EFFECT OF TEMPERATURE ON POLYMER MIGRATION II: CONCENTRATION EQUATION

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Abstract—Polymer migration is a generally well-known phenomenon in a flow field, and it has been verified that the sources of such phenomena are nonhomogeneity of the flow, concentration effects and hydrodynamic interactions between the polymer molecules. In addition, temperature effects were found to be another source of polymer migration. The Langevin equation for a polymer molecule was first derived from single chain dynamics using a kinetic theory for the bead-spring elastic harmonic dumbbell model, as described in part I (reference [1]). In this paper the diffusion equation and concentration profile of the polymer molecules induced by a temperature gradient are obtained from the Fokker-Planck equation. A new differential operator is also introduced to calculate the concentration profile. From the concentration equation obtained in the general flow geometry, we find that in dilute polymer solution there are significant effects on the polymer migration not only due to the nonhomogeneity of the flow field but also due to temperature gradients.

INTRODUCTION

When polymer molecules are exposed to a flow field in a confined geometry, they may not follow the bulk flow. The polymer molecule may be behind or ahead of the bulk flow, or sometimes may cross the streamline. This phenomenon is called "polymer migration".

Polymer migration has been extensively studied due to the many application possibilities, such as chromatography, rheological measurements, polymer processing, or any system that involves flow. The understanding of this phenomenon might provide insight into nonuniform product experienced during extrusion or injection moulding. Migration is also important to the study of red blood cell migration in a blood vessel.

Bird et al. [2] studied the typically well-known kinetic theory of polymers in homogeneous flows. Shafer et al. [3] were the first to show the cross-stream migration of DNA molecules toward the axis in circular Couette flow. In addition, Aubert et al. [4, 5] found that there was some form of migration in all flow, curved or noncurved. However, in parallel flows, they found that the polymer only lags or precedes along a single streamline. The hydrodynamic interactions be-

tween the polymer molecules are also responsible for a new force, leading to another possibility for polymer migration [6-8]. Furthermore, for other polymer molecule models, Brunn [9] used nonlinear elastic dumbbells and found that deformability and hydrodynamic interaction are indispensible pre-requisites for any net migration to take place in viscometric flows.

Most of the work in this field has been done under isothermal conditions. However, in our previous study [1], the temperature gradient effect on polymer dynamics in a flow field was introduced. Applying an elastic dumbbell model, Inn et al. [1] obtained the polymer migration velocity and found that there were significant effects on polymer migration due to the temperature gradient within the flow.

In this study, starting from the continuity equation for the configurational distribution function and developing the nth-moment equation, we further scrutinize the effect of temperature on polymer migration by obtaining a Fokker-Plank type equation and a diffusion equation of the polymer molecules. In addition, we adopt a new differential operator to study polymer migration.

POLYMER CHAIN DYNAMICS

When polymer molecules are immersed in a Newtonian solvent, dynamic couplings between the two re-

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sult. In other words, the polymer molecules disturb the Newtonian solvent, and at the same time the solvent changes the polymer conformation. Therefore, it is important to study the dynamics of polymer solutions [10], to understand the overall rheological properties and polymer molecular behavior. From the dynamics of polymer solutions, we can obtain the force balance equation for the dumbbell beads to investigate polymer migration. The study of polymer dynamics has been well carried out by Freed and other investigators [11-16].

Considering a single polymer chain in a Newtonian solvent, the fundamental equation in fluid dynamics equations are derived from the principles of conservation of mass and momentum. The equation of motion for Newtonian fluids is the following Navier-Stokes equation:

$$\rho\left[\frac{\partial}{\partial t}+\mathbf{v}\cdot\nabla\right]\mathbf{v}-\eta\nabla^2\mathbf{v}+\nabla P=\mathbf{F}^{ext} \tag{1}$$

Here $\mathbf{v}$ is velocity at position $\mathbf{r}$ and time t, ρ is fluid density, P is isotropic pressure, η is viscosity, and $\mathbf{F}^{ext}$ is the body force. If we introduce the Reynolds number (Re) and Strouhal number (Sr) and assume $Re \ll 1$ and $ReSr^{-1} \simeq 1$, Eq. (1) can be approximated by a linearized Navier-Stokes equation [17].

$$\rho\frac{\partial}{\partial t}\mathbf{v}-\eta\nabla^2\mathbf{v}+\nabla P=\mathbf{F}^{ext} \tag{2}$$

When a polymer is immersed in a Newtonian solvent, bead i exerts a force $\sigma_i(t)$ on the fluid. Given that bead i is at position $\mathbf{r}_i(t)$, the force $\sigma_i(t)$ represents a point source. Hence the collection of all polymer beads yields a force density $\sum_{i=1}^{n}\delta[\mathbf{r}-\mathbf{r}_i(t)]\,\delta_i(t)$, acting on the fluid, where δ is the three-dimensional delta function. Therefore, upon introduction of this force into Eq. (2), the fluid flow can be characterized by the following linearized Navier-Stokes equation [11-14]:

$$\rho\frac{\partial}{\partial t}\mathbf{v}-\eta\nabla^2\mathbf{v}+\nabla P(\mathbf{r},\ t)$$
$$=\sum_{i=1}^{n}\delta[\mathbf{r}-\mathbf{r}_i(t)]\,\sigma_i(t)+\mathbf{F}^{ext}$$
$$=\sum_{i=1}^{n}\phi(\mathbf{r},\ t)\,\sigma_i(t)+\mathbf{F}^{ext} \tag{3}$$

Here $\phi(\mathbf{r},\ t)\equiv\delta[\mathbf{r}-\mathbf{r}_i(t)]$.

