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Brownian dynamics simulation of diffusion-limited polymerization of rodlike molecules: Anisotropic translation diffusion

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Step-growth polymerization of rodlike molecules is qualitatively different from flexible molecules, because rotational and translational diffusion limitations result in a rate of reaction which is dependent on the molecular weights of the reacting oligomers. An understanding of the kinetics of polymerization is important for the manufacture of such polymers which have many applications. The theoretical basis and computation details of the pairwise Brownian dynamics method [Northrup et al., J. Chem. Phys. 80, 1517 (1984)] to determine the effective rate constant for reaction between rodlike molecules are presented. In this method the effective rate constant is obtained in terms of the first visit flux (for which an analytical expression is derived) and the reaction probability (which is obtained using Brownian dynamics simulations). A simple derivation for finite domain correction for the simulations is presented, which explicitly accounts for the spatial and orientational variations of the reaction probability. Computations are presented to validate assumptions of the technique. The computed rate constants decrease with decreasing rotational diffusivity to approach an asymptotic value, and decrease with decreasing values of the translational diffusivity perpendicular to the rod axis. The computations show that the effective rate constants obtained for the case of dilute solutions when ratio of the translational diffusivities perpendicular and parallel to the rod axis is equal to 1/5, is close to the case of isotropic translational diffusion. © 1998 American Institute of Physics. [S0021-9606(98)51312-8]

I. INTRODUCTION

Polymerization of rodlike molecules is qualitatively different from flexible molecules. Such polymers are typically synthesized by a step growth polymerization process,1-3 and the slow rotational diffusion and translational diffusion of the oligomers strongly limits the rate of polymerization once the oligomers become long enough.1,4,5 Thus the rate of reaction is dependent on the molecular weight of the reacting oligomers, in contrast to flexible polymers for which the reactivity is equal for all oligomers. Diffusion control affects both the average molecular weight and the molecular weight distribution,5 and consequently the properties of the polymer produced. An understanding of the kinetics of polymerization is of particular relevance to the manufacture of rodlike polymers (e.g., Kevlar) which find wide applications as anchoring ropes, reinforcement in aircrafts, composites for sporting goods, bullet proof vests, etc., due to their high strength and modulus.

Previous analytical and computational studies6-8 have provided some insight into the diffusion controlled polymerization of rodlike molecules, considering various simplifying assumptions. In this paper we present a computational technique for the analysis of diffusion controlled reactions between rodlike molecules based on Brownian dynamics simulations. The method, first proposed by Northrup et al.9 involves the evaluation of the second-order reaction rate constant by considering the diffusion of a single molecule in the neighborhood of a second test molecule. The method has several advantages over other numerical techniques (e.g., finite element method) and we list some of these below. The mathematical formulation of the problem is relatively simple even for complex boundary conditions. The effective rate constant is obtained directly without first obtaining the concentration field. The effective rate constants for different reaction conditions can be obtained from a single simulation. From a purely computational viewpoint, the method requires no inversion of large matrices, and thus memory requirements are minimal. Furthermore the computations can be easily parallelized, and in fact different parts of the computation can be carried out on different computers. Finally, another attractive feature of the method is the possibility of sequentially refining the results: Any single computation gives a value of the rate constant with a particular error, and repeating the computation N times results in reduction of the error by a factor 1/√N. This reveals the main disadvantage of the method which appears to be the slow convergence of the error. Time consuming computations would be required for highly accurate results. The flexibility and simplicity of the method, however, makes it well suited for the problem under study.

In a previous work we presented the pairwise Brownian dynamics method for the analysis of diffusion-limited polymerization of rodlike molecules, but with the simplification of isotropic translational diffusion.10 Here we extend the analysis to the case of anisotropic translational diffusion of the molecules. The extension is nontrivial since the basic theory for the Brownian dynamics must be modified, as must several computational procedures. The main objective of the
current work is to present the theoretical and computational details of the pairwise Brownian dynamics method for the case of rodlike polymers, and to illustrate the method by means of sample computations.

The mathematical formulation of the problem is given in the following section followed by the theory of pairwise Brownian dynamics and computational details. Results and discussion are given in Sec. V and conclusions in Sec. VI.

II. PROBLEM FORMULATION

We consider the diffusion controlled reaction between rodlike molecules in solution when the molecules require near-parallel alignment for reaction. Based on the approximations given elsewhere, the problem essentially reduces to the reaction of a rod with a stationary spherical sink, with the reaction conditions \(|r|<R\) and \(\theta<\theta_r\), where \(\theta\) is the angle made by the molecule axis with the axis of symmetry of the sink, and \(r\) is the position of the center of mass of the diffusing rod (Fig. 1). A fraction of the molecules that satisfy the reaction conditions actually react, as determined by the surface reaction rate constant at the sink surface \((k')\).

The steady-state diffusion equation in the absence of an interaction potential between the molecules and assuming axisymmetry (i.e., number density is independent of \(\phi\)) is

\[
0 = D_\perp \nabla^2 C + (D_\parallel - D_\perp) \mathcal{R}^2 C + D_r \mathcal{R}^2 C,
\]

where \(C\) is the number density, \(\mathcal{R} = u \cdot \nabla\), \(u = \mathcal{R} \times \partial f / \partial \mathcal{R}\) and \(u\) is a unit vector aligned along the rod axis. The diffusivities \(D_\perp\) (translational diffusivity perpendicular to the rod axis), \(D_\parallel\) (translational diffusivity parallel to the rod axis), and \(D_r\) (rotational diffusivity) are assumed to be constant since the total number concentration at any position is nearly constant. Expressions for the diffusivities as a function of the number concentration are available, and we use these results to estimate parameter values. The first term on right hand side of Eq. (1) corresponds to the isotropic component of the translational diffusion, the second term to the anisotropic translational diffusion along the rod axis and the third term to the rotational diffusion.

