

DISPERSION OF FLEXIBLE POLYMER CHAINS IN CONFINED GEOMETRIES

O Ok PARK

Department of Chemical Engineering, Korea Advanced Institute of Science and Technology, Seoul, Korea

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Abstract—Molecular model approach has been used to predict the dispersion characteristics of flexible polymer chains in confined geometries. The analysis ranges from the early stage dispersion to the steady Taylor dispersion of the simple linear dumbbell model polymer chains. For the early stage dispersion, the ray method was applied; an Aris type moments method was useful for the Taylor dispersion. Two parallel plates were chosen as a confining geometry and the specific initial condition of a point source in the midway of the gap was chosen for simplicity. It was found that the qualitative difference in dispersion properties of deformable polymer chains starts from the early stage compared with those of single Brownian particles. And it turns out that one parameter, which is similar to the relative spacing of the dumbbell to the gap of confining geometries, is useful to see the dispersion characteristics of the dumbbells.

INTRODUCTION

The dispersion of spherical particles in a flowing solution was first rigorously considered by Taylor [1] over thirty years ago. It was pointed out in that work that the dispersion is the result of the coupling of Brownian motion to the convection arising from the flow. One remarkable result of Taylor's analysis was a demonstration of the fact that, after a sufficiently long period of time, the dispersion of the solute could be described by a simple diffusion equation and an associated effective diffusivity or dispersion coefficient. Later, Aris [2] extended that analysis and added the effect of pure Brownian diffusion to the problem. The form for the dispersion coefficient for viscous flow in a straight tube of radius "b" is given by

$$K = D + \frac{b^2 U^2}{48 D} \quad (1)$$

where D is the translational diffusivity and U is the mean solvent velocity in the tube.

The first term in equation (1) is the contribution from pure diffusion along the flow direction, and the second is due to the coupling of radial diffusion and axial convection. This result, however, has limited application and is only strictly useful when the solute is isotropic and its size is very small compared to the size of the vessel supporting the flow. As the particles become large relative to the vessel, the interactions between the particles and the solid boundaries become increasingly im-

portant as pointed out by Brenner [3]. This consideration was later taken into account in the work of Foister and van de Ven [4] where the effect of hydrodynamic interactions between the boundary and the particles were taken into account.

At long times the nature of the dispersion is nicely described by the single parameter K and there is often little need to bother to calculate the detailed form of the concentration profile of the solute. Indeed, it is normally only necessary to evaluate certain moments of the concentration profile. At short times, however, it is normally necessary to evaluate the actual concentration distribution in space and time. A number of authors have addressed this problem, including Lighthill [5] and more recently Smith [6]. The approach typically used for such problems is to find an asymptotic solution for the concentration distribution which is valid at short times. The method employed by Smith [6] was an extension of the ray method developed by Cohen and Lewis [7] and Keller et al. [8]. The early stage characteristics are important because for many applications, such as arterial blood flow there is insufficient time for complete cross-mixing of the solute across the supporting channel to be achieved.

Clearly, the dispersion coefficient will also be a function of the detailed structure of the solute. Recently, Brenner et al. [9-11] have considered the dispersion of sedimenting, non-spherical, rigid particles. In contrast with a spherical particle, the dispersion of a non-spherical particle generally depends upon its orientation

relative to the direction of shear flow. The goal of this work was to consider the specific problem of flexible chains (as modelled using a simple elastic dumbbell) dispersing under shear flow in order to examine the effects of deformability of flexible polymer chains due to shear flow. This work also attempts to describe the initial stages of dispersion in addition to the case of steady Taylor dispersion at long times. In section 2, general convective diffusion equation governing the motion of the elastic dumbbell is developed and associated averaged functions are defined for further uses. The early dispersion characteristic of the elastic dumbbell in simple shear flow is examined in section 3 with the aid of ray method. In section 4, the steady Taylor dispersion at long times is considered for both simple shear and Poiseuille flows in order to examine the effects of flow profiles on the dispersion characteristics. Finally section 5 is devoted to summarize the results. This work does neglect, however, the existence of hydrodynamic interactions between the polymer and solid boundaries.

Throughout this study, the results for the elastic dumbbell model will be compared against the predictions for single Brownian particles. The theory for the dispersion of single Brownian particles can be found in Appendices A and B.

GENERAL CONVECTIVE DIFFUSION EQUATION

The model which will be used here is that of the linear elastic dumbbell pictured in Figure 1. This model is the simplest possible description of a flexible polymer and has been used extensively in the description of the fluid dynamics of polymeric liquids. An extensive review of the applications of this model for bulk solution properties can be found in the book of Bird et al. [12]. Recently this model has been used by Aubert and Tirrell [13] for the calculation of the effective viscosity of polymeric liquids flowing through confined geometries. Their work specifically dealt with evaluating the effect of the confining boundaries on the stresses contributed by the polymer chains. The model envisions the polymer chain as two beads connected by a linear spring force with all of the frictional resistance of the chain imbed-

