Theory of Polymer Dynamics

1 Introduction

This document summarizes information related to the construction of theoretical models representing polymers. It is mainly drawn from the book by Doi [1].

2 The freely jointed chain

From [1].We start with a simple model: a chain consisting of N links, each of length b_0 and able to point in any direction independently of each other. The conformation of the model is represented by $(N+1)$ position vectors $\{R_n\} = \{R_0, R_1, ..., R_N\}$, or by the set of bond vectors $\{r_n\} = (r_1, r_2, ..., r_N)$, where $r_n = R_n - R_{n-1}$.

Since the bonds are independent, the configuration distribution is defined as

$$\Psi(\{\vec{r}_n\}) = \prod_{n=1}^{N} \psi(\vec{r}_n)$$

for vector of constant length b_0

$$\psi(\vec{r}) = \frac{1}{4\pi b_0^2}\delta(|\vec{r}| - b_0)$$

we then normalize such that

$$\int \psi(\vec{r})d\vec{r} = 1$$

2.1 The end-to-end vector

We define the end-to-end vector as $\vec{R} = \vec{R}_N - \vec{R}_0 = \sum_{n=1}^{N} \vec{r}_n$. The quantity $\langle R^2 \rangle$ characterizes the length of the chain. The standard deviation of the end-to-end vector

$$\bar{R} = \langle R^2 \rangle^{0.5} = \langle (R_N - R_0)^2 \rangle^{0.5} = \sqrt{N}b_0$$

since

$$\langle R^2 \rangle = \left\langle \left(\sum_{n=1}^{N}(r_n) \right)^2 \right\rangle = \sum_{n=1}^{N}\sum_{m=1}^{N} \langle r_n r_m \rangle + \sum_{n=1}^{N} \langle r_n^2 \rangle + 2\sum_{m>n}^{N} \langle r_n r_m \rangle = \sum_{n=1}^{N} \langle r_n^2 \rangle = Nb_0^2$$

therefore, $\langle R^2 \rangle^{0.5} = \sqrt{N} b_0$. Here we used $\langle r_n r_m \rangle = \langle r_n \rangle \langle r_m \rangle = 0$. Note that this is just the sum of variances of the bond vectors (each of which has variance of b_0)

3   distribution of the end-to-end vector

We denote $\Phi(R, N)$ as the probability distribution function that the end-to-end vector of a chain of N beads is R.

$$\Phi(R, N) = \int \int \int \ldots \int \delta(R - \sum_{n=1}^{N} r_n) \Psi(\{r_n\})) dr_1 dr_2 \ldots dr_N$$

in short, we take all chain configurations for which the end-to-end vector is exactly R. Using the Fourier transform identity for the delta function

$$\delta(r) = \frac{1}{(2\pi)^3} \int e^{ikr} dk$$

see wikipedia. where, after some manipulation and using polar coordinates for solving the integral, we get

$$\Phi(R, N) = \frac{1}{(2\pi)^3} \int e^{ikR} \left(\frac{\sin(kb)}{kb} \right)^N dk$$

Continuing with a series of approximations to the integral above, we get

$$\Phi(R, N) = (3/2\pi N b^2)^{1.5} \exp(-\frac{3R^2}{2Nb^2})$$

4   The Gaussian Chain

From [1]. We consider a chain whose bond length has a Gaussian distribution

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

in 3D, with bond-length variance $< r^2 >= b^2$. The Gaussian chain represent the model of beads on a strings, with the harmonic potential energy

$$U_0(\{R_n\}) \frac{3k_B T}{2b^2} \sum_{n=1}^{N} (R_n - R_{n-1})^2$$

Since the sum of two Gaussian random variables is again a random variable, it turns out that the distribution of the bond between any two beads m and n is Gaussian with

$$\Phi(R_n - R_m, n - m) = \left[\frac{3}{2\pi b^2 |n - m|} \right]^{3/2} \exp\left[-\frac{3(R_n - R_m)^2}{2|n - m|b^2} \right]$$

and for any m and n

$$< (R_n - R_m)^2 >= |n - m|b^2$$

5   The center of mass

The center of mass is defined as the mean bead position over time

$$cm(t) = \frac{1}{N+1} \sum_{i=0}^{N} R_n(t)$$

therefore, the differential equation for the center of mass is

$$\frac{dcm}{dt} = \frac{1}{N+1} \sum_{i=0}^{N} \frac{dR_i}{dt} = \frac{1}{N+1} \sum_{i=0}^{N} f_n(t)$$