On the other hand, the equation of motion for the ith bead follows Newton's second law as follows:

$$m_i\frac{d^2}{dt^2}\mathbf{r}_i(t)=-\sigma_i(t)+\mathbf{f}_i^*+\mathbf{F}_i^{(c)}, \tag{4}$$

where, m_i is the mass of the ith bead, $\mathbf{f}_i^*$ is the random Brownian force and $\mathbf{F}_i^{(c)}$ is the connector force. The presence of the solvent will produce a force equal to $-\sigma_i(t)$ on the polymer bead from Newton's third law. The simplest model for the connector force (known as a linear spring or Rouse chain) is given as [11]

$$-\mathbf{F}_i^{(c)}=\sum_j\frac{3kT}{l^2}A_{ij}\,\mathbf{r}_j(t)\equiv\Delta_i\,\mathbf{r}_i(t), \tag{5}$$

where $A_{ij}=2\delta_{i,j}-\delta_{i-1,j}-\delta_{i+1,j}$ is an element of the Rouse matrix [2], l is the mean distance between the beads, k is the Boltzmann constant, and T is the absolute temperature. Neglecting the inertia term, Eq. (4) can be written as

$$\Delta_i\,\mathbf{r}_i(t)=H(2\mathbf{r}_i-\mathbf{r}_{i-1}-\mathbf{r}_{i+1})=-\sigma_i+\mathbf{f}_i^*, \tag{6}$$

where $H=3kT/l^2$ is the Hookean spring constant. In Eq. (6) we still require a hydrodynamic boundary condition to determine the unknown force $\sigma_i(t)$. A boundary condition requiring no slip at the bead surface is mathematically the simplest one and implies that [14]

$$\dot{\mathbf{r}}_i(t)=\mathbf{v}[\mathbf{r}_i(t),\ t]=\int d^3r\varphi_i(\mathbf{r})\mathbf{v}(\mathbf{r},\ t)\equiv\varphi_i(\mathbf{r})\bar{\mathbf{v}}(\mathbf{r},\ \bar{t}), \tag{7}$$

where the over-barred variables imply integration.

Now we can calculate the velocity of the fluid in the presence of a polymer molecule. We can formally solve $\mathbf{v}$ in terms of the Green function of a pure fluid [15];

$$\mathbf{v}(\mathbf{r},\ t)=\mathbf{v}_0(\mathbf{r},\ t)+\mathbf{G}(\mathbf{r}-\bar{\mathbf{r}};\ t-\bar{t})\cdot\sum_{i=1}^{n}\varphi_i(\bar{\mathbf{r}})\,\sigma_i(\bar{t}) \tag{8}$$

Where $\mathbf{v}_0$ is the velocity profile in the absence of the polymer molecule, which can be calculated from the Navier-Stokes and continuity equations. It is well known in simple confined geometry. By assuming creeping flow, $\mathbf{G}$ can be expressed as the following Oseen tensor [10]:

$$\mathbf{G}(\mathbf{r})=\frac{1}{8\pi\eta r}\left(\mathbf{I}+\frac{\mathbf{rr}}{r^2}\right). \tag{9}$$

From Eqs. (7) through (9) we obtain the explicit expression for single chain dynamics for the ith bead [11, 14, 16] in the following form:

$$\dot{\mathbf{r}}_i(t)=\varphi_i(\bar{\mathbf{r}})\,\mathbf{v}_0(\bar{\mathbf{r}},\ t)+\varphi_i(\bar{\mathbf{r}})\mathbf{G}(\bar{\mathbf{r}},\ \bar{\mathbf{r}};\ t-\bar{t})$$
$$\cdot\sum_{j=1}^{n}\varphi_j(\bar{\mathbf{r}})\{-\Delta_j\mathbf{r}_j(t)+\mathbf{f}_j^*(\bar{t})\}$$
$$=\mathbf{v}_0(\mathbf{r}_i,\ t)+\sum_j\mathbf{T}_{ij}\cdot(-\Delta_j\mathbf{r}_j(t)+\mathbf{f}_j^*) \tag{10}$$

Where $T_{ij}(t-t') = G[r_i(t) - r_j(t'); t-t']$. Eq. (10) implies that the velocity of the ith bead is the summation of the undisturbed velocity of the fluid at r_i, and the velocity disturbances created by the beads. The term involving T_{ij} can arise from two different physical origins: the Stokes law type of drag force on the same bead i for i=j and the Oseen type of hydrodynamic interaction from the different beads j if i≠j [15]. The calculation of T_{ij} requires fluid mechanical calculations.

An alternative method is to express the dynamics of the polymer chain in terms of a probability function Ψ, which yields the Fokker-Plank equation. Eq. (10) is known as the chain Langevin equation for a single chain. In deriving this equation, the n-bead model is used. In practice the n-bead model involves extensive bookkeeping problems. To avoid this complexity, we use a two-bead dumbbell model. Even though this dumbbell model in no way accounts for the details of the molecular architecture, it has been found that the dumbbell qualitatively reproduces most features of the N-bead response [18]. It is orientable and stretchable, and these two properties are essential for the qualitative description of steady-state rheological properties and those involving slow changes with time. Especially from the relaxation process viewpoint, the slowest and in many ways most important relaxation process is the relaxation of the entire molecule. This process affects the end-to-end vector of the entire molecule and its dynamics are captured by a simple model with just one spring having a bead at each end, that is the two-bead elastic dumbbell model [19]. For the dumbbell model, the Langevin equation for each bead 1 and 2 can be written in the form:

$$\dot{r}_1 = v_0(r_1, t) + T_{11}(t-\bar{t}) \cdot [F_1^{(c)}(\bar{t}) + f_1^*(\bar{t})] + T_{12}(t-\bar{t}) \cdot [F_2^{(c)}(\bar{t}) + f_2^*(\bar{t})]$$

$$r_2 = v_0(r_2, t) + T_{21}(t-\bar{t}) \cdot [F_1^{(c)}(\bar{t}) + f_1^*(\bar{t})] + T_{22}(t-\bar{t}) \cdot [F_2^{(c)}(\bar{t}) + f_2^*(\bar{t})] \qquad (11)$$

where $F_i^{(c)}$ (i=1, 2) is the connector for the two-bead elastic dumbbell model.

