Theory of Diffusion-Controlled Reactions in Polymers under Flow

Glenn H. Fredrickson*

Departments of Chemical Engineering and Materials, University of California, Santa Barbara, California 93106

Ludwik Leibler

Laboratoire de Physico-Chimie Theorique, ESPCI, 75231 Paris Cedex 05, France

Received October 16, 1995; Revised Manuscript Received January 11, 1996[⊗]

ABSTRACT: We extend the theoretical framework of de Gennes for treating diffusion-controlled reactions in complex fluid systems to situations in which a steady, linear flow is externally imposed. Consideration is restricted to systems that are dilute in reactive sites and for which the reaction occurs instantaneously and irreversibly when a pair of sites are brought in close contact. Illustrative calculations are presented for the long-time intermolecular trapping rate constant in polymer melts where a small fraction of chains have a single terminally attached reactive group. Both shear and extensional flows are considered, as well as Rouse and reptation models of chain dynamics. Extensions of the analysis may have applications in modeling free radical termination processes and reactive blending.

I. Introduction

Chemical reactions that occur in complex fluid systems are frequently under diffusion control due to the reduced mobility of reactive sites—particularly when such sites are tethered to macromolecules or other supramolecular assemblies. For example, the familiar termination reactions that occur during free radical polymerization are controlled by the mobilities of the macroradical species present, and dramatic effects can occur (e.g., the Trommsdorff effect) when these mobilities are reduced by chain growth and entanglements at the late stages of reaction.[1] Another classic example is the cyclization reaction between pendant groups at the two ends of a polymer chain, where internal Brownian dynamics of the macromolecule are critical in establishing the cyclization rate.[2] Besides such cases involving an actual chemical reaction, a variety of phenomena arising from purely physical interactions can also be mathematically described by the framework used to treat diffusion-controlled reactions, e.g. flocculation of polymeric or colloidal systems or photophysical processes such as fluorescence quenching.[3]

Interest in diffusion-controlled reactions in *simple* fluid systems dates back to Smoluchowski.[4] He showed that in a very dilute suspension of diffusing (spherical) reactants and after a short induction period, the decay of the spatially-averaged reactant number density, $\rho(t)$, satisfies

$$\mathrm{d}\rho/\mathrm{d}t = -k_{\mathrm{s}}\rho^2 \tag{1.1}$$

where the effective reaction rate coefficient, k_{s}, is given by

$$\mathrm{k}_{\mathrm{s}} = 4\pi D a \tag{1.2}$$

In deriving this expression, it was assumed that the reaction occurs instantaneously and irreversibly when two reactants are separated by a distance less than a, the so-called “capture radius”, and D is the diffusion coefficient associated with the relative motion of the two reactants. (If the reactants are all identical, then $D = 2D_0$, where D_0 is the self-diffusion coefficient of a single reactant). Smoluchowski used generalizations of this result to build a successful theory of colloidal aggregation phenomena.[5]

In subsequent years, the Smoluchowski formula has been generalized in many important ways. One active area of research has been to explore corrections to eq 1.2 associated with larger concentrations of reactive particles.[6,7] Short-time corrections to eq 1.2 have also been explored in some detail,[8,9] as well as corrections associated with potential interactions[10] and hydrodynamic interactions[11] between approaching reactants. Alternatives to the purely absorbing boundary condition (instantaneous reaction) assumed by Smoluchowski have also been examined.[12]

Theoretical methods have also emerged in recent years to treat diffusion-controlled reactions among sites attached to polymers. This area of research was pioneered by Wilemski and Fixman,[13] and important conceptual advances were made by Doi,[14] de Gennes,[15] and others.[16] Most recently, Friedman and O’Shaughnessy[17] have developed a unifying framework to describe both intra- and intermolecular reactions over a broad range of reactive polymer concentrations.

In spite of this considerable body of work on diffusion-controlled reactions in polymers, and in view of the fact that commercial reacting polymer systems are often subjected to processing flows, e.g. reactive blending, it is surprising that very little attention has been paid to the effect of *flow* on inter- and intramolecular reaction rates in polymers.[18] Convective transport of reactive sites would generally be expected to increase intermolecular reaction rates, although intramolecular reactions might actually be slowed due to conformational extension under flow.

While the literature on flow effects in reacting polymer systems is quite limited, reasonably complete results are available for *small* molecule reactants in steady linear flows of the form

$$\mathbf{u}(\mathbf{r}) = \mathbf{\Gamma}\cdot\mathbf{r} \tag{1.3}$$

where Γ_{ij} is a traceless uniform velocity gradient tensor. The associated “modified Smoluchowski” problem re-

---

[⊗] Abstract published in *Advance ACS Abstracts,* March 1, 1996.

0024-9297/96/2229-2674$12.00/0

quires the solution of the following convected-diffusion equation exterior to a sphere of radius a[19]

$$D\nabla^2 c(\mathbf{r}) - \mathbf{u}(\mathbf{r})\cdot\nabla c(\mathbf{r}) = 0 \tag{1.4}$$

subject to absorbing boundary conditions at the sphere surface, $c(r=a) = 0$, and uniform concentration at infinity, $c(r\rightarrow\infty) = 1$. (The reaction rate is obtained by integrating the diffusive flux over the surface of the capture sphere at $r = a$.) The solution of this problem has been most fully explored in the context of an analogous problem of convective heat transfer caused by flow past a sphere,[20-22] although some differences exist due to the assumed form of the velocity field near the particle.[23]

The results of these studies can be summarized by referring to a dimensionless Peclet number for mass transfer

$$Pe = \kappa a^2/D \tag{1.5}$$

where κ is the characteristic scale of the velocity gradient tensor Γ_{ij} (e.g. in the case of simple shear flow in the $x-y$ plane, $\kappa = \Gamma_{xy}$ is the shear rate). For weak flows, $Pe \ll 1$, the leading correction to the Smoluchowski reaction rate eq 1.2 is given by

$$k = k_s[1 + \alpha Pe^{1/2} + O(Pe)] \tag{1.6}$$

where α is a constant prefactor whose value depends on the type of flow (form of Γ_{ij}). The nonanalytic dependence on Peclet number is a consequence of the fact that imposition of flow is a singular perturbation to the Smoluchowski problem. The unperturbed problem has a diffusive field that decays algebraically ($\sim 1/r$) at large distances r; however, an arbitrarily weak linear flow causes $O(1)$ changes to this concentration field at distances exceeding $(D/\kappa)^{1/2}$. Thus, the problem is fundamentally changed when $\kappa \neq 0$; i.e. flow is a singular perturbation.

At large Peclet number, $Pe \gg 1$ (but where fluid inertia can still be neglected), a diffusive boundary layer is set up and one can again infer results from the heat transfer studies for the asymptotic reaction rate. The situation is a bit more complicated in this regime, however, depending on the type of flow and boundary conditions assumed at the sphere surface. If the flow around the sphere has no closed streamlines,[20] then one can argue quite generally that the asymptotic scaling behavior is

$$k/k_s \sim Pe^{1/3} \qquad Pe \rightarrow \infty \tag{1.7}$$

However, if closed streamlines exist, such as in the case of simple shear flow past a freely rotating sphere (with no-slip conditions at the sphere surface),[24] the asymptotic behavior is quite different:

$$k/k_s \sim 1 \qquad Pe \rightarrow \infty \tag{1.8}$$

The numerical prefactors in both cases will depend on the specific type of flow. It is important to note, however, that in problems of diffusion-controlled reaction in polymers it is generally not appropriate to impose non-slip boundary conditions on the velocity field at the capture sphere surface.[23] This can be crucial, because, e.g. in the case of simple shear flow, it is precisely these boundary conditions that produce closed streamlines and result in the behavior summarized in eq 1.8. In contrast, if the linear shear flow is taken to be unperturbed at the surface of the capture sphere (the assumption made throughout the present paper), then no closed streamlines exist and the asymptotic behavior is changed to that given in eq 1.7.

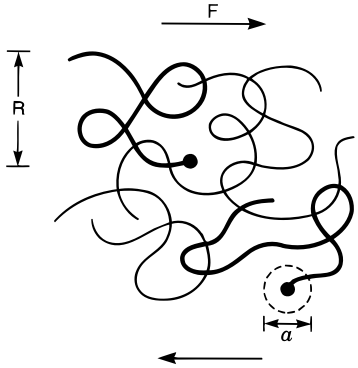

Figure 1. Reacting polymer system studied in the present paper consisting of a melt of linear polymer chains, with a small fraction of the chains possessing one terminally attached raective site (solid dot). When two sites approach within a "capture radius" a, an instantaneous and irreversible reaction occurs. The melt is assumed to be monodisperse with degree of polymerization N and equilibrium radius-of-gyration R. A linear flow (F) is imposed on the system and is characterized by a uniform velocity gradient tensor Γ_{ij}.

In the present paper, we consider the effect of flows of the form of eq 1.3 on the rates of diffusion-controlled reactions in *polymers*. For concreteness, we restrict attention to the simple case of polymer melts where a small fraction of the chains have a *single* terminally attached reactive group (Figure 1). We also assume for simplicity that all the labeled chains are identical in size, mobility, and reactivity. In section II we outline a general theoretical approach, modeled after that of de Gennes,[15] that can be used to analyze such problems. Although the approach is also capable of dealing with *intramolecular* reactions between groups attached to the same macromolecule, we defer such studies to a future paper. In sections III and IV we apply the formalism to examine intermolecular reaction kinetics in entangled and unentangled melts under both weak and strong flow conditions. Finally, in section V we summarize our results and discuss additional applications of the formalism.

Our weak flow results can be anticipated on the basis of eq 1.6 for small molecules. Studies of intermolecular reaction rates in polymer melts under quiescent conditions[15] have established that the analog of the Smoluchowski formula, eq 1.2, for polymeric systems is

$$k = \alpha_1 D_0 R \tag{1.9}$$

where D_0 is the center-of-mass diffusivity of a labeled polymer and the chain radius-of-gyration, R, plays the role of the capture radius. The numerical value of the constant prefactor, α_1, is approximately insensitive to the details of the mechanism assumed for the chain dynamics, e.g. Rouse (unentangled) or reptation (entangled) (see section III below). A particularly interesting feature of eq 1.9 is the dissappearance of a microscopic (monomer size scale) capture radius from the formula. This results from the fact that the rate-controlling step in intermolecular reactions in polymers (at low concentrations of reactive chains) is the slow diffusive process of bringing the centers-of-mass of two reactive coils together. Once this has occurred, the combination of the reactive sites occurs on a short time scale dictated by the internal-mode Brownian dynamics of the chains.