ed on the two beads. Throughout this study comparisons will be made between the dumbbell model and the case of a single Brownian particle represented by single bead of friction. (See Figure 1). The conformation of the chain is described through a distribution function $\psi(r_1, r_2; t)$ which prescribes the probability that bead 1 is located at r_1 , and bead 2 at location r_2 at time t . The diffusion equation describing the evolution of ψ can be developed by considering the appropriate force balance for each of the beads. This approach is thoroughly discussed in reference [12] and leads to the following equation:

$$\frac{\partial \psi}{\partial t} + \frac{\partial}{\partial r_1} [U_1 \psi + \frac{H}{\zeta} (r_1 - r_2) \psi] - \frac{kT}{\zeta} \frac{\partial^2 \psi}{\partial r_1^2} + \frac{\partial}{\partial r_2} [U_2 \psi - \frac{H}{\zeta} (r_1 - r_2) \psi] - \frac{kT}{\zeta} \frac{\partial^2 \psi}{\partial r_2^2} = 0 \quad (2)$$

where H is the force constant of the spring, ζ is the friction coefficient of each bead and kT is the Boltzmann energy. The velocity of the fluid at each of the bead positions are U_1 and U_2 respectively. First term in equation (2) is the accumulation of the probability of distribution function, second represents the hydrodynamic friction due to flow, third is the spring force term which is taking care of the deformability of flexible polymer chains, and the last is due to the Brownian movement. Since we are interested in the dispersion of the dumbbell, it is necessary to solve the time dependent problem and we have chosen to restrict our attention to the following initial condition:

$$\psi(r_1, r_2; 0) = \delta(r_1) \delta(r_2) \quad (3)$$

The choice of this specific initial condition will only affect the initial dispersion of the dumbbell and not the steady Taylor dispersion. Even for case of the initial dispersion the important qualitative results reported here are independent of the initial condition chosen.

It is convenient to introduce dimensionless variables by scaling against a characteristic length λ , velocity gradient α and time T_c . It is appropriate to pick the gap width of the confined geometries as a characteristic length, since we are interested in the dispersion of the solute due to the confining geometries. As far as a characteristic is concerned, we can have two choices. First one is related to the time scale with which the solute can diffuse across the gap width of the boundaries. The steady Taylor type dispersion will be interpreted with this time scale as will be shown in section 4. And second choice is the relaxation time scale of the anisotropic deformable solutes like macromolecules. The early dispersion characteristic will be explained with this time scale in section 3. Equation (2) can be then rewritten in the following form where the variables r_1, r_2 and t and parameter U are understood to be dimensionless.

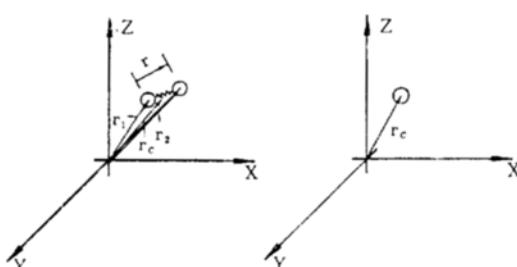


Fig. 1. (a) The Elastic Dumbbell model and (b) Spherical Brownian model.

sionless.

$$\begin{aligned} \frac{\partial \psi}{\partial t} + \frac{\partial}{\partial \underline{r}_1} [\beta \underline{U}_1 \psi + \frac{1}{4\epsilon} (\underline{r}_2 - \underline{r}_1) \psi] - 2 \frac{\partial^2 \psi}{\partial \underline{r}_1^2} \\ + \frac{\partial}{\partial \underline{r}_2} [\beta \underline{U}_2 \psi + \frac{1}{4\epsilon} (\underline{r}_1 - \underline{r}_2) \psi] - 2 \frac{\partial^2 \psi}{\partial \underline{r}_2^2} = 0 \quad (4) \end{aligned}$$

Here $\beta = \alpha T_c$, $T_c = \lambda^2/D$, $D = kT/2\zeta$, $T_p = \zeta/4H$ and finally $\epsilon = T_c/T_p$. In addition to being the ratio of the time scale for the dumbbell to diffuse across the gap to the relaxation time of the dumbbell, the parameter ϵ is also proportional to the square of the ratio of the dumbbell's radius of gyration to the channel gap. D has a dimension of (length)²/time and it is known as the translational diffusivity of the elastic dumbbells. The boundary condition which will be used is that the flux of probability normal to any surface is zero. If a surface has a normal vector \underline{n} , the boundary conditions are:

\underline{r}_1 on the boundary:

$$[\beta \underline{U}_1 \psi + \frac{1}{4\epsilon} (\underline{r}_2 - \underline{r}_1) \psi - 2 \frac{\partial \psi}{\partial \underline{r}_1}] \cdot \underline{n} = 0 \quad (5)$$

\underline{r}_2 on the boundary:

$$[\beta \underline{U}_2 \psi + \frac{1}{4\epsilon} (\underline{r}_1 - \underline{r}_2) \psi - 2 \frac{\partial \psi}{\partial \underline{r}_2}] \cdot \underline{n} = 0 \quad (6)$$

