Theory of Polymer Dynamics

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0.1 Introduction

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

0.2 The freely jointed chain

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

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

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

$$\langle R^2 \rangle = \left\langle \left(\sum_{n=1}^{N} (r_n) \right)^2 \right\rangle = \sum_{n=1}^{N}\sum_{m=1}^{N} \langle r_n r_m \rangle + \sum_{n=1}^{N} \langle r_n^2 \rangle + 2\sum_{m>n}^{N} \langle r_n r_m \rangle = \sum_{n=1}^{N} \langle r_n^2 \rangle = N b_0^2$$

therefore, $\langle R^2 \rangle^{0.5} = \sqrt{N} b_0$. Here we used $\langle r_n r_m \rangle = \langle r_n \rangle \langle r_m \rangle = 0$

0.2.1 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.

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

in short, we take all chain configurations for which the end- to-end vector is exactly R.

0.2.2 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

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

0.2.3 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 $\frac{1}{N}\sum_{i\neq n}^{N} f_n(t)$

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0.2.4 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 $\vec{r_i} = [x_i, y_y, z_i]$ 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 mean $\mu = b^2/3 + b^2/3 + b^2/3 = b^2$.

0.2.5 The dynamic 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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0.3 Simulations

0.3.1 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

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

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

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

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

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

0.3.2 Relaxation time

The relaxation time is determined according to the formula

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