$\begin{aligned} \psi_0(n) &= \frac{1}{\sqrt{N}} \\ \psi_j(n) &= \sqrt{\frac{2}{N}} \cos\left(\frac{(2n-1)j\pi}{2N}\right), \quad j \in \{1, \dots, N-1\} \end{aligned}$$

The completeness and orthonormality relations are

$$\sum_{j=0}^{N-1} \psi_j(n) \psi_j(n') = \delta_{nn'}, \quad \sum_{n=1}^N \psi_j(n) \psi_{j'}(n) = \delta_{jj'}, \quad (6.6.21)$$

with eigenvalues $\lambda_j = 4 \sin^2(\pi j/2N)$. Note that $\lambda_0 = 0$.

We now work in the basis of normal modes $\{\eta_j^\mu\}$, where

$$\eta_j^\mu(t) = \sum_{n=1}^N \psi_j(n) x_n^\mu(t) \quad , \quad x_n^\mu(t) = \sum_{j=0}^{N-1} \psi_j(n) \eta_j^\mu(t) \quad . \quad (6.6.22)$$

We then have

$$\frac{d\eta_j}{dt} = -\frac{1}{\tau_j} \eta_j + \mathbf{g}_j(t) \quad , \quad (6.6.23)$$

where the j^{th} relaxation time is

$$\tau_j = \frac{\gamma}{4k \sin^2(\pi j/2N)} \quad (6.6.24)$$

and

$$g_j^\mu(t) = \gamma^{-1} \sum_{n=1}^N \psi_j(n) f_n^\mu(t) \quad . \quad (6.6.25)$$

Note that

$$\langle g_j^\mu(t) g_{j'}^\nu(t') \rangle = 2\gamma^{-1} k_B T \delta_{jj'} \delta^{\mu\nu} \delta(t-t') \quad . \quad (6.6.26)$$

Integrating Equation 6.6.23, we have for, $j = 0$,

$$\eta_0(t) = \eta_0(0) + \int_0^t dt' \mathbf{g}_0(t') \quad . \quad (6.6.27)$$

For the $j > 0$ modes,

$$\eta_j(t) = \eta_j(0) e^{-t/\tau_j} + \int_0^t dt' \mathbf{g}_j(t') e^{(t'-t)/\tau_j} \quad . \quad (6.6.28)$$

Thus,

$$\begin{aligned} \langle \eta_0^\mu(t) \eta_0^\nu(t') \rangle_c &= 2\gamma^{-1} k_B T \delta^{\mu\nu} \min(t, t') \\ \langle \eta_j^\mu(t) \eta_j^\nu(t') \rangle_c &= \gamma^{-1} k_B T \delta^{\mu\nu} \tau_j \left(e^{-|t-t'|/\tau_j} - e^{-(t+t')/\tau_j} \right) \quad , \end{aligned}$$

where the ‘connected average’ is defined to be $\langle A(t) B(t') \rangle_c \equiv \langle A(t) B(t') \rangle - \langle A(t) \rangle \langle B(t') \rangle$. Transforming back to the original real space basis, we then have

$$\langle x_n^\mu(t) x_{n'}^\nu(t') \rangle_c = \frac{2k_B T}{N\gamma} \delta^{\mu\nu} \min(t, t') + \frac{k_B T}{\gamma} \delta^{\mu\nu} \sum_{j=1}^{N-1} \tau_j \psi_j(n) \psi_j(n') \left(e^{-|t-t'|/\tau_j} - e^{-(t+t')/\tau_j} \right) \quad . \quad (6.6.29)$$

In particular, the ‘connected variance’ of $\mathbf{x}_n(t)$ is

$$\text{CVar}[\mathbf{x}_n(t)] \equiv \langle [\mathbf{x}_n(t)]^2 \rangle_c = \frac{6k_B T}{N\gamma} t + \frac{3k_B T}{\gamma} \sum_{j=1}^{N-1} \tau_j [\psi_j(n)]^2 (1 - e^{-2t/\tau_j}) \quad . \quad (6.6.30)$$