It is also convenient to introduce the center of mass coordinates \underline{r}_c and the bead separation vector \underline{r} according to the following definitions:

$$\underline{r}_c = (\underline{r}_1 + \underline{r}_2)/2 \quad (7)$$

$$\underline{r} = \underline{r}_2 - \underline{r}_1 \quad (8)$$

We shall restrict our attention to the case of unidirectional flows in the x -direction between parallel plates with gradients only in the y -direction. Furthermore, it is useful to define the following averaged functions which will be used in later calculations. The first such function, $\Phi(x_c, y_1, y_2; t)$ is defined as:

$$\Phi = \iiint dx dz_1 dz_2 \psi(x_1, y_1, z_1, x_2, y_2, z_2; t) \quad (9)$$

It is a kind of simplified distribution function and the reason why we are interested in this distribution function is that we would like to examine the x direction dispersion due to y directional boundaries so that the integration over x_1, z_1 and z_2 will leave the distribution function to depend upon only x_c , y_1 and y_2 and it will be easy to handle. This function is described by the following equation:

$$\begin{aligned} \frac{\partial \Phi}{\partial t} + \beta U \frac{\partial \Phi}{\partial x_c} + \frac{1}{4\epsilon} \frac{\partial}{\partial y_1} [(\underline{y}_2 - \underline{y}_1) \Phi - 8\epsilon \frac{\partial \Phi}{\partial y_1}] \\ + \frac{1}{4\epsilon} \frac{\partial}{\partial y_2} [(\underline{y}_1 - \underline{y}_2) \Phi - 8\epsilon \frac{\partial \Phi}{\partial y_2}] = 0 \quad (10) \end{aligned}$$

subject to the following boundary conditions:

\underline{y}_1 on the boundary:

$$(\underline{y}_2 - \underline{y}_1) \Phi - 8\epsilon \frac{\partial \Phi}{\partial y_1} = 0 \quad (11a)$$

\underline{y}_2 on the boundary:

$$(\underline{y}_1 - \underline{y}_2) \Phi - 8\epsilon \frac{\partial \Phi}{\partial y_2} = 0 \quad (11b)$$

$$\text{where } U = \frac{1}{2} [U(y_1) + U(y_2)] \quad (12)$$

and U denotes x component of velocity vector. The initial condition for equation (10) is

$$\Phi(x_c, y_1, y_2; 0) = \delta(x_c) \delta(y_1) \delta(y_2) \quad (13)$$

The second set of averaged functions are the moment P^k defined by:

$$P^k(y_1, y_2; t) = \int_{-\infty}^{\infty} dx_c \Phi(x_c, y_1, y_2; t) x_c^k \quad (14)$$

These moments obey the following equation:

$$\begin{aligned} \frac{\partial P^k}{\partial t} + \frac{1}{4\epsilon} \frac{\partial}{\partial y_1} [(\underline{y}_2 - \underline{y}_1) P^k - 8\epsilon \frac{\partial P^k}{\partial y_1}] \\ + \frac{1}{4\epsilon} \frac{\partial}{\partial y_2} [(\underline{y}_1 - \underline{y}_2) P^k - 8\epsilon \frac{\partial P^k}{\partial y_2}] \\ = \beta k U P^{k-1} + k(k-1) P^{k-2} \quad (15a) \end{aligned}$$

with the initial condition that

$$P^k(y_1, y_2; 0) = \delta_{k,0} \delta(y_1) \delta(y_2) \quad (15b)$$

The boundary conditions for equations (15) are identical to equation (11a) and (11b). Finally, the following additional averaged functions are defined:

$$\bar{P}^k(t) = \int dy_1 \int dy_2 P^k(y_1, y_2; t) \quad (16)$$

These functions evolve in time according to:

$$\frac{d\bar{P}^k(t)}{dt} = \beta k \bar{U} P^{k-1} + k(k-1) \bar{P}^{k-2} \quad (17a)$$

$$\text{with } \bar{P}^k(0) = \delta_{k,0} \quad (17b)$$

Analogous averaged functions have been used in the past for the solution of problems involving single Brownian particles and were first introduced by R. Aris [2]. By solving for P^1 and P^2 from equation (17), we obtain

$$\frac{1}{2} \frac{d\bar{P}^2}{dt} = \beta \bar{U} P^1 + 1 \quad (18)$$

$$\frac{d\bar{P}^1}{dt} = \beta \bar{U} P^0 \quad (19a)$$

$$\bar{P}^1 = \bar{U} P^0 t \quad (19b)$$

The dispersion coefficient K_i for dispersion in the i direction is formally defined as one half of the time differential of the variance of the particle concentration distribu-

tion. The dispersion coefficient in the direction of x_c can be related to the first and second moments defined so far and is given by

$$\frac{K_{x_c}}{D} = \frac{1}{2} \frac{d\bar{P}^2}{dt} - \bar{P}^1 \frac{d\bar{P}^1}{dt} \quad (20a)$$

$$= 1 + \beta h_1(t; \epsilon) \quad (20b)$$

Similarly in the case of the y_c -dispersion coefficient we can easily obtain the following result:

$$\frac{K_{y_c}}{D} = h_2(t; \epsilon) \quad (21)$$

Here h_1 and h_2 are unknown functions which only depend on t and ϵ . They can be determined once the specific velocity field is given. Since the x_c dispersion coefficient is of main concern, K without any subscript will denote x_c dispersion coefficient from now on. It can be easily verified that these results are valid for any unidirectional flow in the x -direction when the boundaries are taken to be parallel to the flow. It can be also shown that the dispersion coefficients for the single Brownian particles are of the same form as equations (20b) and (21) except that ϵ is zero. Having introduced the above definitions, we shall now proceed to analyze two specific flow fields.

