

EFFECT OF TEMPERATURE ON POLYMER MIGRATION

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Abstract—In this study, we investigated the temperature gradient effect on the polymer dynamics in a flow field. To simplify our analysis, we adopted a two-bead harmonic dumbbell model, and found that there were significant effects on the polymer migration not only due to the nonhomogeneity of the flow field, but also due to the temperature difference.

INTRODUCTION

Both the theoretical and experimental aspect of polymer migration in nonhomogeneous flow fields have been widely published [1-8]. In studying a rheological separation method for DNA molecules, Dill and Zimm [7] investigated the macromolecular migration phenomenon in the nonhomogeneous flow set up in a DNA solution confined between rotating concentric cones.

Shaler et al. [8] also found that cross-streamline migration of DNA molecules occurs radially in a circular Couette flow resulting from the geometry. Cross-streamline migration here implies that a suspended polymer molecule moves perpendicular to the streamlines of the flow. Neglecting hydrodynamic interaction among the beads, Aubert et al. [1,2] showed that the migration is the result of viscous drag with the solvent and it occurs only when the flow is nonhomogeneous; that is, there exists some form of migration such that the polymer lags the flow along a single streamline in pressure-driven flow in a slit. In curvilinear flow, cross-streamline migration was also found to occur considering hydrodynamic interaction. Sekhon et al. [3] suggested that the hydrodynamic interactions inside the polymer molecules are responsible for a new force, leading to another possibility for polymer migration even in the dilute solution limit and parallel flows. Using the theory of Edwards and Freed [9], Jhon and Freed [5] recently developed a multiple scattering theory to more explicitly describe the concentration

dependence of migration of Rouse-Zimm type polymers, and also to extend previous theories with the inclusion of complete hydrodynamic interactions.

However, all of these previous works were studied under isothermal conditions. Our aim in this study is to extend the polymer migration in a temperature gradient field, and to derive the origin of the forces that produce a deviation in the trajectory of the polymer from the main stream. The migration of polymer molecules is characterized by computing \triangle , defined by

$$\triangle \equiv \dot{\mathbf{r}}_c - \mathbf{v}(\mathbf{r}_c, t), \quad (1)$$

where \mathbf{r}_c is the center of mass of polymer, $\dot{\mathbf{r}}_c$ is the velocity of the center of mass. Eq. (1) considers the migration of the polymer from the unperturbed flow of the fluid. When $\triangle \neq 0$ and \triangle is perpendicular to $\mathbf{v}(\mathbf{r}_c, t)$, polymer migration will occur across the streamline. Therefore, to study other source of polymer migration besides the nonhomogeneity effect of the flow field, we will adopt the bead-spring elastic dumbbell model in nonisothermal system of the flow. The theory developed here can be easily generalized for an n -bead chain, and we will come up with a qualitative solution.

DEVELOPMENT

Here, we choose a bead-spring model to describe the polymer for simplicity. It consists of two beads of equal mass connected by a linear spring as shown in Fig. 1. A force balance written for each bead of the dumbbell (eliminating acceleration terms) gives [10],

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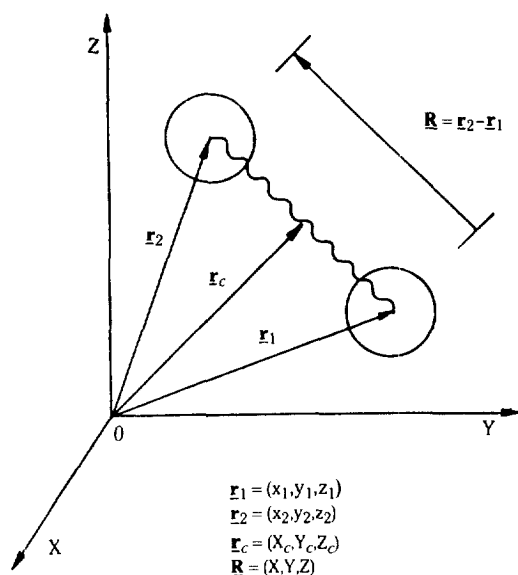


Fig. 1. Elastic dumbbell, made up of two beads connected by a Hookean spring.

$$0 = -\zeta_1 (\dot{\underline{r}}_1 - \underline{v}_1) - kT_1 \frac{\partial}{\partial \underline{r}_1} \ln \Psi + H \underline{R},$$

$$0 = -\zeta_2 (\dot{\underline{r}}_2 - \underline{v}_2) - kT_2 \frac{\partial}{\partial \underline{r}_2} \ln \Psi - H \underline{R}. \quad (2)$$