Since R clearly plays the role of the capture radius a in polymeric systems under quiescent conditions, one might anticipate that in the presence of flow an appropriate Peclet number for polymers would be

$$Pe = \kappa R^2/D_0 \sim \kappa\tau \tag{1.10}$$

where τ is the longest internal relaxation time of a chain. (Note that the final expression in eq 1.10 is often referred to as a Deborah number). By reference to eq 1.6, we might expect that the first correction term to eq 1.9 for weak flows would be of the form

$$k \approx \alpha_1 D_0 R[1 + \alpha_2(\kappa\tau)^{1/2}] \tag{1.11}$$

where α_2 is a second constant that depends on the flow type. Indeed, in section III we shall see that this expression is appropriate for both entangled and nonentangled melts in weak linear flows of the form given in eq 1.3. Explicit results will be given for α_1 and α_2 in cases of weak shear and uniaxial extensional flows and we argue that, with proper interpretation of D_0 and τ, the formulas hold equally well for entangled and nonentangled melts.

By strict analogy with eq 1.7 for small molecules, one might expect that strong flows ($\kappa\tau \gg 1$) with no closed streamlines would lead to reaction rate coefficients of the form $k \sim D_0R(\kappa\tau)^{1/3}$, where we have again replaced the capture radius by R and the Peclet number by the Deborah number $\kappa\tau$. However, due to the conformational changes that result from the application of strong flows and the associated changes in chain dynamics, this formula is not found to universally hold. Indeed, we find distinct results for the asymptotic reaction rate ($\kappa\tau \to \infty$) in cases of entangled and unentangled chains.

II. General Approach

In the present section we closely follow the formalism developed by de Gennes,[15] but explicitly incorporate an externally imposed linear flow described by eq 1.3. The system under consideration consists of n macromolecules (or other complex objects, e.g. micelles), each with a single reactive site at some precise location. At present we do not specify that location, but in later calculations assume linear chains with terminal reactive sites. The n reactive macromolecules are placed in contact with otherwise identical, but unlabeled, macromolecules to form a melt of volume V. We shall ultimately only be concerned with the thermodynamic limit: $n \to \infty$, $V \to \infty$, $\rho = n/V$ constant.

An object of primary importance is the pair distribution function defined by

$$\psi(\mathbf{r},\mathbf{r}';t) = \sum_{i}^{n}\sum_{j(\neq i)}^{n}\langle\delta(\mathbf{r}-\mathbf{r}_i(t))\delta(\mathbf{r}'-\mathbf{r}_j(t))\rangle \tag{2.1}$$

where $\mathbf{r}_i(t)$ is the position of the ith reactive group at time t and $\langle ...\rangle$ denotes an ensemble average with an appropriate probability distribution of reactant positions at time t, $P(\{\mathbf{r}_i\},t)$. Physically, $\psi(\mathbf{r},\mathbf{r}';t)$ represents the joint probability density that any of the n reactive groups lies near position $\mathbf{r}$ and any of the remaining $n - 1$ reactive groups lies near position $\mathbf{r}'$ at time t. At $t = 0$, we assume that the initial ensemble consists of a random distribution of unreacted particles, $P(\{\mathbf{r}_i\},0) = 1/V^n$. Thus,

$$\psi(\mathbf{r},\mathbf{r}';0) = \rho^2 \tag{2.2}$$

A simple model for the time evolution of $\psi(\mathbf{r},\mathbf{r}';t)$ can be written in the symbolic form

$$L\psi(\mathbf{r},\mathbf{r}';t) = -Q(|\mathbf{r}-\mathbf{r}'|)\psi(\mathbf{r},\mathbf{r}';t) \tag{2.3}$$

where L is a differential operator describing the evolution of ψ associated with the diffusive and convective motion of reactive sites near $\mathbf{r}$ and $\mathbf{r}'$. The object $Q(|\mathbf{r}-\mathbf{r}'|)$ is a sink function that describes the rate of disappearance of reactants due to pairwise combination. Following de Gennes,[15] we adopt a simple model for the sink function:

$$Q(r) = \begin{cases} Q_0, & r \le a \\ 0, & r > a \end{cases} \tag{2.4}$$

Thus, two reactive sites that approach within a "capture radius" a react and dissappear from the system at a uniform rate Q_0. No reaction takes place between sites separated by distances larger than a. The capture radius a will be assumed throughout to be a monomer size scale, although its precise value will prove unimportant, since it does not enter rate expressions like eq 1.11.

Models for L depend on the type of dynamics appropriate for the macromolecules of interest. For spherical, rigid particles undergoing *independent* Brownian dynamics in the linear flow eq 1.3, L takes the form

$$L = \frac{\partial}{\partial t} - D_0{\nabla_{\mathbf{r}}}^2 - D_0{\nabla_{\mathbf{r}'}}^2 + \mathbf{r}\cdot\mathbf{\Gamma}^{\mathrm{T}}\cdot\nabla_{\mathbf{r}} + \mathbf{r}'\cdot\mathbf{\Gamma}^{\mathrm{T}}\cdot\nabla_{\mathbf{r}'} \tag{2.5}$$

where $\mathbf{\Gamma}^{\mathrm{T}}$ is the transpose of the velocity gradient tensor $\mathbf{\Gamma}$ and D_0 is the self-diffusion coefficient of a single particle. For reactive sites attached to the ends of flexible polymers, simple diffusion is not appropriate; instead, a generalized non-Markovian operator is required:

$$\begin{aligned} Lf(\mathbf{r},\mathbf{r}';t) \equiv [\partial/\partial t + \mathbf{r}\cdot\mathbf{\Gamma}^{\mathrm{T}}\cdot\nabla_{\mathbf{r}} + \\ \mathbf{r}'\cdot\mathbf{\Gamma}^{\mathrm{T}}\cdot\nabla_{\mathbf{r}'}]f(\mathbf{r},\mathbf{r}';t) - \int_0^t \mathrm{d}\tau \int \mathrm{d}\mathbf{x} \int \mathrm{d}\mathbf{y}\, \mathbf{D}(\mathbf{y}-\mathbf{x},t-\tau) : \\ \nabla_{\mathbf{x}}\nabla_{\mathbf{x}}[f(\mathbf{x},\mathbf{r}';\tau)\delta(\mathbf{y}-\mathbf{r}) + f(\mathbf{r},\mathbf{x};\tau)\delta(\mathbf{y}-\mathbf{r}')] \end{aligned} \tag{2.6}$$

In this expression, $D_{ij}(\mathbf{r},t)$ is a nonlocal generalized diffusion tensor describing the Brownian dynamics of a single site, the form of which depends on the symmetry of the flow and whether the polymers are long enough to be entangled. As in eq 2.5, we assume that, regardless of the complexity of the single particle motion, sites attached to different polymers move *independently*.

Actually constructing the tensor $D_{ij}(\mathbf{r},t)$ for an assumed model of chain dynamics is a rather difficult task that involves projecting the dynamics of the large number of degrees of freedom associated with the conformations of a macromolecule onto an equation of motion for the three spatial coordinates of the reactive site. de Gennes,[15] however, made the important observation that for the problem at hand (albeit without flow) it is actually easier to avoid constructing L and work instead with its inverse, an integral operator. We adopt this approach below and show that the addition of an external flow presents no additional difficulties. For this purpose, it is convenient to introduce a Green's function that is the kernel of the operator L^{-1}:

$$LG^{(2)}(\mathbf{r},\mathbf{r}_0;\mathbf{r}',\mathbf{r}'_0;t) = \delta(\mathbf{r}-\mathbf{r}_0)\delta(\mathbf{r}'-\mathbf{r}'_0)\delta(t) \tag{2.7}$$

This two-particle propagator, $G^{(2)}(\mathbf{r},\mathbf{r}_0;\mathbf{r}',\mathbf{r}'_0;t)$, represents the conditional probability density that two reactive sites with positions $\mathbf{r}_0$ and $\mathbf{r}'_0$ at time $t = 0$ are found at $\mathbf{r}$ and $\mathbf{r}'$, respectively, a time t later. Because the dynamical evolution described by L conserves the number of reactive particles, $G^{(2)}$ is normalized according to

$$\int \mathrm{d}\mathbf{r} \int \mathrm{d}\mathbf{r}'\, G^{(2)}(\mathbf{r},\mathbf{r}_0;\mathbf{r}',\mathbf{r}'_0;t) = 1 \tag{2.8}$$

We continue to assume that the dynamics of reactive sites attached to different macromolecules are uncorrelated, owing to the low concentration of sites. This allows the factorization of $G^{(2)}$ into a product of single-particle Green's functions:

$$G^{(2)}(\mathbf{r},\mathbf{r}_0;\mathbf{r}',\mathbf{r}'_0;t) = G(\mathbf{r},\mathbf{r}_0;t)G(\mathbf{r}',\mathbf{r}'_0;t) \tag{2.9}$$

Next, we use eq 2.7 to invert the differential operator L appearing in eq 2.3. This leads to the integral equation

$$\psi(\mathbf{r},\mathbf{r}';t) = \int \mathrm{d}\mathbf{r}_0 \int \mathrm{d}\mathbf{r}'_0\, [\rho^2 G(\mathbf{r},\mathbf{r}_0;t)G(\mathbf{r}',\mathbf{r}'_0;t) - \int_0^t \mathrm{d}\tau\, G(\mathbf{r},\mathbf{r}_0;t-\tau)G(\mathbf{r}',\mathbf{r}'_0;t-\tau)Q(|\mathbf{r}_0-\mathbf{r}'_0|)\psi(\mathbf{r}_0,\mathbf{r}'_0;\tau)] \tag{2.10}$$

where we have incorporated the initial condition eq 2.2.