To simplify our analysis, we neglect the hydrodynamic interaction between the beads and set [15]

$$T_{ij}(t-t') \cong \zeta^{-1}\delta_{ij}\delta(t-t'). \qquad (12)$$

The Brownian random force, f^*, can be defined as follows:

$$f_i^* = -kT\frac{\partial}{\partial r_i} \ln\Psi. \qquad (13)$$

In polymer kinetic theory, one of the important parameters is the configurational distribution function (Ψ). With these simplifications, Eq. (11) can be written as follows:

$$\dot{r}_1 = v_0(r_1) + \zeta_{-1}\left(F_1^{(c)} - kT\frac{\partial}{\partial r_1} \ln\Psi\right),$$

$$\dot{r}_2 = v_0(r_2) + \zeta_{-1}\left(F_2^{(c)} - kT\frac{\partial}{\partial r_2} \ln\Psi\right). \qquad (14)$$

The coordinates of Eq. (14) are transformed into center of mass coordinates $[r_c = (r_1 + r_2)/2]$ and internal coordinates ($R = r_2 - r_1$) by the following procedure [1]:

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

$$= v_+ - \frac{1}{2}\left[\zeta_1\left(-\frac{\partial}{\partial R} + \frac{1}{2}\frac{\partial}{\partial r_c}\right) + \zeta_2\left(\frac{\partial}{\partial R} + \frac{1}{2}\frac{\partial}{\partial r_c}\right)\right]\ln\Psi - \frac{1}{2}\beta_- R, \qquad (15)$$

where we define $A_+ = \frac{1}{2}(A_1 + A_2)$, $A_- = A_2 - A_1$,

$$\frac{kT_i}{\zeta_i} \equiv \xi_i \text{ and } \frac{H}{\zeta_i} \equiv \beta_i.$$

In this study, since we express the temperature as a function of position in the field, viscosity will also be a function of position. In addition, from the Stokes equation, the friction coefficient also depends on the position. Simplifying Eq. (15), we have the velocity of the center of mass of the dumbbell in the following form:

$$\dot{r}_c = v_+ - \frac{1}{2}\xi_-\frac{\partial}{\partial R} \ln\Psi - \frac{1}{2}\xi_+\frac{\partial}{\partial r_c} \ln\Psi - \frac{1}{2}\beta_- R. \qquad (16)$$

Again from Eq. (14), we have

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

$$= v_- - 2\xi_+\frac{\partial}{\partial R} \ln\Psi - \frac{1}{2}\xi_-\frac{\partial}{\partial r_c} \ln\Psi - 2\beta_+ R. \qquad (17)$$

Using the translation operator, the quantities A_+ and A_- are arranged as follows:

$$A_+ = \frac{1}{2}[\exp(r_1 \cdot \nabla') + \exp(r_2 \cdot \nabla')] A(r')|_{r'=0}$$

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

$$A_- = \frac{1}{2}[\exp(r_2 \cdot \nabla') - \exp(r_1 \cdot \nabla')] A(r')|_{r'=0}$$

$$= 2\exp(r_c \cdot \nabla')\sinh\left(\frac{R}{2} \cdot \nabla'\right) A(r')|_{r'=0} \qquad (18)$$

where the translation operator is defined as: $f(r) = \exp[r \cdot \nabla']f(r')|_{r'=0}$. From the definition of polymer migration velocity, $\Delta = \dot{r}_c - v(r_c, t)$, we obtain the following

equation [1]:

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

$$-\frac{1}{2}\left\langle\xi_+\frac{\partial}{\partial\mathbf{r}_c}\ln\Psi\right\rangle$$

$$\underline{-\frac{1}{2}\left\langle\xi_-\frac{\partial}{\partial\mathbf{R}}\ln\Psi\right\rangle-\frac{1}{2}\langle\beta_-\mathbf{R}\rangle.}\qquad(19)$$

Here, the angular brackets denote the average over the internal coordinates and the underlined term is the new result of migration due to the temperature gradient.

EQUATION OF CONCENTRATION

The configurational distribution function of the polymer molecules satisfies the following equation of continuity which has similarity with the equation of continuity in hydrodynamics in the six-dimensional configurational space [2]:

$$\frac{\partial\Psi}{\partial t}=-\frac{\partial}{\partial\mathbf{R}}\cdot(\dot{\mathbf{R}}\Psi)-\frac{\partial}{\partial\mathbf{r}_c}\cdot(\dot{\mathbf{r}}_c\Psi).\qquad(20)$$

Substituting Eqs. (16) and (17) into Eq. (20), we obtain

$$\frac{\partial\Psi}{\partial t}=-\frac{\partial}{\partial\mathbf{R}}\cdot(\mathbf{v}_-\Psi)+\left[\frac{\partial}{\partial\mathbf{R}}\cdot(2\xi_+)\frac{\partial}{\partial\mathbf{R}}\Psi\right]$$

$$+\frac{1}{2}\frac{\partial}{\partial\mathbf{R}}\cdot\left(\xi_-\frac{\partial}{\partial\mathbf{r}_c}\Psi\right)+\frac{\partial}{\partial\mathbf{R}}\cdot(2\beta_+\mathbf{R}\Psi)$$

$$-\frac{\partial}{\partial\mathbf{r}_c}\cdot(\mathbf{v}_+\Psi)+\frac{1}{2}\frac{\partial}{\partial\mathbf{r}_c}\cdot\left(\xi_-\frac{\partial}{\partial\mathbf{R}}\Psi\right)$$

$$+\frac{1}{2}\frac{\partial}{\partial\mathbf{r}_c}\cdot\left(\xi_+\frac{\partial}{\partial\mathbf{r}_c}\Psi\right)+\frac{\partial}{\partial\mathbf{r}_c}\cdot\frac{1}{2}(\beta_-\mathbf{R}\Psi).\qquad(21)$$

Eq. (21) is a second-order partial differential equation, often referred to as the Fokker-Planck equation.

Since the calculation of the probability function is very difficult we try to obtain an approximate solution. The standard procedure is to construct the moment equations, and to calculate the first few moments.

