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Dynamics of end-to-end loop formation: A flexible chain in the presence of hydrodynamic interaction

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ABSTRACT

Based on the Wilemski–Fixman approach [G. Wilemski, M. Fixman, J. Chem. Phys. 60 (1974) 866], we show that, for a flexible chain in θ solvent, hydrodynamic interaction treated with a pre-averaging approximation makes ring closing faster if the chain is not very short. We also show that the ring closing time for a long chain with hydrodynamic interaction in θ solvent scales with the chain length (N) as $N^{1.5}$, in agreement with the previous renormalization group calculation based prediction by Freidman and O'Shaughnessy [B. Friedman, B. O'Shaughnessy, Phys. Rev. A 40 (1989) 5950].

1. introduction

The dynamics of loop formation in long chain molecules has been a subject of immense interest to experimentalists [1–4] and theoreticians [5–17] for over a decade. Recently, the dynamics of loop formation has found greater importance because of its relevance in biophysics. Advances in single molecule techniques made it possible to monitor the kinetics of loop formation involving biomolecules at the single molecule level [18,19]. Loop formation is a prime step in protein [20] and RNA folding [21]. Also, a measure of the intrinsic flexibility of DNA can be found from the rate at which it undergoes cyclization [18].

Loop formation in polymers is essentially a many-body problem, as a polymer is made of many connected segments, and hence an exact analytical solution is impossible. All the theories of loop closing dynamics are approximate [5,8]. Although many theoretical and simulation attempts have been made to investigate the effect of flexibility [17] and solvent quality [13] on the loop closing dynamics, not much theoretical investigation has been performed to shed light on the effects of hydrodynamic interaction on the loop closing dynamics other than the renormalization group calculation by Freidman et al. [22]. Hydrodynamic interaction which is essentially nonlocal in space has been shown to have profound effects on the dynamics of long chain molecules [23,24]. The rate of translocation of polymer through a nanopore has been shown to be affected by the presence of hydrodynamic interaction [24,25]. Recently, it has been theoretically shown [23] that the breakage rate of stretched polymer tethered to soft bond is enhanced in the presence of hydrodynamic interaction.

In this paper, we investigate the effect of hydrodynamic interaction on the ring closing dynamics of a flexible chain in θ solvent. It is well known that the ring closing time (τ) for a flexible chain without excluded volume and hydrodynamic interaction (a Rouse chain; see [26]) scales with the chain length (N) as N^2 in the Wilemski–Fixman [5] theoretical framework. Here, we use the Zimm model [26] for the polymer, which actually takes care of the hydrodynamic interaction at the simplest possible level. Our calculation shows that hydrodynamic interaction profoundly affects the rate of loop formation and also has a different scaling relation with the chain length, N. The rest of the paper is arranged as follows. In Section 2, the Wilemski–Fixman (WF) theory for the chain closure [5] is briefly discussed. The WF formalism gives a

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prescription to calculate the ring closing time as an integral over a sink–sink time correlation function. Section 3 deals with a brief description of the radial delta function sink which is used later in the calculation of the ring closing time. A time correlation formalism for a flexible chain with and without hydrodynamic interaction is discussed in Section 4. Section 5 presents the results, and 6 is devoted to conclusions.

2. Theory of chain closure

In an stochastic environment, the dynamics of a single polymer chain having reactive end groups is modeled by the following Smoluchowski equation:

$$\frac{\partial P(\{\mathbf{R}\},t)}{\partial t} = LP(\{\mathbf{R}\},t) - kS(\{\mathbf{R}\})P(\{\mathbf{R}\},t). \tag{1}$$

Here, $P(\{R\},t)$ is the distribution function for a chain that has the conformation $\{R\} \equiv R_1, R_2, \ldots R_n$ at time t, where R_i denotes the position of the ith monomer in the chain of n monomers. $S(R)$ is called the sink function; it actually models the reaction between the ends, and thus is usually a function of an end-to-end vector. L is a differential operator, defined as

$$L = D_0 \sum_{i=1}^{n} \frac{\partial}{\partial \mathbf{R}_i} \cdot \left[\frac{\partial}{\partial \mathbf{R}_i} + \frac{\partial U}{\partial \mathbf{R}_i}\right] P(\{\mathbf{R}\},t). \tag{2}$$