From this we see that at long times, when $t \gg \tau_1$, the motion of $\mathbf{x}_n(t)$ is diffusive, with diffusion constant $D = k_B T / N\gamma \propto B^{-1}$, which is inversely proportional to the chain length. Recall the Stokes result $\gamma = 6\pi\eta R/M$ for a sphere of radius R and mass M moving in a fluid of dynamical viscosity η . From $D = k_B T / \gamma M$, shouldn't we expect the diffusion constant to be $D = k_B T / 6\pi\eta R \propto N^{-1/2}$, since the radius of gyration of the polymer is $R_g \propto N^{1/2}$? This argument smuggles in the assumption

that the only dissipation is taking place at the *outer surface* of the polymer, modeled as a ball of radius R_g . In fact, for a Gaussian random walk in three space dimensions, the density for $r < R_g$ is $\rho \propto N^{-1/2}$ since there are N monomers inside a region of volume $(\sqrt{N})^3$. Accounting for Flory swelling due to steric interactions (see below), the density is $\rho \sim N^{-4/5}$, which is even smaller. So as $N \rightarrow \infty$, the density within the $r = R_g$ effective sphere gets small, which means water molecules can easily penetrate, in which case the entire polymer chain should be considered to be in a dissipative environment, which is what the Rouse model says – each monomer executed overdamped motion.

A careful analysis of Equation 6.6.30 reveals that there is a subdiffusive regime¹² where $\text{CVar}[\mathbf{x}_n(t)] \propto t^{1/2}$. To see this, first take the $N \gg 1$ limit, in which case we may write $\tau_j = N^2 \tau_0 / j^2$, where $\tau_0 \equiv \gamma / \pi^2 k$ and $j \in \{1, \dots, N-1\}$. Let $s \equiv (n - \frac{1}{2}) / N \in [0, 1]$ be the scaled coordinate along the chain. The second term in Equation 6.6.30 is then

$$S(s, t) \equiv \frac{6k_B T}{\gamma} \cdot \frac{\tau_1}{N} \sum_{j=1}^{N-1} \frac{\cos^2(\pi j s)}{j^2} (1 - e^{-2j^2 t / \tau_1}) \quad (6.6.31)$$

Let $\sigma \equiv (t / \tau_1)^{1/2}$. When $t \ll \tau_1$, $\sigma \ll 1$, we have

$$S(s, t) \simeq \frac{6k_B T}{\gamma} \cdot \frac{\tau_1}{N} \sigma \int_0^{N\sigma} du \frac{\cos^2(\pi u s / \sigma)}{u^2} (1 - e^{-2u^2}) \quad (6.6.32)$$

Since $s / \sigma \gg 1$, we may replace the cosine squared term by its average $\frac{1}{2}$. If we further assume $N\sigma \gg 1$, which means we are in the regime $1 \ll t / \tau_0 \ll N^2$, after performing the integral we obtain the result

$$S(s, t) = \frac{3k_B T}{\gamma} \sqrt{2\pi\tau_0 t} \quad (6.6.33)$$

provided $s = \mathcal{O}(1)$, the site n is not on either end of the chain. The result in Equation 6.6.33 dominates the first term on the RHS of Equation \ref{Rousevar} since $\tau_0 \ll t \ll \tau_1$. This is the subdiffusive regime.

When $t \gg \tau_1 = N^2 \tau_0$, the exponential on the RHS of Equation 6.6.31 is negligible, and if we again approximate $\cos^2(\pi j s) \simeq \frac{1}{2}$, and we extend the upper limit on the sum to infinity, we find $S(t) = (3k_B T / \gamma)(\tau_1 / N)(\pi^2 / 6) \propto t^0$, which is dominated by the leading term on the RHS of Equation 6.6.30. This is the diffusive regime, with $D = k_B T / N\gamma$.

Finally, when $t \ll \tau_0$, the factor $1 - \exp(-2t / \tau_j)$ may be expanded to first order in t . One then obtains $\text{CVar}[\mathbf{x}_n(t)] = (6k_B T / \gamma) t$, which is independent of the force constant k . In this regime, the monomers don't have time to respond to the force from their neighbors, hence they each diffuse independently. On such short time scales, however, one should check to make sure that inertial effects can be ignored, that $t \gg M / \gamma$.

