

POLYMER CONFORMATION IN AN EXTENSIONAL FLOW WITH BEAD-WALL HYDRODYNAMIC INTERACTION

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Abstract—A simplified investigation into the properties of polymers near surfaces in a flow field is presented. A kinetic theory for a two-bead harmonic dumbbell model is derived, centering primarily on the effect of anisotropic hydrodynamics due to the presence of a wall. A comparison of the anisotropic and isotropic cases is made, and it is found that the difference manifest in the polymer concentration is only substantial at relatively high strain rates, or within a few molecular diameters of the wall for realistic values of molecular parameters.

INTRODUCTION

The study of polymer dynamics at interfaces has become more important recently[1,2] due to the many application possibilities, such as the understanding of oil recovery enhancement with polymer injected into porous rock, coating films, adhesion, and lubrication. A related system is the study of blood cell behavior in small capillaries to predict biomedical-related phenomena[3], and, clearly, gel permeation chromatography must also be a benefit of any investigation related to polymers at interfaces[4].

Our purpose in this paper is to present some of our findings involving polymer solutions with anisotropic hydrodynamic effects due to the presence of a wall. Polymer systems modeled by an n bead-spring chain surrounded by a Newtonian fluid[5,6] are expected to represent the characteristics of polymeric solutions fairly well. However, such a model is rather intractable to solve exactly even for simple systems, and even then a system involving anisotropic diffusion is certainly not simple. A simplification often made in the past is to consider only one "unit cell" of the n -bead chain, that is, the dumbbell model (two beads connected with one spring). It is hoped that by ignoring the cumbersome bookkeeping involved in considering

the n -bead chain, and still retaining the elementary physics of the model, we will come up with an intuitive (possibly qualitative) solution. What we have given up is molecular weight dependence and most probably some detailed structural information. What we have gained is the ability to construct a description of the system which is virtually impossible to develop on a more detailed level.

Once the decision has been made to consider only the two-bead model, a spring potential must be chosen to characterize the interaction between the beads. Most often the Hookean potential is chosen, which is the most studied due to the simplicity in its mathematical structure. Other potentials have been also studied, primarily ones that limit the maximum length of extension, such as the FENE (Finitely Extendable Non-linear Elastic) potential[7] or the Fraenkel model[8]. Normally, hydrodynamic interactions between the beads are ignored and only the Stokes forces are considered. These hydrodynamic interactions should be included to describe the dynamics of the system; however, their inclusion causes the problem to become complicated. A formal but virtually rigorous theory for the system involving flow with hydrodynamic interaction is given in Jhon et al.[9]. In our analysis, we will consider the hydrodynamic effects of bead-wall interactions but not bead-bead interactions.

The flow regime most studied in the dumbbell system is homogeneous flow, a flow which has the most linear gradients in velocity and can be represented by

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the truncated Taylor series: $\mathbf{v} = \mathbf{v}_0 + \mathbf{K} \cdot \mathbf{r}^*$, where \mathbf{v} is the fluid velocity and \mathbf{r} is the coordinate. Flows involving higher-order terms in the series have been partially studied, particularly with regard to polymer migration [6,10]. Potential flow is also a favorite of investigators, because the flow enters the problem as an extra applied potential and can be handled rather easily.

The equilibrium results for n -bead chains are relatively easy to find without imposed flow, and much has been studied on this subject in the past [11-14]. However, only limited studies of wall effects on polymers in the presence of a flow field have been performed [15-17]. In this paper, we wish to point out the salient effects of this case by using a simple polymer model and a simple flow field. In order to keep our results clear, we will not consider hydrodynamic interactions between the beads, only interactions involving the beads and the wall. It is further assumed that dumbbells do not interact with one another hydrodynamically; that is, the combined effect of a dumbbell solution is the sum of the effects of the individual dumbbells. Our defense for these simplifications is not that they are unimportant—they are important, but we must decline to be concerned with these so that the effects strictly related to anisotropic diffusion can be isolated.

If one looks at the diffusion of a sphere near a wall, the mobility of the sphere drops off uniformly to zero as the distance from the wall decreases to zero; this is due to the hydrodynamic interaction between the sphere and the wall through the fluid. Although others have considered wall-related polymer phenomena [1, 18, 19], we have succeeded in inserting the wall-dependent diffusion coefficient into the harmonic dumbbell model. Clearly, the imperatives of thermodynamics will leave the equilibrium polymer conformation unchanged with the addition of anisotropic diffusion. Consequently, the steady-state effect of a spatially changing diffusion coefficient must be investigated in conjunction with a competing phenomenon, such as a velocity gradient in the surrounding fluid. Therefore, the effect at steady state of adding anisotropic diffusion to the polymer model, which is purely a dynamic process, can only be investigated in the presence of another dynamic process.