SIMPLE SHEAR FLOW

The first situation which we shall consider is a simple shear flow between two parallel plates which are separated by a distance $2l$ as shown in Figure 2. The coordinate system will be taken midway between the plates and the dimensionless velocity field is given by $\underline{U} = (y, 0, 0)$. The x component of velocity of the center of mass of a dumbbell is then $U = (y_1 + y_2)/2$. The analysis will be carried out over two time domains. The first case is that of the initial dispersion of a point source of dumbbells initially located at the origin. In this case we need to stretch the time scale into the relaxation time scale of the dumbbells to examine the effects of the anisotropic deformability of the dumbbells.

Using equation (10) and defining $\tau = \beta E$, and a new dimensionless time $t' = \epsilon t$, the following equations for

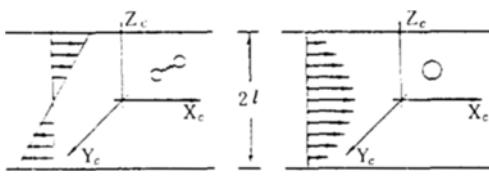


Fig. 2. The flow geometries for (a) Simple shear flow and (b) Rectilinear Poiseuille flow between two parallel plates.

the moments of the distribution can be written:

$$\frac{d}{dt} \langle x_c^2 \rangle = 2\epsilon + 2\tau \langle x_c y_c \rangle \quad (22)$$

$$\frac{d}{dt} \langle x_c y_c \rangle = \tau \langle y_c^2 \rangle - 2\epsilon \langle x_c^2 \rangle \quad (23)$$

$$\frac{d}{dt} \langle y_c^2 \rangle = 2\epsilon + 4\epsilon \langle y_c \rangle \quad (24)$$

$$\text{where } \langle B \rangle = \int_{-\infty}^{\infty} dx_c \int_{-1}^1 dy_c \int_{2y_c-2}^{2-2y_c} dy \ B \cdot \Phi \quad (25)$$

$$\langle C \rangle = \int_{-\infty}^{\infty} dx_c \int_{-1}^1 dy_c [C \cdot \Phi]_{y_1=1} - [C \cdot \Phi]_{y_1=-1} \quad (26)$$

In writing equations (22)-(24), we have dropped the prime on the time. And these second moments are directly related to the dispersion coefficients by definition.

In order to evaluate the moments specified by equations (22)-(24) it is necessary to determine the averages $\langle x_c \rangle$ and $\langle y_c \rangle$ which arise due to the boundary conditions. For this purpose we require a solution for the distribution function Φ . To proceed we shall use the ray method developed by Cohen and Lewis [7] (1967) and Keller and coworkers [8]. This method can be used to obtain asymptotic estimates of diffusion process at small time. In our situation the expansion parameter will be taken to be ϵ . This analysis technique was recently applied to the dispersion of single Brownian particles by R. Smith [6] and we shall largely follow the procedure he developed in order to study the elastic dumbbell. One first assumes a solution for Φ of the following form:

$$\Phi = A \exp\left(-\frac{S}{16\epsilon}\right) \quad (27)$$

Here both A and S are functions of x_c, y_1, y_2 and t . Substituting this into equation (10) and collecting similar terms in the parameter ϵ , we obtain the following results at order $O(1)$ and $O(\epsilon)$:

$$S_t + (y_2 - y_1) (S_{y_1} - S_{y_2}) + (S_{y_1^2} + S_{y_2^2}) + \tau (y_1 + y_2) \frac{S_{x_c^2}}{2} + \frac{S_{x_c^2}}{16} = 0 \quad (28)$$

$$A_t + (y_1 - y_2) \frac{(A_{y_1} - A_{y_2})}{4} + \frac{(A_{y_1} S_{y_1} + A_{y_2} S_{y_2})}{4} + \tau (y_1 + y_2) \frac{A_{x_c}}{2} + \frac{A_{x_c} S_{x_c}}{8} + \left[\frac{S_{y_1 y_1}}{8} + \frac{S_{y_2 y_2}}{8} + \frac{S_{x_c x_c}}{8} - \frac{1}{2} \right] A = 0 \quad (29)$$