One serious defect of the Rouse model is its prediction of the relaxation time of the $j = 1$ mode, $\tau_1 \propto N^2$. The experimentally observed result is $\tau_1 \propto N^{3/2}$. We should stress here that the Rouse model applies to ideal chains. In the theory of polymer solutions, a *theta solvent* is one in which polymer coils act as ideal chains. An extension of the Rouse model, due to my former UCSD colleague Bruno Zimm, accounts for hydrodynamically-mediated interactions between any pair of 'beads' along the chain. Specifically, the Zimm model is given by

$$\frac{dx_n^\mu}{dt} = \sum_{n'} H^{\mu\nu}(\mathbf{x}_n - \mathbf{x}_{n'}) \left[k(x_{n'+1}^\nu + x_{n'-1}^\nu - 2x_{n'}^\nu) + f_{n'}^\nu(t) \right] \quad (6.6.34)$$

where

$$H^{\mu\nu}(\mathbf{R}) = \frac{1}{6\pi\eta R} (\delta^{\mu\nu} + \hat{R}^\mu \hat{R}^\nu) \quad (6.6.35)$$

is known as the **Oseen hydrodynamic tensor** (1927) and arises when computing the velocity in a fluid at position \mathbf{R} when a point force $\mathbf{F} = \mathbf{f} \delta(\mathbf{r})$ is applied at the origin. Typically one replaces $H(\mathbf{R})$ by its average over the equilibrium distribution of polymer configurations. Zimm's model more correctly reproduces the behavior of polymers in θ -solvents.

Flory Theory of Self-Avoiding Walks

What is missing from the random walk free energy is the effect of *steric interactions*. An argument due to Flory takes these interactions into account in a mean field treatment. Suppose we have a chain of radius R . Then the average monomer density within the chain is $c = N/R^d$. Assuming short-ranged interactions, we should then add a term to the free energy which effectively counts the number of near self-intersections of the chain. This number should be roughly Nc . Thus, we write

$$F(\mathbf{R}, N) = F_0 + u(T) \frac{N^2}{R^d} + \frac{1}{2} dk_B T \frac{R^2}{Na^2} \quad (6.6.36)$$

The effective interaction $u(T)$ is positive in the case of a so-called ‘good solvent’.

The free energy is minimized when

$$0 = \frac{\partial F}{\partial R} = -\frac{dvN^2}{R^{d+1}} + dk_B T \frac{R}{Na^2} \quad (6.6.37)$$

which yields the result

$$R_F(N) = \left(\frac{ua^2}{k_B T} \right)^{1/(d+2)} N^{3/(d+2)} \propto N^\nu \quad (6.6.38)$$

Thus, we obtain $\nu = 3/(d+2)$. In $d = 1$ this says $\nu = 1$, which is exactly correct because a SAW in $d = 1$ has no option but to keep going in the same direction. In $d = 2$, Flory theory predicts $\nu = \frac{3}{4}$, which is also exact. In $d = 3$, we have $\nu_{d=3} = \frac{3}{5}$, which is extremely close to the numerical value $\nu = 0.5880$. Flory theory is again exact at the SAW upper critical dimension, which is $d = 4$, where $\nu = \frac{1}{2}$, corresponding to a Gaussian random walk¹³. Best. Mean. Field. Theory. Ever.

How well are polymers described as SAWs? Figure 6.6.4 shows the radius of gyration R_g versus molecular weight M for polystyrene chains in a toluene and benzene solvent. The slope is $\nu = d \ln R_g / d \ln M = 0.5936$. Experimental results can vary with concentration and temperature, but generally confirm the validity of the SAW model.