The boundary condition at the reaction surface \((r=R)\) is given by

\[
-D_0 \frac{\partial C}{\partial r} = \begin{cases} k' C \quad \text{for } \theta<\theta_c, \\ 0 \quad \text{for } \theta>\theta_c, \end{cases}
\]

where \(k'\) is the surface reaction rate constant and \(D_0\) is the radial component of the translational diffusivity given by

\[
D_0 = D_\perp + (D_\parallel - D_\perp) \{ \cos \theta \cos \theta_r \\ \sin \theta \sin \theta_r \cos (\phi - \phi_r) \}.
\]

The far field boundary conditions, and the symmetry boundary conditions for the problem are

\[
C = C_\infty, \quad r \to \infty,
\]

\[
\frac{\partial C}{\partial \theta} = 0, \quad \theta = 0,
\]

\[
\frac{\partial C}{\partial \theta} = 0, \quad \theta = \pi/2,
\]

\[
\frac{\partial C}{\partial \theta_r} = 0, \quad \theta_r = 0,
\]

\[
\frac{\partial C}{\partial \theta_r} = 0, \quad \theta_r = \pi/2.
\]

The second-order effective rate constant is then obtained as

\[
k_{\text{eff}} = 4 \pi R^2 k' \int_0^{\pi/2} \int_0^{\theta_r} (C(R, \theta_r, \theta)/C_\infty) \times \sin \theta d\theta \sin \theta_r d\theta_r.
\]

The homogeneous rate constant \((k_H)\), i.e., the rate constant in the absence of diffusional resistance, is related to the surface reaction rate constant \((k')\) by

\[
k' = \frac{k_H}{4 \pi R^2 (1 - \cos \theta_c)}.
\]

The above equation is obtained by putting \(C(R) = C_\infty\) in Eq. (6). Rescaling the variables as \(\tilde{C} = C/C_\infty\), \(\tilde{r} = r/R\), \(\tilde{k}_{\text{eff}} = k_{\text{eff}}/(4 \pi R D_r)\) and \(\tilde{D}_0 = D_0/D_\perp\) the diffusion equation in dimensionless form is

\[
\gamma \tilde{\nabla}^2 \tilde{C} + (1 - \gamma) \tilde{\mathcal{R}}^2 \tilde{C} + \frac{1}{\tilde{s}} \tilde{\mathcal{R}}^2 \tilde{C} = 0,
\]

with the boundary conditions at the reaction surface given by

\[
k' = \frac{k_H}{4 \pi R^2 (1 - \cos \theta_c)}.
\]
where \(D_0 = \gamma + (1 - \gamma) \cos(\theta - \theta_c)\).

The effective rate constant in dimensionless form is then

\[ k_{\text{eff}} = \alpha \int_0^{\pi/2} \int_0^{\pi/2} C(1, \theta_r, \theta) \sin \theta d\theta \sin \theta_r d\theta_r. \]

The above scaling reveals that the rate constant for the reaction depends on the following dimensionless parameters

\[ \gamma = \frac{D_1}{D_\parallel}, \quad s = \frac{D_\parallel}{R^2 D_r}, \quad \alpha = \frac{k^* R}{D_\parallel}, \]

in addition to the critical orientation \(\theta_c\). The anisotropy of the translational diffusion is reflected by \(\gamma\) which falls to very small values \(O(10^{-2})\) with increasing molecular lengths; \(s\) is a measure of the rotational diffusion resistance which is \(O(10^6)\) for cases of practical interest. The parameter \(\alpha\) is measure of the intrinsic reaction rate, and depends on the system under consideration. Values for the critical orientation are not available, but previous estimates\(^5\) indicate \(\theta_c \sim O(10^{-2})\).

We consider next the theory underlying the pairwise Brownian dynamics method to numerically obtain the effective rate constant \((k_{\text{eff}})\) for the problem defined in this section.

### III. THEORY

At steady state, the reaction flux is equal to the total normal flux of molecules through any surface enclosing the reactive sink. Considering a spherical surface of radius \(r = b\) (Fig. 1), the effective rate constant is obtained as

\[ k_{\text{eff}} = \frac{4 \pi b^2}{C_\infty} \int_0^{r} j(b, \theta_r, \theta) \sin \theta d\theta \sin \theta_r d\theta_r, \]

\[ = \frac{4 \pi \sigma^2}{C_\infty} \langle j \rangle, \]

where \(j(b, \theta_r, \theta)\) is the radial component of the translational diffusion flux to the surface \(r = b\) and \(\langle \cdot \rangle\) denotes an average taken over all orientations and positions on surface \(r = b\). The basic idea of the pairwise Brownian dynamics (PWBD) approach is to write the radial flux as

\[ j(b, \theta_r, \theta) = j_0(b, \theta_r, \theta) \beta_0(\theta_r, \theta), \]

where \(j_0\) is the first visit flux (i.e., the flux of particles starting from \(r = \infty\) that visit the surface \(r = b\) for the first time) and \(\beta_0(\theta_r, \theta)\) is the reaction probability (i.e., the fraction of particles of starting from \(r = b\) that react rather than escape to \(r = \infty\)).