Equation (28) is referred to as the eikonal equation. This is a nonlinear first order partial differential equation and can be solved by the method of characteristics. If we

choose the ray parameter as time t , then the characteristic equations are given by:

$$\frac{dy_1}{dt} = \frac{(y_2 - y_1)}{4} + \frac{S_{y_1}}{4} \quad (30a)$$

$$\frac{dy_2}{dt} = \frac{(y_1 - y_2)}{4} + \frac{S_{y_2}}{4} \quad (30b)$$

$$\frac{dx_c}{dt} = \frac{(y_1 + y_2)}{2} + \frac{S_{x_c}}{8} \quad (30c)$$

$$\frac{dS_{y_1}}{dt} = \frac{(S_{y_2} - S_{y_1})}{4} - \tau \frac{S_{x_c}}{2} \quad (30d)$$

$$\frac{dS_{y_2}}{dt} = \frac{(S_{y_1} - S_{y_2})}{4} - \tau \frac{S_{x_c}}{2} \quad (30e)$$

$$\frac{dS_{x_c}}{dt} = 0 \quad (30f)$$

Along these rays both equation (28) and (29) can be shown to be the following ordinary differential equations respectively:

$$\frac{dS}{dt} = \frac{S_{y_1}^2}{8} + \frac{S_{y_2}^2}{8} + \frac{S_{x_c}^2}{16} \quad (31)$$

$$\frac{dA}{dt} = \left[\frac{1}{2} - \frac{S_{y_1}^2}{8} - \frac{S_{y_2}^2}{8} - \frac{S_{x_c}^2}{16} \right] A \quad (32)$$

In order to solve equations (30a) to (30f), initial conditions need to be specified. The initial values for S_{y_1} , S_{y_2} , and S_{x_c} will be taken to be $4q$, $4r$ and $8p$ respectively. These ray parameters identify the rays through which information is transmitted. The solutions to equations (30a) to (30f) are:

$$\begin{aligned} x_c - x_{c0} - \frac{\tau}{2} (y_{10} + y_{20}) t &= pt \left(1 - \frac{1}{6} \tau^2 t^2 \right) \\ &= \frac{\tau}{4} (q + r) t^2 \end{aligned} \quad (33a)$$

$$(y_1 - y_2) - (y_{10} - y_{20}) \exp \left(-\frac{t}{2} \right) = 2(q - r) \sinh \left(\frac{t}{2} \right) \quad (33b)$$

$$(y_1 + y_2) - (y_{10} + y_{20}) = (q + r) t - \tau pt \quad (33c)$$

$$S_{y_1} - S_{y_2} = 4(q - r) - 8\tau pt \quad (33d)$$

$$S_{x_c} = 8p \quad (33e)$$

where x_{c0} , y_{10} and y_{20} are the initial values of x_c , y_1 and y_2 respectively. Using these results, equation (28) can be integrated to yield:

$$\begin{aligned} S &= (q - r)^2 [e^t - 1] + 4p^2 t + (q + r)^2 t - 2\tau p (q + r) t^2 \\ &+ \frac{4}{3} \tau^2 p^2 t^3 \end{aligned} \quad (34)$$

For the specific initial condition (13) we can eliminate the ray parameters to obtain:

$$S = \frac{4[x_c - \tau t \frac{(y_1 + y_2)}{4}]^2}{t(1 + \frac{1}{12} \tau^2 t^2)} + \frac{[(y_1 + y_2)^2}{t} + \frac{[(y_1 - y_2)^2}{[1 - e^t]} \quad (35)$$

Following the procedure of Smith [6], in order to evaluate the amplitude factor A , it is useful to define the following Jacobian which is related to the separation between rays.

$$J = \frac{\partial (x_c, y_1, y_2)}{\partial (p, q, r)} \quad (36)$$

This function obeys the following equation.

$$\frac{dJ}{dt} = J \left[-\frac{1}{2} + \frac{S_{y_1} y_1}{4} + \frac{S_{y_2} y_2}{4} + \frac{S_{x_c} x_c}{8} \right] \quad (37)$$

Combining (37) and (29) it is clear that

$$A \sqrt{J} \exp \left(-\frac{t}{4} \right) = \text{constant along rays} \quad (38)$$

This constant can be determined either from the solution for sufficiently small time (Smith, p112), or from the conservation of total probability. The final result is:

$$A = \frac{1}{16(\epsilon\pi)^{1.5} t (1 - e^t)^{0.5} (1 + \frac{1}{12} \tau^2 t^2)^{0.5}} \quad (39)$$

These results for Φ obtained from equations (27), (35) and (39) can be shown to be identical to the exact solution obtained for the single Brownian model by Foister [4] if our result is integrated over all values of $y = y_2 - y_1$. Using the ray method one can therefore obtain the exact solution for the dispersion of the center of mass of the dumbbells in the absence of boundaries. Furthermore, one can show that both the single Brownian model and the elastic dumbbell model predict identical dispersion characteristics. This similarity between the two models will disappear, however, once boundaries are included due to the fact that the linear dumbbell cannot sample the entire region between the boundaries with equal probability. The solution obtained so far is referred to as the incident solution and the effect of boundaries can be taken into account by considering the reflection of the rays at the boundaries. As time passes the reflected rays increase in importance relative to the incident rays and in general, multiply reflected rays must be considered at longer times. In this calculation, however, we have only considered the effect of the first reflected rays at either the bottom or top boundaries. With reflected rays taken into account, the following form for Φ is assumed.