We now define the integration of any function of the orientation vector, B(R), over the entire configuration space:

$$\langle B\rangle\equiv\int d^3R\,B(\mathbf{R})\Psi(\mathbf{r}_c,\mathbf{R},t)\qquad(22)$$

Using Eq. (22), Eq. (21) can be integrated over all configuration space as follows:

$$\frac{\partial}{\partial t}\langle B\rangle=\left\langle\frac{\partial B}{\partial\mathbf{R}}\cdot\mathbf{v}\right\rangle+\left\langle\frac{\partial}{\partial\mathbf{R}}\cdot(2\xi_+)\frac{\partial B}{\partial\mathbf{R}}\right\rangle$$

$$+\frac{1}{2}\left\langle\frac{\partial B}{\partial\mathbf{R}}\cdot\frac{\partial\xi_-}{\partial\mathbf{r}_c}\right\rangle-\frac{1}{2}\frac{\partial}{\partial\mathbf{r}_c}\cdot\left\langle\frac{\partial B}{\partial\mathbf{R}}\xi_-\right\rangle$$

$$-\left\langle\frac{\partial B}{\partial\mathbf{R}}\cdot2\beta_+\mathbf{R}\right\rangle-\frac{\partial}{\partial\mathbf{r}_c}\cdot\langle\mathbf{v}_+B\rangle$$

$$-\frac{1}{2}\frac{\partial}{\partial\mathbf{r}_c}\cdot\left\langle\frac{\partial}{\partial\mathbf{R}}(B\xi_-)\right\rangle$$

$$+\frac{1}{2}\frac{\partial}{\partial\mathbf{r}_c}\cdot\frac{\partial}{\partial\mathbf{r}_c}\langle B\xi_+\rangle$$

$$-\frac{1}{2}\frac{\partial}{\partial\mathbf{r}_c}\cdot\left\langle\frac{\partial}{\partial\mathbf{r}_c}(B\xi_+)\right\rangle$$

$$+\frac{1}{2}\frac{\partial}{\partial\mathbf{r}_c}\cdot\langle B\beta_-\mathbf{R}\rangle.\qquad(23)$$

In the case of B=1, Eq. (23) becomes an equation for the concentration profile:

$$\langle1\rangle\equiv\int d^3R\Psi(\mathbf{r}_c,\mathbf{R},t)=C(\mathbf{r}_c,t)\qquad(24)$$

Therefore, substituting B=1 into Eq. (23), we obtain

$$\frac{\partial C}{\partial t}=-\frac{\partial}{\partial\mathbf{r}_c}\cdot\left[\langle\mathbf{v}_+\rangle+\frac{1}{2}\left\langle\frac{\partial}{\partial\mathbf{R}}\xi_-\right\rangle\right.$$

$$\left.-\frac{1}{2}\frac{\partial}{\partial\mathbf{r}_c}\langle\xi_+\rangle+\frac{1}{2}\left\langle\frac{\partial}{\partial\mathbf{r}_c}\xi_+\right\rangle-\frac{1}{2}\langle\beta_-\mathbf{R}\rangle\right].$$

$$\qquad(25)$$

By taking Taylor expansions of each term in Eq. (25) and neglecting higher order terms, we finally obtain the following equation (details are given in Appendix A.):

$$\frac{\partial C}{\partial t}=-\nabla\cdot\left[\left(\mathbf{v}(\mathbf{r}_c)+\frac{1}{8}\frac{kT}{H}\nabla'^2\mathbf{v}(\mathbf{r}')|_{r'=0}\right.\right.$$

$$\left.+\frac{1}{2}\nabla'\xi(\mathbf{r}')|_{r'=0}-\frac{1}{2}\frac{kT}{H}\delta\cdot\nabla'\beta(\mathbf{r}')|_{r'=0}\right)C$$

$$\left.-\frac{1}{2}\left(\xi(\mathbf{r}_c)+\frac{1}{8}\frac{kT}{H}\nabla'^2\xi(\mathbf{r}')|_{r'=0}\right)\nabla\,C\right].\qquad(26)$$

Eq. (26) turns out to be a general diffusion equation of the following form:

$$\frac{\partial C}{\partial t}+\nabla\cdot\mathbf{J}=0\qquad(27)$$

where $\mathbf{J}$ is the flux. Therefore, we can simply transform Eq. (26) in term of the flux as follows:

$$\mathbf{J}=\underline{-\frac{1}{2}\left[\xi(\mathbf{r}_c)+\frac{1}{8}\frac{kT}{H}\nabla'^2\xi(\mathbf{r}')|_{r'=0}\right]\nabla C}$$
$$\text{(a)}$$

$$\underline{\left[\mathbf{v}(\mathbf{r}_c)+\frac{1}{8}\frac{kT}{H}\nabla'^2\mathbf{v}(\mathbf{r}')|_{r'=0}\right.}$$
$$\text{(b)}$$

$$+\frac{1}{2}\nabla'\xi(\mathbf{r}')|_{r'=0}-\frac{1}{2}\frac{kT}{H}\nabla'\beta(\mathbf{r}')|_{r'=0}\Big]C \qquad (28)$$

$$\underbrace{\phantom{+\frac{1}{2}\nabla'\xi(\mathbf{r}')|_{r'=0}-\frac{1}{2}\frac{kT}{H}\nabla'\beta(\mathbf{r}')|_{r'=0}}}_{(c)}$$

In Eq. (28), term (a) implies a diffusion coefficient, term (b) comes from the nonhomogeneity of flow and term (c) is the new source of polymer migration due to a temperature gradient.

EQUATION WITH DIFFERENTIAL OPERATOR

An alternative way to calculate the concentration equation, is to introduce a new differential operator. First we define the differential operator $\mathscr{D}$ as:

$$\frac{\partial\Psi}{\partial t}\equiv\mathscr{D}\Psi. \qquad (29)$$

We apply this equation to Eq. (21) and then obtain the following definition for the differential operator.

$$\mathscr{D}=\frac{\partial}{\partial\mathbf{R}}\cdot\mathbf{v}_-+\frac{\partial}{\partial\mathbf{R}}\cdot(2\xi_+)\frac{\partial}{\partial\mathbf{R}}+\frac{1}{2}\frac{\partial}{\partial\mathbf{R}}\cdot\xi_-\frac{\partial}{\partial\mathbf{r}_c}$$
$$+2\frac{\partial}{\partial\mathbf{R}}\cdot(\beta_+\mathbf{R})-\frac{\partial}{\partial\mathbf{r}_c}\cdot\mathbf{v}_++\frac{1}{2}\frac{\partial}{\partial\mathbf{r}_c}\cdot\xi_-\frac{\partial}{\partial\mathbf{R}}$$
$$+\frac{1}{2}\frac{\partial}{\partial\mathbf{r}_c}\cdot\xi_+\frac{\partial}{\partial\mathbf{r}_c}+\frac{1}{2}\frac{\partial}{\partial\mathbf{r}_c}\cdot\beta_-\mathbf{R}. \qquad (30)$$