Taking all the above into account, we want to solve the problem of the stagnation flow [20] of a dumbbell solution onto a single fixed wall. Although this model

* In general, the flow field can be expressed as $\mathbf{v} = \mathbf{v}_0 + \mathbf{r} \cdot \nabla \mathbf{v}_0 + \frac{1}{2} \mathbf{r} \mathbf{r} : \nabla \nabla \mathbf{v}_0 + \dots$. For the homogeneous flow, the higher order gradients vanish, and $\mathbf{v} = \mathbf{v}_0 + \mathbf{K} \cdot \mathbf{r}$, where $\mathbf{K} = (\nabla \mathbf{v}_0)^+$.

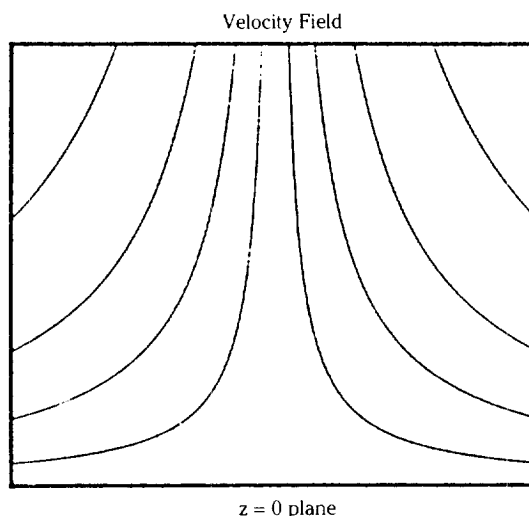


Fig. 1. This represents the streamlines of flow near the wall ($z=0$). The flow direction along the streamlines is determined by the sign of ϵ .

is admittedly simple, it facilitates the necessarily complicated calculations. We must also use a simple flow field for the same reason. The flow field we have selected is an irrotational pure extensional flow, pictured in Figure 1. To use a flow that has a nonzero rotational component would force us to recast the problem into one that rotates with the local fluid elements, complicating the problem immensely. The new work presented here deals with the effects of anisotropic diffusion and the flow field. As mentioned before, if there were no flow field, the equilibrium conformation would be unaffected by anisotropic diffusion, so we are looking for the interaction of two dynamic phenomena, the flow field and anisotropic diffusion. Again, we will, unfortunately, have to use an approximation for the spatial dependence of the diffusion coefficient, as given by Cox and Brenner [21].

What we hope to accomplish by these approximations is an understanding of the important effects of anisotropic diffusion in pores, not an exact calculation of any particular case (though we do this as an illustration for potential flow). It will become evident during the following developments that anisotropic diffusion cannot be ignored in all dynamic pore-related systems, and, using extensional flow, we will compare results with and without anisotropic diffusion. After we have specified the internal part of the diffusion equation precisely, we will obtain an equation relating the local concentration of molecules by averaging over the internal coordinate. This will give us the observable concentration dependence as a function of the distance

from the wall, and will be compared to the case with isotropic(Stokes-Einstein) diffusion.

DEVELOPMENT

We will begin by seeking a solution to the diffusion equation for the two-bead(dumbbell) model, for the case of isotropic diffusion in the presence of a wall. For this, we will seek an approximation that will allow us to determine the effect of anisotropic diffusion on the model. In each case, though, we will impose a homogeneous extensional-potential flow generated by

$$xz + yz = \text{constant}, \quad (1)$$

which is schematically represented in Figure 1. Note that this velocity description allows for slip at the wall, as do all potential flows. Our purpose in this paper, however, is not to present the most physically detailed account of a wall; rather, we wish to point out the coupling of diffusion and the flow field in the most mathematically unencumbered way possible. The introduction of vorticity to the velocity field complicates the situation tremendously, even for problems not involving a wall. Thus, we shall settle for a little less physical realism in our flow field in order to obtain an intuitive sense of the role anisotropic diffusion will play involving polymers near interfaces.

1. The Probability Density with Isotropic Diffusion

With isotropic diffusion, the equation for the bead velocity is(neglecting acceleration)[5]:

$$\dot{\mathbf{r}}_i = \mathbf{v}(\mathbf{r}_i) - \frac{kT}{\zeta} \frac{\partial \ln \Psi}{\partial \mathbf{r}_i} - \frac{1}{\zeta} \frac{\partial \phi_r}{\partial \mathbf{r}_i} \quad (i=1, 2), \quad (2)$$

where \mathbf{r}_i is the position vector of i th bead and $\mathbf{v}(\mathbf{r})$ is the velocity of the surrounding fluid evaluated at \mathbf{r}_i as if the bead was not there. Ψ is the probability function, kT/ζ is the part of the diffusion coefficient($\zeta = 6\pi\eta a$; "a" is radius of bead) and ϕ_r is the part of the potential explained below. $\mathbf{v}(\mathbf{r}_i)$ is given by:

$$\mathbf{v}(\mathbf{r}_i) = \mathbf{K} \cdot \mathbf{r}_i; \quad \mathbf{K} = (\nabla \mathbf{v})^+ = \begin{bmatrix} -\frac{1}{2}\epsilon & 0 & 0 \\ 0 & -\frac{1}{2}\epsilon & 0 \\ 0 & 0 & +\epsilon \end{bmatrix} \quad (3)$$

