

## DYNAMICS OF RIGID AND FLEXIBLE POLYMER CHAINS IN CONFINED GEOMETRIES

### III. WALL-BEAD HYDRODYNAMIC INTERACTION

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**Abstract**—As a continuation of the previous paper, dynamics of rigid and flexible polymer chains in viscous medium was reexamined in order to include the interaction of boundary and polymer chains. As models for rigid and flexible chains, rigid and linear elastic dumbbells were considered, which are essentially composed of two beads of frictional sources. The orientation distribution function was obtained by including anisotropic diffusivities of the bead due to the presence of the walls, and rheological properties were predicted to give us the dependence on an additional parameter,  $\epsilon_0 h$  relative size of bead to the gap width, as expected. Dynamics of flexible polymer chains showed a similar dependence on the relative size of bead, but exhibited no dependence on the shear rate as the case of no boundaries.

### INTRODUCTION

In the previous paper [1], dynamics of rigid and flexible polymer chains in viscous Newtonian fluid was presented in case of simple shear flow between two parallel plates, and applied to obtain the rheological properties of such solution for any size of channel gap compared with that of polymer chains. One of most important feature of Rigid Dumbbell(hereafter called R.D.) solution in that paper is that a distribution function which describes the motion of R.D. polymer chain can be constructed from the unbounded distribution function when no boundary exists.

At that time, however, the boundaries were simply taken as a solid wall through which both solvent and polymer can not penetrate so that there assumed no change in flow characteristic after introducing the boundaries. It is well-known, however, that such boundaries alter the diffusivity of the finite size of particles due to the change of friction exerted by fluid. Hydrodynamics [2,3,4, and 5] tells us that the frictional force exerted by fluid rises up tremendously as a particle approaches boundaries. Furthermore, there would be an anisotropic increase of such frictional drag when a particle moves toward the boundary or along it. This anisotropy can cause new kind of dynamics as far as polymer is concerned.

This phenomenon is called "wall-bead hydrodynamic interaction". It is possible to consider another kind of hydrodynamic interaction if we deal with the finite

size of bead of which polymer chains are composed. That is the bead-bead interaction which was extensively studied by from Kirkwood [6] to Bird et al.[7] in case of unbounded media, and it made the shear thinning rate in the rheological properties less than that of no interaction and decreased the flow effect by increasing the relaxation time of R.D.. This interaction can be characterized by the relative length of R.D.

$$h = d/L \quad (1)$$

where  $d$  is diameter of bead and  $L$  is length of R.D.. As a first approximation, interaction effect is of order  $h$  when  $h$  is small enough. On the other hand, wall-bead interaction can be characterized by the factor how often the polymer chain can be located near the boundary, because in that region the frictional force increases tremendously. This factor can be quantitized by  $h$  and  $\epsilon_0$

$$\epsilon_0 = L/l \quad (2)$$

where  $l$  is channel gap of the boundaries. It turned out that for small  $\epsilon_0 h$  the interaction effect in averaged diffusivity of the polymer chain is of order  $\epsilon_0 h \ln(\epsilon_0 h)$  which is greater than order of  $\epsilon_0 h$ . Therefore bead-bead interaction can be neglected if  $\epsilon_0$  is greater than unity. Furthermore if  $\epsilon_0$  is not too small compared to 1, then wall-bead interaction could be dominant, provided that  $h$  is small. In this paper, I will restrict myself to the topic of wall-bead interaction by ignoring bead-bead interaction entirely. In chapter II, kinetic theory for R.D. model

polymer in confined geometries will be developed and then applied to the specific case namely the case of simple shear flow between two parallel plates. In chapter III, anisotropic factor will be determined in the sense of preaveraging by utilizing the hydrodynamic results about the frictional drag near the wall. After discussing the results of R.D., in chapter IV, Linear Elastic Dumbbell(hereafter called as E.D.) will be analyzed with the same line used before [1].

### KINETIC EQUATION FOR R.D.

The model used here is that of rigid dumbbell pictured in Figure 1 which was the same as used before [1]. The only difference arises from the factor that each bead has a finite size so that it allows us to consider the wall-bead hydrodynamic interaction effect. The kinetic equation for the orientation distribution function which governs the motion of R.D. chain can be derived from the force balances to exerted to each bead by neglecting acceleration terms.

$$0 = \xi (\dot{r}_j) (\dot{r}_j - \dot{y}_j) + \frac{kT}{\xi_0} \nabla_{r_j} \ln \psi \quad \text{for } j=1, 2 \quad (3)$$

Here  $\xi(\dot{r}_j)$  is a diagonal tensor in general which is non-dimensionalized by where  $\xi_0$  is a the Stoke's friction factor, and  $\dot{y}_j$  is a bead velocity which is determined by the macroscopic velocity field.  $\dot{r}_j$ 's are the position vectors of each bead.  $kT$  is the Boltzman temperature. After defining  $\underline{A} = [\xi(\dot{r}_1) - \xi(\dot{r}_2)]/2$  and  $\underline{B} = \xi(\dot{r}_1) - \xi(\dot{r}_2)$  and assuming the homogeneous velocity field  $\underline{f}$ , the following sets of equation can be derived.

$$4\underline{A}(\dot{r}_c - \underline{f} \cdot \dot{r}_c) + \underline{B}(\dot{r} - \underline{f} \cdot \underline{r}) + \frac{2kT}{\xi_0} \nabla_{r_c} \ln \psi = 0 \quad (4)$$

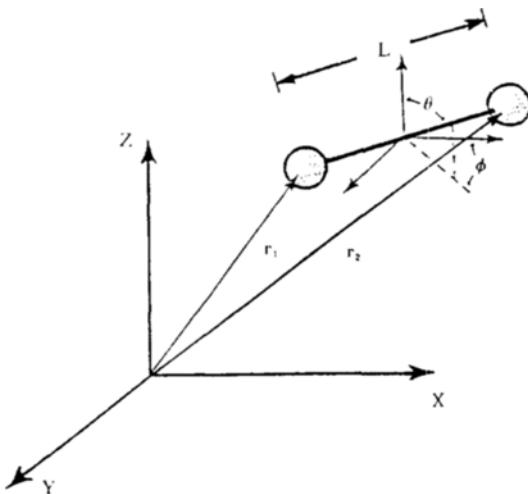


Fig. 1. The rigid dumbbell model.