The first term is the friction force with ζ as the friction coefficient. The second term represents Brownian motion. $\Psi(\underline{r}_1, \underline{r}_2, t)$ is the configurational distribution function. The third term is the spring force, and H is the Hookean spring constant. The friction coefficient and the temperature of each bead are given as functions of position. Our treatment, which includes explicit position dependence, is more general than Bird et al. [10]. The coordinates of eq. (2) are transformed into center of mass coordinates (\underline{r}_c) and internal coordinates (\underline{R}) by the following procedure:

$$\underline{r}_c = \frac{1}{2} (\underline{r}_1 + \underline{r}_2)$$

$$= \underline{v}_+ - \frac{1}{2} \left(\xi_1 \left(-\frac{\partial}{\partial \underline{R}} + \frac{\partial}{\partial \underline{r}_c} \right) + \xi_2 \left(\frac{\partial}{\partial \underline{R}} + \frac{\partial}{\partial \underline{r}_c} \right) \right) \ln \Psi - \frac{1}{2} \nu_- \underline{R}, \quad (3)$$

where we define $A_+ = 1/2(A_1 + A_2)$, $A_- = A_2 - A_1$, $\frac{kT_i}{\zeta_i} \equiv \xi_i$, and $\frac{H}{\zeta_i} \equiv \nu_i$. Simplifying eq. (3), we have the velocity of the center of mass of the dumbbell.

$$\dot{\underline{r}}_c = \underline{v}_+ - \frac{1}{2} \xi_- \frac{\partial}{\partial \underline{R}} \ln \Psi - \frac{1}{2} \xi_+ \frac{\partial}{\partial \underline{r}_c} \ln \Psi - \frac{1}{2} \nu_- \underline{R}. \quad (4)$$

Again from eq. (2), we can have

$$\underline{R} = \dot{\underline{r}}_2 - \dot{\underline{r}}_1$$

$$= \underline{v}_- - 2\xi_+ \frac{\partial}{\partial \underline{R}} \ln \Psi - \frac{1}{2} \xi_- \frac{\partial}{\partial \underline{r}_c} \ln \Psi - 2\nu_+ \underline{R}. \quad (5)$$

The translation operator: $\underline{f}(\underline{r}) = \exp[\underline{r} \cdot \nabla'] \underline{f}(\underline{r}')|_{r'=0}$ is adopted to express an arbitrary velocity field in terms of a polynomial of the spatial coordinates. Using the equations, $\underline{r}_1 = \underline{r}_c - \underline{R}/2$ and $\underline{r}_2 = \underline{r}_c + \underline{R}/2$, we can represent the velocity field at positions \underline{r}_1 and \underline{r}_2 as

$$\underline{v}(\underline{r}_1) = \exp\left[\left(\underline{r}_c - \frac{\underline{R}}{2}\right) \cdot \nabla'\right] \underline{v}(\underline{r}')|_{r'=0}, \text{ and}$$

$$\underline{v}(\underline{r}_2) = \exp\left[\left(\underline{r}_c + \frac{\underline{R}}{2}\right) \cdot \nabla'\right] \underline{v}(\underline{r}')|_{r'=0}. \quad (6)$$

We will calculate the migration velocity defined in eq. (1), where $\underline{v}(\underline{r}) = \exp[\underline{r} \cdot \nabla'] \underline{v}(\underline{r}')|_{r'=0}$. Using the translation operator, the quantities A_+ and A_- can be simplified as follows:

$$A_+ = \frac{1}{2} [\exp(\underline{r}_1 \cdot \nabla') + \exp(\underline{r}_2 \cdot \nabla')] A(\underline{r}')|_{r'=0}$$

$$= \exp(\underline{r}_c \cdot \nabla') \cosh\left(\frac{\underline{R}}{2} \cdot \nabla'\right) A(\underline{r}')|_{r'=0},$$

and

$$A_- = [\exp(\underline{r}_2 \cdot \nabla') - \exp(\underline{r}_1 \cdot \nabla')] A(\underline{r}')|_{r'=0}$$

$$= 2 \exp(\underline{r}_c \cdot \nabla') \sinh\left(\frac{\underline{R}}{2} \cdot \nabla'\right) A(\underline{r}')|_{r'=0}. \quad (7)$$

Substituting eq. (4) into the definition of Δ , we obtain

$$\Delta = 2 \exp(\underline{r}_c \cdot \nabla') \sinh^2\left(\frac{\underline{R}}{4} \cdot \nabla'\right) \underline{v}(\underline{r}')|_{r'=0}$$

$$- \frac{\xi_-}{2} \frac{\partial}{\partial \underline{r}_c} \ln \Psi - \frac{\xi_-}{2} \frac{\partial}{\partial \underline{R}} \ln \Psi - \frac{1}{2} \nu_- \underline{R}. \quad (8)$$