It is now convenient to recall some general properties of space–time correlation functions in steady flows of the form given in eq 1.3. As discussed, for example, by Onuki and Kawasaki,[25] *equal-time* correlation functions retain the usual translational invariance in the thermodynamic limit. Thus, the pair distribution function $\psi(\mathbf{r},\mathbf{r}';t)$ is a function only of the relative coordinate $\mathbf{r} - \mathbf{r}'$:

$$\psi(\mathbf{r},\mathbf{r}';t) = \psi(\mathbf{r}-\mathbf{r}';t) \tag{2.11}$$

The single-particle Green function $G(\mathbf{r},\mathbf{r}_0;t)$, in contrast, is proportional to the two-time correlation function $\langle\delta(\mathbf{r}-\mathbf{r}_i(t))\delta(\mathbf{r}_0-\mathbf{r}_i(0))\rangle$ and has a distinct dependence on $\mathbf{r}$ and $\mathbf{r}_0$ imposed by Galilean invariance[25]

$$G(\mathbf{r},\mathbf{r}_0;t) = G(\mathbf{r}-\exp(\boldsymbol{\Gamma}t)\cdot\mathbf{r}_0;t) \tag{2.12}$$

where $\exp(\boldsymbol{\Gamma}t)$ is the familiar exponential matrix defined by its Taylor series about the origin. With these specific forms for ψ and G, eq 2.10 can be reduced to the following form by a change of integration from $\mathbf{r}_0$ to $\mathbf{x} \equiv \mathbf{r}_0 - \mathbf{r}'_0$:

$$\psi(\mathbf{r}-\mathbf{r}';t) = \rho^2 - \int \mathrm{d}\mathbf{x} \int \mathrm{d}\mathbf{r}'_0 \int_0^t \mathrm{d}\tau\, Q(x)\psi(\mathbf{x};\tau)G(\mathbf{r}-\exp[(t-\tau)\boldsymbol{\Gamma}]\cdot(\mathbf{x}+\mathbf{r}'_0);t-\tau)G(\mathbf{r}'-\exp[(t-\tau)\boldsymbol{\Gamma}]\cdot\mathbf{r}'_0;t-\tau) \tag{2.13}$$

In deriving this expression, we have also invoked the normalization of G implied by eq 2.8 and made use of the following identity (which holds for the specific forms of $\boldsymbol{\Gamma}$ considered in the present paper and ensures the Jacobian of the transformation is unity):

$$\det[\exp(-\boldsymbol{\Gamma}t)] = 1 \tag{2.14}$$

Our next step is to integrate the variable $\mathbf{y} \equiv \mathbf{r} - \mathbf{r}'$ on both sides of eq 2.13 over a volume $V_a = 4\pi a^3/3$, i.e. the "capture sphere". Defining

$$\Psi(t) = \int_{V_a} \mathrm{d}\mathbf{y}\, \psi(\mathbf{y};t) \tag{2.15}$$

this leads to

$$\Psi(t) = \rho^2 V_a - Q_0 \int_{V_a} \mathrm{d}\mathbf{x} \int_{V_a} \mathrm{d}\mathbf{y} \int \mathrm{d}\mathbf{r}'_0 \times \int_0^t \mathrm{d}\tau\, \psi(\mathbf{x};\tau)G(\mathbf{y}+\mathbf{r}'-\exp[(t-\tau)\boldsymbol{\Gamma}]\cdot(\mathbf{x}+\mathbf{r}'_0);t-\tau)G(\mathbf{r}'-\exp[(t-\tau)\boldsymbol{\Gamma}]\cdot\mathbf{r}'_0;t-\tau) \tag{2.16}$$

where we have inserted the form of the sink function given in eq 2.4.

Up to this point, our various manipulations have been exact. It is now appropriate to introduce an approximation, invoking the fact that the capture radius a is a monomeric length scale much smaller than the characteristic root-mean-square displacement, $d_{\mathrm{rms}}(t)$, that controls the effective reaction rate. Because the integrals over $\mathbf{x}$ and $\mathbf{y}$ are restricted to a sphere of radius a about the origin, to leading order for $a/d_{\mathrm{rms}}(t) \to 0$ we can eliminate $\mathbf{x}$ and $\mathbf{y}$ in the first factor of G appearing on the right hand side of eq 2.16. Corrections for finite a could evidently be systematically developed by Taylor expansion. With this simplification, eq 2.16 reduces to

$$\Psi(t) = \rho^2 V_a - Q_0 V_a \int_0^t \mathrm{d}\tau\, \Psi(\tau)S(t-\tau) \tag{2.17}$$

where

$$S(t) \equiv \int \mathrm{d}(\mathbf{d}(t))\, [G(\mathbf{d}(t);t)]^2 \tag{2.18}$$

and

$$\mathbf{d}(t) \equiv \mathbf{r} - \exp(\boldsymbol{\Gamma}t)\cdot\mathbf{r}_0 \tag{2.19}$$

is the difference between the position of a reactive site at time t and the position that the site would have at time t if it moved only by advection (i.e. diffusion was suppressed). We subsequently refer to $\mathbf{d}(t)$ as the "diffusive particle displacement".

The quantity $S(t)$ plays a central role in both the present theory and earlier theories for quiescent systems.[15] Physically, $S^{-1}(t)$ is proportional to the average volume swept out in a time t by a *single* reactive site undergoing an arbitrarily complex Brownian motion. An important distinction with earlier work is that when a flow is present, only the average *diffusive* displacement enters the calculation of this volume and the diffusion becomes *anisotropic*.

Another useful physical interpretation can be ascribed to $S(t)$. We note that $G(\mathbf{d}(t);t)$ can generally be written in the form

$$G(\mathbf{d}(t);t) = (\det \mathbf{M}(t))^{-1/2} g(\mathbf{d}(t)\cdot\mathbf{M}^{-1}(t)\cdot\mathbf{d}(t)) \tag{2.20}$$

where the mean-squared diffusive displacement tensor, $M_{ij}(t)$, is defined by

$$M_{ij}(t) \equiv \langle d_i(t) d_j(t)\rangle \tag{2.21}$$

and $g(x)$ is a dimensionless scaling function that describes the shape of the distribution of $\mathbf{d}(t)$. The prefactor on the right hand side of eq 2.20 ensures proper normalization of G. For certain models of reactive site dynamics, e.g. sites attached to Rouse chains, $\mathbf{d}(t)$ is a Gaussian random variable and G has the explicit form

$$G_{\mathrm{gaus}}(\mathbf{d}(t);t) = (2\pi)^{-3/2}(\det \mathbf{M}(t))^{-1/2} \exp[-(1/2)\mathbf{d}(t)\cdot\mathbf{M}^{-1}(t)\cdot\mathbf{d}(t)] \tag{2.22}$$

For this specific case, the integral in eq 2.18 leads to

$$S_{\mathrm{gaus}}(t) = 2^{-3}\pi^{-3/2}(\det \mathbf{M}(t))^{-1/2} \tag{2.23}$$

In the more general case of eq 2.20, it is apparent that $S(t)$ remains proportional to $(\det \mathbf{M}(t))^{-1/2}$, although with a different numerical prefactor. Regardless of the prefactor, we see that

$$S(t) \sim G(\mathbf{0};t) \sim (\det \mathbf{M}(t))^{-1/2} \tag{2.24}$$

which indicates that $S(t)$ can also be interpreted as being proportional to the conditional probability density that a pair of reactive sites that are together at time zero (i.e. within a capture radius), are also found together at time t. It should be noted that eqs 2.20 and 2.23 reduce to corresponding expressions of de Gennes[15] in the limit of no flow, $[\exp(t\mathbf{\Gamma})]_{ij} \to \delta_{ij}$.

Our final step is to solve eq 2.17 and deduce an effective reaction rate. Equation 2.17 is a simple Volterra integral equation that can be solved by Laplace transformation. Defining transforms by

$$\hat{f}(s) = \int_0^\infty \mathrm{d}t \, \exp(-st) f(t) \tag{2.25}$$

we obtain for the Laplace transform of $\Psi(t)$:

$$\hat{\Psi}(s) = \frac{\rho^2 V_a}{s + sQ_0 V_a \hat{S}(s)} \tag{2.26}$$

The rate of reaction can be expressed as

$$-\frac{\mathrm{d}}{\mathrm{d}t}\rho \equiv k(t)\rho^2 = Q_0 \int_{V_a} \mathrm{d}\mathbf{y} \; \psi(\mathbf{y};t) \tag{2.27}$$

or, Laplace transforming, we have the following frequency-dependent rate coefficient:

$$\hat{k}(s) = Q_0 \rho^{-2} \hat{\Psi}(s) \tag{2.28}$$

Combining this expression with eq 2.26 and taking the limit of instantaneous reaction on contact of sites, $Q_0 \to \infty$, the following simple rate expression is obtained:

$$\hat{k}(s) = \frac{1}{s\hat{S}(s)} \tag{2.29}$$

It is important to note that the dependence on both Q_0 and a is lost in this limiting expression, indicating an insensitivity to the microscopic details of the reaction event. Hence, we expect that eq 2.29 has more general validity than the specific choice of trapping model (eq 2.4) might suggest.

In general, the inverse Laplace transform of eq 2.29 leads to a time-dependent reaction rate coefficient $k(t)$. As discussed by de Gennes,[15] situations exist ("compact exploration") in which $k(t)$ does not settle down to a nonzero constant value at long times, and for such cases no effective reaction rate "constant" can be defined. For the cases of interest in the present paper, however, the quantity $\hat{S}(s)$ has a finite $s \to 0$ limit and a long-time rate constant exists. Moreover, we shall focus exclusively on this object, defined by

$$k \equiv \lim_{t\to\infty} k(t) = \left[\int_0^\infty \mathrm{d}t \; S(t)\right]^{-1} \tag{2.30}$$

In the following sections we explore the application of eqs 2.23, 2.24, and 2.30 to situations in which the reactive sites are attached to linear chains in entangled and unentangled polymer melts and subjected to shear and extensional flows.