The first visit flux can be obtained by solving the diffusion equation for the rods [Eq. (1)] with the following boundary conditions

\[ C = 0, \quad r = b, \quad \text{(14a)} \]
\[ C = C_\infty, \quad r = \infty. \quad \text{(14b)} \]

Since the boundary conditions are isotropic, \(C = C(r)\) and the diffusion equation [Eq. (1)] becomes

\[ \frac{d}{dr} \left( r^2 \frac{dC}{dr} \right) = 0. \quad \text{(15)} \]

The concentration profile is then

\[ C = C_\infty \left[ 1 - \frac{b}{r} \right], \quad \text{(16)} \]

and the first visit flux is given by

\[ j_0 = \frac{D_0 C_\infty}{b}. \quad \text{(17)} \]

Thus, in this case, the concentration field is isotropic, however, the flux \(j_0\) is not. Using the above result the rate constant is obtained as

\[ k_{\text{eff}} = 4 \pi b (D_0 \beta_0). \quad \text{(18)} \]

To calculate the effective rate constant we require the reaction probability \((\beta_0(\theta_r, \theta))\) which is obtained numerically by means of Brownian dynamics simulations. Simulations, however, can be carried out only for a finite domain and we consider next a method to correct for this.

#### Finite domain correction

Defining the bounded domain reaction probability \(\beta_0\) as the fraction of molecules that react rather than escape to the surface \(r = q\), we obtain a relationship between the finite domain and infinite domain reaction probabilities.

The infinite domain reaction probability \((\beta_\infty)\) can be expressed in terms of fluxes at \(r = b\) as

\[ \beta_\infty(\theta_r, \theta) = \frac{j(b, \theta_r, \theta)/j(b, \theta_r, \theta) + j_\infty(b, \theta_r, \theta)}{j(b, \theta_r, \theta)/j(b, \theta_r, \theta) + j_\infty(b, \theta_r, \theta)} = \frac{\int_{\theta_r}^{\theta} (j_\infty(b, \theta_r, \theta) + j_{\text{eq}}(b, \theta_r, \theta))}{\int_{\theta_r}^{\theta} (j_\infty(b, \theta_r, \theta) + j_{\text{eq}}(b, \theta_r, \theta))}, \]

where \(j_\infty\) is the reaction flux and \(j_{\text{eq}}\) is the escape flux both for a finite domain. A balance of fluxes at \(r = b\) gives

\[ j_0(b, \theta_r, \theta) = j(b, \theta_r, \theta) + j_\infty(b, \theta_r, \theta), \quad \text{(20)} \]

so that the flux of molecules arriving at \(r = b\) is split into a reaction flux \((j)\) and an escape flux \((j_{\text{eq}})\).

Similarly, in the case of a finite domain we can write

\[ \beta_\infty(\theta_r, \theta) = \frac{\int_{\theta_r}^{\theta} (j_{\text{eq}}(b, \theta_r, \theta) + j_{\text{eq}}(b, \theta_r, \theta))}{\int_{\theta_r}^{\theta} (j_{\text{eq}}(b, \theta_r, \theta) + j_{\text{eq}}(b, \theta_r, \theta))}, \quad \text{(21)} \]

where \(j_\infty\) is the reaction flux and \(j_{\text{eq}}\) is the escape flux both for a finite domain. A balance of fluxes at \(r = b\) gives

\[ j_0^* = j_\infty + j_{\text{eq}}, \quad \text{(22)} \]

where \(j_0^*\) is the first visit flux for a finite domain. The boundary conditions for obtaining the first visit flux in this case are

\[ C^* = 0, \quad r = b, \quad \text{(23a)} \]
\[ C^* = C_q, \quad r = q. \quad \text{(23b)} \]

As in the case of the infinite domain the concentration field is isotropic, and using Eq. (1) we get
\[ C^* = C_q - \frac{C_q b q}{(q-b)} \left( \frac{1}{r} - \frac{1}{q} \right) \]  
\[ j_0^* = \frac{D_0 C_q q}{(q-b) b}. \]  
(24)  
(25)

In the above equations \( C_q \) is the unknown (uniform) concentration at \( r = q \).

The average reaction flux in an infinite domain is given by

\[ \langle j \rangle = \langle j_0 \beta_\infty \rangle, \]  
\[ \text{using Eqs. (19) and (20). Substituting for } j_0 \text{ using Eq. (17) we have} \]  
\[ \langle j \rangle = \frac{C_\infty}{b} \langle D_0 \beta_\infty \rangle = \chi(D_0 \beta_\infty). \]  
(26)  
(27)

Similarly, the average reaction flux for a finite domain is given by

\[ \langle j^* \rangle = \langle j_0^* \beta_\infty \rangle = \frac{C_q b q}{(q-b) b} \langle D_0 \beta_\infty \rangle = \chi^* \langle D_0 \beta_\infty \rangle. \]  
(28)

Choosing \( C_q \) such that the finite and infinite domain reaction fluxes are equal \( \langle j^* \rangle = \langle j \rangle \) we get

\[ \chi^* \langle D_0 \beta_\infty \rangle = \chi(D_0 \beta_\infty). \]  
(29)