The measurable quantity is the average of some quantity Δ over the internal coordinates. This average is denoted by angular brackets: $\langle A \rangle = \int d^3R A \Psi$

$$\langle \Delta \rangle = 2 \langle \exp(\underline{r}_c \cdot \nabla') \sinh^2\left(\frac{\underline{R}}{4} \cdot \nabla'\right) \underline{v}(\underline{r}')|_{r'=0} \rangle$$

$$- \frac{1}{2} \langle \xi_- \left(\frac{\partial}{\partial \underline{r}_c} \ln \Psi \right) \rangle - \frac{1}{2} \langle \xi_- \frac{\partial}{\partial \underline{R}} \ln \Psi \rangle$$

$$- \frac{1}{2} \langle \nu_- \underline{R} \rangle. \quad (9)$$

Ψ can be conveniently expressed as the composite of two functions:

$$\Psi = C(\underline{r}_c, t) \psi(\underline{R}, \underline{r}_c, t), \quad (10)$$

where C is the local dumbbell concentration

$$C(\underline{r}_c, t) \equiv \int d^3R \Psi(\underline{R}, \underline{r}_c, t). \quad (11)$$

Using these definitions we can rearrange eq. (9) as

$$\langle \Delta \rangle = (V_F + V_T)C - D \frac{\partial}{\partial \underline{r}_c} C, \quad (12)$$

with

$$V_F = 2 \left[\exp(\underline{r}_c \cdot \nabla') \sinh^2 \left(\frac{\underline{R}}{4} \cdot \nabla' \right) \underline{v}(\underline{r}') \right]_{r=0},$$

$$V_T = \frac{1}{2} \left[\left\langle \frac{\partial \xi}{\partial \underline{R}} \right\rangle - (\underline{v} \cdot \underline{R}) \right],$$

and

$$D = \frac{1}{2} \langle \xi_+ \rangle. \quad (13)$$

By taking Taylor expansions of the averaged values in eq. (13) and neglecting higher order terms, we obtained the following result (Details are given in the Appendix).

$$V_F = \frac{kT}{8H} \nabla'^2 \underline{v}(\underline{r}')|_{r=0},$$

$$V_T = \frac{1}{2} \left[\nabla' \xi(\underline{r}') - \frac{kT}{H} \nabla' \underline{v}(\underline{r}') \right]_{r=0},$$

and

$$D = \frac{1}{2} \left[\xi(\underline{r}_c) + \frac{kT}{8H} \nabla'^2 \xi(\underline{r}')|_{r=0} \right]. \quad (14)$$

RESULT AND DISCUSSION

Clearly V_F in eq. (13) is the general expression of polymer migration due to a nonhomogeneous flow field effect; V_F is zero for homogeneous flows, while nonzero for nonhomogeneous flow. A quadratic form of nonhomogeneity was well investigated by Aubert and Tirrell [1]. Considering the second order terms in Taylor series expansion for the velocity field, they obtained $V_F = \frac{1}{8} \langle \underline{RR} \rangle : \nabla \nabla \underline{v}$, where $\langle \underline{RR} \rangle$ is the dyadic product of the end-to-end vector. Obviously, we can obtain the same result by only considering the second order expansion terms of the first term of eq. (9). D contains information about migration resulting from Fickian diffusion and yields the same result in the case of the free-draining limit [3]. V_T accounts for migration due to the temperature gradient, which is the new result of this paper. Thermal migration has not been previously studied.

When we consider V_T in eq. (14), we can easily find the effect of the temperature gradient.

$$\nabla' \xi(\underline{r}') = \nabla' \xi(T(\underline{r}')) = (\nabla' T) \xi'(T),$$

$$\frac{kT}{H} \nabla' \underline{v}(\underline{r}') = \frac{kT(\underline{r}')}{H} (\nabla' T) \underline{v}'(T), \quad (15)$$

and V_T is proportional to the direction of temperature gradient, and

$$V_T = \frac{1}{2} \left[\xi'(T) - \frac{kT}{H} \underline{v}'(T) \right] \nabla' T. \quad (16)$$

Our present analysis is valid only for unbounded flows and dilute polymer solutions. We ignore the interactions between solid boundaries and the beads and the hydrodynamic interactions between the beads. For simplicity, even though we have chosen the dumbbell model, the results can be extended to the n -bead chain. We are currently carrying out numerical studies on concentration profile and higher order moments (e.g. second moments will give rheological equation of state).