We now redefine $\mathscr{L}$ using the integral formula:

$$\int d^3\mathbf{R}\,\mathscr{D}\,\Psi_{eq}(\mathbf{R})\equiv\mathscr{L}, \qquad (31)$$

where Ψ_{eq} is the value of a Hookean spring in equilibrium as follows [2]:

$$\Psi_{eq}=\left(\frac{H}{2\pi kT}\right)^{3/2}\exp\left(-\frac{H\mathbf{R}^2}{2kT}\right) \qquad (32)$$

Using Eq. (31), we calculate each term in Eq. (30) (details are given in Appendix B). Therefore $\mathscr{L}$ is obtained at $\mathbf{r}'=\mathbf{r}$ as follows:

$$\mathscr{L}=-\frac{\partial}{\partial\mathbf{r}}\cdot\exp\left(\frac{kT\nabla'^2}{8H}\right)\mathbf{v}(\mathbf{r}')|_{r'=r}$$
$$-\frac{1}{2}\frac{\partial}{\partial\mathbf{r}}\cdot\exp\left(\frac{kT\nabla'^2}{8H}\right)\nabla'\xi(\mathbf{r}')|_{r'=r}$$
$$+\frac{1}{2}\frac{\partial}{\partial\mathbf{r}}\cdot\frac{\partial}{\partial\mathbf{r}}\exp\left(\frac{kT\nabla'^2}{8H}\right)\xi(\mathbf{r}')|_{r'=r}$$
$$+\frac{kT}{2H}\frac{\partial}{\partial\mathbf{r}}\cdot\exp\left(\frac{kT\nabla'^2}{8H}\right)\nabla'\mathbf{v}(\mathbf{r}')|_{r'=r}. \qquad (33)$$

If we integrate Eq. (29) using Eqs. (30) and (31), we obtain the concentration equation in the following form.

$$\frac{\partial}{\partial t}C(\mathbf{r},\,t)\simeq\mathscr{L}C(\mathbf{r},\,t) \qquad (34)$$

Applying the quantity $\mathscr{L}$ to Eq. (34) we obtain

$$\frac{\partial}{\partial t}C(\mathbf{r},\,t)=-\frac{\partial}{\partial\mathbf{r}}\cdot\Big[-\frac{1}{2}\frac{\partial}{\partial\mathbf{r}}\exp\left(\frac{kT\nabla'^2}{8H}\right)\xi(\mathbf{r}')|_{r'=r}$$
$$+\exp\left(\frac{kT\nabla'^2}{8H}\right)\mathbf{v}(\mathbf{r}')|_{r'=r}$$
$$+\frac{1}{2}\exp\left(\frac{kT\nabla'^2}{8H}\right)\nabla'\xi(\mathbf{r}')|_{r'=r}$$
$$-\frac{kT}{2H}\exp\left(\frac{kT\nabla'^2}{8H}\right)\nabla'\beta(\mathbf{r}')|_{r'=r}\Big]C(\mathbf{r},\,t). \qquad (35)$$

In Eq. (35), $C(\mathbf{r},\,t=0)=C_0$ in the initial state $(t=0)$ and at steady state Eq. (35) is

$$\nabla\cdot\mathbf{J}=0. \qquad (36)$$

Therefore, the flux $(\mathbf{J})$ can be written as follows:

$$\mathbf{J}=-\frac{1}{2}\frac{\partial}{\partial\mathbf{r}}\exp\left(\frac{kT\nabla'^2}{8H}\right)\xi(\mathbf{r}')|_{r'=r}\,C(\mathbf{r},\,t)$$
$$+\Big[\exp\left(\frac{kT\nabla'^2}{8H}\right)\mathbf{v}(\mathbf{r}')|_{r'=r}$$
$$+\frac{1}{2}\exp\left(\frac{kT\nabla'^2}{8H}\right)\nabla'\xi(\mathbf{r}')|_{r'=r}$$
$$-\frac{kT}{2H}\exp\left(\frac{kT\nabla'^2}{8H}\right)\nabla'\beta(\mathbf{r}')|_{r'=r}\Big]C(\mathbf{r},\,t). \qquad (37)$$

By taking Taylor expansions in Eq. (37) and neglecting higher order terms, we obtain the following result.

$$\mathbf{J}=-\frac{1}{2}\Big[\xi(\mathbf{r})+\frac{kT}{8H}\nabla'^2\xi(\mathbf{r}')|_{r'=r}\Big]\nabla C(\mathbf{r},\,t)$$
$$+\Big[\mathbf{v}(\mathbf{r})+\frac{kT}{8H}\nabla'^2\mathbf{v}(\mathbf{r}')|_{r'=r}+\frac{1}{2}\nabla'\xi(\mathbf{r}')|_{r'=r}$$
$$-\frac{kT}{2H}\nabla'\beta(\mathbf{r}')|_{r'=r}\Big]C(\mathbf{r},\,t). \qquad (38)$$

It can be easily seen that Eq. (38) gives the same result as Eq. (28).

SUMMARY

This work has shown that, in general, polymer molecules move relative to the fluid when the undisturbed flow field is nonhomogeneous, and that there also exists an effect of a temperature gradient in the flow field of polymer migration. Starting from the well-known result of polymer dynamics on a single polymer chain located in a Newtonian solvent, we obtain the force balance equation for a bead-spring dumbbell model. Since obtaining a solution of the configu-

rational probability function is rather difficult, the moment analysis method is adopted and the polymer concentration is derived from the zeroth moment of the nth-moment equation. The results from this study are then compared with those from our previous study [1].