For a SAW under an external force, we compute the Gibbs partition function,

$$Y(\mathbf{F}_{ext}, N) = \int d^d R P_N(\mathbf{R}) e^{\mathbf{F}_{ext} \cdot \mathbf{R} / k_B T} = \int d^d x f(x) e^{\hat{\mathbf{n}} \cdot \mathbf{x}} \quad (6.6.39)$$

where $x = R/R_F$ and $s = k_B T / R_F F_{ext}$ and $\hat{\mathbf{n}} = \hat{\mathbf{F}}_{ext}$. One then has $R(F_{ext}) = R_F \Phi(R_F/\xi)$, where $\xi = k_B T / F_{ext}$ and $R(F_{ext}) = F_{ext} R_F^2 / k_B T$. For small values of its argument one has $\Phi(u) \propto u$. For large u it can be shown that $R(F_{ext}) \propto (F_{ext} R_F / k_B T)^{2/3}$.

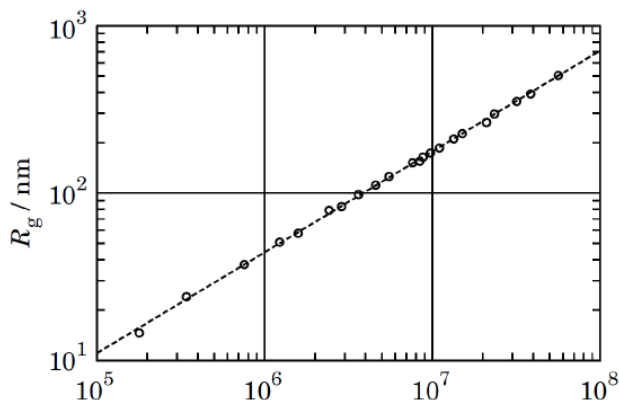


Figure 6.6.4: Radius of gyration R_g of polystyrene in a toluene and benzene solvent, plotted as a function of molecular weight of the polystyrene. The best fit corresponds to a power law $R_g \propto M^\nu$ with $\nu = 0.5936$. From J. Des Cloizeaux and G. Jannink, *Polymers in Solution: Their Modeling and Structure* (Oxford, 1990).

On a lattice of coordination number z , the number of N -step random walks starting from the origin is $\Omega_N = z^N$. If we constrain our random walks to be self-avoiding, the number is reduced to

$$\Omega_N^{SAW} = C N^{\gamma-1} y^N \quad (6.6.40)$$

where \mathcal{C} and γ are dimension-dependent constants, and we expect $y \propto z - 1$, since at the very least a SAW cannot immediately double back on itself. In fact, on the cubic lattice one has $z = 6$ but $y = 4.68$, slightly less than $z - 1$. One finds $\gamma_{d=2} \simeq \frac{4}{3}$ and $\gamma_{d=3} \simeq \frac{7}{6}$. The RMS end-to-end distance of the SAW is

$$R_F = a N^\nu, \quad (6.6.41)$$

where a and ν are d -dependent constants, with $\nu_{d=1} = 1$, $\nu_{d=2} \simeq \frac{3}{4}$, and $\nu_{d=3} \simeq \frac{3}{5}$. The distribution $P_N(\mathbf{R})$ has a scaling form,

$$P_N(R) = \frac{1}{R_F^d} f\left(\frac{R}{R_F}\right) \quad (a \ll R \ll Na). \quad (6.6.42)$$

One finds

$$f(x) \sim \begin{cases} x^g & x \ll 1 \\ \exp(-x^\delta) & x \gg 1, \end{cases} \quad (6.6.43)$$

with $g = (\gamma - 1)/\nu$ and $\delta = 1/(1 - \nu)$.