Appendix A: derivation of $\langle \Delta \rangle$

Each term of eq. (12) can be expanded by using the Taylor series expansion and by the definition of the average of some quantity as follows:

$$\begin{aligned} & \langle \exp(\underline{r}_c \cdot \nabla') \sinh^2 \left(\frac{\underline{R}}{4} \cdot \nabla' \right) \underline{v}(\underline{r}') \rangle_{r=0} \\ &= \left\langle \sum_{n=0}^{\infty} \frac{(\underline{r}_c \cdot \nabla')^n}{n!} \sum_{m=1}^{\infty} \frac{(\frac{\underline{R}}{2} \cdot \nabla')^{2m}}{(2m)!} \underline{v}(\underline{r}') \right\rangle_{r=0} \\ &= \left\langle \left[1 + (\underline{r}_c \cdot \nabla') + \frac{1}{2!} (\underline{r}_c \cdot \nabla')^2 + \dots \right] \right. \\ & \quad \left. \left[\frac{1}{2!} \left(\frac{\underline{R}}{2} \cdot \nabla' \right)^2 : \nabla' \nabla' + \frac{1}{4!} \left(\frac{\underline{R}}{2} \cdot \nabla' \right)^4 : \nabla' \nabla' \nabla' \nabla' + \dots \right] \underline{v}(\underline{r}') \right\rangle_{r=0} \\ &= \frac{1}{8} \langle \underline{RR} \rangle : \nabla' \nabla' \underline{v}(\underline{r}')|_{r=0} + \frac{1}{8} \langle \underline{r}_c \underline{RR} \rangle : \nabla' \nabla' \nabla' \underline{v}(\underline{r}')|_{r=0} + \dots \\ &\cong \frac{1}{8} \langle \underline{RR} \rangle : \nabla' \nabla' \underline{v}(\underline{r}')|_{r=0} \\ &= \frac{1}{8} \frac{kT}{H} \nabla'^2 \underline{v}(\underline{r}')|_{r=0} \quad (A. 1) \\ & \langle \xi_+ \rangle = \left\langle \sum_{n=0}^{\infty} \frac{(\underline{r}_c \cdot \nabla')^n}{n!} \sum_{m=0}^{\infty} \frac{(\frac{\underline{R}}{2} \cdot \nabla')^{2m}}{(2m)!} \xi(\underline{r}') \right\rangle_{r=0} \\ &= \langle \xi(\underline{r}') \rangle_{r=0} + \underline{r}_c \cdot \nabla' \xi(\underline{r}')|_{r=0} \end{aligned}$$

$$\begin{aligned}
& + \frac{1}{2!} \underline{\mathbf{r}}_c \underline{\mathbf{r}}_c : \nabla' \nabla' \xi(\underline{\mathbf{r}}') |_{\underline{\mathbf{r}}=0} \\
& + \frac{1}{8} \underline{\mathbf{R}} \underline{\mathbf{R}} : \nabla' \nabla' \xi(\underline{\mathbf{r}}') |_{\underline{\mathbf{r}}=0} + \dots > \\
& \equiv \xi(\underline{\mathbf{r}}_c) + \frac{1}{8} \langle \underline{\mathbf{R}} \underline{\mathbf{R}} \rangle : \nabla' \nabla' \xi(\underline{\mathbf{r}}') |_{\underline{\mathbf{r}}=0} \\
& = \xi(\underline{\mathbf{r}}_c) + \frac{1}{8} \frac{kT}{H} \nabla'^2 \xi(\underline{\mathbf{r}}') |_{\underline{\mathbf{r}}=0} \quad (\text{A. 2})
\end{aligned}$$

$$\begin{aligned}
\langle \frac{\partial \xi}{\partial \underline{\mathbf{R}}} \rangle &= 2 \langle \frac{\partial}{\partial \underline{\mathbf{R}}} \left\{ \sum_{n=0}^{\infty} \frac{(\underline{\mathbf{r}}_c \cdot \nabla')^n}{n!} \sum_{m=0}^{\infty} \frac{(\frac{\underline{\mathbf{R}}}{2} \cdot \nabla')^{2m}}{(2m+1)!} \right. \\
&\quad \left. \xi(\underline{\mathbf{r}}') |_{\underline{\mathbf{r}}=0} \right\} \rangle \\
&\equiv 2 \langle \frac{\partial}{\partial \underline{\mathbf{R}}} \left[\frac{\underline{\mathbf{R}}}{2} \cdot \nabla' \xi(\underline{\mathbf{r}}') |_{\underline{\mathbf{r}}=0} \right] \rangle \\
&= 2 \langle \frac{\partial}{\partial R_i} \left[\frac{R_i}{2} \frac{\partial}{\partial r_j} \cdot \xi(\underline{\mathbf{r}}') |_{\underline{\mathbf{r}}=0} \right] \rangle \delta_i \\
&= \langle \delta_{ij} \frac{\partial}{\partial r_j} \cdot \xi(\underline{\mathbf{r}}') |_{\underline{\mathbf{r}}=0} \rangle \delta_i \\
&= \nabla' \xi(\underline{\mathbf{r}}') |_{\underline{\mathbf{r}}=0} \quad (\text{A. 3})
\end{aligned}$$