$$\Phi = A_I \exp \left(-\frac{S_I}{16\epsilon} \right) + A_R \exp \left(-\frac{S_R}{16\epsilon} \right) \quad (40)$$

where the subscripts I and R refer to incident and reflected rays respectively. The following conditions are used

at a point of reflection:

$$S_I = S_R \quad (41)$$

$$\frac{A_I}{A_R} = - \left[(y_2 - y_1) + \frac{S_I y_1}{2} \right] / \left[(y_2 - y_1) + \frac{S_R y_1}{2} \right] \quad (42)$$

Using the boundary conditions and the results given for S_I and A_I in equation (35) and (39), S_R and A_R can be obtained. The integrals $\langle x_c \rangle$ and $\langle y_c \rangle$ in equations (22)-(24) can then be evaluated approximately as:

$$\begin{aligned} \langle x_c \rangle &= \frac{\sqrt{t} e_1(t)}{\pi t e_2(t)} \left\{ \exp \left[-\frac{1}{4\epsilon e_1(t)} \right] - \exp \left[-\frac{1}{4\epsilon t} \right] \right\} \\ &+ \frac{t \exp \left[-\frac{1}{4\epsilon e_2(t)} \right]}{2\sqrt{\pi \epsilon e_2(t)} \sqrt{e_2(t)}} \left\{ \operatorname{erf} \left[\frac{\dot{e}_1(t)}{4\epsilon e_2(t)} \right]^{0.5} \right. \\ &\quad \left. + \operatorname{erf} \left[\frac{t e_2(t)}{4\epsilon e_1(t)} \right]^{0.5} \right\} \end{aligned} \quad (43)$$

$$\langle x_c \rangle = \frac{\tau t}{2} \langle y_c \rangle \quad (44)$$

assuming that $A_I/A_R = 1$ for small time $\epsilon t \ll \sqrt{\epsilon}$ and $e_1(t) = 1 - \exp(-t)$ and $e_2(t) = 1 + t - \exp(-t)$.

Inserting these functions of time into equations (22)-(24) these equations can be numerically integrated to obtain the moments $\langle x_c^2 \rangle$, $\langle x_c y_c \rangle$ and $\langle y_c^2 \rangle$. The dispersion coefficients K_{xc} and K_{yc} can then be calculated directly from these second moments since the first moments, $\langle x_c \rangle$ and $\langle y_c \rangle$, are always zero in a simple shear flow. The result of this analysis for K_{xc} is shown in Figure 3 where the time dependent dispersion coefficient is plotted for several values of ϵ .

APPROACH TO STEADY STATE (TAYLOR) DISPERSION OF THE ELASTIC DUMBBELL

Simple shear flow

The approach to steady state dispersion can be solved by considering equations (10)-(17) where U is y_c . First of all, we know that the moment $P^0(y_1, y_2; t \rightarrow \infty)$ is only a function of y of the form:

$$P^0(y_1, y_2; t \rightarrow \infty) \rightarrow C_0 \exp \left[-\frac{y^2}{16\epsilon} \right] \quad (45)$$

$$\text{where } C_0 = \frac{C_1}{8\sqrt{\pi\epsilon}} \quad (46a)$$

$$\frac{1}{C_1} = \operatorname{erf} \left[\frac{1}{2\sqrt{\epsilon}} \right] + \frac{2\sqrt{\epsilon}}{\sqrt{\pi}} \left[\exp \left(-\frac{1}{4\epsilon} \right) - 1 \right] \quad (46b)$$

This result can be easily obtained from equation (15a) for P^0 . This function is directly related to the center of mass distribution function $C(y_c; t)$ which will be defined later. Using this result in the same equation for $P^1(y_1, y_2; t \rightarrow \infty)$ we have:

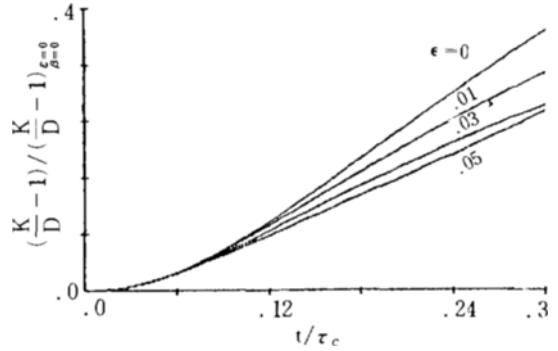


Fig. 3. Initial x_c dispersion of Elastic Dumbbell for simple shear flow for various values of ϵ (The only coupling effect of radial diffusion and axial convection is shown and it is based on equations (22)-(24), (43) and (44)).

$$\begin{aligned} \frac{\partial P^1}{\partial t} - 4 \frac{\partial}{\partial y} \left\{ \exp \left[-\frac{y^2}{16\epsilon} \right] \frac{\partial}{\partial y} [P^1 \exp \left(\frac{y^2}{16\epsilon} \right)] \right\} \\ - \frac{\partial^2 P^1}{\partial y^2} = \beta y_c C_0 \exp \left(-\frac{y^2}{16\epsilon} \right) \end{aligned} \quad (47a)$$

$$2 \exp \left(-\frac{y^2}{16\epsilon} \right) \frac{\partial}{\partial y} \{P^1 \exp \left(\frac{y^2}{16\epsilon} \right)\} \pm \frac{\partial P^1}{\partial y_c} = 0 \quad (47b)$$

at $y = \pm (2 - 2y_c)$

This function is also directly related to the centroid $Q(y_c; t)$ which will be defined later.