6   Centralizing the chain

The differential equation describing the dynamics R_n in $3D$ is

$$\frac{dR_n}{dt} = -\frac{3D}{b^2} \left(2R_n(t) - R_{n-1}(t) - R_{n+1}(t) \right) + f_n(t)$$

If we shift the chain so that its new center of mass always lays at the origin, we get

$$\frac{d(R_n - cm)}{dt} = -\frac{3D}{b^2} \left(2R_n - R_{n-1} - R_{n+1} \right) + f_n - \frac{1}{N+1} \sum_{i=0}^{N} f_i$$

for such a new system, the new center of mass, cm^* should have zero derivative, indeed.

$$\frac{dcm^*}{dt} = \frac{1}{N+1} \left[\sum_{i=1}^{N} \frac{dR_i}{dt} - (N+1) \sum_{i=0}^{N} \frac{1}{N+1} f_i \right] = \vec{0}$$

Of course, this process is only valid post simulation. It seems not plausible to simulate a random process such that its center of mass remains in one point.

Subtracting the center of mass from the position of each bead should not affect the distribution of bond lengths, and it is indeed obvious to see it by subtracting two consecutive beads equation that the center of mass cancels out. However, the distribution of bead position is affected.

since each f_n is normally distributed with std $\sqrt{2D}$ and mean 0, the random variable $\frac{1}{N} \sum_{i \neq n}^{N} f_n(t)$

[UNFINISHED]

7   The distribution of the bond lengths

The bond length behaves like the central χ^2 with d degrees of freedom, where d is the dimension of the problem. In $3D$, since each $\vec{r}_i = [x_i, y_i, z_i]$ has 3

coordinates, each i.i.d normally distributed with $\langle x_i^2 \rangle = \langle y_i^2 \rangle = \langle z_i^2 \rangle = \frac{b^2}{3}$, the length squared $\|\vec{r_i}\|^2 = x_i^2 + y_i^2 + z_i^2 \sim \chi^2(3)$ with variance $\mu = b^2/3 + b^2/3 + b^2/3 = b^2$ which is the sum of variances.

To calculate the cumulative distribution function (CDF) of the bond length, we use result from the analysis of quadratic forms [3] (chapter 3). From the CDF we will obtain the *survival probability*, which its first moment is the *mean first passage time* for the two ends of the polymer. We start with a definition of a quadratic form in random variables. Let $X = (X_1, X_2, ..., X_n)'$ denote a random vector with mean $\mu = (\mu_1, \mu_2, ..., \mu_n)'$ and covariance matrix Σ. The quadratic form in the random variables X associated with an $n \times n$ symmetric matrix $A = (a_{ij})$ is defined as

$$Q(X) = Q(X_1, X_2, ..., X_n) = X'AX = \sum_{i=1}^{n} \sum_{j=1}^{n} a_{ij} X_i X_j$$

E will denote the expected value, $\mu = E(X)$ and $\Sigma = E[(X - \mu)(X - \mu)'] = Cov(X)$.

The density of the quadratic form $Y = X'AX$, $A = A' \geq 0$, $X \sim N_p(\mu, \Sigma)$ is given by

$$f_p(\lambda; b; y)$$

8   The dynamics of bond length

In simulations we would like to determine Δt such that no 'blow-ups' will occur. For this end, we constrain the mean of squared difference between bond length in consecutive steps to lay below some predefined small value.