$$\begin{aligned}
\langle \nu \cdot \underline{\mathbf{R}} \rangle &= 2 \left\langle \sum_{n=0}^{\infty} \frac{(\underline{\mathbf{r}}_c \cdot \nabla')^n}{n!} \sum_{m=0}^{\infty} \frac{(\frac{\underline{\mathbf{R}}}{2} \cdot \nabla')^{2m+1}}{(2m+1)!} \right. \\
&\quad \left. \nu(\underline{\mathbf{r}}') |_{\underline{\mathbf{r}}=0} \right\rangle \underline{\mathbf{R}} > \\
&= \langle \underline{\mathbf{R}} \underline{\mathbf{R}} \rangle : \nabla' \nu(\underline{\mathbf{r}}') |_{\underline{\mathbf{r}}=0} \\
&= \frac{kT}{H} \nabla' \cdot \nu(\underline{\mathbf{r}}') |_{\underline{\mathbf{r}}=0} \quad (\text{A. 4})
\end{aligned}$$

Inserting equations (A.1), (A.2), (A.3) and (A.4) into eq. (13), we can finally obtain eq. (14).

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NOMENCLATURE

a : radius of bead
 A : arbitrary quantity
 $A_{+} = (A_1 + A_2)/2$
 $A_{-} = A_2 - A_1$

C : local dumbbell concentration
 H : spring constant
 k : Boltzmann's constant
 $\underline{\mathbf{r}}$: position vector
 $\underline{\mathbf{r}}_i$: position vector of i th bead
 $\underline{\mathbf{r}}_c$: center-of-mass, $= (\underline{\mathbf{r}}_1 + \underline{\mathbf{r}}_2)/2$
 $\underline{\mathbf{R}}$: internal configuration coordinate, $= \underline{\mathbf{r}}_2 - \underline{\mathbf{r}}_1$
 t : time
 T : absolute temperature
 $\underline{\mathbf{v}}$: fluid velocity
 $\underline{\mathbf{v}}_c$: fluid velocity at the center of mass
 $\underline{\mathbf{v}}_o$: fluid velocity at the origin

Greek Letters

ζ : friction coefficient
 η : viscosity
 ν : $1/\zeta$
 ξ : kT/ζ
 Ψ : probability function
 ϕ : probability function (normalized with respect to internal coordinates)

REFERENCES

1. Aubert, J.H. and Tirrell, M.: *J. Chem. Phys.*, **72**(4), 2694 (1980).
2. Aubert, J.H., Prager, S. and Tirrell, M.: *J. Chem. Phys.*, **73**(8), 4103 (1980).
3. Sekhon, G., Armstrong, R.C. and Jhon, M.S.: *J. Poly. Sci.; Poly. Phys. Ed.*, **20**, 947 (1982).
4. Brunn, P.O. and Chi, S.: *Rheol. Acta*, **23**, 163 (1984).
5. Jhon, M.S. and Freed, K.F.: *J. Poly. Sci.; Poly. Phys. Ed.*, **23**, 955 (1985).
6. Aubert, J.H. and Tirrell, M.: *Rheol. Acta*, **19**, 452 (1980).
7. Dill, K.A. and Zimm, B.H.: *Nucleic Acids Research*, **7**(3), 735 (1979).
8. Shafer, R.H., Laiken, N. and Zimm, B.H.: *Biophys. Chem.*, **2**, 180 (1974).
9. Edwards, S.F. and Freed, K.F.: *J. Chem. Phys.*, **61**, 1189 (1974); Freed, K.F., in "Progress in Liquid Physics", Croxton, C.A. ed., Wiley, New York, p.343 (1978).
10. Bird, R.B., Curtiss, C.F., Armstrong, R.C. and Hassager, O.: "Dynamics of Polymeric Liquids", Vol. 2, Wiley, New York (1987).