$$\underline{B}(\dot{r}_c - \underline{f} \cdot \dot{r}_c) + [\underline{A}(\dot{r} - \underline{f} \cdot \underline{r})] \cdot \frac{2kT}{\xi_0} \frac{\partial \ln \psi}{\partial \theta} = 0 \quad (5)$$

$$\underline{B}(\dot{r}_c - \underline{f} \cdot \dot{r}_c) + [\underline{A}(\dot{r} - \underline{f} \cdot \underline{r})] \cdot \frac{2kT}{\xi_0 S} \frac{\partial \ln \psi}{\partial \phi} = 0 \quad (6)$$

where  $\underline{r}_c = (\underline{r}_1 + \underline{r}_2)/2$  and  $\underline{r} = \underline{r}_2 - \underline{r}_1$ , and  $S$  and  $C$  denote  $\sin \phi$  and  $\cos \phi$  respectively, and small  $s$  and  $c$  will denote  $\sin \theta$  and  $\cos \theta$  later.  $\hat{g}_\theta$  and  $\hat{g}_\phi$  are the unit vectors along  $\theta$  and  $\phi$  direction, respectively. Once we have  $\dot{\theta}$  and  $\dot{\phi}$  from equations (5) and (6) and  $\dot{r}_c$  from equation (4), it is easy to construct the kinetic equation for R.D. from the conservation of probability in space where polymer chains can be located.

$$\frac{\partial \psi}{\partial t} + \frac{1}{s} \cdot \frac{\partial (s \dot{\theta} \psi)}{\partial \theta} - \frac{\partial (\dot{\phi} \psi)}{\partial \phi} - \frac{\partial \dot{r}_c \psi}{\partial \underline{r}_c} = 0 \quad (7)$$

Details are the same as in the textbook of Bird et al. [8]. It is hard to obtain  $\dot{\theta}$ ,  $\dot{\phi}$  and  $\dot{r}_c$  in general from the equation (4)-(6). Now let us apply to the specific case, namely, the case of simple shear flow between two parallel plates as shown in Figure 2. External flow field is given by the following velocity gradient tensor.

$$\underline{f} = \alpha \begin{pmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \quad (8)$$

Then we have

$$\begin{aligned} \dot{\theta} &= \frac{\alpha c^2 C}{1 + \lambda s^2} - \frac{D_r}{D_1} \cdot \frac{1}{1 + \lambda s^2} \cdot \frac{\partial \ln \psi}{\partial \theta} \\ &+ \epsilon_0 \frac{B_3}{4A_3} \cdot \frac{D_r}{D_1} \cdot \frac{1}{1 + \lambda s^2} \cdot \frac{\partial \ln \psi}{\partial z_c} \end{aligned} \quad (9)$$

$$\dot{\phi} = -\alpha \frac{c S}{s^2} - \frac{1}{s^2} \cdot \frac{D_r}{D_1} \cdot \frac{\partial \ln \psi}{\partial \phi} \quad (10)$$

$$\dot{z}_c = \frac{B_3}{4A_3} \epsilon_0 \dot{\theta} - \frac{\epsilon_0^2}{4} \cdot \frac{D_r}{A_3} \cdot \frac{\partial \ln \psi}{\partial z_c} \quad (11)$$

where  $D_1 = A_1 - B_1^2$ ,  $D_3 = A_3 - B_3^2$ , and  $\lambda = (D_3 - D_1)/D_1$ .  $A_i$  and  $B_i$  are the diagonal elements of tensor  $\underline{A}$  and  $\underline{B}$ , and  $D_i$  turned out to be the harmonic averages of the

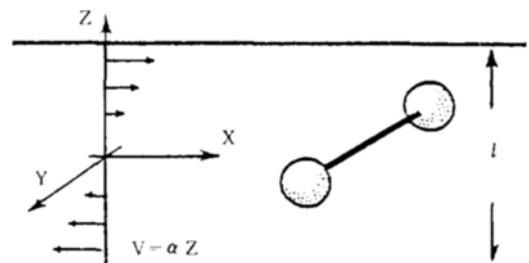


Fig. 2. The flow geometry.

diagonal elements of  $\underline{\underline{\zeta}}(r_1)$  and  $\underline{\underline{\zeta}}(r_2)$ .  $D_r$  is the rotational diffusivity of R.D. which is given by  $2kT/\zeta_0 L^2$  can be called the anisotropic factor in the diffusivity. By introducing the concept of preaveraging,  $B_3$  terms can be neglected and then after integrating over  $x_c$  and  $y_c$ , we have

$$\frac{\partial \psi}{\partial t} + \beta Q(\psi) - A(\psi) - \frac{\epsilon^2}{4^2} \cdot \frac{\partial^2 \psi}{\partial z_c^2} = 0 \quad (12)$$

$$\text{where } Q = \frac{c^2 C}{1 - \lambda s^2} \cdot \frac{\partial}{\partial \theta} - \frac{c S}{s} \cdot \frac{\partial}{\partial \phi}$$

$$- \frac{3(1+\lambda) \cos C (1+\lambda s^2/3)}{(1+\lambda s^2)^2} \quad (13)$$

$$A = \frac{1}{s} \cdot \frac{\partial}{\partial \theta} \left( \frac{s}{1+\lambda s^2} \cdot \frac{\partial}{\partial \theta} \right) + \frac{1}{s^2} \cdot \frac{\partial^2}{\partial \phi^2} \quad (14)$$

$$\beta = \frac{\alpha}{D_r < 1/D_1 >} \quad (15)$$

subject to the no flux boundary condition of each bead and the normalization condition of the total probability. One different thing is that length was scaled by the factor  $(1-\epsilon_0 h)$  further than before [1]. So hereafter  $\epsilon$  means  $\epsilon_0/(1-\epsilon_0 h)$ . This is the simply the extrusion effect of bead. Normalization condition looks like exactly same as before except modified definition of.

$$1(\psi) = 1 \quad (16)$$

$$1 = (1-\epsilon) \int_{-1}^1 dt \int_0^{2\pi} d\phi + \epsilon \int_0^1 dt_0 \int_{-t_0}^{t_0} dt \int_0^{2\pi} d\phi \\ \epsilon \leq 1 \quad (17)$$

$$1 = \epsilon \int_0^1 dt_0 \int_{-t_0}^{t_0} dt \int_0^{2\pi} d\phi \quad \epsilon > 1 \quad (18)$$