In the above equation the unknown quantities are \( \langle D_0 \beta_\infty \rangle \) and \( \chi^* \). Thus we need an additional equation, and this is obtained by putting the ratio of the average escape fluxes \( \langle j_0 \rangle/\langle j_0 \beta_\infty \rangle = \Omega \). From Eqs. (20) and (22) we have

\[ \langle j_0 \beta_\infty \rangle = \langle j_0 \rangle - \langle j \rangle \]  
(30)

and

\[ \langle j_0 \rangle = \langle j_0^* \rangle - \langle j^* \rangle. \]  
(31)

From the above equations we get

\[ \Omega = \frac{\langle j_0 \beta_\infty \rangle}{\langle j_0 \rangle} = \frac{\chi(D_0) - \chi(D_0 \beta_\infty)}{\chi^*(D_0) - \chi^*(D_0 \beta_\infty)}. \]  
(32)

Using Eq. (29) and simplifying we obtain

\[ \langle D_0 \beta_\infty \rangle = \frac{\langle D_0 \rangle \langle D_0 \beta_\infty \rangle}{\langle D_0 \rangle - \langle D_0 \beta_\infty \rangle} \Omega. \]  
(33)

To utilize Eq. (33) we need to estimate \( \Omega \). Northrup et al. proposed using the value obtained when the escape fluxes are isotropic for \( r > b \). This gives

\[ \Omega = 1 - b/q. \]  
(34)

Here we generalize the above result to the case when the diffusive flux may not be isotropic for \( r > b \) as

\[ \Omega = 1 - a(b/q) + \cdots. \]  
(35)

Thus if \( \langle D_0 \beta_\infty \rangle \) is computed for two or more values of \( b/q \), \( \langle D_0 \beta_\infty \rangle \) can be calculated, and the dimensionless rate constant is then

\[ k_{\text{eff}} = 4\pi b \langle D_0 \beta_\infty \rangle = \frac{4\pi b \langle D_0 \rangle \langle D_0 \beta_\infty \rangle}{\langle D_0 \rangle - \langle D_0 \beta_\infty \rangle} \Omega. \]  
(36)

In the limit \( (b/q) \to 0 \) we obtain \( \Omega \to 1 \) and \( \beta_\infty = \beta_\infty \) so that the above equation reduces to an identity as expected. Further, for isotropic translation diffusion \((D_1 = D_\perp = D_\parallel)\) we recover our earlier result.

The overall approach presented above is more accurate than that of Northrup et al. who proposed to calculate \( k_{\text{eff}} \) by putting

\[ k_{\text{eff}} = \langle j_0 \rangle \langle \beta_\infty \rangle 4\pi b^2 / C_\infty. \]  
(37)

This approximation need not be made in our analysis.

Using the rescaled variables defined earlier, the effective rate constant in dimensionless form is

\[ \tilde{k}_{\text{eff}} = \frac{\bar{b} \langle \bar{D}_0 \rangle \langle \bar{D}_0 \beta_\infty \rangle}{\langle \bar{D}_0 \beta_\infty \rangle + (\langle \bar{D}_0 \rangle - \langle \bar{D}_0 \beta_\infty \rangle)} \Omega, \]  
(38)

and the ratio of escape fluxes in dimensionless form is \( \tilde{\Omega} = 1 - a(\bar{b} / \bar{q}) \) where \( \bar{b} = b l \) and \( \bar{q} = q / R \).

**IV. COMPUTATIONS**

In this section, we detail the computation of the average reaction probability \( \langle \bar{D}_0 \beta_\infty \rangle \) of molecules starting at \( r = b \) in the presence of an absorbing boundary at \( r = q \). The main steps in the computation are: (i) Generation of a Brownian trajectories, (ii) calculation of the survival probability of the molecule during each step of a trajectory, and (iii) averaging the reaction probability over appropriate initial conditions.

**A. Generation of a Brownian trajectory**

The Brownian motion of a rodlike molecule is simulated by subjecting the molecule to small random, spatial, and angular displacements over small time steps. The probability density for the displacements is obtained by solving the following diffusion equation

\[ \frac{\partial P}{\partial t} = D_r \nabla^2 P + (D_\perp - D_\parallel) J^2 P + D_r \beta^2 P, \]  
(39)

subject to the initial condition

\[ P(r, u, 0) = \delta(r - r_0) \delta(u - u_0). \]  
(40)

In addition, appropriate symmetry and far-field boundary conditions apply.

Since the total number density of molecules is nearly constant, the rotational diffusion is independent of the translational diffusion and is given by

\[ \frac{\partial P_u}{\partial t} = D_r \beta^2 P_u. \]  
(41)

For \( \theta = \Delta \theta \ll 1 \) the distribution is

\[ P_u(\theta, \phi, t) = \frac{1}{4\pi D_r t} \exp \left\{ - \frac{\theta^2 + \theta_0^2 - 2 \theta \theta_0 \cos(\phi - \phi_0)}{4D_r t} \right\}, \]  
(42)

and for \( \Delta \theta \ll \theta \) the distribution is Gaussian

\[ P_u(\theta, \phi, t) = \frac{1}{4\pi D_r t} \exp \left\{ - \frac{\Delta \theta^2 - \sin^2 \theta_0 \Delta \phi^2}{4D_r t} \right\}, \]  
(43)
where \((\theta_0, \phi_0)\) are the orientation angles at the start of the step, and \(\Delta \theta\) and \(\Delta \phi\) are the angular displacements.

