

2.1.2 The Gaussian Chain Model

Important Concepts: fluctuating bond, Hamiltonian for the Gaussian Chain Model

We consider a chain made up of orientationally uncorrelated (freely-jointed) links where the length of any link vector is no longer constant but has a probability distribution

$$G(\mathbf{r}) = \left(\frac{3}{2\pi b^2}\right)^{3/2} \exp\left(-\frac{3\mathbf{r}^2}{2b^2}\right) \quad (2.36)$$

with the expectation for the link length being

$$\langle \mathbf{r}^2 \rangle = b^2 \quad . \quad (2.37)$$

The probability distribution for the end-to-end vector is then

$$P(\mathbf{R}_e) = P(\{\mathbf{r}_n\}) \quad (2.38)$$

$$= \prod_{n=1}^N \left(\frac{3}{2\pi b^2}\right)^{3/2} \exp\left(-\frac{3\mathbf{r}_n^2}{2b^2}\right) \quad (2.39)$$

$$= \left(\frac{3}{2\pi b^2}\right)^{3/2} \exp\left(-\sum_{n=1}^N \frac{3(\mathbf{R}_n - \mathbf{R}_{n-1})^2}{2b^2}\right) \quad (2.40)$$

and hence for the entropy

$$S = \ln P = \sum_{n=1}^N \ln P(\mathbf{r}_n) \quad (2.41)$$

$$= \text{const} - \frac{3}{2b^2} \sum_{n=1}^N \mathbf{r}_n^2 \quad . \quad (2.42)$$

From this we obtain the free energy

$$F(\{\mathbf{r}_n\}) = E + \frac{3T}{2b^2} \sum_{n=1}^N \mathbf{r}_n^2 \quad (2.43)$$

with the internal energy E being independent of $\{\mathbf{r}_n\}$.

Hence we obtain the same equilibrium distribution as for the freely-jointed chain. Eq (2.40) also results if we start off with the Hamiltonian for a chain of springs

$$H = \frac{3}{2} \frac{k_B T}{b^2} \sum_{n=1}^N (\mathbf{R}_n - \mathbf{R}_{n-1})^2 \quad (2.44)$$

and we also obtain the scaling of the end-to-end distance

$$\langle R_e^2 \rangle \propto N \quad (2.45)$$

Further Reading 2.1.4 (Continuous scales)

For the later development we note the generalization to all scales for the Gaussian model at fixed contour length L

$$P(\mathbf{R}) = \int_{\mathbf{r}(0)=0}^{\mathbf{r}(L)=\mathbf{R}} \mathcal{D}[\mathbf{r}(s)] \exp \left[\frac{3L}{2b^2} \int_0^L ds \left(\frac{\partial \mathbf{r}(s)}{\partial s} \right)^2 \right] \quad (2.46)$$

where $\mathbf{r}(s)$ denotes the contour or conformation of the chain. This is solved by

$$P(\mathbf{R}) = \left(\frac{3}{2\pi b^2} \right)^{3/2} \exp \left(-\frac{3\mathbf{R}^2}{2b^2} \right) \quad (2.47)$$

and is the proper continuum limit of the FJC, where the limits $N \rightarrow \infty$ and $b \rightarrow 0$ were taken, such that Nb^2 stayed finite.

We further generalize the effective Hamiltonian

$$H = \frac{3}{2} \frac{k_B T}{b^2} \int_0^L ds \dot{\mathbf{r}}^2(s) \quad (2.48)$$

where the derivation is to be taken along the contour.

2.1.3 Worm-like Chain Model

Important Concepts: bending rigidity and the relation with the persistence length

A short-coming of the above models (besides they being phantom chains, i.e. no self-avoidance) is that there is no intrinsic stiffness. Intuitively, we expect a bending of the chain to cost energy. A model that provides this is the *worm-like chain model* (WLC)