III. Weak Convection Effects

A. Unentangled Melts. We begin our study of convection on diffusion-controlled reactions in polymers by considering an unentangled melt (Rouse dynamics[26]) subjected to a weak linear flow of arbitrary type. A small fraction of the chains have a single, *terminally* attached reactive site that can undergo irreversible reaction by combining with a second site on a different chain. In the analysis below, we adopt the nomenclature for Rouse dynamics employed in the text of Doi and Edwards.[26]

Due to the linearity of the Rouse Langevin equations in the flow eq 1.3, it is straightforward to construct the diffusive displacement tensor, $\mathbf{M}(t)$, defined in eq 2.21. We obtain the expression

$$\mathbf{M}(t) = 2D_0 \int_0^t \mathrm{d}t' \exp(\mathbf{\Gamma}t') \exp(\mathbf{\Gamma}^{\mathrm{T}}t') + 4\sum_{p=1}^{\infty}\left\{(\mathrm{e}^{-t/\tau_p} - 1)^2 \exp(\mathbf{\Gamma}t)\mathbf{C}_p \exp(\mathbf{\Gamma}^{\mathrm{T}}t) + \frac{2k_{\mathrm{B}}T}{\zeta_p}\int_0^t \mathrm{d}t' \, \mathrm{e}^{-2t'/\tau_p} \exp(\mathbf{\Gamma}t') \exp(\mathbf{\Gamma}^{\mathrm{T}}t')\right\} \tag{3.1}$$

where $D_0 = k_{\mathrm{B}}T/(N\zeta)$ is the (reactive) chain center-of-mass diffusion coefficient, N is the degree of polymerization, ζ is the monomeric friction coefficient, and $\zeta_p \equiv 2N\zeta$ for $p \geq 1$. The Rouse relaxation times are given by $\tau_p = \tau_1/p^2$, where τ_1 is the longest Rouse internal mode relaxation time:

$$\tau_1 = \frac{\zeta N^2 b^2}{3\pi^2 k_{\mathrm{B}}T} \tag{3.2}$$

and b is the statistical segment length. The object, $(\mathbf{C}_p)_{ij}$, appearing in eq 3.1 is defined as the matrix of equal-time pair correlations of the pth Rouse mode: $(\mathbf{C}_p)_{ij} = \langle[\mathbf{X}_p(0)]_i[\mathbf{X}_p(0)]_j\rangle$. This quantity satisfies the matrix equation[26]

$$\mathbf{C}_p = \frac{k_{\mathrm{B}}T}{k_p}\mathbf{I} + \frac{1}{2}\tau_p\mathbf{\Gamma}\mathbf{C}_p + \frac{1}{2}\tau_p\mathbf{C}_p\mathbf{\Gamma}^{\mathrm{T}} \tag{3.3}$$

where $\mathbf{I}$ is the identity matrix and $k_p = (6\pi^2 k_{\mathrm{B}}T/Nb^2)p^2$ is the "spring constant" of the pth Rouse mode. We also note the relation $\tau_p = \zeta_p/k_p$.

As a means of characterizing the strength of the flow, it proves convenient to reexpress the velocity gradient tensor in the form

$$\Gamma_{ij} = \kappa E_{ij} \tag{3.4}$$

where κ is the flow strength (shear or extension rate) and E_{ij} is a dimensionless tensor expressing the flow type. The two cases of interest in the present paper are *simple shear flow* in the $x-y$ plane

$$\mathbf{E} = \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \tag{3.5}$$

and *uniaxial extensional flow* with principal extension axis z:

$$\mathbf{E} = \begin{pmatrix} -1/2 & 0 & 0 \\ 0 & -1/2 & 0 \\ 0 & 0 & +1 \end{pmatrix} \tag{3.6}$$

It is also convenient to define a *Deborah number* based on the longest Rouse relaxation time by

$$De \equiv \kappa \tau_1 \tag{3.7}$$

and introduce a dimensionless time $\tilde{t} = t/\tau_1$ in eq 3.1 for $\mathbf{M}(t)$. This leads to the expression

$$\mathbf{M}(\tilde{t}) = 2D_0\tau_1\int_0^{\tilde{t}}\mathrm{d}t\ \exp(De\mathbf{E}t)\exp(De\mathbf{E}^{\mathrm{T}}t) + 4\sum_{p=1}^{\infty}\{(\mathrm{e}^{-\tilde{t}p^2} - 1)^2\exp(De\mathbf{E}\tilde{t})\mathbf{C}_p\exp(De\mathbf{E}^{\mathrm{T}}\tilde{t}) + D_0\tau_1\int_0^{\tilde{t}}\mathrm{d}t\ \mathrm{e}^{-2tp^2}\exp(De\mathbf{E}t)\exp(De\mathbf{E}^{\mathrm{T}}t)\} \tag{3.8}$$

We are now in a position to consider the influence of *weak flows*, defined by $De \ll 1$, on the long-time reaction rate. For $De \ll 1$, it is straightforward to show that the first integral on the right hand side of eq 3.8, which represents the dynamics of the center-of-mass Rouse mode, dominates the remaining terms for any $\tilde{t} \gg 1$. The internal mode terms involving the sum over p dominate only for $\tilde{t} \ll 1$, in which case the flow effect is negligible:

$$\mathbf{M}(\tilde{t}) \approx 2c_1(D_0\tau_1)\tilde{t}^{1/2}[1 + O(\tilde{t}^{1/2}De)] \qquad \tilde{t} \ll 1,\ De \ll 1 \tag{3.9}$$

The constant c_1 appearing in this expression is obtained by converting the sum over p to an integral with the result

$$c_1 \equiv \int_0^{\infty}\mathrm{d}x\ x^{-3/2}[1 - \exp(-x)] \approx 3.5449 \tag{3.10}$$

A simple approximation for $\mathbf{M}(\tilde{t})$ that is asymptotic for $De \ll 1$ and uniform in $\tilde{t}$ is thus

$$\mathbf{M}(\tilde{t}) \approx 2D_0\tau_1(1 + c_1\tilde{t}^{-1/2})\int_0^{\tilde{t}}\mathrm{d}t\ \exp(De\mathbf{E}t)\exp(De\mathbf{E}^{\mathrm{T}}t) \tag{3.11}$$

Next, we insert forms of $\mathbf{E}$ appropriate for shear and extensional flows (eqs 3.5 and 3.6) into eq 3.11 and evaluate $S(t)$ according to eq 2.23. (Note that $\mathbf{d}(t)$ is a Gaussian random variable in the Rouse model). For simple shear flow, one obtains

$$S_{\mathrm{shear}}(\tilde{t}) = [8\pi D_0\tau_1(\tilde{t} + c_1\tilde{t}^{1/2})]^{-3/2}[1 + (1/12)(\tilde{t}De)^2]^{-1/2} \tag{3.12}$$

while, for uniaxial extensional flow, the corresponding expression is

$$S_{\mathrm{ext}}(\tilde{t}) = \frac{2^{1/2}De^{3/2}}{[8\pi D_0\tau_1(1 + c_1\tilde{t}^{-1/2})]^{3/2}(1 - \exp(-\tilde{t}De))(\exp(2\tilde{t}De) - 1)^{1/2}} \tag{3.13}$$

Substitution of these expressions into eq 2.30 and asymptotic evaluation of the integrals for $De \rightarrow 0$ leads to the following results for the long-time reaction rate coefficient:

$$k_{\mathrm{shear}} = \frac{32\sqrt{\pi}}{c_2}D_0R[1 + (c_3/c_2)De^{1/2} + ...] \tag{3.14}$$

$$k_{\mathrm{ext}} = \frac{32\sqrt{\pi}}{c_2}D_0R[1 + c_2^{-1}(c_1 + c_4)De^{1/2} + ...] \tag{3.15}$$

where $R = N^{1/2}b/\sqrt{6}$ is the chain radius-of-gyration and c_2, c_3, and c_4 are constants defined by the following numerical integrals:

$$c_2 \equiv \int_0^{\infty}\mathrm{d}x\ \frac{1}{(x + c_1x^{1/2})^{3/2}} \approx 1.1284 \tag{3.16}$$

$$c_3 \equiv \int_0^{\infty}\mathrm{d}x\ \frac{(1 + x^2/12)^{1/2} - 1}{x^{3/2}(1 + x^2/12)^{1/2}} \approx 0.9104 \tag{3.17}$$

$$c_4 \equiv \int_0^{\infty}\mathrm{d}x\ \frac{\mathrm{e}^{-x}[(1 - \mathrm{e}^{-x})(1 - \mathrm{e}^{-2x})^{1/2} - \sqrt{2}x^{3/2}]}{x^{3/2}(1 - e^{-x})(1 - \mathrm{e}^{-2x})^{1/2}} \approx -2.1253 \tag{3.18}$$

Inserting these numerical coefficients, we finally obtain

$$k_{\mathrm{shear}} = 50.26D_0R[1 + 0.8068De^{1/2} + ...] \tag{3.19}$$

$$k_{\mathrm{ext}} = 50.26D_0R[1 + 1.258De^{1/2} + ...] \tag{3.20}$$

In the absence of flow, $De = 0$, the leading term in these expressions has the scaling form previously obtained by de Gennes,[15] although we provide an explicit estimate of the numerical prefactor.[27] For both types of flows, it is evident that the first correction scales as $De^{1/2} = (\kappa\tau_1)^{1/2}$; this is expected to be a general feature of linear flows characterized by a traceless velocity gradient tensor $\mathbf{\Gamma}$ (with a few exceptions,[20] e.g. purely rotational fluid motion). Moreover, the numerical prefactor depends on the type of flow. The finding that $k_{\mathrm{shear}} < k_{\mathrm{ext}}$ at small Deborah number is consistent with our expectation that "strong flows", such as uniaxial extension, are more effective at bringing reactive sites together than "weaker" flows, such as simple shear. Additionally, the fact that both flow correction terms are *positive* could have been anticipated for irreversible reactions, since in such cases the reverse reaction cannot be accelerated by flow.

B. Entangled Melts. Next, we turn to consider weak convection effects on the reaction rate in situations where the active chains are sufficiently long to be dynamically entangled. We assume the reptation model to be applicable in such cases, and again adopt the nomenclature of the text by Doi and Edwards.[26]

For entangled chains, the flow strength is to be compared with a longer relaxation time than the Rouse time τ_1, which for convenience we choose to be τ_{d}, the disengagement time of the reptation model:

$$\tau_{\mathrm{d}} = \frac{\zeta b^4N^3}{\pi^2k_{\mathrm{B}}Ta_{\mathrm{t}}^{\,2}} \tag{3.21}$$

The quantities appearing in this expression have their previous interpretations and a_{t} is the step length of the primitive chain (tube diameter). A new Deborah number can now be defined as

$$De = \kappa\tau_d \tag{3.22}$$

and weak convection again corresponds to $De \ll 1$.