and the wall was chosen to be the plane at $z = 0$. Here, ϵ is known as the elongational rate, and can be positive or negative depending upon the flow direction, as shown in Figure 1. Written in this way, the velocity can be expressed in terms of a potential:

$$\mathbf{v}(\mathbf{r}_i) = -\frac{1}{\zeta} \nabla \phi_{r,i}; \quad \phi_{r,i} = \frac{\zeta \epsilon}{4} \sum_{i=1}^2 (x_i^2 + y_i^2 - 2z_i^2), \quad (4)$$

to which the rest of the potential(ϕ_r) can be added. The potential ϕ_r can further be split up into the connector potential(ϕ_c) and a potential due to the wall located at $z = 0$ (ϕ_w):

$$\phi_r = \phi_w + \phi_c, \quad (5)$$

where

$$\phi_w = \begin{cases} 0 & z_i > a \\ \infty & z_i \leq a \end{cases} \quad (i=1, 2); \quad \phi_c = \frac{1}{2} H(\mathbf{r}_2 - \mathbf{r}_1)^2. \quad (6)$$

Here, "a" is the radius of a bead and H is the Hooke's law constant. So the equation for the velocity becomes:

$$\dot{\mathbf{r}}_i = -\frac{kT}{\zeta} \frac{\partial \ln \Psi}{\partial \mathbf{r}_i} - \frac{1}{\zeta} \frac{\partial \phi_r}{\partial \mathbf{r}_i}. \quad (7)$$

Here, ϕ_r is total potential and

$$\phi_r = \phi_{r,i} + \phi_r = \phi_{r,i} + \phi_w + \phi_c. \quad (8)$$

The continuity equation of the probability function[5] is:

$$\frac{\partial \Psi}{\partial t} = - \sum_{i=1}^2 \frac{\partial}{\partial \mathbf{r}_i} \cdot (\dot{\mathbf{r}}_i \Psi). \quad (9)$$

We shall start by finding the steady-state solution to the diffusion equation. Trivially, we can find the result for $\partial \Psi / \partial t = 0$ by setting $\dot{\mathbf{r}}_1 = \dot{\mathbf{r}}_2 = 0$, which gives

$$\Psi_h = C \exp\left(-\frac{\phi_r}{kT}\right), \quad (10)$$

where C is a constant. Clearly this is not the solution we want, because $\dot{\mathbf{r}}_c$ is the center of mass velocity; $\dot{\mathbf{r}}_c = (\dot{\mathbf{r}}_1 + \dot{\mathbf{r}}_2)/2 = 0$; rather, this solution can only be regarded as the homogeneous solution of eq.(7). We need to attach an additional constraint to this solution, which is

$$\dot{\mathbf{r}}_c = \frac{\mathbf{v}(\mathbf{r}_1) + \mathbf{v}(\mathbf{r}_2)}{2} = \mathbf{K} \cdot \mathbf{r}_c = \mathbf{v}_c. \quad (11)$$

The general solution can be considered to be of the form,

$$\Psi = f(\mathbf{r}_1, \mathbf{r}_2) \Psi_h(\mathbf{r}_1, \mathbf{r}_2), \quad (12)$$

where $f(\mathbf{r}_1, \mathbf{r}_2)$ is the contribution due to the nonhomogeneous condition imposed by eq. (11), or written as

$$\dot{\mathbf{r}}_c = -\frac{kT}{2\zeta} \frac{\partial \ln f}{\partial \mathbf{r}_c} = \mathbf{v}_c = -\frac{1}{\zeta} \frac{\partial \phi_{r,i}(\mathbf{r}_c)}{\partial \mathbf{r}_c}, \quad (13)$$

where

$$\phi_{r,i,c}(\mathbf{r}_c) = \frac{\zeta \epsilon}{4} (x_c^2 + y_c^2 - 2z_c^2).$$

Then f is easily solved for:

$$f \propto \exp \left[-\frac{2}{kT} \phi_{rl,c}(\mathbf{r}_c) \right], \quad (15)$$

Therefore, the solution now becomes,

$$\Psi = f \Psi_h = C \exp \left\{ -\frac{1}{kT} [\phi_r - 2\phi_{rl,c}(\mathbf{r}_c)] \right\}, \quad (16)$$

which can be written in center of mass $[\mathbf{r}_c = (\mathbf{r}_1 + \mathbf{r}_2)/2]$ and relative or internal coordinates $(\mathbf{R} = \mathbf{r}_2 - \mathbf{r}_1)$ explicitly:

$$\Psi = C \exp \left\{ -\frac{H}{2kT} [(X^2 + Y^2 + Z^2) + \lambda_h \epsilon (X^2 + Y^2 - 2Z^2)] \right\} \theta(z_c - a) \theta[(2z_c - a) - |Z|], \quad (17)$$

where θ represents the Heaviside step function and $\lambda_h = \xi/4H$ is a characteristic time constant for the Hookean dumbbells. This solution satisfies eq.(9) exactly for the case $D\Psi/Dt = 0$, where D/Dt stands for the material time derivative. This solution assumes that the molecule sees no change in its surroundings with respect to time. This is not quite true, because z_c is a function of time, and, therefore, so is the molecule's distance from the wall. However, near the wall the velocity z_c declines uniformly to zero, and far away from the wall the molecule will adopt its usual Gaussian shape, unaffected by the wall. So it can be expected, at least for small values of ϵ in eq.(3), that the drift of the molecule towards the wall can be neglected and the solution for $D\Psi/Dt = 0$ will closely represent the true solution.