For steady simple shear flow we have already known that  $z_c$  dependence can be neglected with the no-flux boundary condition with the same argument used before [1]. It means that the wall can be felt by polymer chains only when they reach the wall provided that no adsorption of polymer occurs on the wall. Solution of equation (12) can be expressed as following

$$\psi(\theta, \phi, z_c) = \psi_{\beta=0} f(\epsilon, \beta) \sum_{k=0}^{\infty} \beta^k \Phi_k \quad (19)$$

where

$$\psi = \frac{1}{2\pi(2-\epsilon)} \quad \epsilon \leq 1 \quad (20)$$

$$= \frac{\epsilon}{2\pi} \quad \epsilon > 1 \quad (21)$$

and

$$f(\epsilon, \beta) = 1/[1 + \frac{\epsilon}{2-\epsilon} \sum_{k=0}^{\infty} a_k(1) \beta^{2k}] \quad \epsilon \leq 1 \quad (22)$$

$$= \sum_{k=0}^{\infty} g_k(\epsilon) \beta^{2k} \quad \epsilon > 1 \quad (23)$$

$a_k(1)$  and  $g_k(\epsilon)$  are given by equation (26) and (30)-(31), later.

The basic solution  $\Phi$  has a general form as following.

$$\Phi_{2k} = \sum_{i=1}^{k+1} \sum_{j=i}^{2k+1} E(k, i, j) P_{2j-2}^{2i} C_{2i-2} \quad (24)$$

$$\Phi_{2k+1} = \sum_{i=1}^{k+1} \sum_{j=i}^{2k+1} O(k, i, j) P_{2j-1}^{2i-1} C_{2i-1} \quad (25)$$

where the coefficients  $E(k, i, j)$  and  $O(k, i, j)$  are now functions of  $\lambda$ . First four  $\Phi$ 's are given in Appendix for reference. We can use the same definition of  $a_k(\epsilon)$ ,  $b_k(\epsilon)$ ,  $c_k(\epsilon)$ ,  $K_{2g, 2r}^p(\epsilon)$  and  $g_k(\epsilon)$  of the previous paper by using the modified definition of  $\epsilon$ .

$$a_k(\epsilon) = \sum_{j=1}^{2k+1} E(k, 1, j) K_{0, 2j-2}^0(\epsilon) \quad (26)$$

$$b_k(\epsilon) = \sum_{j=1}^{2k+1} E(k, 1, j) K_{2, 2j-2}^0(\epsilon) \quad (27)$$

$$c_k(\epsilon) = \sum_{j=1}^{2k+1} O(k, 1, j) K_{2, 2j}^1(\epsilon) \quad (28)$$

$$K_{2g, 2r}^p(\epsilon) = \epsilon^2 \int_0^{1/\epsilon} dt_0 \int_{-t_0}^{t_0} dt P_{2g}^p(t) P_{2r}^p(t) \quad (29)$$

$$g_k(\epsilon) = - \sum_{j=1}^k a_{k-j+1}(\epsilon) g_{j-1}(\epsilon) \quad k \geq 1 \quad (30)$$

$$g_0(\epsilon) = 1 \quad (31)$$

Then it is straightforward to obtain the rheological properties.

$$\epsilon \leq 1 \quad (\eta - \eta_s)_{\beta=0} = \frac{n_0 k T}{6D_r < 1/D_1 >} \cdot \frac{1 - 3\epsilon/4}{1 - \epsilon/2} \quad (32)$$

$$\frac{(\eta - \eta_s)}{(\eta - \eta_s)_{\beta=0}} = f(\epsilon, \beta) \{ 1 + \frac{1}{1 - 3\epsilon/4} \sum_{k=1}^{\infty} [\frac{\epsilon}{2} a_k(1) + \frac{2(1-\epsilon)}{5} E(k, 1, 2) + \epsilon b_k(1)] \beta^{2k} \} \quad (33)$$

$$\psi_{\beta=0}^1 = \frac{n_0 k T}{30D_r^2 < 1/D_1 >} \cdot \frac{1+\lambda}{1+\lambda/2} \cdot \frac{1-5\epsilon/8}{1-\epsilon/2} \quad (34)$$

$$\frac{\psi^1}{\psi_{\beta=0}^1} = f(\epsilon, \beta) \{ 1 - \frac{1+\lambda}{1+\lambda/2} \cdot \frac{1}{1-5\epsilon/8} [\sum_{k=1}^{\infty} 6(1-\epsilon) O(k, 1, 1) + 5\epsilon c_k(1)] \beta^{2k} \} \quad (35)$$

$$\epsilon \geq 1$$

$$(\eta - \eta_s)_{\beta=0} = \frac{n_0 k T}{6D_r < 1/D_1 >} \cdot \frac{1}{2\epsilon^2} \quad (36)$$

$$\frac{(\eta - \eta_s)}{(\eta - \eta_s)_{\beta=0}} = 2\epsilon^2 [1 + 2f(\epsilon, \beta) \sum_{k=1}^{\infty} b_k(\epsilon) \beta^{2k}] \quad (37)$$

$$\phi_{\beta=0}^1 = \frac{n_0 k T}{30 D_r^2 \langle 1/D_r \rangle^2} \cdot \frac{1+\lambda}{1-\lambda/2} \cdot \left( \frac{5}{4\epsilon^2} - \frac{1}{2\epsilon^4} \right) \quad (38)$$

$$\phi_{\beta=0}^1 = f(\epsilon, \beta) \left[ 1 + \sum_{k=1}^{\infty} \frac{c_k(\epsilon)}{c_0(\epsilon)} \beta^{2k} \right] \quad (39)$$

Therefore it is clear that in order to consider the wall-bead interaction effect, we need modified concept of  $\epsilon$  with  $h$ ,  $\lambda$ , and  $D_r$ . These  $\lambda$  and  $D_r$  are also functions of  $\epsilon$  and  $h$  so that in fact we need only one additional parameter  $h$  like the case of bead-bead interaction. Next chapter will be devoted to determine  $\lambda$  and  $D_r$  for given  $\epsilon$  and  $h$ .