Based on the above, we put

\[ P = P_u(u, t)P_r(r, u, t), \]  

so that the governing equation for the probability density for translational diffusion becomes

\[ \frac{\partial P_r}{\partial t} = D_\perp \nabla^2 P_r + (\Delta \theta - D_\perp) \frac{\partial^2 P_r}{\partial \theta^2} + D_r \frac{\partial^2 P_r}{\partial \phi^2}. \]  

We further separate the translational diffusion probability density into an isotropic and anisotropic part as

\[ P_r = P_{ri}P_{ra}, \]  

and we assume these to be independent so that

\[ \frac{\partial P_{ri}}{\partial t} = D_\perp \nabla^2 P_{ri}, \]  

and

\[ \frac{\partial P_{ra}}{\partial t} = (D_\theta - D_\perp) \frac{\partial^2 P_{ra}}{\partial \theta^2} + D_r \frac{\partial^2 P_{ra}}{\partial \phi^2}. \]  

In making the above decomposition we take \(P_{ri} = P_{ri}(r_i, t)\) where \(r_i\) the isotropic part of the displacement and \(P_{ra} = P_{ra}(u, \eta, t)\) where \(\eta\) is the additional anisotropic displacement. The total displacement is then \(r = r_i + \eta u\).

Neglecting the rotational contribution to \(P_{ra}\) (which is reasonable for small displacements), and defining \(\eta\) as a curve tangent to the rod axis during anisotropic diffusion, we have on neglecting the curvature of \(\eta\)

\[ \frac{\partial P_{ra}}{\partial t} = (D_\theta - D_\perp) \frac{\partial^2 P_{ra}}{\partial \theta^2}. \]  

The above equation describes the motion of the molecule along its axis, when the change in orientation of the molecule is small. Thus the probability density for \(\Delta \eta\) is also Gaussian but with diffusivity \((D_\theta - D_\perp)\).

The probability densities for rotation and translation in dimensionless form are given by

\[ P_u(\theta, \phi, \tau) = \frac{s}{4\pi \tau} \exp \left[ -\frac{(g - g_0)^2 + (h - h_0)^2}{4 \tau} \right], \]  

\[ \Delta \theta \ll \tau \ll 1, \]  

\[ P_u(\theta, \phi, \tau) = \frac{s}{4\pi \tau} \exp \left[ -\frac{(\Delta \theta)^2 + \sin^2 \theta_0 (\Delta \phi)^2}{4 \tau} \right], \]  

\[ \Delta \theta \ll \sigma \ll \tau \ll 1, \]  

\[ P_r(t, \tau) = \frac{1}{4\pi \tau \gamma} \exp \left[ -\frac{(\Delta \bar{\eta})^2 + (\Delta \bar{\phi})^2}{4 \tau \gamma} \right], \]  

\[ \bar{P}_r(\Delta \bar{\eta}, \tau) = \frac{1}{4\pi (1 - \gamma) \tau} \exp \left[ -\frac{(\Delta \eta)^2}{4 (1 - \gamma) \tau^2} \right], \]  

where \(\tau = tD_\perp R^2\), \(g = \theta \sin \phi\), \(h = \theta \cos \phi\), \(g_0 = \theta_0 \sin \phi_0\) and \(h_0 = \theta_0 \cos \phi_0\). All distances are made dimensionless with respect to \(R\).

Based on the above analysis, we use the following algorithm for computation of Brownian steps in the trajectory:

(i) Calculate \((\theta, \phi)\) using Eqs. (50) or (51).

(ii) Calculate the isotropic displacements \((\Delta \bar{\eta}, \Delta \bar{\phi})\) using a Gaussian distribution with diffusivity \(\gamma\) [Eq. (52)].

(iii) Obtain a Gaussian displacement \(\Delta \bar{\eta}\) with diffusivity \((1 - \gamma)\) [Eq. (53)]. Calculate the anisotropic displacement using

\[ \Delta \bar{\eta}_a = \Delta \bar{\eta} \cos \theta_m, \]  

\[ \Delta \bar{\phi}_a = \Delta \bar{\eta} \sin \theta_m \cos \phi_m, \]  

\[ \Delta \bar{\eta}_a = \Delta \bar{\eta} \sin \theta_m \sin \phi_m, \]  

where \(\theta_m = (\theta_0 + \Delta \theta/2)\) and \(\phi_m = (\phi_0 + \Delta \phi/2)\). In step (iii) the average values of \(\theta\) and \(\phi\) for a step are used in calculating the anisotropic part of the displacement. This is equivalent to assuming that \(\theta\) and \(\phi\) vary linearly with \(\eta\) during the step, and that \(\Delta \theta\) and \(\Delta \phi \ll 1\).

We use a variable time step in all these computations which in dimensionless form is given by

\[ \tau = \tau_{min} \frac{\bar{r}}{R_{c}}, \]  

where \(\tau_{min}\), \(\bar{r}\), and \(R_{c}\) are the predetermined constants which are obtained as explained elsewhere.\(^{10}\)

**B. Computation of the single-step survival probability**

The reaction probability \((\beta_q)\) for a single trajectory is given by

\[ \beta_q = 1 - \prod_k \omega_k, \]  

where \(\omega_k\) is the survival probability of the molecule for a single Brownian step. The survival probability can be obtained from the probability densities for diffusion near a reflective or reactive surface, and we detail the derivation of the expression to calculate \(\omega_k\) in this section.