It remains, then, to define the constant C given in eq. (17) by observing that

$$\int \Psi|_{z_c \rightarrow \infty} d^3\mathbf{R} = C_\infty, \quad (18)$$

where C_∞ is the bulk concentration. The resulting function for the total probability density then becomes:

$$\Psi = C_\infty \left(\frac{H}{2\pi kT} \right)^{3/2} (1 + \lambda_h \epsilon)^{-1} (1 - 2\lambda_h \epsilon)^{1/2} \exp \left\{ -\frac{H}{2kT} [(X^2 + Y^2 + Z^2) + \lambda_h \epsilon (X^2 + Y^2 - 2Z^2)] \right\} \theta(z_c - a) \theta[2(z_c - a) - |Z|]. \quad (19)$$

It may seem rather mathematically melodramatic to go to such pains to get such a simple solution for isotropic diffusion, but the concepts used in the foregoing development involving anisotropic diffusion will rely heavily on the method presented above. In particular, we will find it necessary to approximate the equation for the nonhomogenous part [eqs. (13) and (14)] in order to obtain an explicit relation for Ψ .

2. The Probability Density with Anisotropic Diffusion

When a sphere is in the proximity of a wall, diffu-

sion is inhibited both parallel and perpendicular to the wall. The perpendicular component, however, drops off much faster than the parallel one. We will assume, therefore, that the parallel component remains unchanged from free diffusion. The perpendicular part of the mobility was calculated by Cox and Brenner[22]; $[\xi_i^{-1}(h)]_{zz} = 1/\xi_i(h)$, where $h = (z_i - a)/a$, $(z_i - a)$ is the distance of i th sphere to the wall. The term $f_i(h)$ has the asymptotic form

$$f_i(h) \sim \begin{cases} h & \text{as } h \rightarrow 0 \\ \frac{h-1/8}{h+1} & \text{as } h \rightarrow \infty. \end{cases} \quad (20)$$

We will adopt for the ensuing development the combined asymptotic form, stated for simplicity as

$$(\xi_i^{-1})_{zz} = \frac{1}{\xi} \frac{h}{h+1}. \quad (21)$$

Now the diffusion coefficient becomes a tensor:

$$\xi_i^{-1} = \frac{1}{\xi} \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & \frac{h}{h+1} \end{pmatrix} = \frac{1}{\xi} \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & \frac{z_i/\epsilon - 1}{z_i/a} \end{pmatrix}. \quad (22)$$

The equation of motion for the individual beads then becomes,

$$\dot{\mathbf{r}}_i = \mathbf{v}(\mathbf{r}_i) - \xi_i^{-1}(\mathbf{r}_i) \cdot (kT \frac{\partial \ln \Psi}{\partial \mathbf{r}_i} + \frac{\partial \phi_r}{\partial \mathbf{r}_i}). \quad (23)$$

Similarly, as in the isotropic case,

$$\dot{\mathbf{r}}_i = -\xi_i^{-1}(\mathbf{r}_i) \cdot (kT \frac{\partial \ln \Psi}{\partial \mathbf{r}_i} + \frac{\partial}{\partial \mathbf{r}_i} (\phi_r + \phi'_{rl})), \quad (24)$$

where we define the potential for the flow part of the anisotropic case (ϕ'_h) as follows:

$$\frac{\partial \phi'_{rl}}{\partial \mathbf{r}_i} = -\xi_i(\mathbf{r}_i) \cdot \mathbf{v}(\mathbf{r}_i), \quad (25)$$

and from eqs. (4), (22), and (25)

$$\phi'_{rl} = \frac{\epsilon \xi}{4} \sum_{i=1}^2 (x_i^2 + y_i^2 - 2z_i^2) - \epsilon \xi \sum_{i=1}^2 (z_i a + a^2 \ln[z_i/a - 1]). \quad (26)$$

Note that for the $a \rightarrow 0$ limit, eq. (26) reduces to eq.(4) as expected. Therefore, we can obtain the homogenous solution ($\dot{\mathbf{r}}_1 = \dot{\mathbf{r}}_2 = 0$);

$$\Psi_h = C \exp \left[-\frac{1}{kT} (\phi_r + \phi'_{rl}) \right]. \quad (27)$$

Again, the equation that relates the nonhomogenous solution giving $\dot{\mathbf{r}}_c = \mathbf{v}_c$ is

$$\mathbf{v}_c = -\frac{kT}{2} \underline{\underline{\zeta}}_+^{-1} \cdot \frac{\partial \ln f}{\partial \mathbf{r}_c} - \frac{kT}{2} \underline{\underline{\zeta}}_-^{-1} \cdot \frac{\partial \ln f}{\partial \mathbf{R}}, \quad (28)$$

where $\underline{\underline{\zeta}}_+^{-1} = (\underline{\underline{\zeta}}_1^{-1} + \underline{\underline{\zeta}}_2^{-1})/2$ and

$$\underline{\underline{\zeta}}_-^{-1} = \underline{\underline{\zeta}}_2^{-1} - \underline{\underline{\zeta}}_1^{-1}.$$