The center of mass distribution $C(y_c; t)$ is defined as

$$C(y_c; t) = \int_{2y_c-2}^{2-2y_c} dy P^0(y_1, y_2; t) \quad (48a)$$

Using equation (45), the steady concentration distribution can be obtained, and it is clear that it does not depend on the specific velocity profile. This is plotted in Figure 5.

The centroid Q of the concentration distribution is defined as

$$Q(y_c; t) = \int_{2y_c-2}^{2-2y_c} dy P^1(y_1, y_2; t) \quad (48b)$$

Using equation (47), Q can be shown to obey the following equation:

$$\frac{\partial Q}{\partial t} - 4 \left\{ \exp \left(-\frac{y^2}{16\epsilon} \right) \frac{\partial}{\partial y} [P^1 \exp \left(\frac{y^2}{16\epsilon} \right)] \right\} \Big|_{y=2-2y_c-2}^{y=2-2y_c}$$

$$- \frac{\partial^2 Q}{\partial y_c^2} = \frac{1}{2} \beta C_0 y_c \left[\operatorname{erf} \left(\frac{1-y_c}{2\sqrt{\epsilon}} \right) \right] \quad (49)$$

$$\frac{\partial Q}{\partial y_c} = 0 \quad \text{at } y_c = \pm 1 \quad (50a)$$

$$\int_{-1}^1 Q dy_c = 0 \quad (50b)$$

From equation (45), P^0 will be independent of y_c at long time and from equation (9), it is also clear that at long time, the x_c dependence of $\Phi(x_c, y, y_c; t)$ will become increasingly smaller and can be neglected. From these two facts and the relationship between P^0 and Φ given in equation (14), $\partial P^0 / \partial y_c$ and $\partial \Psi / \partial y_c$ approach to zero at long time. It can then be concluded that $\partial P^0 / \partial y_c$ approaches zero along with these two derivatives by the similar argument. The second term in equation (49) will then disappear from the boundary conditions given in equation (47b), and that equation is easily solved giving:

$$\begin{aligned} \frac{Q(y_c; t \rightarrow \infty)}{\beta} = & \frac{C_1}{2} \left\{ \left[\frac{z^3}{6a^3} - \frac{z^2}{2a^2} - \frac{z}{4a^3} - \frac{1}{4a^2} \right] \operatorname{erf}(z) \right. \\ & + \frac{1}{\sqrt{\pi}} \left[\frac{z^2}{6a^3} - \frac{z}{2a^2} - \frac{1}{3a^3} \right] \exp(-z^2) + \frac{(z-a)}{\sqrt{\pi a^2}} \\ & \left. + \left[\frac{1}{2a^2} + \frac{1}{3} \right] \operatorname{erf}(a) + \left(\frac{1}{3a^3} + \frac{1}{3a} \right) \frac{\exp(-a^2)}{\sqrt{\pi}} \right\} \quad (51) \end{aligned}$$

$$\text{where } z = a(1-y_c) \text{ and } a = \frac{1}{2\sqrt{\epsilon}}.$$

The dispersion coefficient can be found directly from the centroid function to be

$$\begin{aligned} \frac{K_{xc} - D}{\beta^2 D} = & \left(\frac{2C_1}{15} \right) \left\{ \left[1 + \frac{5}{8a^2} - \frac{15}{16a^4} \right] \operatorname{erf}(a) \right. \\ & + \left[\frac{\exp(-a^2)}{\sqrt{\pi}} \right] \left(\frac{1}{a} + \frac{1}{8a^3} - \frac{1}{16a^5} \right) + \left[\frac{1}{\sqrt{\pi}} \right] \\ & \left. - \frac{5}{2a} + \frac{5}{4a^3} + \frac{1}{2a^5} \right\} \quad (52) \end{aligned}$$

As $\epsilon \rightarrow 0$ (or as the channel width becomes large compared with the dumbbell), this ratio approaches a value of 2/15 which is identical to the result for a single Brownian particle as one would expect. On the other hand, as ϵ approaches infinity, the ratio in (52) tends to a value of 13/24, slightly greater than half of the previous value.

Rectilinear Poiseuille Flow

First of all, let us calculate the average velocity of the dispersing cloud of elastic dumbbells. This is calculated by simply averaging the Poiseuille velocity field against the function $P^0(y_1, y_2; t \rightarrow \infty)$ in equation (45). If we define λ as the ratio of the average velocity for the elastic dumbbell model to that for a Brownian particle, we have that:

$$\frac{\lambda}{C_1} = \left[1 - \frac{3}{2a^2} \right] \operatorname{erf}(a) + \frac{e^{-a^2}}{\sqrt{\pi}} \left[\frac{1}{a} - \frac{2}{a^3} \right] + \frac{2}{\sqrt{\pi a^2}} \quad (53)$$

where C_1 is given in (46).