### $\lambda$ AND $D_r$ FOR R.D.

For the preaveraging friction factor, the bead concentration profile and the functional form of frictional factor are needed. From the distribution function given in equation (19), bead concentration profile can be easily obtained.

$$\epsilon \leq 1/2$$

$$\text{for } 1/2 - \epsilon \leq |z_1| \leq 1/2$$

$$C(z_1) = \frac{f(\epsilon, \beta)}{2 - \epsilon} [1 + t_0 + \sum_{k=1}^{\infty} \beta^{2k} G_k(t_0; \lambda)] \quad (40a)$$

$$\text{for } 0 \leq |z_1| \leq 1/2 - \epsilon$$

$$C(z_1) = \frac{f(\epsilon, \beta)}{2 - \epsilon} \quad (40b)$$

$$1/2 \leq \epsilon \leq 1$$

$$\text{for } 0 \leq |z_1| \leq \epsilon - 1/2$$

$$C(z_1) = \frac{f(\epsilon, \beta)}{2 - \epsilon} \sum_{k=1}^{\infty} \beta^{2k} [G_k(t_0; \lambda) - G_k(t_0 - 1/\epsilon; \lambda)] \quad (40c)$$

$$\text{for } \epsilon - 1/2 \leq |z_1| \leq 1/2$$

$$C(z_1) = \frac{f(\epsilon, \beta)}{2 - \epsilon} [1 + t_0 + \sum_{k=1}^{\infty} \beta^{2k} G_k(t_0; \lambda)] \quad (40d)$$

$$\epsilon \geq 1$$

$$C(z_1) = \epsilon^2 f(\epsilon, \beta) \{ \sum_{k=1}^{\infty} \beta^{2k} [G_k(t_0; \lambda) - G_k(t_0 - 1/\epsilon; \lambda)] \} \quad (40e)$$

$$\text{where } \epsilon t_0 = 1/2 - z_1 \text{ and}$$

$$G_k(t; \lambda) = \int_0^t dt' \sum_{j=1}^{2k+1} E(k, 1, j) P_{2j-2}^0(t) \quad (41)$$

For the mathematical simplicity, the equilibrium profile was used here so that it would be said to be "equilibrium

Table 1. Dimensionless force on a sphere moving parallel to a plane wall [3, 4].

$\xi$	$\zeta_3(\xi)$	eq. (42a)	eq. (42b)
9.0677	1.0591	—	1.0592
2.7622	1.1738	—	1.1758
1.3524	1.3079	—	1.3143
0.5431	1.5675	1.2844	1.5736
0.1276	2.1514	2.0569	1.9954
0.0453	2.6475	2.6092	2.1651
0.0050	3.7863	3.7841	2.2772
0.0032	4.0223	4.0223	2.2857

um averaged hydrodynamic interaction". In qualitative sense, it could give the right answer. Next thing we need is the specific friction factor. Brenner et al. [2,3,4, and 5] reported the variable friction factor for the single sphere near a solid boundary in their series of papers. The results were quoted here in Table 1 and Table 2. Both exact results and approximate values obtained the following formulars are tabulated and for the computational purpose the following functions were chosen for each case.

$$\zeta_1(\xi) = -\frac{8}{15} \ln \xi + 0.9588 \quad \xi \leq 0.157 \quad (42a)$$

$$\zeta_1(\xi) = 1/[1 - \frac{9}{16(1+\xi)}] \quad \xi > 0.157 \quad (42b)$$

$$\zeta_3(\xi) = 1/\xi + 0.2 \ln(1/\xi) + 0.9713 \quad \xi \leq 1.839 \quad (43a)$$

Table 2. Dimensionless force on a sphere moving perpendicular to a plane wall [2, 5].

$\xi$	$\zeta_3(\xi)$	eq. (43a)	eq. (43b)
9.0677	1.1253	—	1.1258
5.1323	1.2220	—	1.2247
2.7622	1.4129	—	1.4266
1.3524	1.8375	—	1.9166
0.5431	3.0361	2.9347	—
0.1276	9.2518	9.2201	—
0.0201	51.594	51.500	—
0.0050	201.86	202.57	—
0.0013	802.15	802.31	—

$\xi$  is relative gap between bead and plane wall divided by the diameter of the bead.

$$\xi_3(\xi) = 1/(1 - \frac{9}{8(1+\xi)}) \quad \xi > 1.839 \quad (43b)$$

Here direction "1" means  $x$  direction parallel to the boundary and "3" means the perpendicular direction  $z$ . Since two beads are identical,

$$\langle 1/D_1 \rangle = \langle 1/\xi_1(z_1) \rangle \quad (44a)$$

$$\langle 1/D_3 \rangle = \langle 1/\xi_3(z_1) \rangle \quad (44b)$$

Here  $\langle \cdot \rangle$  means an average over all possible configurations of polymer chains. And we have two walls to be considered, so that we simply assumed that the effects due to two walls could be multiplied to give us the whole effects. Then we have the following expression for  $\langle 1/D_1 \rangle$  and  $\langle 1/D_3 \rangle$  which can be integrated numerically.

$$\epsilon < 1/2$$

$$\langle 1/D_1 \rangle = F_1(\epsilon h)/(1 - \epsilon/2) - \epsilon B_1(\epsilon, h)/(2 - \epsilon) \quad (45a)$$

$$1/2 \leq \epsilon \leq 1$$

$$\langle 1/D_1 \rangle = F_1(\epsilon h)/[\epsilon(2 - \epsilon)] - \frac{\epsilon}{2 - \epsilon} [B_1(\epsilon, h) - B_2(\epsilon, h)] \quad (45b)$$

$$1 \leq \epsilon$$

$$\langle 1/D_1 \rangle = F_1(\epsilon h) \quad (45c)$$

where

$$F_1(x) = \frac{1}{x} \int_0^x dy \left[ \frac{1}{\xi_1(y) \xi_1(2x-y)} \right] \quad (46a)$$

$$B_1(\epsilon, h) = \frac{h}{2} \int_0^{2\epsilon h} dy \left[ \frac{2-hy}{\xi_1(y) \xi_1(2\epsilon h-y)} \right] \quad (46b)$$

$$B_2(\epsilon, h) = \frac{h}{2} \int_0^{2\epsilon h} dy \left[ \frac{2-hy}{\xi_1(y) \xi_1(2\epsilon h-y)} \right] \quad (46c)$$

Now it is clear that we need one more parameter  $h$  in order to consider the wall-bead interaction effect.  $\langle 1/D_3 \rangle$  can be obtained by similar method with  $\xi_3(y)$  instead of  $\xi_1(y)$ .