Considering very small time steps so that \(\omega_k = 1\) except very close to the reactive surface, we can neglect the curvature of the surface, and the translational diffusion can be assumed to be one-dimensional. The diffusion equation in this case is

\[ \frac{\partial P}{\partial t} = D_r \frac{\partial^2 P}{\partial x^2} + D_0 \frac{\partial^2 P}{\partial x^2}, \]  

where \(D_0(\theta, \theta_0)\) is given by Eq. (3). Since the rotational diffusion is unaffected by the translational diffusion we write

\[ P = P_u P_x, \]  

so that the governing equation for \(P_x\) is

\[ \frac{\partial P_x}{\partial t} = D_0 \frac{\partial^2 P_x}{\partial x^2} + D_r \frac{\partial^2 P_x}{\partial x^2}. \]  

We require to obtain the probability density for a molecule initial at \(x = d\) for the cases of reflective and reactive boundaries at \(x = 0\), and the boundary conditions for each case are given below.
\begin{align}
\bar{P}_{\text{refl}}(x,0|d) &= \delta(x-d), \\
\frac{\partial \bar{P}_{\text{refl}}}{\partial x} &= 0, \quad x=0, \\
\bar{P}_{\text{refl}}(x,0, x \to \infty, \\
\bar{P}_{\text{rxn}}(x,0|d) &= \delta(x-d), \\
D_0 \frac{\partial \bar{P}_{\text{rxn}}}{\partial x} &= k' \bar{P}_{\text{rxn}}, \quad x=0, \\
\bar{P}_{\text{rxn}}(x,0, x \to \infty, \\
\end{align}

If we assume that the contribution of rotational diffusion to \( P_x \) [last term of Eq. (59)] is small, we can assume \( D_0 \) to be nearly constant, and the governing equations are essentially the same as that for isotropic diffusion. The results are then

\begin{align}
\bar{P}_{\text{refl}}(x,t|d) &= \bar{P}_f(x,t|d) + \bar{P}_f(x,t|-d), \\
\bar{P}_{\text{rxn}}(x,t|d) &= \bar{P}_{\text{refl}}(x,t|d) + \bar{P}_2(x,t|d) \\
\end{align}

where

\begin{align}
\bar{P}_f(x,t|d) &= \frac{1}{\sqrt{4 \pi D_0 m t}} \exp \left\{ -\frac{(x-d)^2}{4 D_0 m t} \right\} \\
\end{align}

and

\begin{align}
\bar{P}_2(x,t|d) &= -\frac{k'}{D_0 m} \exp \left\{ \frac{k'}{D_0 m} (k't + x + d) \right\} \\
&\quad \times \text{erfc} \left\{ \frac{2k't + x + d}{\sqrt{4 D_0 m t}} \right\}, \\
\end{align}

where \( D_0 m = D_0 (\theta_m, \theta_m) \).

The above equations are similar to those of Allison et al.\textsuperscript{11} for the case of no direct charge. Only here we use an average value of the translational diffusivity \( D_0 m = D_0 (\theta_m, \theta_m) \).

The fraction of particles starting from \( x=d \) and present in \((x,x+d x)\) at time \( t \) that do not react (i.e., the survival probability) is

\begin{equation}
\omega_x = \frac{\bar{P}_{\text{rxn}}(x,t|d)}{\bar{P}_{\text{refl}}(x,t|d)},
\end{equation}

Denoting \( \mathbf{r}' \) and \( \mathbf{r} \) as the position vectors of the molecule before and after a Brownian step, we have

\begin{equation}
d = |\mathbf{r}'| - R; \quad x = |\mathbf{r}| - R,
\end{equation}

so that the probability densities can be easily calculated.

The probability densities in dimensionless form are

\begin{align}
\bar{P}_{\text{refl}}(\bar{x},\bar{t}|\bar{d}) &= \bar{P}_f(\bar{x},\bar{t}|\bar{d}) + \bar{P}_f(\bar{x},\bar{t}|-\bar{d}), \\
\bar{P}_{\text{rxn}}(\bar{x},\bar{t}|\bar{d}) &= \bar{P}_{\text{refl}}(\bar{x},\bar{t}|\bar{d}) + \bar{P}_2(\bar{x},\bar{t}|\bar{d}), \\
\bar{P}_f(\bar{x},\bar{t}|\bar{d}) &= \frac{1}{\sqrt{4 \pi D_0 m \tau}} \exp \left\{ -\frac{(\bar{x}-\bar{d})^2}{4 D_0 m \tau} \right\},
\end{align}

C. Initialization of trajectories

When the rotational diffusivity is small, only those molecules which are initiated close to the critical orientation for reaction (\( \theta_c \)) have the possibility of reacting. Thus molecules should be initiated in the range

\begin{equation}
\theta \in (0, \theta_c + \delta),
\end{equation}

where \( \delta \) is chosen such that \( \beta_c (\theta_c + \delta, \theta_c) < \epsilon \), and \( \epsilon \) is a preset limit. \( \delta \) is evaluated as \( \delta = A \tilde{g}/\sqrt{s} \) where \( A \) is a predetermined constant. Similarly molecules should be initiated with their angular position

\begin{equation}
\theta_c \in (0, \pi/2),
\end{equation}

\( \beta_c (\theta_c, \theta) \) can be computed at equally spaced intervals in the above ranges, and then numerically integrated.

V. RESULTS AND DISCUSSION

Brownian dynamic simulations were carried out for different values of the ratio of perpendicular to parallel translational diffusivities of the rod molecule (\( \gamma \)), and the rotational diffusion resistance (\( s \)). All the computations were carried out for a fixed value of the initiation radius (\( b \)) and four different values of the truncation radius (\( \tilde{q} \)). All the results reported here are the averages of five iterations, carried out for 500 trajectories for \( s = 10^8, 10^9, \) and \( 10^{10}; \) \( \gamma = 1.0 \) and 0.5, 750 trajectories for \( s = 10^7; \) \( \gamma = 1.0 \) and 0.5) and 2000 trajectories (for \( s = 10^5, 10^6, 10^7, \) and \( 10^{10}; \) \( \gamma = 0.1 \)) respectively. The value of the critical orientation angle for reaction used was \( \theta_c = 0.01 \) radians.