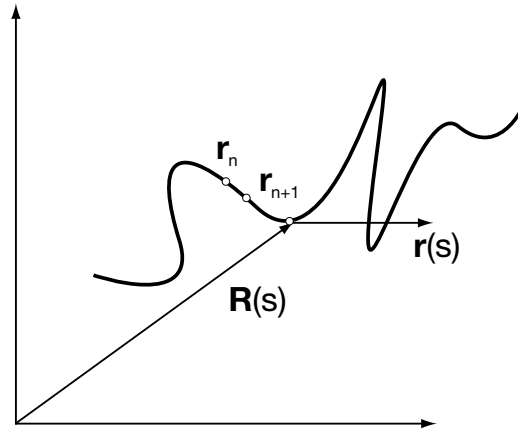


Figure 2.10: Definition of the coordinates used to describe the chain as a continuous curve

$$H = -\epsilon \sum_{n=1}^{N-1} \mathbf{r}_n \cdot \mathbf{r}_{n+1} \quad (2.49)$$

which is simply the one-dimensional Heisenberg model for ferromagnets. Here $|\mathbf{r}_n| = b$. This model can be treated in the continuum limit where $N \rightarrow \infty$, $b \rightarrow 0$ and $\epsilon \rightarrow \infty$ with

$$\epsilon/N = \text{constant} \quad , \quad (2.50)$$

keeping the contour length also constant. Using

$$-\mathbf{r}_{n+1} \cdot \mathbf{r}_n = \frac{1}{2} [(\mathbf{r}_n - \mathbf{r}_{n+1})^2 - 2b^2] \quad (2.51)$$

we have

$$H = \lim_{b \rightarrow 0, \epsilon, N \rightarrow \infty} \frac{\epsilon b}{2} \sum_{n=1}^{N-1} b \left(\frac{\mathbf{r}_n - \mathbf{r}_{n+1}}{b} \right)^2 \quad . \quad (2.52)$$

To cross over to the continuum limit we use the tangent vector with the arc length s

$$\frac{\partial \mathbf{r}(s)}{\partial s} = \lim_{b \rightarrow 0} \left(\frac{\mathbf{r}_{n+1} - \mathbf{r}_n}{b} \right) \quad (2.53)$$

and $\sum_{n=1}^{N-1} b \rightarrow \int_0^L ds$ to find

$$H = \frac{\kappa}{2} \int_0^L ds \left(\frac{\partial \mathbf{r}(s)}{\partial s} \right)^2 = \frac{\kappa}{2} \int_0^L ds \left(\frac{\partial^2 \mathbf{R}(s)}{\partial s^2} \right)^2 \quad (2.54)$$

with the *bending modulus* $\kappa = \epsilon b$.

Thus the partition function is given by

$$Z = \int \mathcal{D}[\mathbf{r}(s)] \delta(|\mathbf{r}(s)| - 1) \exp(-\beta H[\mathbf{r}(s)]) \quad . \quad (2.55)$$

The bending modulus must have a relation with the persistence length. To find this relation we need to calculate the correlation function

$$\langle \mathbf{r}(s) \mathbf{r}(s') \rangle \propto \exp(-|s - s'|/\xi_p) \quad . \quad (2.56)$$

We can now calculate the mean squared end-to-end-distance and the mean squared radius of gyration

$$\langle R_e^2 \rangle = \left\langle \left(\int_0^L ds \mathbf{r}(s) \right)^2 \right\rangle \quad (2.57)$$

$$= \int_0^L ds \int_0^L ds' \langle \mathbf{r}(s) \cdot \mathbf{r}(s') \rangle \quad (2.58)$$

$$= 2\xi_p^2 \left(\frac{L}{\xi_p} - 1 + e^{-L/\xi_p} \right) \quad (2.59)$$

$$= L^2 f_D \left(\frac{L}{\xi_p} \right) \quad , \quad (2.60)$$

where $f_D(x) = 2(x - 1 + e^{-x})/x^2$ being the Debye-function (see figure 2.11).

Further Reading 2.1.5 (Lattice Chains)

We can also go about calculating the average end-to-end distance staying discrete (Kratky-Porod model [36]). For this we write

$$H = -\epsilon \sum_{n=1}^{N-1} \mathbf{r}_n \cdot \mathbf{r}_{n+1} = -\epsilon \sum_{n=1}^N \cos \theta_n \quad . \quad (2.61)$$

The partition function is given by

$$Z_N = \prod_{n=1}^N \int d\Omega_n e^{\beta \epsilon \cos \theta_n} = Q_l^N \quad (2.62)$$