## RESULTS FOR R.D.

Wall hydrodynamic effect in diffusivity is calculated numerically and plotted in Figure 3 in forms of  $1/\langle 1/D_1 \rangle$ ,  $1/\langle 1/D_3 \rangle$  and  $\lambda$ . As expected,  $\lambda$  is an increasing function of  $\epsilon$ , and in both  $h = 0.1$  0.2 linear relationship between  $\lambda$  and  $\epsilon$  holds as shown in Figure 3. Relative size effect on zero shear viscosity is plotted in Figure 4. One maximum is predicted near  $\epsilon = 1$ . It is due to the increase of the frictional resistance exerted by fluid with the presence of the wall, and anisotropy  $\lambda$  is also responsible for the increase of zero shear properties.

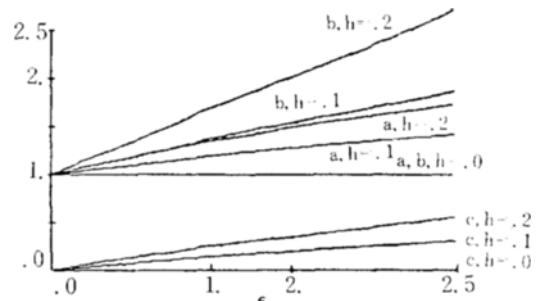


Fig. 3. (a)  $1/\langle 1/D_1 \rangle$ , (b)  $1/\langle 1/D_3 \rangle$ , and (c)  $\lambda$  as functions of  $\epsilon$  with the parameter  $h$  for R. D..

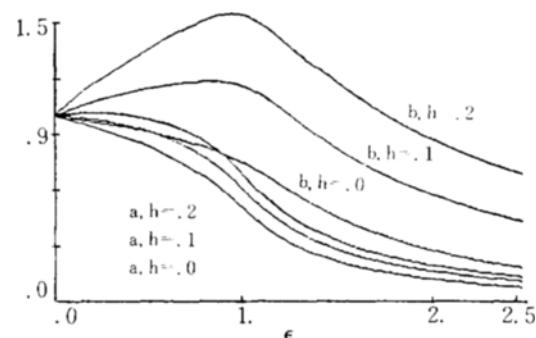


Fig. 4. (a) First Normal Stress Coefficient and (b) Shear Viscosity at zero-shear rate normalized by those with no boundary as functions of  $\epsilon$  with parameter  $h$  for R. D..

Both viscosity and first normal stress difference have substantial dependence on the relative thickness (here  $h$ ) of polymer chains compared with their length. In Figure 5, weak flow dependence on the dimensionless rheological properties are plotted as functions of modified shear rate. In general shear thinning rate increases as  $h$  increases, which is of reverse tendency predicted in case of bead-bead hydrodynamic interaction[7]. When  $\epsilon$  is 0.75, hydrodynamic interaction decreased the shear thinning effect, though.

## ELASTIC DUMBBELL MODEL

Kinetic equation with preaveraged hydrodynamic interaction can be derived for elastic dumbbell model polymer from the force balance of each bead.

$$\begin{aligned} \frac{\partial \psi}{\partial t} + \nabla \cdot (\Gamma \cdot \Gamma) \psi - \frac{2K}{\zeta_0} \left( \frac{1}{D_1} \cdot \frac{\partial x \psi}{\partial x} + \frac{1}{D_2} \cdot \frac{\partial y \psi}{\partial y} \right. \\ \left. + \frac{1}{D_3} \cdot \frac{\partial z \psi}{\partial z} \right) - \frac{2kT}{\zeta_0} \cdot \frac{1}{D_1} \cdot \frac{\partial^2 \psi}{\partial x^2} + \frac{1}{D_2} \cdot \frac{\partial^2 \psi}{\partial y^2} \end{aligned}$$

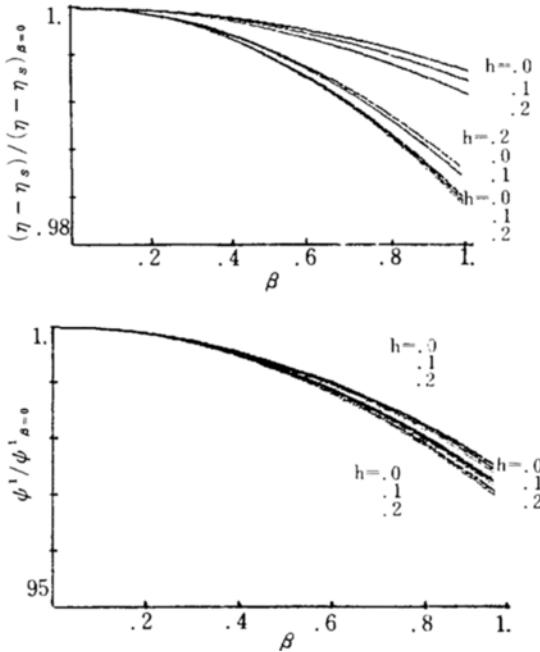


Fig. 5. (a) Dimensionless viscosity and (b) First Normal Stress Coefficient as functions of shear rate for R. D. (From the bottom,  $\epsilon = 1.25$ ,  $\epsilon = 0.75$ ,  $\epsilon = 0.0$  respectively).

$$+\frac{1}{D_3} \cdot \frac{\partial^2 \psi}{\partial z^2} - \frac{kT}{2\zeta_0} \left( \frac{1}{D_1} \cdot \frac{\partial^2 \psi}{\partial x_c^2} + \frac{1}{D_2} \cdot \frac{\partial^2 \psi}{\partial y_c^2} + \frac{1}{D_3} \cdot \frac{\partial^2 \psi}{\partial z_c^2} \right) = 0 \quad (47)$$