The result show that

$$\gamma = \ll \|r_n(t + \Delta t) - r_n(t)\|^2 \gg = \left(\frac{3D\Delta t}{b} \right)^2 + 6D\Delta t$$

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9   Eigenvalues of the Rouse Ring

Connecting bead 1 and N to form a ring, we now search for the eigenvalues of the new *Rouse ring* matrix, R, harboring such a connection. For this end, we have to calculate the determinant of the matrix

$$D_N = |R - \lambda I| = \begin{vmatrix} x & -1 & 0 & 0 & ... & & -1 \\ -1 & x & -1 & 0 & ... & & 0 \\ 0 & -1 & x & -1 & ... & & 0 \\ . & & & & . & & . \\ . & . & & & & . & \\ . & & & -1 & x & -1 & 0 \\ 0 & & & & -1 & x & -1 \\ -1 & . & . & . & 0 & -1 & x \end{vmatrix}_{N \times N}$$

with $x = 2 - \lambda$. We can apply to the matrix of size $(N-1) \times (N-1)$ the same procedure as before and try to solve it recursively. The boundary conditions now read

$$D_1 = x; D_2 = x^2 - 1$$

According to the solution in section **??** and in [2], we have

$$D_{N-1} = \frac{\sin(N\theta)}{\sin(\theta)}$$

The relationship between D_N and D_{N-1} is found by developing the determinant of D_N according to the last column

$$D_N = x(-1)^{2N} D_{N-1} + (-1)(-1)^{2N-1} D^* + (-1)(-1)^{N+1} D^{**} = x D_{N-1} + D^* + (-1)^{N+2} D^{**}$$

with the determinant D^* and D^{**} defined as the minors

$$D^* = \begin{vmatrix} x & -1 & 0 & 0 & \dots & 0 \\ -1 & x & -1 & 0 & \dots & 0 \\ 0 & -1 & x & -1 & \dots & \\ . & & & . & & \\ . & & & . & & \\ . & & & -1 & x & -1 \\ -1 & & & 0 & -1 \end{vmatrix}_{(N-1) \times (N-1)} \qquad D^{**} = \begin{vmatrix} -1 & x & -1 & 0 & \dots & 0 \\ 0 & -1 & x & -1 & \dots & 0 \\ . & & & & . & \\ . & & & & . & \\ . & & & -1 & x & -1 \\ 0 & & & & -1 & x \\ -1 & & & & 0 & -1 \end{vmatrix}_{(N-1) \times (N-1)}$$

We calculate the determinants D^* and D^{**} by minors according to the last row to get

$$D^* = (-1)(-1)^{2N-2} D_{N-2} + (-1)(-1)^{N-1+1}(-1)^{N-2} = (-1)^{2N-1}[D_{N-2} + 1]$$

$$D^{**} = (-1)(-1)^{2N-2}(-1)^{N-2} + (-1)(-1)^{1+N-1} D_{N-2} = (-1)^{3N-3} + (-1)^{N+1} D_{N-2}$$

Therefore,

$$
\begin{aligned}
D_N &= x D_{N-1} + (-1)^{2N-1}[D_{N-2} + 1] + (-1)^{N+2}[(-1)^{3N-3} + (-1)^{N+1} D_{N-2}] \\
&= x D_{N-1} + (-1)^{2N-1}[D_{N-2} + 1] + (-1)^{4N-1} + (-1)^{2N+3} D_{N-2} \\
&= x D_{N-1} + D_{N-2}[(-1)^{2N-1} + (-1)^{2N+3}] + (-1)^{2N-1} + (-1)^{4N-1} \\
&= x D_{N-1} - 2 D_{N-2} - 2
\end{aligned}
$$

Substituting the solution for D_{N-1} and D_{N-2}, we get

$$D_N = \frac{x \sin(N\theta) - 2 \sin((N-1)\theta) - 2 \sin(\theta)}{\sin(\theta)} = 0$$

Further simplification of D_N leads to

$$
\begin{aligned}
D_N &= 2\frac{\cos(\theta)\sin(N\theta) - [\sin((N-1)\theta) + \sin(\theta)]}{\sin(\theta)} \\
&= \frac{2}{\sin(\theta)}[\cos(\theta)\sin(N\theta) - [2\sin(\frac{N\theta}{2})\cos(\frac{(N-2)\theta}{2})]] \\
&= \frac{4}{\sin(\theta)}[\cos(\theta)\sin(\frac{N\theta}{2})\cos(\frac{N\theta}{2}) - \sin(\frac{N\theta}{2})[\cos(\frac{N\theta}{2})\cos(\theta) + \sin(\frac{N\theta}{2})\sin(\theta)]] \\
&= -4\sin^2(\frac{N\theta}{2})
\end{aligned}
$$