A shortcut to obtaining results for the reptation model in weak flows can be identified by returning to the approximate form of $\mathbf{M}(t)$ deduced for the Rouse model in the last section, eq 3.11. Returning to dimensional time, this expression can be rewritten in the form

$$\mathbf{M}(t) = \frac{\langle r^2(t)\rangle_0}{3t}\int_0^t \mathrm{d}t'\, \exp(\mathbf{\Gamma}t')\exp(\mathbf{\Gamma}^{\mathrm{T}}t') \tag{3.23}$$

where $\langle r^2(t)\rangle_0$ is the mean-squared displacement of a reactive site *in the absence of flow*. The factor involving the integral in this expression describes the effect of flow on the dynamics of the center-of-mass mode of the polymer. Thus, this approximation involves only the *equilibrium dynamics* of the internal modes of the polymer, while providing an exact description of convection and diffusion for the $p = 0$ (center-of-mass) mode. Such a factorization is evidently exact for $\kappa\tau_1 \to 0$, since the flow is sufficiently weak in this limit that the internal mode dynamics can be treated as unperturbed. The effect of the flow on the center-of-mass dynamics, however, cannot be described perturbatively; indeed, this is the source of the nonanalytic flow corrections obtained in the previous section.

The factorization expressed by eq 3.23 holds for reptation dynamics as well. Provided that $De = \kappa\tau_d \ll 1$, the effect of the flow on the internal mode dynamics can be neglected and we are left with the simple task of developing an expression for $\langle r^2(t)\rangle_0$ appropriate to the reptation model. Indeed, Doi and Edwards[26] provide an explicit derivation of this quantity for times greater than τ_1 (cf. their eq 6.36):

$$\frac{1}{3}\langle r^2(t)\rangle_0 = 2D_0t + \sum_{p=1}^{\infty}\frac{8R^2}{p^2\pi^2}[1 - \exp(-tp^2/\tau_d)] \tag{3.24}$$

The center-of-mass diffusion coefficient is now that appropriate for the reptation model:

$$D_0 = \frac{k_BTa_t^{\,2}}{3N^2\zeta b^2} \tag{3.25}$$

Equation 3.24, however, is identical in form to an expression for $\langle r^2(t)\rangle_0/3$ derived from the Rouse model (cf. Doi and Edwards eq 4.III.6), provided the appropriate definition of D_0 is used along with the following replacement in the latter, $\tau_1 \to \tau_d$. Next, we note that the first factor in eq 3.11 is simply an approximation for the function $\langle r^2(t)\rangle_0/(3t)$ expressed as a series in eq 3.24. Thus, we conclude that eq 3.11 can still be applied for the reptation model if the dimensionless time $\tilde{t}$ is redefined according to $\tilde{t} = t/\tau_d$ and the new definitions of D_0 and De (eqs 3.22 and 3.25) are employed. It follows immediately that the long-time reaction rate coefficients appropriate for reptating chains in weak shear and uniaxial extensional flows are given identically by eqs 3.19 and 3.20 with these redefinitions of D_0 and De:

$$k_{\text{shear}} = 50.26D_0R[1 + 0.8068De^{1/2} + ...] \tag{3.26}$$

$$k_{\text{ext}} = 50.26D_0R[1 + 1.258De^{1/2} + ...] \tag{3.27}$$

There are actually a couple of hidden assumptions in the derivation of these equations for the reptation model. The first is that we employ the numerical prefactor $(2^{-3}\pi^{-3/2})$ appropriate for $S(t)$ if the distribution of diffusive displacements $\mathbf{d}(t)$ are Gaussian. This is not strictly the case for reptation dynamics, so the prefactor (50.26) in the front of eqs 3.26 and 3.27 would seem to be in question. However, the dynamics of the center-of-mass mode for the reptation model can be quite accurately described as a Gaussian random variable (albeit with colored noise) and the key role of this mode in determining the limiting behavior of k for $De \to 0$ has been previously established. Thus, we expect that the numerical prefactor in eqs 3.26 and 3.27 is reasonably accurate, although probably not exact. A second hidden assumption in our analysis is that eq 3.24 holds only for times greater than the Rouse time τ_1, while the rate coefficient k depends on the behavior of $S(t)$ at all times (cf. eq 2.30). Nevertheless, it is easily demonstrated that the strict correspondence between expressions [for $\mathbf{M}(t)$] for the Rouse and reptation models is asymptotically correct to leading order for $\tau_1/\tau_d \to 0$. Provided that the reactive chains are well-entangled, these time scales are widely separated and the correspondence should be very closely met.

IV. Strong Convention Effects

A. Unentangled Melts. Next, we turn to consider strong flow effects, i.e. $De \gg 1$, in unentangled melts. Our starting point is eq 3.8, an exact expression for the diffusive displacement tensor $\mathbf{M}(\tilde{t})$ of a Rouse chain in a flow of arbitrary strength and type. Because of a well-known instability of Rouse dynamics under strong extensional flows[28] (chain extension becomes unbounded due to the Hookean force law), we shall restrict our discussion to strong *shear* flows described by a tensor $\mathbf{E}$ of the form of eq 3.5. In the present section, the Deborah number is defined in accordance with eq 3.7 and the dimensionless time $\tilde{t}$ is defined as $\tilde{t} = t/\tau_1$.

We proceed as in section III.A by developing an approximation for $\mathbf{M}(\tilde{t})$ that is uniformly accurate in $\tilde{t}$, while asymptotic for $De \to \infty$. For long times, $\tilde{t} \gg 1$, the center-of-mass term (first term) on the right hand side of eq 3.8 is dominant for $De \gg 1$, just as in the case of $De \ll 1$. We find for $De \gg 1$ and $\tilde{t} \gg 1$

$$\mathbf{M}(\tilde{t}) \approx 2D_0\tau_1\begin{pmatrix} \tilde{t} + \frac{1}{3}De^2\tilde{t}^3 & \frac{1}{2}De\tilde{t}^2 & 0 \\ \frac{1}{2}De\tilde{t}^2 & \tilde{t} & 0 \\ 0 & 0 & \tilde{t}\end{pmatrix} \tag{4.1}$$

where we have retained a linear term in $\tilde{t}$ in the element M_{xx} for symmetry in later expressions, even though it is subdominant. For $\tilde{t} \ll 1$ and $De \gg 1$, the internal mode terms (terms involving the p sum) in eq 3.8 provide the dominant contribution to $\mathbf{M}(\tilde{t})$. In this regime,

$$\mathbf{M}(\tilde{t}) \approx 2D_0\tau_1\begin{pmatrix} c_1\tilde{t}^{1/2} + (\pi^2/12)De^2\tilde{t}^2 & (c_5/2)De\tilde{t}^{3/2} & 0 \\ (c_5/2)De\tilde{t}^{3/2} & c_1\tilde{t}^{1/2} & 0 \\ 0 & 0 & c_1\tilde{t}^{1/2}\end{pmatrix} \tag{4.2}$$

The numerical coefficient c_5 entering this expression is defined by the integral

$$c_5 \equiv \int_0^\infty \mathrm{d}x\, x^{-5/2}[(1 - 2\mathrm{e}^{-x})(1/2 + x) + 1/2] \approx 4.7261 \tag{4.3}$$

An approximation, uniform in $\tilde{t}$ and asymptotic for $De \to \infty$, is obtained by superimposing these asymptotic forms:

$$\mathbf{M}(\tilde{t}) \approx 2D_0\tau_1 \begin{pmatrix} \tilde{t}+c_1\tilde{t}^{1/2}+De^2\left(\frac{\pi^2}{12}\tilde{t}^2+\frac{1}{3}\tilde{t}^3\right) & \frac{1}{2}De(\tilde{t}^2+c_5\tilde{t}^{3/2}) & 0 \\ \frac{1}{2}De(\tilde{t}^2+c_5\tilde{t}^{3/2}) & \tilde{t}+c_1\tilde{t}^{1/2} & 0 \\ 0 & 0 & \tilde{t}+c_1\tilde{t}^{1/2} \end{pmatrix} \tag{4.4}$$

Next, we use this approximation for $\mathbf{M}(\tilde{t})$ in eq 2.23, which leads to the expression

$$S_{\text{shear}}(\tilde{t}) = (8\pi D_0\tau_1)^{-3/2}(\tilde{t} + c_1\tilde{t}^{1/2})^{-1/2}[(\tilde{t} + c_1\tilde{t}^{1/2})^2 + De^2(\tilde{t} + c_1\tilde{t}^{1/2})(\pi^2\tilde{t}^2/12 + \tilde{t}^3/3) - De^2(\tilde{t}^2 + c_5\tilde{t}^{3/2})^2/4]^{-1/2} \tag{4.5}$$

Finally, we insert this expression into eq 2.30 for the long-time rate coefficient, rescale the integration variable to $x = \tilde{t}De^{4/3}$, and asymptotically evaluate the integral to leading order for $De \to \infty$. This leads to

$$k_{\text{shear}} \approx \frac{32\sqrt{\pi}c_1^{\,3/2}}{c_6} D_0RDe^{1/3} \tag{4.6}$$

where c_6 is the following integral:

$$c_6 \equiv \int_0^\infty \mathrm{d}x\, x^{-3/4}[1 + (\pi^2/12c_1)x^{3/2}]^{-1/2} \approx 7.1550 \tag{4.7}$$

Inserting this numerical coefficient finally leads to

$$k_{\text{shear}} \approx 52.908 D_0RDe^{1/3} \qquad De \to \infty \tag{4.8}$$

indicating that the reaction rate coefficient increases without bound as the shear rate is increased.