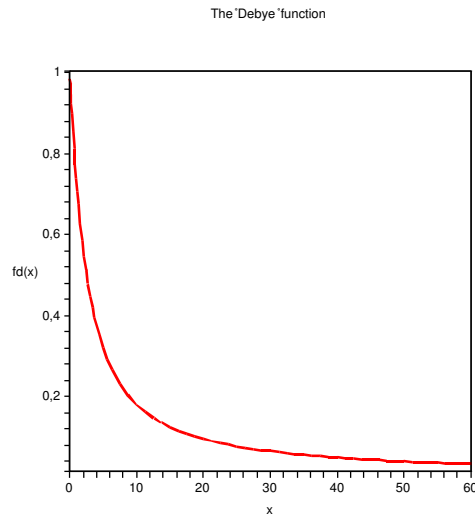


Figure 2.11: The Debye-function

with

$$Q_l = 2\pi \int_{-1}^1 d(\cos\theta) e^{\beta\epsilon \cos\theta} = 4\pi \frac{\sinh \beta\epsilon}{\beta\epsilon} \quad (2.63)$$

With this we can calculate the distance

$$\langle R_e^2 \rangle = b^2 \langle (\sum r_n)^2 \rangle = b^2 \sum_{n,m} \langle \mathbf{r}_n \cdot \mathbf{r}_m \rangle \quad (2.64)$$

again as the correlation between the directions of bonds. For the nearest neighbour correlation we have

$$\langle \mathbf{r}_n \cdot \mathbf{r}_{n+1} \rangle = \langle \cos \theta \rangle \quad (2.65)$$

$$= \frac{\int d\Omega \cos \theta e^{\beta\epsilon \cos \theta}}{\int d\Omega e^{\beta\epsilon \cos \theta}} \quad (2.66)$$

$$= \frac{d \ln Q_l}{d(\beta\epsilon)} \quad (2.67)$$

$$= \coth(\beta\epsilon) - 1/\beta\epsilon \quad (2.68)$$

$$= f_L(\beta\epsilon) \quad (2.69)$$

where f_L is the *Langevin function*. In general the correlation is given by [37]

$$\langle \mathbf{r}_n \cdot \mathbf{r}_{n+1} \rangle = e^{-N \ln(1/c)} \quad , \quad (2.70)$$

which can be written in terms of the persistence length ξ_p

$$\langle \mathbf{r}_n \cdot \mathbf{r}_{n+1} \rangle = e^{-Nb/\xi_p} \quad (2.71)$$

with

$$\xi_p = \frac{b}{\ln(1/c)} \quad (2.72)$$

If the macromolecule is stiff $\epsilon\beta \gg 1$ and

$$c \approx 1 - k_B T / \epsilon \quad , \quad (2.73)$$

then

$$\ln(1/c) \approx k_B T / \epsilon \quad (2.74)$$

and thus

$$\xi_p = b\beta\epsilon \quad . \quad (2.75)$$

Let us rewrite the end-to-end distance in terms of c

$$\frac{1}{b^2} \langle R_e^2 \rangle = \sum_{i=1}^N \left(\sum_{j=1}^{i-1} c^{i-j} + 1 + \sum_{j=i+1}^N c^{j-i} \right) \quad , \quad (2.76)$$

then for most i the two sums in the braces can be replaced by $\sum_{k=1}^{\infty} c^k = \frac{c}{1-c}$ and with this we obtain

$$\langle R_e^2 \rangle \approx Nb^2 \left(1 + \frac{2c}{1-c} \right) = Nb^2 \frac{1+c}{1-c} \quad . \quad (2.77)$$

$\frac{1+c}{1-c}$ is the Flory factor. The Kuhn segment length l_K is then given by

$$l_K = \frac{1+c}{1-c} b \quad . \quad (2.78)$$

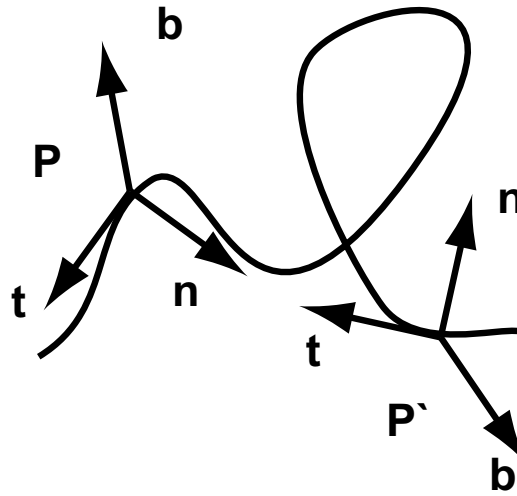


Figure 2.12: Motion of the Frenet triad along a curve

Since we are dealing in some sense with mathematical curves in three dimensional space recall that a curve in space is *mathematically* determined by the two parameters: *curvature* κ and *torsion* τ (the basic triad $\{\mathbf{t}_k\}$)

$$\frac{d\mathbf{b}}{ds} = -\tau\mathbf{n} \quad , \quad \frac{d\mathbf{n}}{ds} = -\kappa\mathbf{t} + \tau\mathbf{b} \quad , \quad \frac{d\mathbf{t}}{ds} = \kappa\mathbf{n} \quad (2.79)$$