This is, of course, a more difficult equation to solve than the one obtained with isotropic hydrodynamics. However, if we require that this equation be solved exactly only at $\mathbf{R} = \mathbf{0}$, then the problem reverts to the simpler form obtained for the isotropic case

$$\frac{\partial \ln f}{\partial \mathbf{r}_c} = \frac{2}{kT} \cdot \frac{\partial \phi'_{i,c}(\mathbf{r}_c)}{\partial \mathbf{r}_c}, \quad (29)$$

with

$$\begin{aligned} \phi'_{i,c}(\mathbf{r}_c) &= \frac{\epsilon \zeta}{4} (x_c^2 + y_c^2 - 2z_c^2) - \epsilon \zeta \\ &\quad (z_c a + a^2 \ln[z_c/a - 1]). \end{aligned} \quad (30)$$

Then, similar to eq.(17) for the isotropic case, $f = C \exp[(2/kT) \phi'_{i,c}(\mathbf{r}_c)]$. Again, the general solution using the approximate Ψ_h can be found:

$$\Psi = f \Psi_h = \exp\left[-\frac{1}{kT}(\phi_r + \phi'_{i,c} - 2\phi'_{i,c})\right]. \quad (31)$$

This approximation basically relies on the fact that $\mathbf{R} = \mathbf{0}$, a dumbbell, must behave as an equivalent sphere. As in the isotropic case, this result can be written explicitly in center of mass and internal coordinates, and using the boundary condition that $C = C_\infty$ when $z_c \rightarrow \infty$:

$$\begin{aligned} \Psi &= C_\infty \left(\frac{H}{2\pi kT}\right)^{3/2} (1 + \lambda_h \epsilon) (1 - 2\lambda_h \epsilon)^{1/2} \\ &\quad \exp\left\{-\frac{H}{2kT}[(1 + \lambda_h \epsilon)(X^2 + Y^2) \right. \\ &\quad \left. + (1 - 2\lambda_h \epsilon)Z^2]\right\} \left[1 - \left(\frac{Z}{2(z_c - a)}\right)^2\right]^{\zeta a^2 \epsilon / kT} \\ &\quad \theta(z_c - a) \theta[2(z_c - a) - |Z|]. \end{aligned} \quad (32)$$

3. Computation of Moments

In this section, we will calculate the first few moments of Ψ . Here, the n th moments can be defined as [9]

$$\langle \mathbf{RR} \cdots \mathbf{RR} \rangle \equiv \int d^3\mathbf{R} \mathbf{RR} \cdots \mathbf{RR} \Psi(\mathbf{R}, \mathbf{r}_c). \quad (33)$$

The zeroth moment evaluated at $\mathbf{r}_c = \mathbf{r}[C(\mathbf{r}, t)]$ gives the concentration profile of the polymer molecules; that is

$$C(\mathbf{r}) \equiv \langle 1 \rangle \equiv \int d^3\mathbf{R} \Psi(\mathbf{R}, \mathbf{r}_c) |_{\mathbf{r}_c = \mathbf{r}}. \quad (34)$$

For the isotropic Ψ [cf. eq.(19)], the resulting concentration profile is simply given as

$$C(z)/C_\infty = \text{erf}[\sqrt{2} \mu^{1/2} (1 - 2\lambda_h \epsilon) (z/a - 1)]. \quad (35)$$

Here, $\mu = Ha^2/kT$ and erf is the error function.

For the anisotropic Ψ [cf. eq.(32)], the result is somewhat more complicated:

$$C(z)/C_\infty = AB(\alpha, 1/2) {}_1F_1(1/2; \alpha + 1/2; \beta(z)), \quad (36)$$

where B represents the Beta function and ${}_1F_1$ represents the degenerate hypergeometric function;

$$\begin{aligned} {}_1F_1(\alpha; \gamma; x) &= \\ &= \frac{1}{B(\alpha; \gamma - \alpha)} \int_0^1 (1-t)^{\gamma-\alpha-1} t^{\alpha-1} \exp(xt) dt, \end{aligned} \quad (37)$$

and A , α and β are defined as

$$\begin{aligned} A &= 2(2\pi)^{-1/2} \mu^{1/2} (1 - 2\lambda_h \epsilon)^{1/2} (z/a - 1), \\ \alpha &= 1 + 4(\lambda_h \epsilon) \mu, \\ \beta(z_c) &= -2\mu [1 - 2(\lambda_h \epsilon)] (z/a - 1)^2. \end{aligned} \quad (38)$$

We have calculated the concentrations for both of the above cases with the aid of a computer, and the results are presented in the next section.