From this qualitative analysis, the effect of temperature gradient on polymer migration is found from the equation of migration velocity, the equation of concentration and an approximate result using a differential operator, gives the same effect on polymer migration. The physical origins of polymer migration, so far, are associated with the nonhomogeneous flow field, confined geometry, and concentration gradient. This paper demonstrates that the inclusion of a temperature gradient changes the migration behavior by contributing an additional source term.

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APPENDIX A : Derivation of Eq. (26)

Each term in Eq. (25) can be rewritten using a Taylor series expansion and the definition of the average of some quantity as follows:

$$(i) \quad \langle \mathbf{v}_+ \rangle = \left\langle \left[\mathbf{v} + \mathbf{r}_c \cdot \nabla' \mathbf{v}(\mathbf{r}') + \frac{1}{2!} \mathbf{r}_c \mathbf{r}_c : \nabla' \nabla' \mathbf{v}(\mathbf{r}') \right. \right.$$
$$\left. \left. + \frac{1}{8} \mathbf{R} \mathbf{R} : \nabla' \nabla' \mathbf{v}(\mathbf{r}') \right]_{r'=0} \right\rangle_{eq} C$$
$$= \left[\mathbf{v} + \mathbf{r}_c \cdot \nabla' \mathbf{v}(\mathbf{r}') + \frac{1}{2!} \mathbf{r}_c \mathbf{r}_c : \nabla' \nabla' \mathbf{v}(\mathbf{r}') \right.$$
$$\left. + \frac{1}{8} \frac{kT}{H} \nabla'^2 \mathbf{v}(\mathbf{r}') \right]_{r'=0} C$$
$$= \left[\mathbf{v}(\mathbf{r}_c) + \frac{1}{8} \frac{kT}{H} \nabla'^2 \mathbf{v}(\mathbf{r}')|_{r'=0} \right] C \quad (A1)$$

$$(ii) \quad \frac{1}{2} \left\langle \frac{\partial}{\partial \mathbf{R}} \xi_- \right\rangle = \frac{1}{2} \left\langle \frac{\partial}{\partial \mathbf{R}} \xi_- \right\rangle_{eq} C$$
$$= \left\langle \frac{\partial}{\partial \mathbf{R}} \left[\exp(\mathbf{r}_c \cdot \nabla') \sinh\left(\frac{\mathbf{R}}{2} \cdot \nabla' \right) \xi(\mathbf{r}') \right]_{r'=0} \right\rangle C$$
$$= \left\langle \frac{\partial}{\partial \mathbf{R}} \left[\frac{\mathbf{R}}{2} \cdot \nabla' \xi(\mathbf{r}') \right]_{r'=0} \right\rangle C$$
$$= -\left\langle \delta_{ij} \frac{\partial}{\partial r_j} \xi(\mathbf{r}')|_{r'=0} \right\rangle C$$
$$= \frac{1}{2} \nabla' \xi(\mathbf{r}')|_{r'=0} C \quad (A2)$$

$$(iii) \quad \frac{1}{2} \frac{\partial}{\partial \mathbf{r}_c} \langle \xi_+ \rangle = \frac{1}{2} \frac{\partial}{\partial \mathbf{r}_c} \langle \xi_+ \rangle_{eq} C$$

$$= \frac{1}{2} \frac{\partial}{\partial \mathbf{r}_c} \left\langle \left[\xi + \mathbf{r}_c \cdot \nabla' \xi(\mathbf{r}') + \frac{1}{2!} \mathbf{r}_c \mathbf{r}_c : \nabla' \nabla' \xi(\mathbf{r}') \right. \right.$$
$$\left. \left. + \frac{1}{8} \mathbf{R} \mathbf{R} : \nabla' \nabla' \xi(\mathbf{r}') \right]_{r'=0} \right\rangle_{eq} C$$
$$= \frac{1}{2} \frac{\partial}{\partial \mathbf{r}_c} \left[\xi(\mathbf{r}_c) + \frac{1}{8} \frac{kT}{H} \nabla'^2 \xi(\mathbf{r}') \right]_{r'=0} C$$
$$= \frac{1}{2} \frac{\partial \xi}{\partial \mathbf{r}_c} C + \frac{1}{2} \frac{\partial C}{\partial \mathbf{r}_c} \left[\xi(\mathbf{r}_c) + \frac{1}{8} \frac{kT}{H} \nabla'^2 \xi(\mathbf{r}') \right]_{r'=0}$$
$$(A3)$$

$$(iv) \quad \frac{1}{2} \left\langle \frac{\partial}{\partial \mathbf{r}_c} \xi_+ \right\rangle = \frac{1}{2} \left\langle \frac{\partial}{\partial \mathbf{r}_c} \xi_+ \right\rangle_{eq} C$$
$$= \frac{1}{2} \left\langle \frac{\partial}{\partial \mathbf{r}_c} \left[\xi(\mathbf{r}_c) + \frac{1}{8} \mathbf{R} \mathbf{R} : \nabla' \nabla' \xi(\mathbf{r}')_{r'=0} \right] \right\rangle_{eq} C$$
$$= \frac{1}{2} \left\langle \frac{\partial}{\partial \mathbf{r}_c} \xi(\mathbf{r}_c) \right\rangle_{eq} C = \frac{1}{2} \frac{\partial}{\partial \mathbf{r}_c} \xi(\mathbf{r}_c) C \quad (A4)$$

$$(v) \quad \frac{1}{2} \langle \beta_- \mathbf{R} \rangle = \frac{1}{2} \langle \beta_- \mathbf{R} \rangle_{eq} C$$
$$= \frac{1}{2} \langle [2\beta + \mathbf{R} \cdot \nabla' \beta(\mathbf{r}') + \cdots]_{r'=0} \mathbf{R} \rangle_{eq} C$$
$$= \frac{1}{2} \langle \mathbf{R} \mathbf{R} \rangle_{eq} \cdot \nabla' \beta(\mathbf{r}')|_{r'=0} C$$
$$= \frac{1}{2} \frac{kT}{H} \delta \cdot \nabla' \beta(\mathbf{r}')|_{r'=0} C \quad (A5)$$

Inserting Eqs. (A1)-(A4) into Eq. (25), we obtain Eq. (26).