Specifically for steady simple shear flow between two parallel plates, it can be simplified into

$$\beta z \frac{\partial \psi}{\partial x} - \frac{1}{2} \left( \frac{\partial x \psi}{\partial x} - \frac{1}{1+\lambda} \cdot \frac{\partial z \psi}{\partial z} \right) - \frac{1}{4} \left( \frac{\partial^2 \psi}{\partial x^2} + \frac{1}{1-\lambda} \cdot \frac{\partial^2 \psi}{\partial z^2} + \frac{1}{4(1+\lambda)} \cdot \frac{\partial^2 \psi}{\partial z_c^2} \right) = 0 \quad (48a)$$

with

$$\int_{-\sqrt{6/4\epsilon}}^{\sqrt{6/4\epsilon}} dz_c \int_{-t}^t dz \int_{-\infty}^{\infty} dx \psi = 1 \quad (48b)$$

$$2z\psi + \frac{\partial \psi}{\partial z} - \frac{1}{2} \cdot \frac{\partial \psi}{\partial z_c} = 0$$

$$\text{at } z = 2z_c \pm \frac{\sqrt{6}}{2\epsilon} \quad (48c)$$

$$2z\psi + \frac{\partial \psi}{\partial z} + \frac{1}{2} \cdot \frac{\partial \psi}{\partial z_c} = 0$$

$$\text{at } z = -2z_c \pm \frac{\sqrt{6}}{2\epsilon} \quad (48d)$$

$$t = \frac{\sqrt{6}}{2\epsilon} - 2|z_c| \quad (48e)$$

where length was scaled by  $(2kT/K)^{1/2}/[1-\epsilon_0 h]$ , with  $h=d/l$  and  $\epsilon_0 = (6\lambda_p/\lambda_c)^{1/2}$ . Characteristic time  $\lambda_p$  is defined by  $\zeta_0/4K$  and  $\lambda_c = \zeta_0 l^2/2kT$ . Dimensionless shear strength  $\beta$  is defined by  $\alpha \zeta_0 < D_1 > / 4K$  and anisotropic factor  $\lambda$  is defined by  $(D_3 - D_1)/D_1$  and  $\epsilon = \epsilon_0/(1-\epsilon_0 h)$ . Solution for no flow has exactly same form as before [1].

$$\psi_{\beta=0} = \frac{C_1}{\pi} e^{-(x^2+z^2)} \quad (49)$$

$$\text{where } C_1 = 1/[2a \text{erf}(2a) + \{\exp(-4a^2) - 1\}/\pi] \quad (50a)$$

$$a = \sqrt{6}/4\epsilon \quad (50b)$$

And the probability distribution of center of mass given by the following will not be changed by the presence of a one-dimensional flow along x direction.

$$C(z_c) = \int_{-t}^t dz \int_{-\infty}^{\infty} dx \psi = C_1 \text{erf}(t) \quad (51)$$

Therefore if we assume  $\psi(x, z/z_c)$  as following

$$\psi(x, z/z_c) = \sum_{k=0}^{\infty} \beta^k \psi_k(x, z) \quad (52)$$

$\psi_k(x, z; \lambda)$  can be expressed as following.

$$\psi_k(x, z; \lambda) = H_k(x) Z_k(z; \lambda) \exp[-(x^2+z^2)] \quad (53)$$

Here  $H_k(x)$  is  $k$ th order Hermite polynomial. Equation for  $Z_k(z; \lambda)$  is

$$\frac{d^2 Z_k}{dz^2} - 2z \frac{dZ_k}{dz} - 2k(1+\lambda) Z_k = -4(1+\lambda) z Z_{k-1} \quad (54a)$$

subject to

$$\frac{dZ_k}{dz} = 0 \text{ at } z = |t| \quad (54b)$$

$Z_0(z; \lambda)$  and  $Z_1(z; \lambda)$  for integer  $\lambda$  are solved explicitly.

$$Z_0(z; \lambda) = C_1 / \pi \quad (55)$$

$$Z_1(z; \lambda) = \frac{C_1(1+\lambda)}{\pi(1+\lambda/2)} \left[ z + \exp(z^2 - t^2) \frac{O_\lambda(t)}{E_{\lambda-1}(t) - 2t O_\lambda(t)} \right] \quad (56)$$

Here  $O_n(t)$  and  $E_n(t)$  are odd and even parts of  $i^n \text{erfc}(t)$  [9], the repeated integral of the complementary error function. Because of the orthogonality of Hermite polynomial, we only need the following 4 integrals for the numerical calculation of the rheological properties of E.D..

$$\int_{-t}^t Z_0 \exp(-z^2) dz, \int_{-t}^t Z_0 z^2 \exp(-z^2) dz,$$

$$\int_{-t}^t Z_1 z \exp(-z^2) dz \text{ and } \int_{-t}^t Z_2 \exp(-z^2) dz$$

And as shown before, the last two integrals are identical for any  $\lambda$ ,  $Z_0$  and  $Z_1$  obtained by equations (55) and (56) are enough for the evaluation of the rheological properties. The results are

$$\frac{(\eta - \eta_s)}{(\eta - \eta_s)_{\epsilon=0}} = \frac{\psi^1}{\psi^1_{\epsilon=0}} = \frac{2}{\beta} \int_0^{2a} dt \langle xz/z_c \rangle \quad (57)$$

because

$$\begin{aligned} \langle xz/z_c \rangle &= \frac{2\beta C_1}{\sqrt{\pi}} \frac{1+\lambda}{1+\lambda/2} \left\{ \frac{\sqrt{\pi}}{4} \operatorname{erf}(t) \right. \\ &\quad \left. - t \exp(-t^2)/2 + \exp(-t^2) \right\} \\ &\quad \left[ \frac{t E_{\lambda,0}(t) + O_{\lambda+2}(t)}{2t O_{\lambda}(t) - E_{\lambda-1}(t)} \right] \quad (58a) \end{aligned}$$

$$\langle x^2/z_c \rangle = -C_1 \operatorname{erf}(t) + 2\beta \langle xz/z_c \rangle \quad (58b)$$

$$\langle z^2/z_c \rangle = -C_1 (\operatorname{erf}(t) - \frac{2t}{\sqrt{\pi}} \exp(-t^2)) \quad (58c)$$

In order to evaluate  $D_1$  and  $\lambda$ , we need the bead concentration profile at equilibrium.

$$C(z_1) = C_1 (\operatorname{erf}(a-z_1) + \operatorname{erf}(a+z_1)) \quad (59)$$

Then we have

$$\begin{aligned} \langle 1/D_1 \rangle &= \frac{\sqrt{6} C_1 h}{4} \int_0^{1/\epsilon h} dt \frac{\operatorname{erf}(\frac{\sqrt{6}h}{4} - t) + \operatorname{erf}(\frac{\sqrt{6}h}{2\epsilon} - \frac{\sqrt{6}ht}{4})}{\xi_1(t) \xi_1(\frac{2}{\epsilon h} - t)} \\ &\quad (60) \end{aligned}$$