Here, D_0 is the diffusion coefficient of the chain, defined as the inverse of the friction coefficient per unit length, and U is the potential energy of the chain. Wilemski and Fixman [5] then derived an approximate expression for the mean first passage time from Eq. (1). This mean first passage time is actually the loop closing time for the chain. The expression for this loop closing time reads

$$\tau = \int_0^\infty \mathrm{d}t \left(\frac{C(t)}{C(\infty)} - 1\right), \tag{3}$$

where $C(t)$ is the sink–sink correlation function, defined as

$$C(t) = \int \mathrm{d}\mathbf{R} \int \mathrm{d}\mathbf{R}_0 S(\mathbf{R}) G(\mathbf{R},t|\mathbf{R}_0,0) S(\mathbf{R}_0) P(\mathbf{R}_0). \tag{4}$$

In the above expression, $G(\mathbf{R},t|\mathbf{R}_0,0)$ is the Green function, or the conditional probability that a chain with end-to-end distance R_0 at time $t = 0$ has end-to-end distance R at time t; $P(R_0)$ is the equilibrium distribution of the end-to-end distance since the chain was in equilibrium at time $t = 0$. $S(R)$ is the sink function [27–29], which depends only on the separation between the chain ends. We would like to comment that Eq. (3) is valid in the limit of infinite sink strength, as this closing time is nothing but the mean first passage time [30,31].

Now, it is obvious that knowledge of the Green function, $G(\mathbf{R},t|\mathbf{R}_0,0)$, is a prerequisite for calculating the sink–sink correlation function $C(t)$ and hence the closing time τ. In the case of a flexible chain, the Green function and the end-to-end probability distribution function are known and Gaussian.

For a flexible chain, the Green function is given by

$$G(\mathbf{R},t|\mathbf{R}_0,0) = \left(\frac{3}{2\pi \langle R^2\rangle_{eq}}\right)^{3/2} \frac{1}{\left(1-\phi^2(t)\right)^{3/2}} \times \exp\left[-\frac{3(\mathbf{R}-\phi(t)\mathbf{R}_0)^2}{2\langle R^2\rangle_{eq}(1-\phi^2(t))}\right], \tag{5}$$

where

$$\phi(t) = \frac{\langle \mathbf{R}(t)\cdot\mathbf{R}(0)\rangle_{eq}}{\langle R^2\rangle_{eq}} \tag{6}$$

is the normalized end-to-end vector correlation function for the chain. The above ensemble average is taken over the initial equilibrium distribution for end-to-end vector $P(\mathbf{R}_0)$.

Similarly, the end-to-end equilibrium distribution for a flexible chain with $L_1 = Nb^2$ (b is the size of the each monomer and N is the number of monomers) at time $t = 0$ is given by (see Refs. [26,15])

$$P(R_0) = \left(\frac{3}{2\pi L_1^2}\right)^{3/2} \exp\left[-\frac{3R_0^2}{2L_1^2}\right]. \tag{7}$$

With the above Gaussian functions, the sink–sink correlation function can be written as a radial double integral.

$$\begin{aligned} C(t) &= \left(\frac{3}{2\pi L_1^2}\right)^3 \frac{1}{\left(1-\phi^2(t)\right)^{3/2}} \int_0^\infty 4\pi R^2 S(R)\,\mathrm{d}R \int_0^\infty 4\pi R_0^2 S(R_0)\,\mathrm{d}R_0 \\ &\quad \times \exp\left[-\frac{3}{2L_1^2}\frac{(R^2+R_0^2)}{(1-\phi^2(t))}\right] \frac{\sinh\left[(3\phi(t)RR_0)/(L_1^2(1-\phi^2(t)))\right]}{(3\phi(t)RR_0)/(L_1^2(1-\phi^2(t)))}. \end{aligned} \tag{8}$$

The above integral can be evaluated analytically for some specific choice of the sink functions. For a radial delta function sink, the above integral can be evaluated analytically.