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

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

with the expectation for the link length being

$$< \mathbf{r}^2 >= b^2 \quad . \tag{2.37}$$

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

$$\begin{aligned} P(\mathbf{R}_e) &= P(\{\mathbf{r}_n\}) && (2.38)\\ &= \prod_{n=1}^{N} \left(\frac{3}{2\pi b^2}\right)^{3/2} \exp\left(-\frac{3\mathbf{r}_n^2}{2b^2}\right) && (2.39)\\ &= \left(\frac{3}{2\pi b^2}\right)^{3/2} \exp\left(-\sum_{n=1}^{N} \frac{3(\mathbf{R}_n - \mathbf{R}_{n-1})^2}{2b^2}\right) && (2.40) \end{aligned}$$

and hence for the entropy

$$\begin{aligned} S &= \ln P = \sum_{n=1}^{N} \ln P(\mathbf{r}_n) && (2.41)\\ &= \text{const} - \frac{3}{2\mathrm{b}^2} \sum_{\mathrm{n}=1}^{\mathrm{N}} \mathbf{r}_{\mathrm{n}}^2 \quad . && (2.42) \end{aligned}$$

From this we obtain the free energy

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

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

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

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

$$< R_e^2 > \propto N \quad . \tag{2.45}$$

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

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

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

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

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

We further generalize the effective Hamiltonian

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

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)

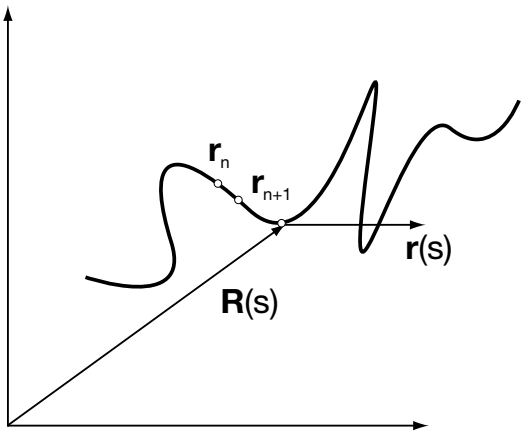

Figure 2.10: Definition of the coordinates used to describe the chain as a continuous curve

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

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 $N \to \infty$, $b \to 0$ and $\epsilon \to \infty$ with

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

keeping the contour length also constant. Using

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

we have

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

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

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

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

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

with the *bending modulus* $\kappa = \epsilon b$.
Thus the partition function is given by

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

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

$$< \mathbf{r}(s)\mathbf{r}(s') > \propto \exp(-|s - s'|/\xi_p) \quad . \tag{2.56}$$

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

$$\begin{aligned} < R_e^2 > &= < \left(\int_0^L ds \mathbf{r}(s)\right)^2 > & (2.57)\\ &= \int_0^L ds \int_0^L ds' < \mathbf{r}(s) \cdot \mathbf{r}(s') > & (2.58)\\ &= 2\xi_p^2 \left(\frac{L}{\xi_p} - 1 + e^{-L/\xi_p}\right) & (2.59)\\ &= L^2 f_D\left(\frac{L}{\xi_p}\right) \quad , & (2.60) \end{aligned}$$

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

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

The partition function is given by

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

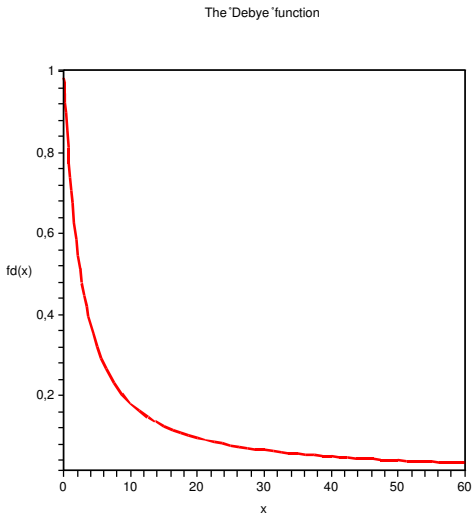

Figure 2.11: The Debye-function

with

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

With this we can calculate the distance

$$< R_e^2 >= b^2 < (\sum r_n)^2 >= b^2 \sum_{n,m} < \mathbf{r}_n \cdot \mathbf{r}_m > \tag{2.64}$$

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

$$\begin{aligned} < \mathbf{r}_n \cdot \mathbf{r}_{n+1} > &= < \cos\theta > & (2.65)\\ &= \frac{\int d\Omega \cos\theta e^{\beta\epsilon\cos\theta}}{\int d\Omega e^{\beta\epsilon\cos\theta}} & (2.66)\\ &= \frac{d \ln Q_l}{d(\beta\epsilon)} & (2.67)\\ &= \coth(\beta\epsilon) - 1/\beta\epsilon & (2.68)\\ &= f_L(\beta\epsilon) \quad , & (2.69) \end{aligned}$$

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

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

which can be written in terms of the persistence length ξ_p

$$< \mathbf{r}_n \cdot \mathbf{r}_{n+1} >= e^{-Nb/\xi_p} \tag{2.71}$$

with

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

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

$$c \approx 1 - k_B T/\epsilon \quad , \tag{2.73}$$

then

$$\ln(1/c) \approx k_B T/\epsilon \tag{2.74}$$

and thus

$$\xi_p = b\beta\epsilon \quad . \tag{2.75}$$

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

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

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

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

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

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

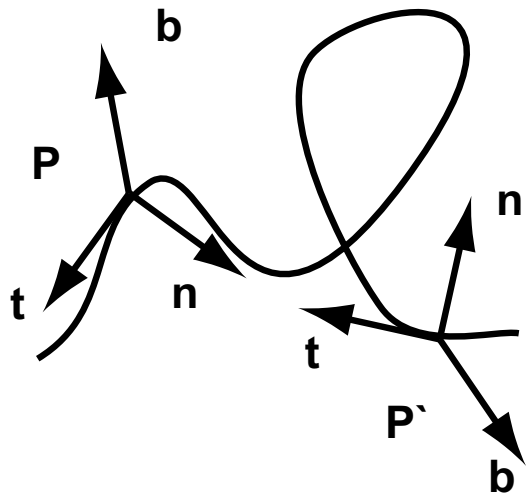

Figure 2.12: Motion of the Fernet triad along a curve

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 $\{\mathbf{t}_k\}$)

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

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

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

and

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

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

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

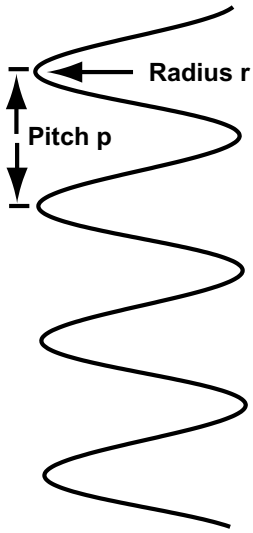

Figure 2.13: Definition of the parameters for a helix

We can generalize the Fernet-frame introducing a third parameter

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

where

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

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

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

The parameters b_k define the rigidity. Defining

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

with

$$A_{ij} = \sum_k \epsilon_{ijk}\omega_k \tag{2.87}$$

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

$$\frac{dv^i}{ds} = Av^i \tag{2.88}$$

which can be discretized as

$$v^i(s + ds) = Ov^i(s) \tag{2.89}$$

with

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

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