A particularly interesting feature of eq 4.8 is that it shows an asymptotic scaling at large Deborah numbers that is consistent with eq 1.7 and highlights the importance of the choice of boundary conditions on the flow near the surface of the "capture sphere". For the present case of Rouse chains, the effective capture radius is the radius-of-gyration, R, and the flow was assumed to be unperturbed from eq 1.3 when two reactive groups are separated by that distance. In the analogous heat transfer studies,[20,24] no-slip conditions were imposed on the flow at the capture radius and the sphere was free to rotate. Because unperturbed shear flow has no closed streamlines, we observe the scaling of eq 1.7, while the no-slip boundary conditions in the heat transfer studies led to closed streamlines and the very different scaling given in eq 1.8.[24]

The correspondence between eqs 4.8 and 1.7 also provides insight into the physics behind this asymptotic formula.[19,20] At high shear rates, a narrow diffusive boundary layer of thickness $\Delta \sim (u_x/D_0R^2)^{-1/3} \sim RDe^{-1/3}$ is set up around the "capture sphere" at radius R. The radial flux of reactive sites is estimated as $j_r \sim D_0\rho\Delta^{-1}$, which after integration over the surface of the capture sphere and normalization by the density of reactive sites ρ, leads to the rate expression $k_{\text{shear}} \sim D_0\Delta^{-1}R^2 \sim D_0RDe^{1/3}$. Thus, it appears that *chain extension* caused by application of strong shear flow to unentangled melts does not influence the scaling in eq 4.8, but does indirectly influence the prefactor.

Another interesting aspect of eq 4.8 is that it predicts a weak dependence of the rate coefficient on molecular weight, $k_{\text{shear}} \sim N^{1/6}\kappa^{1/3}$. If the predominant contribution to k_{shear} in the $\kappa \to \infty$ limit arose from strictly local Rouse dynamics (i.e. motions of segments very near the reactive chain end), one might have expected an asymptotic form independent of N. This would imply a rate expression $k_{\text{shear}} \sim D_0R(\kappa\tau_1)^{1/4} = D_0RDe^{1/4}$, originally suggested by de Gennes.[18] The fact that we find a different scaling, $k_{\text{shear}} \sim D_0RDe^{1/3}$, indicates a residual dependence on larger-scale (N-dependent) dynamics, which is evidently associated with the molecular weight dependence of the diffusive boundary layer.

B. Entangled Melts. Next, we turn to the evaluation of the reaction rate coefficient under strong flow conditions and for chains that are sufficiently long to be entangled. Strong flow calculations with the reptation model tend to be difficult, and the present evaluation of the diffusive displacement tensor $\mathbf{M}(t)$ turns out to be no exception. In order to obtain analytical results, we adopt the so-called "independent alignment approximation" of Doi and Edwards,[26] which leads to *linear* partial differential equations for the correlation functions of interest. Previous experience with the independent alignment approximation in rheological calculations has yielded answers that are in reasonable qualitative and quantitative agreement with exact numerical solutions of the reptation model, so we might hope for similar accuracy in the present application. Unfortunately, rather difficult numerical analysis is required to relax the approximation.

Rather than directly compute the displacement tensor $\mathbf{M}(t)$ for reptation dynamics, we follow the approach in section 6.3 of Doi and Edwards[26] and consider the dynamics of a more general tensor $\mathbf{Q}(s,s';t)$, defined by

$$\mathbf{Q}(s,s';t) \equiv \langle[\mathbf{R}(s,t) - \exp(\mathbf{\Gamma}t)\cdot\mathbf{R}(s',0)][\mathbf{R}(s,t) - \exp(\mathbf{\Gamma}t)\cdot\mathbf{R}(s',0)]\rangle \tag{4.9}$$

where $\mathbf{R}(s,t)$ is the position vector of the primitive chain segment at contour location s and time t. The primitive chain is taken to have a total length L; the tensor $\mathbf{M}(t)$, which contains information only about chain end dynamics, is recovered by setting both s and s' to zero:

$$\mathbf{M}(t) = \mathbf{Q}(0,0;t) \tag{4.10}$$

Within the independent alignment approximation, it is straightforward to derive partial differential equations for space−time correlation functions of segmental displacement. The object $\mathbf{Q}(s,s';t)$ satisfies the equation

$$\frac{\partial}{\partial t}\mathbf{Q}(s,s';t) = D_c\frac{\partial^2}{\partial s^2}\mathbf{Q} + \mathbf{\Gamma Q} + \mathbf{Q\Gamma}^{\mathrm{T}} \tag{4.11}$$

where $D_c = k_BT/(N\zeta)$ is the curvilinear diffusion coefficient of the primitive chain, which also corresponds to the Rouse center-of-mass diffusivity. It is important to note that this simple equation of motion is valid only for times exceeding the Rouse time τ_1. Thus, the subsequent analysis will hold only for flow rates satisfying $\kappa\tau_1 \ll 1$ in order that faster dynamical processes will not be excited. Nevertheless, this restriction is not particularly limiting because the strong flow regime $\tau_d^{-1} \ll \kappa \ll \tau_1^{-1}$ can be very broad for high molecular weight chains.

Following the procedure outlined in section 6.3.2 of Doi and Edwards, the boundary conditions on **Q** are easily found to be:

$$\frac{\partial}{\partial s}Q_{ij}(s,s';t)\Big|_{s=0} = -\frac{1}{3}a_{\mathrm{t}}\delta_{ij} \tag{4.12}$$

$$\frac{\partial}{\partial s}Q_{ij}(s,s';t)\Big|_{s=L} = \frac{1}{3}a_{\mathrm{t}}\delta_{ij} \tag{4.13}$$

where a_{t} is again the step length of the primitive chain. Finally, we need an initial condition, which is given by the second rank tensor

$$\mathbf{U}(s,s') \equiv \mathbf{Q}(s,s';0) = \langle[\mathbf{R}(s) - \mathbf{R}(s')][\mathbf{R}(s) - \mathbf{R}(s')]\rangle \tag{4.14}$$

Equations 4.11−4.14 constitute a well-posed initial-boundary value problem for the displacement tensor $\mathbf{Q}(s,s';t)$, provided an expression for the tensor $\mathbf{U}(s,s')$ is available. To obtain such an expression, we derive a second partial differential equation within the independent alignment approximation:

$$D_{\mathrm{c}}\left(\frac{\partial}{\partial s} + \frac{\partial}{\partial s'}\right)^2\mathbf{U} + \mathbf{\Gamma}\mathbf{U} + \mathbf{U}\mathbf{\Gamma}^{\mathrm{T}} = 0 \tag{4.15}$$

This tensor satisfies the same boundary conditions as **Q**

$$\frac{\partial}{\partial s}U_{ij}(s,s')\Big|_{s=0} = -\frac{1}{3}a_{\mathrm{t}}\delta_{ij} \tag{4.16}$$

$$\frac{\partial}{\partial s}U_{ij}(s,s')\Big|_{s=L} = \frac{1}{3}a_{\mathrm{t}}\delta_{ij} \tag{4.17}$$

and for the present object, we also require s' boundary conditions:

$$\frac{\partial}{\partial s'}U_{ij}(s,s')\Big|_{s'=0} = -\frac{1}{3}a_{\mathrm{t}}\delta_{ij} \tag{4.18}$$

$$\frac{\partial}{\partial s'}U_{ij}(s,s')\Big|_{s'=L} = \frac{1}{3}a_{\mathrm{t}}\delta_{ij} \tag{4.19}$$

At this point it is difficult to go any further without specifying the type of flow. In order to illustrate the method and provide a basis for comparison with the strong flow results obtained in the previous section for the Rouse model, we subsequently restrict our attention to *strong shear* flows. For this choice of the velocity gradient tensor $\mathbf{\Gamma}$ (cf. eqs 3.4 and 3.5), eqs 4.15−4.19 can be solved analytically. It proves convenient to express the solution in terms of the two combination variables

$$s_+ \equiv s + s' \tag{4.20}$$

$$s_- \equiv |s - s'| \tag{4.21}$$

which also diagonalize the partial differential operator appearing in eq 4.15. We find for the various Cartesian components of $\mathbf{U}(s,s')$:

$$U_{xx}(s,s') = \frac{1}{3}a_{\mathrm{t}}s_- + \frac{\kappa^2 a_{\mathrm{t}}s_-}{48D_{\mathrm{c}}^2}\left\{\frac{1}{60}s_-^{\,4} + \frac{1}{3}Ls_+(2L^2 - s_-^{\,2}) + \frac{1}{6}s_-^{\,2}s_+^{\,2} - \frac{1}{3}Ls_+^{\,3} + \frac{1}{12}s_+^{\,4}\right\} \tag{4.22}$$

$$U_{xy}(s,s') = U_{yx}(s,s') = \frac{\kappa a_{\mathrm{t}}s_-}{12D_{\mathrm{c}}}\left\{-\frac{1}{6}s_-^{\,2} + Ls_+ - \frac{1}{2}s_+^{\,2}\right\} \tag{4.23}$$

$$U_{yy}(s,s') = U_{zz}(s,s') = \frac{1}{3}a_{\mathrm{t}}s_- \tag{4.24}$$

and all other matrix elements identically vanish.