In addition, moments for the isotropic and anisotropic cases can be calculated. We will give the results for the second-order moments. The second moments can be written in tensorial form, and

$$\langle \mathbf{RR} \rangle = \begin{bmatrix} \langle X^2 \rangle & 0 & 0 \\ 0 & \langle Y^2 \rangle & 0 \\ 0 & 0 & \langle Z^2 \rangle \end{bmatrix}. \quad (39)$$

When the dumbbell locates far away from the wall $z_c \rightarrow \infty$, it becomes

$$\langle X^2 \rangle_\infty = \langle Y^2 \rangle_\infty = a^2 (\mu [1 + \lambda_h \epsilon])^{-1}, \quad (40)$$

and

$$\langle Z^2 \rangle_\infty = a^2 (\mu [1 - 2\lambda_h \epsilon])^{-1}. \quad (41)$$

The reader can easily see that $\langle X^2 \rangle / \langle X^2 \rangle_\infty = 1$, and $\langle Y^2 \rangle / \langle Y^2 \rangle_\infty = 1$. However, $\langle Z^2 \rangle / \langle Z^2 \rangle_\infty \neq 1$. The zz -component of second moment tensor for the isotropic tensor becomes

$$\begin{aligned} \langle Z^2 \rangle / \langle Z^2 \rangle_\infty &= 2\pi^{-1/2} \gamma[3/2, 2\mu(1 - 2\lambda_h \epsilon)] \\ &\quad (z_c/a - 1)^2. \end{aligned} \quad (42)$$

Here, $\gamma(\alpha, x)$ is the incomplete Gamma function. The zz -component of the second moment tensor for the anisotropic case is:

$$\begin{aligned} \langle Z^2 \rangle / \langle Z^2 \rangle_\infty &= 4\mu (1 - 2\lambda_h \epsilon) [(z_c/a) - 1]^2 \\ &\quad AB(\alpha, 3/2) {}_1F_1[3/2; 3/2 + \alpha; \beta(z_c)]. \end{aligned} \quad (43)$$

CONCLUSION

Although the flow regime used (extensional-homo-

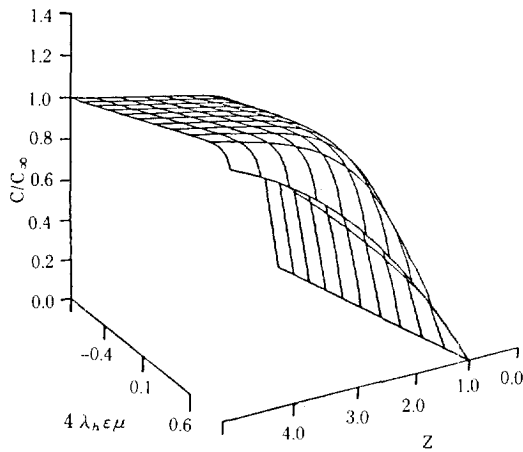


Fig. 2. This is a three-dimensional representation of the equation of the concentration for the isotropic case. The wall is at $z = 0$ and $Ha^2/kT = 0.5$.

geneous) is hypothetical, it serves well to point out the important factors introduced by the anisotropic hydrodynamics induced by the presence of a wall. The results of this analysis should give investigators a good feel for the contribution of anisotropic hydrodynamics to polymers in pores and confined geometries.

The plots given in Figures 2 and 3 are a comparison of the anisotropic and isotropic equations derived in the previous section. The plot involving $-4\lambda_h \epsilon \mu$ should be interpreted as a flow field similar to Figure 1, except when the direction of flow along the streamlines is reversed. In addition to what was discussed in the introduction, it becomes necessary to say a few words about the stability of the molecule in the flow field. Not all values of ϵ are possible for a harmonic dumbbell, because at a certain critical ϵ the dumbbell beads will fly apart indefinitely even in an isotropic medium ($\epsilon = 1/2\lambda_h$ for ϵ positive and $\epsilon = -1/\lambda_h$ for ϵ negative). A commonly used repair of this defect is a FENE potential, or some other potential that allows only finite extension of the spring. A discussion on the relative merits of these potentials is a paper in itself, and we refer those interested to Bird et al.[5]. For this paper, we will deal with a harmonic dumbbell, and the reader would do well to keep in mind that there is some upper bound that ϵ cannot cross.

As we discussed in the introduction, the effects of anisotropic diffusion only manifest when coupled with a flow field. Figure 4 shows clearly that as the flow strength ϵ decreases, the difference between the anisotropic concentration and isotropic concentration vanishes. Indeed, it appears that a fairly large ϵ is needed, one close to the critical ϵ , to effect a substantial dif-