Figure 2 shows the Brownian trajectory of a molecule for three different values of \( \gamma \) equal to 1.0, 0.1, and 0.01, respectively. The molecule is initiated at \( \bar{r} = b, \theta_p = \pi/2 \) with orientation angle \( \theta = 0 \), and \( s = 10^8 \) so that rotational diffusion is small. For \( \gamma = 1.0 \), the translational diffusion is iso-
tropic and the molecule initiated at $\bar{b}$, exhibits a significant transverse motion before it collides with the truncation sphere $\bar{q}$. The translational diffusion is independent of rotational diffusion in this case. For smaller values of $\gamma$ however, transverse motion is greatly restricted, even though rotational diffusion contributes to it.

Figure 3 shows the variation of $\beta_q$ with $\theta$ for the molecules initiated at different $\theta_i$ values for $s = 10^6$ for the different values of $\gamma$ studied. All the graphs show that the reaction probability $\beta_q$ levels off to zero once the initial rod orientation ($\theta$) exceeds the critical angle $\theta_c$ by a significant amount. Further, for $\gamma = 1$ (isotropic translational diffusion) there is no significant change in the reaction probability with $\theta_i$ as expected [Fig. 3(a)]. For $\gamma = 0.1$, in contrast, there is a significant variation with $\theta_i$ [Fig. 3(c)]. The results for $\gamma = 0.5$, which corresponds to the diffusion of rodlike molecules in dilute solutions, has only a slight variation of the reaction probability with $\theta_i$ [Fig. 3(b)].

For small values of $\beta_q$, as obtained here, Eq. (38) simplifies to

$$\bar{k}_\text{eff} = \frac{\bar{b} \langle \tilde{D}_0 \beta_q \rangle}{1 - \alpha (\bar{b}/\bar{q})},$$  

(74)

For all the values of $\gamma$ considered, an appropriate value of the initiation radius ($\bar{b}$) is chosen by plotting graphs of $\bar{b} \langle \tilde{D}_0 \beta_q \rangle$ with $\bar{b}/\bar{q}$ for different values of $\bar{b}$. One such plot is shown in Fig. 4 for $\gamma = 0.5$ and $s = 10^8$. In all the cases straight lines are obtained in accordance with Eq. (74). Furthermore, the intercept ($\bar{k}_\text{eff}$) is the same for all the lines. A sufficiently large value of $\bar{b}$ is taken in each case so that the rate constant computed was independent of $\bar{b}$. The values of initiation radius used are $\bar{b} = 1.10$ for $\gamma = 1.0$ and 0.5, and $\bar{b} = 12.0$ for $\gamma = 0.1$. Figure 4 also shows that the magnitude of slope of the lines ($\alpha \bar{k}_\text{eff}$) increases with $\bar{b}$, and the constant $\alpha \neq 1$ (in the equation $\Omega = 1 - \alpha (\bar{b}/\bar{q})$; refer figure caption for values of $\alpha$). This shows that the flux is not isotropic in the region $r > \bar{b}$ though it approaches this limit with increasing $\bar{b}$. The proposed method, however, can be used for smaller $\bar{b}$ (which is computationally less intensive) and still give accurate results.

Figure 5 shows the variation of $\bar{b} \langle \tilde{D}_0 \beta_q \rangle$ with $\bar{b}/\bar{q}$ for

FIG. 3. Variation of reaction probability ($\beta_q$) with the initial orientation angle of the rod molecule ($\theta$) for different $\theta_i$ values ($s = 10^6$, $\alpha = 1.0$), (a) $\gamma = 1.0$, (b) $\gamma = 0.5$, and (c) $\gamma = 0.1$.

FIG. 4. Variation of $\bar{b} \langle \tilde{D}_0 \beta_q \rangle$ with $\bar{b}/\bar{q}$ for $\alpha = 1.0$, $\theta_i = 0.01$ rad, rotational diffusion resistance $s = 10^8$ and different values of the initiation radius $\bar{b}$ for $\gamma = 0.5$. Error bars give the standard deviation of the computed values and the lines are obtained by a least-square fit. $\square$: $\bar{b} = 1.05$, $\times$: $\bar{b} = 1.10$, $\triangle$: $\bar{b} = 2.0$; ($a = 0.67, 0.69, and 0.87$ for $\bar{b} = 1.05, 1.10$, and 2.0, respectively).

FIG. 5. Variation of $\bar{b} \langle \tilde{D}_0 \beta_q \rangle$ with $\bar{b}/\bar{q}$ for $\alpha = 1.0$, $\theta_i = 0.01$ rad, for different values of the rotational diffusion resistance ($s$) and $\gamma = 0.1$. Error bars give the standard deviation of the computed values and the solid lines are obtained by a least-square fit. $\triangle$: $s = 10^4$, $\times$: $s = 10^6$, $\square$: $s = 10^8$, and $+$: $s = 10^{10}$.
\[ k_{\text{eff}} \times 10^6 \]

\[ \log(s) \]

FIG. 6. Effect of rotational diffusional resistance \((s)\) on the dimensionless effective rate constant \((k_{\text{eff}})\) for \(\alpha = 1.0, \theta = 0.01\) rad and different values of \(\gamma\). Error bars give the standard deviation of the computed values. For \(\gamma = 1.0\): □ denote the computed result and the solid line gives the results for isotropic translational diffusion case,\(^{10}\) ×: \(\gamma = 0.5\), and Δ: \(\gamma = 0.1\).