Next, we turn to the solution of eq 4.11 for $\mathbf{Q}(s,s';t)$. A convenient transformation is

$$Q_{ij}(s,s';t) = \frac{1}{3}a_{\mathrm{t}}|s-s'|\delta_{ij} + W_{ij}(s,s';t) \tag{4.25}$$

where the new tensor $W_{ij}(s,s';t)$ is defined by this relation. Noting that the object $|s - s'|$ is a Green's function of the operator $\partial^2/\partial s^2$, substitution into eq 4.11 leads to the new equation of motion

$$\frac{\partial}{\partial t}\mathbf{W}(s,s';t) = D_{\mathrm{c}}\frac{\partial^2}{\partial s^2}\mathbf{W} + \mathbf{\Gamma}\mathbf{W} + \mathbf{W}\mathbf{\Gamma}^{\mathrm{T}} + \frac{2}{3}a_{\mathrm{t}}D_{\mathrm{c}}\delta(s-s')\mathbf{I} + \frac{1}{3}a_{\mathrm{t}}|s-s'|(\mathbf{\Gamma} + \mathbf{\Gamma}^{\mathrm{T}}) \tag{4.26}$$

The transformation thus generates inhomogeneous terms in the equation of motion (the fourth and fifth terms) but has the advantage of rendering the boundary conditions homogeneous:

$$\frac{\partial}{\partial s}W_{ij}(s,s';t)\Big|_{s=0} = 0 \tag{4.27}$$

$$\frac{\partial}{\partial s}W_{ij}(s,s';t)\Big|_{s=L} = 0 \tag{4.28}$$

The transformed initial condition is

$$\mathbf{W}(s,s';0) = \mathbf{U}(s,s') - \frac{1}{3}a_{\mathrm{t}}|s-s'|\mathbf{I} \tag{4.29}$$

Our next step is to introduce Laplace transforms according to eq 2.25, but with Laplace variable ϵ:

$$\hat{f}(\epsilon) \equiv \int_0^\infty \mathrm{d}t\,\exp(-\epsilon t)f(t) \tag{4.30}$$

This leads to the differential equation (in s only)

$$\left(D_{\mathrm{c}}\frac{\partial^2}{\partial s^2} - \epsilon\right)\hat{\mathbf{W}}(s,s';\epsilon) + \mathbf{\Gamma}\hat{\mathbf{W}} + \hat{\mathbf{W}}\mathbf{\Gamma}^{\mathrm{T}} = -\mathbf{K}(s,s';\epsilon) \tag{4.31}$$

where $\hat{\mathbf{W}}$ still satisfies the homogeneous Neumann boundary conditions given in eqs 4.27 and 4.28. The inhomogeneous term appearing in this equation is defined by

$$\mathbf{K}(s,s';\epsilon) \equiv \frac{2}{3\epsilon}a_{\mathrm{t}}D_{\mathrm{c}}\delta(s-s')\mathbf{I} + \frac{1}{3\epsilon}a_{\mathrm{t}}|s-s'|(\mathbf{\Gamma} + \mathbf{\Gamma}^{\mathrm{T}}) + \mathbf{U}(s,s') - \frac{1}{3}a_{\mathrm{t}}|s-s'|\mathbf{I} \tag{4.32}$$

The solution of eq 4.31 for the case of simple shear flow can be obtained with the help of a Green's function that satisfies

$$\left(D_{\mathrm{c}}\frac{\partial^2}{\partial s^2} - \epsilon\right)\hat{G}(s,s';\epsilon) = -\delta(s-s') \tag{4.33}$$

and subject to the boundary conditions

$$\frac{\partial}{\partial s}\hat{G}(s,s';\epsilon)\Big|_{s=0} = \frac{\partial}{\partial s}\hat{G}(s,s';\epsilon)\Big|_{s=L} = 0 \tag{4.34}$$

A particularly convenient representation of this Green's function is the cosine series

$$\hat{G}(s,s';\epsilon) = \frac{1}{\epsilon L} + \frac{2}{L}\sum_{p=1}^{\infty}\frac{1}{\epsilon + p^2/\tau_d}\cos(p\pi s/L)\cos(p\pi s'/L) \tag{4.35}$$

where we note that the disengagement time of the reptation model, τ_d, naturally enters this expression (cf. eq 3.21). Equation 4.35 can be used to invert the differential operator in eq 4.31 and solve for the various matrix elements of $\hat{\mathbf{W}}$. To express these results, it is convenient to introduce a dimensionless frequency

$$\tilde{\epsilon} \equiv \epsilon\tau_\mathrm{d} \tag{4.36}$$

which is conjugate to the dimensionless time $\tilde{t} \equiv t/\tau_\mathrm{d}$, and recall our definition of the Deborah number appropriate for the reptation model:

$$De \equiv \kappa\tau_\mathrm{d} \tag{4.37}$$

After considerable algebra, we find for $\hat{\mathbf{W}}(0,0;\epsilon)$:

$$\hat{W}_{xx}(0,0;\epsilon) = 2D_0{\tau_\mathrm{d}}^2\left[\frac{1}{\tilde{\epsilon}^2} + 2\sum_{p=1}^{\infty}\frac{1}{\tilde{\epsilon}(\tilde{\epsilon}+p^2)}\right] + De^2D_0{\tau_\mathrm{d}}^2\left\{\frac{\pi^4}{12\tilde{\epsilon}^2} + \frac{\pi^2}{\tilde{\epsilon}^3} + \frac{4}{\tilde{\epsilon}^4} + 8\sum_{p=1}^{\infty}\frac{1}{\tilde{\epsilon}(\tilde{\epsilon}+p^2)^3}\right\} \tag{4.38}$$

$$\hat{W}_{xy}(0,0;\epsilon) = \hat{W}_{yx}(0,0;\epsilon) = DeD_0{\tau_\mathrm{d}}^2\left[\frac{\pi^2}{2\tilde{\epsilon}^2} + \frac{2}{\tilde{\epsilon}^3} + 4\sum_{p=1}^{\infty}\frac{1}{\tilde{\epsilon}(\tilde{\epsilon}+p^2)^2}\right] \tag{4.39}$$

$$\hat{W}_{yy}(0,0;\epsilon) = \hat{W}_{zz}(0,0;\epsilon) = 2D_0{\tau_\mathrm{d}}^2\left[\frac{1}{\tilde{\epsilon}^2} + 2\sum_{p=1}^{\infty}\frac{1}{\tilde{\epsilon}(\tilde{\epsilon}+p^2)}\right] \tag{4.40}$$

where D_0 is the center-of-mass diffusivity of a reptating chain, cf. eq 3.25. All other elements of $\hat{\mathbf{W}}$ identically vanish. Finally, we invert the Laplace transforms, noting that $M_{ij}(t) = W_{ij}(0,0;t)$:

$$M_{xx}(\tilde{t}) = 2D_0\tau_\mathrm{d}\left[\tilde{t} + 2\sum_{p=1}^{\infty}\frac{1}{p^2}(1 - \mathrm{e}^{-p^2\tilde{t}})\right] + De^2D_0\tau_\mathrm{d}\left\{\frac{\pi^4}{12}\tilde{t} + \frac{\pi^2}{2}\tilde{t}^2 + \frac{2}{3}\tilde{t}^3 + 8\sum_{p=1}^{\infty}\frac{1}{p^6}[1 - \mathrm{e}^{-p^2\tilde{t}}(1 + p^2\tilde{t} + p^4\tilde{t}^2/2)]\right\} \tag{4.41}$$

$$M_{xy}(\tilde{t}) = M_{yx}(\tilde{t}) = DeD_0\tau_\mathrm{d}\left\{\frac{\pi^2}{2}\tilde{t} + \tilde{t}^2 + 4\sum_{p=1}^{\infty}\frac{1}{p^4}[1 - \mathrm{e}^{-p^2\tilde{t}}(1 + p^2\tilde{t})]\right\} \tag{4.42}$$

$$M_{yy}(\tilde{t}) = M_{zz}(\tilde{t}) = 2D_0\tau_\mathrm{d}\left[\tilde{t} + 2\sum_{p=1}^{\infty}\frac{1}{p^2}(1 - \mathrm{e}^{-p^2\tilde{t}})\right] \tag{4.43}$$

Having derived general expressions for the diffusive displacement tensor $\mathbf{M}(t)$ in the reptation model, we now follow the approach of the previous section and construct an approximate form that is asymptotic for $De \to \infty$ and uniform in $\tilde{t}$. For $De \gg 1$ and $\tilde{t} \gg 1$, the above equations reduce to an asymptotic form strictly analogous to eq 4.1 for the Rouse model:

$$\mathbf{M}(\tilde{t}) \approx 2D_0\tau_\mathrm{d}\begin{pmatrix} \tilde{t} + \frac{1}{3}De^2\tilde{t}^3 & \frac{1}{2}De\tilde{t}^2 & 0 \\ \frac{1}{2}De\tilde{t}^2 & \tilde{t} & 0 \\ 0 & 0 & \tilde{t} \end{pmatrix} \tag{4.44}$$

In contrast, for $\tilde{t} \ll 1$ and $De \gg 1$, we find

$$\mathbf{M}(\tilde{t}) \approx 2D_0\tau_\mathrm{d}\begin{pmatrix} c_1\tilde{t}^{1/2} + (\pi^4/24)De^2\tilde{t} & (\pi^2/4)De\tilde{t} & 0 \\ (\pi^2/4)De\tilde{t} & c_1\tilde{t}^{1/2} & 0 \\ 0 & 0 & c_1\tilde{t}^{1/2} \end{pmatrix} \tag{4.45}$$

Again, we obtain an approximation for $\mathbf{M}(\tilde{t})$ that is uniform in $\tilde{t}$ and asymptotic for $De \to \infty$ by superimposing these asymptotic forms:

$$\mathbf{M}(\tilde{t}) \approx 2D_0\tau_\mathrm{d}\begin{pmatrix} \tilde{t}+c_1\tilde{t}^{1/2}+De^2\left(\frac{\pi^4}{24}\tilde{t}+\frac{1}{3}\tilde{t}^3\right) & \frac{1}{2}De\left(\tilde{t}^2+\frac{\pi^2}{2}\tilde{t}\right) & 0 \\ \frac{1}{2}De\left(\tilde{t}^2 + \frac{\pi^2}{2}\tilde{t}\right) & \tilde{t}+c_1\tilde{t}^{1/2} & 0 \\ 0 & 0 & \tilde{t}+c_1\tilde{t}^{1/2} \end{pmatrix} \tag{4.46}$$

Substitution into eq 2.23 yields an approximation for $S(t)$ appropriate for the limit of strong shear:[29]

$$S_\mathrm{shear}(\tilde{t}) = (8\pi D_0\tau_\mathrm{d})^{-3/2}(\tilde{t} + c_1\tilde{t}^{1/2})^{-1/2}[(\tilde{t} + c_1\tilde{t}^{1/2})^2 + De^2(\tilde{t} + c_1\tilde{t}^{1/2})(\pi^4\tilde{t}/24 + \tilde{t}^3/3) - De^2(\tilde{t}^2 + \pi^2\tilde{t}/2)^2/4]^{-1/2} \tag{4.47}$$

Finally, we insert this result into eq 2.30 and asymptotically evaluate the integral to leading order for $De \to \infty$. We obtain the following asymptotic form for the long-time rate coefficient of the reptation model under strong shear:

$$k_\mathrm{shear} \approx \frac{(2\pi)^{3/2}c_1}{\sqrt{3}}D_0R\frac{De}{\ln De} \approx 32.234D_0R\frac{De}{\ln De} \qquad 1 \ll De \ll \tau_\mathrm{d}/\tau_1 \tag{4.48}$$

It is interesting to compare this result obtained for the reptation model in the strong shear regime $1 \ll De \ll \tau_\mathrm{d}/\tau_1$ to the corresponding expression derived in the previous section for the Rouse model ($k_\mathrm{shear} \sim D_0RDe^{1/3}$). (Be careful to note that D_0 and De have different definitions in the two sections.) Clearly, a much more rapid increase of the reaction rate with Deborah number is predicted for entangled chains in this range of shear rates. We might hope that the asymptotic scaling given in eq 4.48 will hold even beyond the independent alignment approximation, although this remains to be demonstrated. A careful numerical study of $\mathbf{M}(t)$ for a reptating chain in a shear flow would be quite useful in establishing the robustness of this unusual ($De/\ln De$) scaling of the reaction rate.