APPENDIX B : Derivation of $\mathscr{L}$

Each term of Eq. (30) can be calculated from the definition of Eqs. (31) and (32) as follows [define $\alpha = H/2\pi kT)^{3/2}$]:

$$(i) \quad \int d^3 R \frac{\partial}{\partial \mathbf{R}} \cdot (\mathbf{v}_- \Psi_{eq}) = \int dR_1 \int dR_2 \int dR_3 \frac{\partial}{\partial \mathbf{R}_i} \mathbf{v}_{-i} \Psi_{eq}$$
$$= \int dR_2 \int dR_3 \mathbf{v}_{-1} \Psi_{eq}|_{-\infty}^{+\infty} = 0 \quad (B1)$$

$$(ii) \quad \int d^3 R \frac{\partial}{\partial \mathbf{R}} \cdot (2\xi_+) \frac{\partial}{\partial \mathbf{R}} \Psi_{eq}$$
$$= \int dR_1 \int dR_2 \int dR_3 \left(\frac{\partial}{\partial R_i} 2\xi_+ \frac{\partial}{\partial R_i} \Psi_{eq} \right)$$
$$= \left(2\xi_+ \frac{\partial}{\partial R_1} \Psi_{eq} \right)_{-\infty}^{+\infty} \int dR_2 \int dR_3 = 0 \quad (B2)$$

$$(iii) \quad \int d^3 R \frac{\partial}{\partial \mathbf{R}} \cdot \xi_- \frac{\partial}{\partial \mathbf{r}_c} \Psi_{eq}$$
$$= \int \frac{\partial}{\partial \mathbf{R}} \cdot \left(\frac{\partial}{\partial \mathbf{r}_c} \xi_- \Psi_{eq} \right) d^3 R$$
$$- \int \frac{\partial}{\partial \mathbf{R}} \cdot \left(\frac{\partial \xi_-}{\partial \mathbf{r}_c} \right) \Psi_{eq} d^3 R$$
$$= \int dR_1 \frac{\partial}{\partial \mathbf{R}} \left(\frac{\partial}{\partial \mathbf{r}_c} \xi_- \Psi_{eq} \right) \int dR_2 \int dR_3$$

$$-\int dR_1 \frac{\partial}{\partial \mathbf{R}} \frac{\partial \xi_-}{\partial \mathbf{r}_c} \Psi_{eq} \int dR_2 \int dR_3$$

$$= \left(\frac{\partial}{\partial \mathbf{r}_{c1}} \xi_- \Psi_{eq} \right)_{-\infty}^{+\infty} \int dR_2 \int dR_3$$

$$- \left(\frac{\partial \xi_-}{\partial \mathbf{r}_{c1}} \Psi_{eq} \right)_{-\infty}^{+\infty} \int dR_2 \int dR_3 = 0 \qquad (B3)$$

(iv) $\int d^3R \frac{\partial}{\partial \mathbf{R}} \cdot (\beta_+ \mathbf{R} \Psi_{eq}) = \int \frac{\partial}{\partial \mathbf{R}_i} \beta_+ \mathbf{R}_i \Psi_{eq} dR_1 \int dR_2 \int dR_3$

$$= [\beta_+ \mathbf{R}_1 \Psi_{eq}]_{-\infty}^{+\infty} \int dR_2 \int dR_3 = 0 \qquad (B4)$$

(v) $\int d^3R \frac{\partial}{\partial \mathbf{r}_c} \cdot (\mathbf{v}_+ \Psi_{eq})$

$$= \frac{\partial}{\partial \mathbf{r}_c} \int d^3R \cosh\left(\frac{\mathbf{R}}{2} \cdot \nabla'\right) \alpha \exp\left(-\frac{HR^2}{2kT}\right) \mathbf{v}(\mathbf{r}')|_{\mathbf{r}'=\mathbf{r}_c}$$

$$= \frac{1}{2} \alpha \frac{\partial}{\partial \mathbf{r}_c} \int d^3R \exp\left(\pm \frac{\mathbf{R}}{2} \cdot \nabla'\right) \exp\left(-\frac{HR^2}{2kT}\right) \mathbf{v}(\mathbf{r}')|_{\mathbf{r}'=\mathbf{r}_c}$$

$$= \frac{\partial}{\partial \mathbf{r}_c} \cdot \exp\left(kT \frac{\nabla'^2}{8H}\right) \mathbf{v}(\mathbf{r}')|_{\mathbf{r}'=\mathbf{r}_c} \qquad (B5)$$

(vi) $\int d^3R \frac{\partial}{\partial \mathbf{r}_c} \cdot \left(\xi_- \frac{\partial}{\partial \mathbf{R}} \Psi_{eq}\right)$

$$= 2 \frac{\partial}{\partial \mathbf{r}_c} \cdot \int d^3R \sinh\left(\frac{\mathbf{R}}{2} \cdot \nabla'\right) \xi(\mathbf{r}')|_{\mathbf{r}'=\mathbf{r}_c}$$

$$\frac{\partial}{\partial \mathbf{R}} \alpha \exp\left(-\frac{HR^2}{2kT}\right)$$

$$= -\frac{\alpha H}{kT} \frac{\partial}{\partial \mathbf{r}_c} \cdot \int d^3R \left[\mathbf{R} \exp\left(\frac{\mathbf{R}}{2} \cdot \nabla'\right) \exp\left(-\frac{HR^2}{2kT}\right) \right.$$

$$\left. - \mathbf{R} \exp\left(-\frac{\mathbf{R}}{2} \cdot \nabla'\right) \exp\left(-\frac{HR^2}{2kT}\right) \right] \xi(\mathbf{r}')|_{\mathbf{r}'=\mathbf{r}_c}$$

$$= -\frac{\partial}{\partial \mathbf{r}_c} \cdot \left[\exp\left(\frac{kT\nabla'^2}{8H}\right) \nabla' \xi(\mathbf{r}')|_{\mathbf{r}'=\mathbf{r}_c} \right] \qquad (B6)$$