Polymers and Solvents

Consider a solution of monodisperse polymers of length N in a solvent. Let ϕ be the dimensionless monomer concentration, so ϕ/N is the dimensionless polymer concentration and $\phi_s = 1 - \phi$ is the dimensionless solvent concentration. (Dimensionless concentrations are obtained by dividing the corresponding dimensionful concentration by the overall density.) The entropy of mixing for such a system is given by Equation 2.352. We have

$$S_{mix} = -\frac{Vk_B}{v_0} \cdot \left\{ \frac{1}{N} \phi \ln \phi + (1 - \phi) \ln(1 - \phi) \right\}, \quad (6.6.44)$$

where $v_0 \propto a^3$ is the volume per monomer. Accounting for an interaction between the monomer and the solvent, we have that the free energy of mixing is

$$\frac{v_0 F_{mix}}{Vk_B T} = \frac{1}{N} \phi \ln \phi + (1 - \phi) \ln(1 - \phi) + \chi \phi(1 - \phi). \quad (6.6.45)$$

where χ is the dimensionless polymer-solvent interaction, called the *Flory parameter*. This provides a mean field theory of the polymer-solvent system.

The osmotic pressure Π is defined by

$$\Pi = -\frac{\partial F_{mix}}{\partial V} \Big|_{N_p}, \quad (6.6.46)$$

which is the variation of the free energy of mixing with respect to volume *holding the number of polymers constant*. The monomer concentration is $\phi = NN_p v_0 / V$, so

$$\frac{\partial}{\partial V} \Big|_{N_p} = -\frac{\phi^2}{NN_p v_0} \frac{\partial}{\partial \phi} \Big|_{N_p}. \quad (6.6.47)$$

Now we have

$$F_{mix} = NN_p k_B T \left\{ \frac{1}{N} \ln \phi + (\phi^{-1} - 1) \ln(1 - \phi) + \chi(1 - \phi) \right\}, \quad (6.6.48)$$

and therefore

$$\Pi = \frac{k_B T}{v_0} \left[(N^{-1} - 1) \phi - \ln(1 - \phi) - \chi \phi^2 \right]. \quad (6.6.49)$$

In the limit of vanishing monomer concentration $\phi \rightarrow 0$, we recover

$$\Pi = \frac{\phi k_B T}{N v_0}, \quad (6.6.50)$$

which is the ideal gas law for polymers.

For $N^{-1} \ll \phi \ll 1$, we expand the logarithm and obtain

$$\begin{aligned}\frac{v_0 \Pi}{k_B T} &= \frac{1}{N} \phi + \frac{1}{2} (1 - 2\chi) \phi^2 + \mathcal{O}(\phi^3) \\ &\approx \frac{1}{2} (1 - 2\chi) \phi^2.\end{aligned}$$

Note that $\Pi > 0$ only if $\chi < \frac{1}{2}$, which is the condition for a 'good solvent'.

In fact, Equation ??? is only qualitatively correct. In the limit where $\chi \ll \frac{1}{2}$, Flory showed that the individual polymer coils behave much as hard spheres of radius R_F . The osmotic pressure then satisfies something analogous to a virial equation of state:

$$\begin{aligned}\frac{\Pi}{k_B T} &= \frac{\phi}{N v_0} + A \left(\frac{\phi}{N v_0} \right)^2 R_F^3 + \dots \\ &= \frac{\phi}{N v_0} h(\phi/\phi^*).\end{aligned}$$

This is generalized to a scaling form in the second line, where $h(x)$ is a scaling function, and $\phi^* = N v_0 / R_F^3 \propto N^{-4/5}$, assuming $d = 3$ and $\nu = \frac{3}{5}$ from Flory theory. As $x = \phi/\phi^* \rightarrow 0$, we must recover the ideal gas law, so $h(x) = 1 + \mathcal{O}(x)$ in this limit. For $x \rightarrow \infty$, we require that the result be independent of the degree of polymerization N . This means $h(x) \propto x^p$ with $\frac{4}{5}p = 1$, $p = \frac{5}{4}$. The result is known as the **des Cloiseaux law**:

$$\frac{v_0 \Pi}{k_B T} = C \phi^{9/4}, \quad (6.6.51)$$

where C is a constant. This is valid for what is known as semi-dilute solutions, where $\phi^* \ll \phi \ll 1$. In the dense limit $\phi \sim 1$, the results do not exhibit this universality, and we must appeal to liquid state theory, which is no fun at all.

This page titled 6.6: Polymers is shared under a CC BY-NC-SA license and was authored, remixed, and/or curated by Daniel Arovas.