Choosing $\kappa = \tau = 0$ we obtain a straight line, $r = 1/\kappa$ and $\tau = 0$ for a circle with radius r .

Consider the case of a helix (see figure 2.13) with

$$\mathbf{r}(s) = \left[r \cos \left(\frac{qs}{\sqrt{(qr)^2 + 1}} \right), r \sin \left(\frac{qs}{\sqrt{(qr)^2 + 1}} \right), \frac{s}{\sqrt{(qr)^2 + 1}} \right] \quad (2.80)$$

and

$$\kappa(s) = \frac{rq^2}{1 + (qr)^2} \quad (2.81)$$

$$\tau(s) = \frac{q}{1 + (qr)^2} \quad (2.82)$$

Clearly as $r \rightarrow 0$ we must approach a straight line. The curvature vanishes indeed in this limit but the torsion does not.

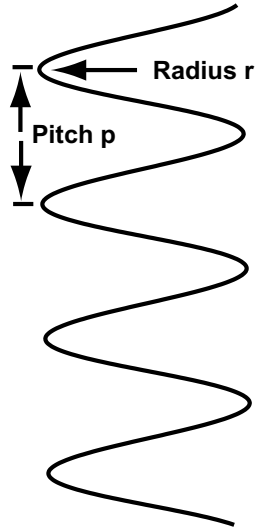


Figure 2.13: Definition of the parameters for a helix

We can generalize the Frenet-frame introducing a third parameter

$$\frac{d\mathbf{t}_i(s)}{ds} = - \sum_{j,k} \epsilon_{ijk} \omega_j(s) t_k(s) \quad (2.83)$$

where

$$\omega_1 = \kappa \cos \alpha \quad , \quad \omega_2 = \kappa \sin \alpha \quad , \quad \omega_3 = \tau + \frac{d\alpha}{ds} \quad (2.84)$$

This could be used to define an elastic energy with spontaneous curvature and torsion $\{\omega_{0k}\}$ (the deviation from equilibrium is denoted by $\delta\omega_k = \omega_k - \omega_{0k}$)

$$U = \frac{1}{2} \sum_k b_k \int_0^L \delta\omega_k^2 ds \quad (2.85)$$

The parameters b_k define the rigidity. Defining

$$A = \begin{bmatrix} 0 & -\kappa & \omega \\ \kappa & 0 & -\tau \\ -\omega & \tau & 0 \end{bmatrix} \quad (2.86)$$

with

$$A_{ij} = \sum_k \epsilon_{ijk} \omega_k \quad (2.87)$$

we can develop also a numerical procedure to generate curves that have a prescribed spontaneous curvature with fluctuations. For this let $v^x = (t_1^x, t_2^x, t_3^x,)$ etc. then we write the equation 2.83 as

$$\frac{dv^i}{ds} = Av^i \quad (2.88)$$

which can be discretized as

$$v^i(s + ds) = Ov^i(s) \quad (2.89)$$

with

$$O = \left(1 + \frac{ds}{2}A\right)\left(1 - \frac{ds}{2}A\right)^{-1} \quad (2.90)$$

Note that O is an orthogonal matrix guaranteeing that we consistently generate orthogonal triads.

In figure is depicted the case for a curve where the spontaneous curvature is set such that a circle is preferred.

2.1.4 Self-Avoiding Chains

The above models all lack the excluded volume interaction between the monomers. Indeed, the ubiquitous polymer model is a self-avoiding random walk.

Let $U(\mathbf{R}_n - \mathbf{R}_m)$ be a monomer-monomer interaction potential assumed to handle the excluded volume. We treat the polymer as gas of disconnected monomers confined within the same volume V as the polymer coil. If \bar{R} denotes the average extent of the chain then the chain occupies a volume $V = \bar{R}^3$. Let ΔF_c be the term that arises from the chemical work done by initially “preparing” the monomers in