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

\[
G(r) = \left(\frac{3}{2\pi b^2}\right)^{3/2} \exp\left(-\frac{3r^2}{2b^2}\right)
\]

with the expectation for the link length being

\[
<r^2> = b^2.
\]

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

\[
P(R_e) = P(\{r_n\}) = \prod_{n=1}^{N} \left(\frac{3}{2\pi b^2}\right)^{3/2} \exp\left(-\frac{3r_n^2}{2b^2}\right)
\]

\[
= \left(\frac{3}{2\pi b^2}\right)^{3/2} \exp\left(-\sum_{n=1}^{N} \frac{3(R_n - R_{n-1})^2}{2b^2}\right)
\]

and hence for the entropy

\[
S = \ln P = \sum_{n=1}^{N} \ln P(r_n)
\]

\[
= \text{const} - \frac{3}{2b^2} \sum_{n=1}^{N} r_n^2.
\]

From this we obtain the free energy

\[
F(\{r_n\}) = E + \frac{3T}{2b^2} \sum_{n=1}^{N} r_n^2
\]

with the internal energy \(E\) being independent of \(\{r_n\}\).
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

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

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

$$\langle R_e^2 \rangle \sim N$$  \hspace{1cm} (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 $L$

$$P(\mathbf{R}) = \int_0^{r(L)=\mathbf{R}} D[\mathbf{r}(s)] \exp \left[ \frac{3}{2 b^2} \int_0^L ds \left( \frac{\partial \mathbf{r}(s)}{\partial s} \right)^2 \right]$$  \hspace{1cm} (2.46)$$

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

$$P(\mathbf{R}) = \left( \frac{3}{2 \pi b^2} \right)^{3/2} \exp \left( -\frac{3R^2}{2b^2} \right)$$  \hspace{1cm} (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

$$H = \frac{3}{2} k_B T \int_0^L d\mathbf{r}^2(s)$$  \hspace{1cm} (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

\[ H = -\epsilon \sum_{n=1}^{N-1} \mathbf{r}_n \cdot \mathbf{r}_{n+1} \]  

(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

\[ \epsilon/N = \text{constant} , \]  

(2.50)

keeping the contour length also constant. Using

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

(2.51)

we have

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

(2.52)

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

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

(2.53)
2.1 GENERAL PROPERTIES OF MACROMOLECULES

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

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

with the bending modulus $\kappa = eb$.

Thus the partition function is given by

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

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

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

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

$$< R_e^2 > = < \left( \int_0^L ds r(s) \right)^2 > \tag{2.57}$$

$$= \int_0^L ds \int_0^L ds' < r(s) \cdot r(s') > \tag{2.58}$$

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

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

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

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

The partition function is given by

$$Z_N = \prod_{n=1}^{N} \int d\Omega_n e^{\beta \epsilon \cos \theta_n} = Q_I^N \tag{2.62}$$
Figure 2.11: The Debye-function

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

With this we can calculate the distance

\[ < R^2_e > = b^2 < (\sum_{n} r_n)^2 > = b^2 \sum_{n,m} < r_n \cdot r_m > \] (2.64)

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

\[ < r_n \cdot r_{n+1} > = < \cos \theta > \]
\[ = \frac{\int d\Omega \cos \theta e^{\beta \epsilon \cos \theta}}{\int d\Omega e^{\beta \epsilon \cos \theta}} \] (2.65)
\[ = \frac{d \ln Q_l}{d(\beta \epsilon)} \] (2.66)
\[ = \coth(\beta \epsilon) - 1/\beta \epsilon \] (2.67)
\[ = f_L(\beta \epsilon) \] (2.68)

where \( f_L \) is the Langevin function. In general the correlation is given by [37]
\[ < r_n \cdot r_{n+1} > = e^{-N \ln(1/c)} \quad , \] (2.70)

which can be written in terms of the persistence length \( \xi_p \)

\[ < r_n \cdot r_{n+1} > = e^{-Nb/\xi_p} \] (2.71)

with

\[ \xi_p = \frac{b}{\ln(1/c)} \] (2.72)

If the macromolecule is stiff \( \epsilon \beta >> 1 \) and

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

then

\[ \ln(1/c) \approx k_B T/\epsilon \] (2.74)

and thus

\[ \xi_p = b\beta \epsilon \quad . \] (2.75)

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

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

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

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

\[ l_K = \frac{1+c}{1-c} b \quad . \] (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 $\kappa$ and torsion $\tau$ (the basic triad $\{t, \kappa, \tau\}$)

\[
\frac{db}{ds} = -\tau n, \quad \frac{dn}{ds} = -\kappa t + \tau b, \quad \frac{t}{ds} = \kappa n
\]  

(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

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

(2.80)

and

\[
\kappa(s) = \frac{rq^2}{1 + (qr)^2} \quad \text{and} \quad \tau(s) = \frac{q}{1 + (qr)^2}
\]

(2.81) and (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.
2.1 General Properties of Macromolecules

We can generalize the Fernet-frame introducing a third parameter

\[
\frac{dt_i(s)}{ds} = - \sum_{j,k} \epsilon_{ijk} \omega_j(s) t_k(s) \tag{2.83}
\]

where

\[
\omega_1 = \kappa \cos \alpha , \quad \omega_2 = \kappa \sin \alpha , \quad \omega_3 = \frac{d\alpha}{ds} \tag{2.84}
\]

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

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\[
A = \begin{bmatrix}
0 & -\kappa & \omega \\
\kappa & 0 & -\tau \\
-\omega & \tau & 0
\end{bmatrix}
\]  \hspace{1cm} (2.86)

with

\[
A_{ij} = \sum_k \epsilon_{ijk} \omega_k
\]  \hspace{1cm} (2.87)

we can develop also a numerical procedure to generate curves that have a prescribed spontaneous curvature with fluctuations. For this let \(v^x = (t^x_1, t^x_2, t^x_3)\) etc. then we write the equation 2.83 as

\[
\frac{dv^i}{ds} = Av^i
\]  \hspace{1cm} (2.88)

which can be discretized as

\[
v^i(s + ds) = Ov^i(s)
\]  \hspace{1cm} (2.89)

with

\[
O = \left(1 + \frac{ds}{2}A\right)\left(1 - \frac{ds}{2}A\right)^{-1}
\]  \hspace{1cm} (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 \(U(R_n - R_m)\) 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 \(\Delta F_c\) be the term that arises from the chemical work done by initially “preparing” the monomers in

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