$\langle 1/D_1 \rangle$  can be obtained from  $\xi_3(t)$  instead of  $\xi_1(t)$ .  $\lambda$  and  $1/\langle 1/D_1 \rangle$  are plotted in Figure 6 as a parameter  $h$  varies. It is interesting that the limiting case of infinity  $\lambda$  could be analyzed. In this case  $E_\lambda(t)$  and  $O_\lambda(t)$  are too small compared with  $\operatorname{erf}(t)$  or  $\exp(-t^2)$  so that we can predict the approximate behavior of dimensionless viscosity. Results are

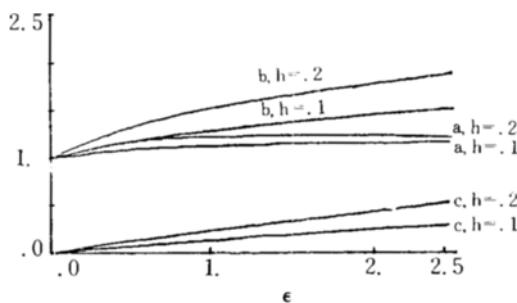


Fig. 6. (a)  $\lambda$  and (b)  $1/\langle 1/D_1 \rangle$  as a function of  $\epsilon$  with the parameter  $h$  for R.D.

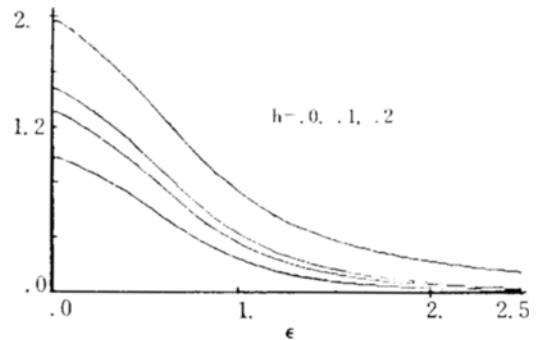


Fig. 7. Dimensionless viscosity or First Normal Stress Coefficient at zero shear rate normalized by those of no boundary as functions of  $\epsilon$  with parameter  $h$  (From the bottom,  $h=0.0, 0.1, 0.2$  and the top one is for the case of infinite  $\lambda$ ).

$$\epsilon \ll 1 \quad \frac{(\eta - \eta_s)}{(\eta - \eta_s)_{\epsilon=0}} = 2 \left( \frac{1 - \frac{2\sqrt{6}}{3\sqrt{\pi}} \epsilon}{1 - \frac{\sqrt{6}}{3\sqrt{\pi}} \epsilon} \right) \quad (61a)$$

$$\epsilon \gg 1 \quad \frac{(\eta - \eta_s)}{(\eta - \eta_s)_{\epsilon=0}} = \frac{1}{\epsilon^2} \quad (61b)$$

Equation (61a) is not much meaningful because when  $\epsilon$  approaches to zero, anisotropy number  $\lambda$  can be large so that there should be little effect on the rheological properties. But it still tells us that there should be limitation on the increase in zero-shear properties even when anisotropy factor increases tremendously. On the other hand, the equation (61b) tells us that if the channel gap is small enough to give us large anisotropy number, then there is no difference between R.D. and E.D. as far as the size effect on the rheological properties are concerned. No flow dependence is detected for E.D. model as same as before [1]. Dimensionless viscosity and first normal stress difference coefficient are plotted in Figure 7 with the parameters  $\lambda$  and  $h$ . For the actual rheological properties interpolation would give the similar size effect shown in Figure 3 for R.D..

## NOMENCLATURE

$\underline{\underline{A}}$	: a diagonal tensor defined by $(\underline{\xi}(r_1) + \underline{\xi}(r_2))/2$
$A_i$	: a diagonal element of tensor $\underline{\underline{A}}$ ( $i=1, 2$ or $3$ )
$a_k(\epsilon)$	: a function defined in the text
$b_k(\epsilon)$	: a function defined in the text

<u>B</u>	: a diagonal tensor defined by $\underline{\underline{\zeta}}(\underline{\underline{\Gamma}}_1) = \underline{\underline{\zeta}}(\underline{\underline{\Gamma}}_2)$	$\psi^i$	: basis of flow strength
$B_i$	: a diagonal element of tensor B ( $i=1, 2$ or $3$ )	$\psi$	: first normal stress coefficient
$B_i(\epsilon, h)$	: a function defined in text ( $i=1$ or $2$ )	$\underline{\partial}_\theta$	: orientation distribution function
$c_s(\epsilon)$	: a function defined in the text	$\underline{\partial}_\phi$	: unit vector in $\theta$
$c_m$	: $\cos[m\theta]$	$\alpha$	: unit vector in $\phi$
$C_n$	: $\cos(n\phi)$	$\beta$	: strength of a shear flow
$C_1$	: constant defined by equation (50a)	$\epsilon_0$	: dimensionless shear strength
$C(z)$	: bead concentration profile	$L/$	: dimensionless parameter defined by $L/$
$D_r$	: rotational diffusivity of R.D.	$\epsilon$	: dimensionless parameter defined by $\epsilon_0/(1-\epsilon_0 h)$
$D_i$	: $A_r B_i^2 / A_i$	$\zeta_0$	: Stoke's friction factor of a bead
$d$	: diameter of bead	$\zeta$	: friction tensor normalized by Stoke's friction factor
$E(k, i, j)$	: coefficients of basic distribution function	$\eta - \eta_s$	: contribution of polymer in viscosity
$E_n(t)$	: even parts of $i^n \operatorname{erfc}(t)$	$\eta$	: viscosity of solution
$f(\epsilon, h)$	: a function defined in the text	$\eta_s$	: viscosity of solvent
$F_i(\epsilon h)$	: a function defined in the text	$\theta$	: an angle coordinate in spherical coordinate system
$g_\kappa(\epsilon)$	: a function defined in the text	$\phi$	: an azimuth angle in spherical coordinate
$G_\kappa(t; \lambda)$	: a function defined in the text	$\lambda$	: anisotropy number in friction of bead
$h$	: $d/L$	$\lambda_p, \lambda_c$	: characteristic time constants defined in the text
$H_n(x)$	: the Hermite polynomials	$\bullet$	: time derivative
$kT$	: Boltzman temperature		
$K_{2g, 2r}^r(t)$	: a function defined in the text		
$L$	: length of R.D.		
$l$	: channel gap of the boundaries		
$n_0$	: number concentration of polymer		
$O(k, i, j)$	: coefficients of basic distribution function		
$O_n(t)$	: odd parts of $i^n \operatorname{erfc}(t)$		
$P_n^m$	: an associated Legendre polynomial		
$\underline{r}_i$	: position vector of a bead ( $i=1$ or $2$ )		
$\underline{r}_c$	: position vector of center of mass of R.D. defined by $(\underline{r}_1 + \underline{r}_2)/2$		
$\underline{r}$	: configuration vector of R.D. defined by $\underline{\underline{\Gamma}}_2 - \underline{\underline{\Gamma}}_1$		
$s_m$	: $\sin[m\theta]$		
$S_n$	: $\sin[n\phi]$		
$t_0$	: $(1/2-z)/\epsilon$		
$\underline{v}_j$	: velocity vector of the position where a bead is located ( $j=1$ or $2$ )		
$W_1, W_2, W_3$	: functions defined in Appendix		
$x, y, z$	: the element of configuration vector $\underline{r}$ in Carteasan coordinate		
$x_c, y_c, z_c$	: the element of position vector of center of mass $\underline{r}_c$ in Carteasan coordinate		
$Z_0, Z_1, Z_2$	: functions defined in the text		