As the Deborah number is increased in an entangled melt beyond a value of order τ_d/τ_1, significant extension of the primitive chain begins to occur and we anticipate a complicated dependence of k_{shear} on the shear rate. However, as the shear rate is increased even further to a Deborah number of order τ_d/τ_e, where $\tau_e \sim a_t^4 \zeta/(k_B T b^2) \ll \tau_1 \ll \tau_d$ is the time for a Rouse displacement of order a tube diameter to occur,[26] the shear will begin to excite localized Rouse modes that are insensitive to the constraints of tube. Thus, asymptotically at very high shear rates in an entangled melt, we anticipate a return to the Rouse strong shear behavior:

$$k_{\text{shear}} \sim \kappa^{1/3} \qquad De \gg \tau_d/\tau_e \tag{4.49}$$

although the molecular weight dependence of the prefactor in this scaling expression is unclear. It would be quite interesting to experimentally examine the nonmonotonic behavior of $dk_{\text{shear}}/d\kappa$ suggested by eqs 4.48 and 4.49.

V. Discussion

In the present paper we have extended a formalism originally developed by de Gennes to examine how convective effects associated with linear flow fields can modify the rates of diffusion-controlled reactions in polymers. For the specific case examined, namely irreversible reactions occurring in melts that are dilute in chains with a single reactive end, we find that the imposition of flow universally accelerates the reaction rate. This prediction is not expected to be robust for reversible reactions, where flow can enhance dissociation by breaking up large aggregates, nor in cases of intramolecular reactions, where conformational extension under flow can cause reactive sites to move farther apart than at equilibrium. Such situations must be examined on a case-by-case basis and represent interesting areas for future investigations.

The nonanalytic dependence of the effective reaction rate coefficient on flow rate found here is also quite interesting. When the convection is weak, as determined by the appropriate Deborah number ($De \equiv \kappa\tau$, $\tau = \tau_1$ or $\tau = \tau_d$) being small compared with unity, we were able to argue that the form of the rate coefficient was the *same* for both entangled and unentangled melts, and sensitive only to the type of flow. As summarized by eqs 3.19 and 3.20, weak convection imparts $O(De^{1/2})$ corrections to the quiescent rate coefficient, with a slightly larger enhancement in the case of extensional as opposed to shear flow. For strong shear flows, we found that unentangled melts exhibit an asymptotic $O(De^{1/3})$ scaling of the rate coefficient with shear rate, while entangled melts show a scaling $k_{\text{shear}} \sim De/\ln De$ for $1 \ll De \ll \tau_d/\tau_1$, where τ_d is the reptation time and τ_1 is the Rouse time at the relevant molecular weight. Only at much higher shear rates in entangled melts, $De \gg \tau_d/\tau_e$, is the Rouse-like prediction of $k_{\text{shear}} \sim \kappa^{1/3}$ expected to be recovered.

Besides reversible reactions and reactions among sites attached to the same macromolecule, there are a number of important directions in which the present work might be generalized. One of these would be to consider the effect of finite concentrations of reactive sites. Previous studies of small molecule systems at rest[6,7] have found an interesting nonanalytic dependence on reactive site concentration; it would be interesting to see if this persists upon application of flow and attaching the sites to macromolecules. With such an extension, it would be possible to construct a theory of polymer flocculation and examine the role of external flow in enhancing the flocculation rate. Another important extension would be to react polymer systems with added solvent. This would be particularly useful in modeling the effect of flow on rates of termination in free radical polymerizations, which are typically carried out in the presence of a solvent or excess monomer. Finally, we note that the present formalism could in principle be generalized to inhomogeneous systems, such as incompatible polymer blends. Such an extension might prove to be a useful starting point for developing theories of reactive blending.

In conclusion, the effects of flow on diffusion-controlled reactions in macromolecular fluids can be quite profound and interesting. Because reactive polymers typically have very small diffusion coefficients and long relaxation times, reaction rates can be exquisitively sensitive to external forces and flow fields. We hope that further investigations of model systems will lead to new insights into commercially important problems such as reactive blending.

Acknowledgment. This work was supported by the National Science Foundation under grant (GHF) DMR-9505599. We are grateful to Mike Weiss for pointing out an algebraic error in an early version of the manuscript.

References and Notes

(1) Odian, G. *Principles of Polymerization*; Wiley-Interscience: New York, 1981.
(2) Winnik, M. A. *Chem. Rev.* **1981**, *81*, 491.
(3) Horie, K.; Mita, I. *Macromolecules* **1978**, *6*, 1175.
(4) Smoluchowski, M. V. *Phys. Z.* **1916**, *17*, 557. Chandrasekhar, S. *Rev. Mod. Phys.* **1943**, *15*, 1.
(5) We note that there has been considerable work in recent years dealing with the effect of fluctuations in the reaction bath on the form of equations like eq 1.1. For certain types of reactions and in low enough dimensions, mean-field theory breaks down at long times and the use of a time-independent reaction rate coefficient is not permissible. (See, e.g.: Kang, K.; Redner, S. *Phys. Rev. A* **1985**, *32*, 435.) For the present case of the reaction A + A → inert, the upper critical dimension is 2, so the use of a constant (long-time) rate coefficient k_S in eq 1.1 and throughout the remainder of the paper is justified.
(6) Felderhof, B. U.; Deutch, J. M. *J. Chem. Phys.* **1976**, *64*, 4551.
(7) Muthukumar, M.; Cukier, R. I. *J. Stat. Phys.* **1981**, *26*, 453.
(8) Bixon, M.; Zwanzig, R. *J. Chem. Phys.* **1981**, *75*, 2354.
(9) Kirkpatrick, T. R. *J. Chem. Phys.* **1982**, *76*, 4255.
(10) Debye, P. *Trans. Electrochem. Soc.* **1942**, *82*, 265.
(11) Deutch, J. M.; Felderhof, B. U. *J. Chem. Phys.* **1973**, *59*, 1669.
(12) Cukier, R. I. *J. Phys. Chem.* **1983**, *87*, 582.
(13) Wilemski, G.; Fixman, M. *J. Chem. Phys.* **1973**, *58*, 4009; **1974**, *60*, 866, 878.
(14) Doi, M. *Chem. Phys.* **1975**, *9*, 455; **1975**, *11*, 107, 115.
(15) de Gennes, P. G. *J. Chem. Phys.* **1982**, *76*, 3316, 3322.
(16) Bernard, D. A.; Noolandi, J. *Phys. Rev. Lett.* **1983**, *50*, 253. Noolandi, J.; Hong, K. M.; Bernard, D. A. *Macromolecules* **1984**, *17*, 2895. Khokhlov, A. R. *Makromol. Chem., Rapid Commun.* **1981**, *2*, 633.
(17) Friedman, B.; O'Shaughnessy, B. *Macromolecules* **1993**, *26*, 4888, 5726. O'Shaughnessy, B. *Phys. Rev. Lett.* **1993**, *71*, 3331.
(18) A comment regarding the role of flow on diffusion-controlled reactions in polymers was made some years ago by de Gennes (de Gennes, P. G. *Radiation Physics Chemistry* **1983**, *22*, 193), but this line of research was apparently never pursued.

(19) Levich, V. G. *Physicochemical Hydrodynamics*; Prentice Hall: Englewood Cliffs, NJ, 1962.

(20) Leal, L. G. *Laminar Flow and Convective Transport Processes: Scaling Principles and Asymptotic Analysis*; Butterworth-Heinemann: Boston, 1992.

(21) Batchelor, G. K. *J. Fluid Mech.* **1979**, *95*, 369.

(22) Acrivos, A. *J. Fluid Mech.* **1980**, *98*, 299.

(23) In the problems considered in the present paper, we assume that the "capture sphere" is penetrable and does not perturb the linear flow, whereas no-slip boundary conditions on the velocity field were generally employed in the heat transfer studies. This assumption is particularly appropriate for reacting polymer melts, since the effective capture radius is a mesoscopic length of order of the radius-of-gyration,[15] while the reactive sites are microscopic (i.e. of order of the monomer size).

(24) Acrivos, A. *J. Fluid Mech.* **1971**, *46*, 233.

(25) Onuki, A.; Kawasaki, K. *Prog. Theor. Phys.* **1980**, *63*, 122.

(26) Doi, M.; Edwards, S. F. *The Theory of Polymer Dynamics*; Oxford University Press: New York, 1986.

(27) This numerical prefactor can be compared with the first-order ϵ expansion result of ref 17. For end-labeled chains of equal lengths, Friedman and O'Shaughnessy obtain a prefactor of $2\pi\epsilon = 2\pi$ for $\epsilon = 4 - d = 1$. The poor agreement of this prefactor with ours (50.26) is presumably due to the fact that these authors renormalized a bare (low-order) perturbation expansion in a parameter proportional to Q_0, while we explicitly take $Q_0 \to \infty$ at the start of our calculations. We believe our coefficient to be considerably more accurate for the problem at hand, although their formalism offers greater flexibility in treating more general situations.

(28) Larson, R. G. *Constitutive Equations for Polymer Melts and Solutions*; Butterworths: Boston, 1988.

(29) Again we note that the use of the prefactor $2^{-3}\pi^{-3/2}$ is predicated on $\mathbf{d}(t)$ being a Gaussian random variable. This is not strictly the case for the reptation model, so the overall numerical prefactors derived for the reptation model should be viewed with some skepticism. Nevertheless, the scaling behavior with the Deborah number is unaffected.

MA951539Y