\(\gamma = 0.1\) for different values of rotational diffusion \(s\). Straight lines are obtained for all the cases, in accordance with Eq. (74). The value of the intercept (which is equal to the rate constant) decreases with increase in the rotational diffusion resistance \((s)\), as there is a reduction in the rotational diffusivity values. Similar trends are obtained for \(\gamma = 0.5\) and \(\gamma = 1.0\).

A comparison of the effect of rotational diffusion resistance \((s)\) on the dimensionless effective rate constant for different \(\gamma\) values is presented in Fig. 6. Also shown in the graph are the results obtained for isotropic translational diffusion.\(^{10}\) There is good agreement between these results and the results obtained from the anisotropic diffusion computations for \(\gamma = 1\); this serves as a confirmation of the technique used. The rate constant decreases significantly with increase in \(\gamma\) values, indicating the importance of translational diffusion perpendicular to the rod axis on the process, particularly for slow rotational diffusion. All the curves become nearly independent of the rotational diffusion at high values of the parameter \(s\). In this limit, the reaction flux is entirely due to translational diffusion of the appropriately oriented molecules \((\theta < \theta_d)\) to the sink surface, and molecular rotation plays a negligible role. The predictions for \(\gamma = 0.5\) are close to those of \(\gamma = 1.0\). Thus, for dilute solutions, for which \(\gamma = 0.5\), the assumption of nearly isotropic diffusion suggested in our earlier study\(^{10}\) is reasonable.

VI. CONCLUSIONS

The theoretical basis and computational details of the pairwise Brownian dynamics method to determine the effective rate constant for reaction between rodlike molecules are presented. The effective rate constant is obtained in terms of the first visit flux (for which an analytical expression is derived) and the reaction probability (which is obtained computationally). A simple derivation for the correction for a finite domain is presented which explicitly accounts for the spatial and orientation dependence of the reaction probability. An empirical function \((\bar{\Omega})\) with a linear dependence on the ratio of the initiation radius \((\bar{b})\) to the truncation radius \((\bar{q})\) is used to calculate the ratio of escape fluxes for a finite and infinite domain. Probability densities are derived for generation of Brownian trajectories and survival probability. The latter are similar in form to the expressions obtained by Lamm and Schulten\(^{12}\) for an isotropic particle near a flat surface.

Computations for \(\gamma = 1\) give results identical to those obtained for computations for isotropic translational diffusion. Computations also show a linear dependence of \(\bar{Q}\) on \(\bar{b}/\bar{q}\) as assumed in the theory; the magnitude constant of proportionality \((\alpha)\) is less than unity; and approaches unit magnitude only for large \(\bar{b}\). The rate constants computed for different initiation radii \((\bar{b})\) are the same further validating the assumed functionality of \(\bar{\Omega}\). Computed values of the rate constant decrease to achieve an asymptotic value at high values of the rotational diffusion resistance \((s)\), and decrease with decrease in the translational diffusivity perpendicular to the rod axis. The results for \(\gamma = 0.5\) close to those of \(\gamma = 1\) indicating that assuming isotropic translational diffusion for dilute solutions gives reasonable predictions of the rate constants.

The results presented here are useful for predicting the dynamic evolution of the molecular weight distribution of a reacting mixture of rodlike molecules, for example, in the polymerization of poly(p-phenylene terephthalamide).\(^{1,4,5}\) Typical values of the constants \((s, \gamma, \alpha)\) required to compute the effective rate constant for the range of values of the dimensionless polymer length \(L\) are given in Table I. As length increases \(s\) increases due to a sharp reduction in the rotational diffusivity and \(\gamma\) decreases because of the fall in the translational diffusivity perpendicular to the rod axis \((D_\perp)\). However, \(\alpha\) remains nearly constant. The translational diffusivities \((D_1\) and \(D_2\)) and the rotational diffusivity \((D_\gamma)\) are calculated using the expressions given in Refs. 13–15. The dimensionless intrinsic reactivity \((\alpha)\) is calculated by using the homogeneous rate constant \((k_\gamma \approx 4.33 \times 10^{-3} \text{ m}^3 \text{mol}^{-1} \text{s}^{-1})\) obtained by fitting theoretical predictions of a population balance analysis for the molecular weight distribution to experimental results.\(^{16}\) We propose to present these results in a separate work.\(^{17}\)

<table>
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<th>(\bar{L})</th>
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\(^{10}\) A simple derivation for the correction for a finite domain is presented which explicitly accounts for the spatial and orientation dependence of the reaction probability. An empirical function \((\bar{\Omega})\) with a linear dependence on the ratio of the initiation radius \((\bar{b})\) to the truncation radius \((\bar{q})\) is used to calculate the ratio of escape fluxes for a finite and infinite domain. Probability densities are derived for generation of Brownian trajectories and survival probability. The latter are similar in form to the expressions obtained by Lamm and Schulten\(^{12}\) for an isotropic particle near a flat surface.

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17 J. Srinivasalu Gupta and D. V. Khakhar, Kinetics of polymerization of rodlike molecules under quiescent conditions (in preparation).