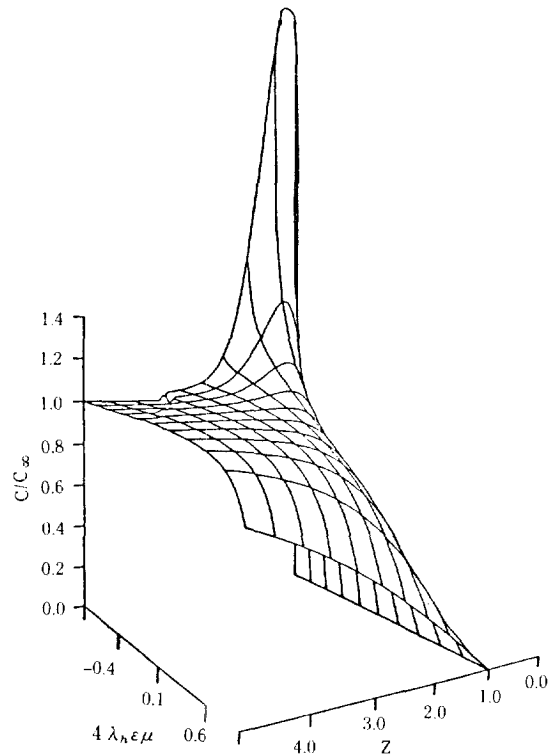


Fig. 3. This is a three-dimensional representation of the equation of the concentration with anisotropic hydrodynamic interactions due to the presence of the wall, again $Ha^2/kT = 0.5$.

ference of 20 or 30 percent. Also, we predict for positive values of ϵ that the anisotropic concentration will be below the isotropic value, and that the situation will reverse itself for negative values of ϵ . When ϵ is positive, the molecule is extending in the z -direction, in the direction of the wall, and it seems that the additional interference from anisotropy depresses the concentration in the near-wall region. This point can be easily explained from the following simple argument.

Let us study the nonhomogenous concentration profile in the presence of the small extensional rate(ϵ). The difference between anisotropic and isotropic concentrations is defined as:

$$C_{aniso} - C_{iso} \equiv \Delta C(z_c, \epsilon). \quad (44)$$

ΔC is computed from eqs.(35) and (36) as

$$\begin{aligned} \Delta C(z_c, \epsilon) &= \sum_{n=0}^{\infty} \frac{\epsilon^n}{n!} \frac{\partial^n}{\partial \epsilon^n} (\Delta C) \big|_{\epsilon=0} \\ &= 0 - \epsilon A + O(\epsilon^2). \end{aligned} \quad (45)$$

In general, we can show that A is positive. Therefore, from eqs.(44) and (45)

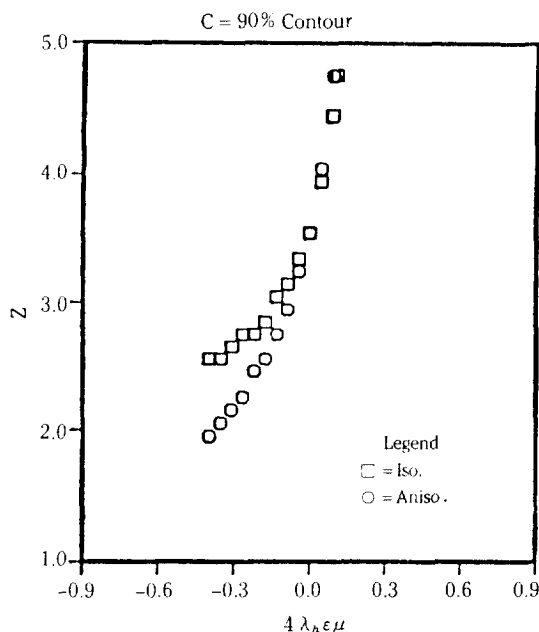


Fig. 4. This gives distance from the wall at which the concentration is at 90% of the bulk as a function of the flow parameters.

$$\varepsilon \geq 0, C_{aniso} \leq C_{iso}; \varepsilon < 0, C_{aniso} > C_{iso} \quad (46)$$

The fact that there is actually a local maximum in concentration above the bulk concentration for ε less than zero is more difficult to explain. We suspect that, since in this case the molecule is extended in the direction parallel to the wall in this case, they are stacking up like coins when encountering the resistance due to anisotropy. It is not sufficient to claim that this local maximum is an artifact of the flow field itself and not due to the polymer nature of the system, because scrutiny of eq.(32) for $z = 0$, the case where the dumbbell behaves as a single sphere, proves that a solution of spheres will have a constant concentration right up to the wall. It is expected, therefore, that this maximum is truly a characteristic of a polymer system near a wall.

Finally, something must be said of the applicability of all this to real polymer systems. We have tried to illustrate as simply as possible the qualitative changes that can be expected due to anisotropic hydrodynamics in polymer systems involving a wall. We have considered a vorticity free flow; but, theoretically, vorticity adds a spin to the "natural" center of mass coordinate of the molecule, causing the shear field and wall potential to oscillate and possibly doing away with the steady-state assumption. We expect that this change in the "natural" coordinate frame will leave

the unchanged tendencies due to isotropy, as described in this paper. We have assumed that there is no hydrodynamic interaction between the beads themselves; while on an order of magnitude basis this assumption is indefensible, we needed this simplification to keep the derivation intuitive and simple. We relegate this potential improvement to the future work file.

We expect that these results will be of interest to researchers concerned with pore and interfacial phenomena involving polymer solutions. At least on a qualitative basis, this analysis should contribute insight into the role of the anisotropic hydrodynamics.