Equating $D_N = 0$ we get the solutions

$$
\theta_p = \frac{2\pi p}{N}
$$

for $p = 0, 1, ..., (N-1)$

Therefore, the eigenvalues of the Rouse ring are

$$
\lambda_p = 2(1 - cos(\theta_p)) = 2(1 - cos(2\pi p/N))
$$

Since $\cos(\frac{2\pi\phi}{N}) = \cos(\frac{2\pi(N-\phi)}{N})$, we have eigenvalues multiplicities. In our case, setting $\phi = p$ we have $\cos(\frac{2\pi p}{N}) = \cos(\frac{2\pi(N-p)}{N})$ for $p = 1, 2, 3, .., (N-2)$. For the end-values, $p = 0$ and $p = N - 1$ the eigenvalues are unique.

10   Center of mass diffusion of the rouse ring

By summing the rows of the Rouse ring matrix, we see that the differential equation describing the diffusion of the center of mass does not change in relation to the chain's organization. inner loops in the ring do not change the center of mass diffusion. Therefore

$$
\frac{dcm}{dt} = \frac{1}{N}\sum_{n=1}^{N} g_n
$$

we follow calculation by

11   Simulations

11.1   Choosing Δt

The dynamics of beads is governed by the equation

$$
\frac{dP}{dt} = -\frac{3D}{b^2}RP + \sqrt{2D}f_n
$$

if we represent the Rouse matrix in its diagonal form

$$
R = Q^{-1}\Lambda Q
$$

where Q is an orthonormal matrix with the eigenvectors of R in its columns,and Λ is a diagonal matrix with the Rouse eigenvalues in the diagonal, we get

$$\frac{dP}{dt} = -\frac{3D}{b^2}Q^{-1}\Lambda Q + \sqrt{2D}f$$

multiplying from the left by Q and setting $S = QP$ we get

$$\frac{dS}{dt} = -\frac{3D}{b^2}\Lambda S + \sqrt{2D}Qf$$

11.1.1   The case with no noise

if we omit the noise term and solve for S the numerical scheme is

$$S(t + \Delta t) - S(t) = (-\frac{3D\Delta t}{b^2}\Lambda)S(t)$$

taking the norm of both sides and dividing

$$\frac{\|S(t + \Delta t) - S(t)\|}{\|S(t)\|} = \|(-\frac{3D\Delta t}{b^2}\Lambda)\| = \frac{3D\Delta t}{b^2}\lambda_{max} = \frac{12D\Delta t}{b^2}$$

where for the Rouse matrix $\lambda_{max} = 4$. Demanding that the quotient be smaller than 1 we have

$$\frac{12D}{b^2} \leq 1 \implies \Delta t \leq \frac{b^2}{12D}$$

11.1.2   The case with noise

using the same procedure as above,

$$\frac{\|S(t + \Delta t) - S(t)\|}{\|S(t)\|} = \|(-\frac{3D}{b^2}\Lambda)S + \sqrt{2D}Qf\|/\|S\| \leq (\frac{3D}{b^2}\|\Lambda)\| + \sqrt{2D}\|Qf\|/\|S\|$$

$$=\leq \frac{3D}{b^2}\lambda_{max} + \sqrt{2D}\frac{\|Q\|\|f\|}{\|S\|} = \frac{12D}{b^2} \leq \frac{3D}{b^2}\lambda_{max}\Delta t + \sqrt{2D}\Delta t$$

Demanding that the quotient be smaller than 1 we have

$$\frac{12D}{b^2} \leq 1 \implies \Delta t \leq \frac{b^2}{12D + \sqrt{2D}b^2}$$

11.2   Relaxation time

The relaxation time is determined according to the formula

$$\tau_p = \frac{b^2\Delta t}{12d^2 \sin^2(\frac{p\pi}{2N})} \tag{1}$$

References

[1] M. Doi and S.F. Edwards. *The theory of polymer dynamics.* International series of monographs on physics. Clarendon Press, 1986.

[2] Y-H Lin. *Polymer Viscoelasticity: Basics, Molecular Theories, Experiments and Simulations.* World Scientific, 2011.

[3] Arakaparampil M Mathai and Serge B Provost. *Quadratic forms in random variables: theory and applications.* M. Dekker New York, 1992.