### Greek Letters

$\underline{\underline{F}}$	: homogeneous velocity gradient tensor
$A$	: operator defined in the text
$\Omega$	: operator defined in the text
$\phi$	: basic function of the orientation distribution function calculated on the

$\psi^i$	: first normal stress coefficient
$\psi$	: orientation distribution function
$\underline{\partial}_\theta$	: unit vector in $\theta$
$\underline{\partial}_\phi$	: unit vector in $\phi$
$\alpha$	: strength of a shear flow
$\beta$	: dimensionless shear strength
$\epsilon_0$	: dimensionless parameter defined by $L/$
$\epsilon$	: dimensionless parameter defined by $\epsilon_0/(1-\epsilon_0 h)$
$\zeta_0$	: Stoke's friction factor of a bead
$\zeta$	: friction tensor normalized by Stoke's friction factor
$\eta - \eta_s$	: contribution of polymer in viscosity
$\eta$	: viscosity of solution
$\eta_s$	: viscosity of solvent
$\theta$	: an angle coordinate in spherical coordinate system
$\phi$	: an azimuth angle in spherical coordinate
$\lambda$	: anisotropy number in friction of bead
$\lambda_p, \lambda_c$	: characteristic time constants defined in the text
$\bullet$	: time derivative

### Subscripts

$\beta = 0$	: refers to the case of no flow
$\epsilon = 0$	: refers to the case of no boundary
$< >$	: refers to the averaged quantity over all possible configuration

## APPENDIX

Basic functions for equation (19) are following.

$$\Phi_0 = 1 \quad (A1)$$

$$\Phi_1 = -\frac{1+\lambda}{1+\lambda/2} \left( \frac{1}{6} P_2^1 C_1 \right) \quad (A2)$$

$$\begin{aligned} \Phi_2 = & -\frac{1+\lambda}{1+\lambda/2} \left( \frac{1}{28} P_2^0 + \frac{1}{70} P_4^0 \right) \\ & + \frac{1+\lambda}{84(2+\lambda)(3+\lambda)} \left[ (5+\lambda) P_2^2 C_2 \right. \\ & \left. + \frac{3+2\lambda}{5} P_4^2 C_2 \right] \quad (A3) \end{aligned}$$

$$\Phi_3 = W_1(\lambda) P_4^1 C_1 + W_2(\lambda) P_4^1 C_1 + W_3(\lambda) P_6^1 C_1 + C_3 \text{ terms} \quad (A4)$$

where

$$W_1(\lambda) =$$

$$W_2(\lambda) = \frac{1 - \lambda + 3\lambda^4 + 158\lambda^3 + 2293\lambda^2 + 7818\lambda + 6840}{315(2 + \lambda)^2(3 + \lambda)(12 + \lambda)(30 + \lambda)} \quad (A5)$$

$$W_3(\lambda) = \frac{(1 - \lambda)(11\lambda^3 + 401\lambda^2 + 2925\lambda + 5274)}{1540(2 + \lambda)(3 + \lambda)(12 + \lambda)(30 + \lambda)} \quad (A6)$$

$$W_4(\lambda) = \frac{(1 + \lambda)(45 + 23\lambda)}{1386(2 + \lambda)(3 + \lambda)(30 + \lambda)} \quad (A7)$$

$P_n^m$ 's are the associates Legendre polynomials defined in [1] and  $C_m$  denotes  $\cos(m\phi)$  as before. One remark for these solution is that as  $\lambda$  grows to infinity only  $W_3(\lambda)$  goes to zero.

## REFERENCES

1. Park, O. O. and Fuller, G.G.: *J. of Non-Newtonian*

- Fluid Mech., **15**, 309(1984).
2. Brenner, H.: *Chem. Eng. Sci.*, **16**, 242(1961).
3. Goldman, A.J., Cox, R.G. and Brenner, H.: *Chem. Eng. Sci.*, **22**, 637(1967).
4. Goldman, A.J., Cox, R.G. and Brenner, H.: *Chem. Eng. Sci.*, **22**, 653(1967).
5. Goldman, A.J., Cox, R.G. and Brenner, H.: *Chem. Eng. Sci.*, **22**, 1753(1967).
6. Kirkwood, J.G. and Auer, P.L.: *J. Chem. Phys.*, **19**, 281(1951).
7. Bird, R.B. and Warner Jr., H.R.: *Trans. Soc. Rheol.*, **15**, 741(1971).
8. Bird, R.B., Hassager, O., Armstrong, R.C. and Curtiss, C.F.: "Dynamics of Polymeric Liquids Vol. 2 'Kinetic Theory'", Wiley, New York (1977).
9. Abramowitz, M. and Stegun, I.A.: "Handbook of Functions", Dover Publication, Inc., New York Ch. 7 (1970).