NOMENCLATURE

a	: Radius of particle
A	: Coefficient in eq.(38)
B	: Beta function
C	: Constant
C_{aniso}	: Anisotropic concentration
C_{iso}	: Isotropic concentration
C_{∞}	: Bulk concentration
ΔC	: Difference of the concentration
D/Dt	: Material time derivative
$f(\mathbf{r}_1, \mathbf{r}_2)$: Function due to nonhomogeneous condition
${}_1F_1$: Degenerate hypergeometric function
h	: $(z_i - a)/a$. Here, $(z_i - a)$ is the distance of i th bead to the wall
H	: Spring constant
k	: Boltzmann's constant
K	: $(\nabla \cdot \mathbf{v}_o)^*$
\mathbf{r}	: Position vector
\mathbf{r}_i	: Position vector of i th bead
\mathbf{r}_c	: Center of mass
R	: Internal configuration coordinate
t	: Time
T	: Absolute temperature
\mathbf{v}	: Fluid velocity
\mathbf{v}_c	: Fluid velocity at the center
\mathbf{v}_o	: Fluid velocity at the origin
x_i, y_i, z_i	: Cartesian coordinate of i th bead
X, Y, Z	: Internal configuration (Cartesian coordinate)

Greek Letters

α	: Coefficient in eq. (38)
β	: Coefficient in eq. (38)
$\gamma(\alpha, x)$: Incomplete Gamma function
ε	: Elongational rate
ϕ_{fl}	: Potential due to the flow
ϕ'_{fl}	: Potential due to the flow of the anisotropic case
$\phi'_{fl,c}$: Potential due to the flow of the anisotropic

	case at the center
ϕ_w	: Potential due to the wall
ϕ_c	: Connector potential
ϕ_r	: Potential ($\phi_w + \phi_c$)
ϕ_T	: Total potential ($\phi_H + \phi_w + \phi_c$)
λ_h	: Characteristic time constant
μ	: Ha^2/kT
θ	: Heaviside step function
ζ_i	: Friction coefficient of i th bead
ζ_i^{-1}	: $1/2 (\zeta_1^{-1} + \zeta_2^{-1})$
ζ_i^{-1}	: $\zeta_2^{-1} - \zeta_1^{-1}$
ζ	: Scalar of the friction coefficient
Ψ	: Probability function
Ψ_h	: Probability function of homogeneous system

Superscript

+	: Transpose
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REFERENCES

1. Aubert, J.H. and Tirrell, M.: *J. Chem. Phys.*, **77**, 553 (1982).
2. Fuller, G.G.: *J. Poly. Sci.; Poly. Phys. Ed.*, **21**, 151 (1983).
3. Cooney, D.O.: "Biomedical Engineering Principles", Marcel Dekker, New York, N.Y. (1976).
4. Casassa, E.F.: *Poly. Letters*, **5**, 773 (1967).
5. Bird, R.B., Hassager, O., Armstrong, R.C. and Curtiss, C.F.: "Dynamics of Polymeric Liquids Vol. 2", Wiley, New York, N.Y. (1978).
6. Jhon, M.S. and Freed, K.: *J. Poly. Sci.; Poly. Phys. Ed.*, **23**, 955 (1985).
7. Warner, H.R. Jr.: *Ind. Eng. Chem. Fundamentals*, **11**, 379 (1972).
8. Fraenkel, G.K.: *J. Chem. Phys.*, **20**, 642 (1952).
9. Jhon, M.S., Sekhon, G. and Armstrong, R.: *Advances in Chemical Physics*, **66**, 153 (1987).
10. Sekhon, G., Armstrong, R. and Jhon, M.S.: *J. Poly. Sci.; Poly. Phys. Ed.*, **20**, 947 (1982).
11. Frisch, H., Simha, R. and Eirich, F.R.: *J. Chem. Phys.*, **21**, 365 (1953).
12. Casassa, E.F. and Tagami, Y.: *Macromolecules*, **2**, 14 (1969).
13. de Gennes, P.G.: "Scaling Concepts in Polymer Physics", Cornell Univ. Press, Ithaca, N.Y. (1979).
14. Scheutjens, J.M.H.M. and Fleer, G.J.: *J. Chem. Phys.*, **21**, 365 (1953).
15. Varoqui, R. and Dejardin, P.: *J. Chem. Phys.*, **66**, 4395 (1977).
16. Dimarzio, E.A. and Rubin, R.J.: *J. Poly. Sci.; Poly. Phys. Ed.*, **16**, 457 (1978).
17. Armstrong, R. and Jhon, M.S.: *J. Chem. Phys.*, **83**, 2475 (1985).
18. Aubert, J.H. and Tirrell, M.: *J. Chem. Phys.*, **72**, 2694 (1980).
19. Aubert, J.H., Prager, S. and Tirrell, M.: *J. Chem. Phys.*, **73**, 4103 (1980).
20. Schlichting, H.: "Boundary-Layer Theory", 7th ed., McGraw-Hill, New York, N.Y. (1979).
21. Cox, R.G. and Brenner, H.: *Chem. Eng. Sci.*, **22**, 1753 (1967).