(vii) $\int d^3R \frac{\partial}{\partial \mathbf{r}_c} \cdot \xi_+ \frac{\partial}{\partial \mathbf{r}_c} \Psi_{eq} = \frac{\partial}{\partial \mathbf{r}_c} \cdot \frac{\partial}{\partial \mathbf{r}_c} \int d^3R \xi_+ \Psi_{eq}$

$$= \frac{\partial}{\partial \mathbf{r}_c} \cdot \frac{\partial}{\partial \mathbf{r}_c} \int d^3R \cosh\left(\frac{\mathbf{R}}{2} \cdot \nabla'\right) \xi(\mathbf{r}')|_{\mathbf{r}'=\mathbf{r}_c}$$

$$\alpha \exp\left(-\frac{HR^2}{2kT}\right)$$

$$= -\frac{\partial}{\partial \mathbf{r}_c} \cdot \frac{\partial}{\partial \mathbf{r}_c} \exp\left[\frac{kT\nabla'^2}{8H}\right] \xi(\mathbf{r}')|_{\mathbf{r}'=\mathbf{r}_c} \qquad (B7)$$

(viii) $\int d^3R \frac{\partial}{\partial \mathbf{r}_c} \cdot \beta_- \mathbf{R} \Psi_{eq}$

$$= 2 \frac{\partial}{\partial \mathbf{r}_c} \cdot \int d^3R \sinh\left(\frac{\mathbf{R}}{2} \cdot \nabla'\right) \beta(\mathbf{r}')|_{\mathbf{r}'=\mathbf{r}_c}$$

$$\mathbf{R} \alpha \exp\left(-\frac{HR^2}{2kT}\right)$$

$$= \alpha \frac{\partial}{\partial \mathbf{r}_c} \cdot \int d^3R \left[\mathbf{R} \exp\left(\frac{\mathbf{R}}{2} \cdot \nabla'\right) \exp\left(-\frac{HR^2}{2kT}\right) \right.$$

$$\left. - \mathbf{R} \exp\left(-\frac{\mathbf{R}}{2} \cdot \nabla'\right) \exp\left(-\frac{HR^2}{2kT}\right) \right] \beta(\mathbf{r}')|_{\mathbf{r}'=\mathbf{r}_c}$$

$$= \frac{kT}{2H} \frac{\partial}{\partial \mathbf{r}_c} \cdot \exp\left(\frac{kT\nabla'^2}{8H}\right) \nabla' \beta(\mathbf{r}')|_{\mathbf{r}'=\mathbf{r}_c} \qquad (B8)$$

Inserting the above equations into Eq. (30), we obtain Eq. (33).

NOMENCLATURE

a   : radius of bead
A   : arbitrary quantity
A_+ $= (A_1 + A_2)/2$ $(A = V, \xi, $ and $\beta)$
A_- $= A_2 - A_1$ $(A = V, \xi, $ and $\beta)$
C   : local dumbbell concentration
H   : spring constant
k   : Boltzmann's constant
r   : position vector
$\mathbf{r}_i$: position vector of ith bead
$\mathbf{r}_c$: center of mass, $= (\mathbf{r}_1 + \mathbf{r}_2)/2$
R   : internal configuration coordinate, $= \mathbf{r}_2 - \mathbf{r}_1$
t   : time
T   : absolute temperature
v   : fluid velocity
$\mathbf{v}_c$: fluid velocity at the center of mass
$\mathbf{v}_o$: 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)
Δ : polymer migration velocity

REFERENCES

1. Inn, Y. W., Choi, H. J. and Jhon, M. S.: *Korean J. Chem. Eng.*, **7**(2), 138 (1990).
2. Bird, R. B., Curtiss, C. F., Armstrong, R. C. and Hassager, O.: "Dynamics of Polymeric Liquids, Vol. 2", Wiley, New York (1987).
3. Shafer, R. H., Laiken, N. and Zimm, B. H.: *Biophys. Chem.*, **2**, 180 (1974).
4. Aubert, J. H. and Tirrell, M.: *J. Chem. Phys.*, **72**(4), 2694 (1980).
5. Aubert, J. H., Prager, S. and Tirrell, M.: *J. Chem. Phys.*, **73**(8), 4103 (1980).
6. Sekhon, G., Armstrong, R. C. and Jhon, M. S.: *J. Poly. Sci.: Poly. Phys. Ed.*, **20**, 947 (1982).

7. Crone, R. M., Jhon, M. S. and Choi, H. J.: *J. Mol. Liquids*, **59**, 115 (1994).

8. Choi, H. J. and Jhon, M. S.: in "Theoretical and Applied Rheology", Moldenaers, P. and Keunings, R. ed, Elsevier Science, Amsterdam, The Netherlands, p. 464 (1992).

9. Brunn, P. O.: *Int. J. Multiphase Flow*, **9**(2), 187 (1983).

10. Doi, M. and Edwards, S. F.: "The Theory of Polymer Dynamics", Oxford Univ. Press, Oxford (1986).

11. Edwards, S. F. and Freed, K. F.: *J. Chem. Phys.*, **61**, 1189 (1974).

12. Freed, K. F. and Edwards, S. F.: *J. Chem. Phys.*, **61**, 3626 (1974).

13. Freed, K. F. and Muthukumar, M.: *J. Chem. Phys.*, **68**, 2088 (1978).

14. Freed, K. F.: in "Progress in Liquid Physics", Croxton, C. A. ed., Wiley, New York, p. 343 (1978).

15. Jhon, M. S., Sekhon, G. and Armstrong, R.: in "Advances in Chemical Physics", Prigogine, I. and Rice, S. A. ed., Wiley, N. Y., p. 66 (1987).

16. Freed, K. F. and Perico, A.: *Macromolecules*, **14**, 1290 (1981).

17. Denn, M. M.: "Process Fluid Mechanics", Prentice-Hall, New Jersey p. 235 (1980).

18. Tanner, R. I.: "Engineering Rheology", Oxford Univ. Press, Oxford, p. 177 (1985).

19. Larson, R. G.: "Constitutive Equations for Polymer Melts and Solutions", Butterworths, Boston, p. 41 (1988).