One interesting result is that λ approaches unity as $\epsilon = 0$ and $\epsilon = \infty$, so that it passes through a maximum at a certain value of ϵ . Now let us replace the longitudinal coordinate, x , with the variable $\epsilon = x - 2\lambda t/3$ because the center of the cloud will be moving with the average speed of $2\lambda/3$. The equation for k 's moments of x_c , P^k becomes

$$\begin{aligned} \frac{\partial P^k}{\partial t} - 4 \frac{\partial}{\partial y} \left\{ \exp \left(-\frac{y^2}{16\epsilon} \right) \frac{\partial}{\partial y} [P^k \exp \left(\frac{y^2}{16\epsilon} \right)] \right\} \\ - \frac{\partial^2 P^k}{\partial y_c^2} = k\beta \left[1 - \frac{2\lambda}{3} - y_c^2 - \frac{y^2}{4} \right] P^{k-1} + k(k-1) P^{k-2} \quad (55a) \end{aligned}$$

with the same boundary condition as before.

And

$$\frac{d\bar{P}^k}{dt} = k\beta \left[1 - \frac{2\lambda}{3} - y_c^2 - \frac{y^2}{4} \right] P^{k-1} + k(k-1) \bar{P}^{k-2} \quad (55b)$$

and again, the boundary condition is unchanged. From the equation for \bar{P}^1 we then obtain the dimensionless centroid function exactly as:

$$\begin{aligned} \frac{4Q(z)}{\beta C_1} = & \left[\frac{4\lambda}{3} + \frac{1}{a^2} \right] \left[\left(\frac{z^2}{2a^2} - \frac{1}{4a^2} \right) \operatorname{erf}(z) \right. \\ & - \frac{z \exp(-z^2)}{2a^2 \sqrt{\pi}} - \frac{2}{a^2 \sqrt{\pi}} + \left(\frac{z^4}{6a^4} - \frac{2z^3}{3a^3} + \frac{z}{a^3} \right. \\ & \left. + \frac{7}{8a^4} \right) \operatorname{erf}(z) - \frac{5z}{3a^4 \sqrt{\pi}} + \left(\frac{z^3}{6a^4} - \frac{2z^2}{3a^3} - \frac{z}{12a^4} + \frac{4}{3a^3} \right. \\ & \left. \left. + \frac{\exp(-z^2)}{\sqrt{\pi}} \right) + C_3 \right] \quad (56) \end{aligned}$$

where

$$\begin{aligned} C_3 = & \left[\frac{2}{15} - \frac{1}{2a^2} - \frac{5}{4a^4} \right] \operatorname{erf}(a) + \frac{\exp(-a^2)}{\sqrt{\pi}} \left[\frac{2}{15a} \right. \\ & - \frac{17}{30a^3} - \frac{9}{10a^5} \left. \right] + \frac{1}{\sqrt{\pi}} \left[\frac{5}{6a^3} - \frac{9}{10a^5} \right] + \left[\frac{4\lambda}{3} \right. \\ & + \frac{1}{a^2} \left. \right] \left\{ \frac{1}{\sqrt{\pi}} \left[\frac{1}{2a} + \frac{1}{6a^3} \right] - \left[\frac{1}{6} + \frac{1}{4a^3} \right] \operatorname{erf}(a) \right. \\ & \left. - \frac{\exp(-a^2)}{\sqrt{\pi}} \left[\frac{1}{a} + \frac{1}{a^3} \right] \right\} \quad (57) \end{aligned}$$

In order to calculate the dispersion coefficient for an inhomogeneous flow field as in the present case, it is necessary to evaluate the function $P^1(y_1, y_2; t \rightarrow \infty)$ in detail instead of simply using the centroid $Q(z)$ which was possible for simple shear flow. This is a formidable task, however, and we shall resort here to a perturbation solution in the parameter ϵ . In the limit of small ϵ , any variation of the velocity gradient over the length scale of the dumbbell can be neglected. Therefore it is only necessary to consider the average velocity of the center

of mass of the dumbbell and not the velocities of the individual beads. If this approximation is made, the relative average velocity λ and the centroid are:

$$\frac{\lambda}{C_1} = \left(1 - \frac{3}{4a^2}\right) \operatorname{erf}(a) + \left(\frac{1}{a} - \frac{1}{2a^3}\right) \frac{\exp(-a^2)}{\sqrt{\pi}} + \frac{1}{2a^3\sqrt{\pi}} \quad (58)$$

$$\frac{Q(z)}{\beta} = \left(\frac{2\lambda}{3}\right) \left\{ \left[\frac{z^2}{2} + \frac{1}{4}\right] \operatorname{erf}(z) + \frac{z\exp(-a^2)}{2\sqrt{\pi}} - \frac{z}{\sqrt{\pi}} \right\} + \left[\frac{z^4}{12a^2} - \frac{z^3}{3a} - \frac{z}{2a} + \frac{3}{16a^2}\right] \operatorname{erf}(z) - \frac{z}{3a^2\sqrt{\pi}} + \left[\frac{z^3}{12a^2} - \frac{z^2}{3a} - \frac{z}{24a^2} + \frac{2}{3a}\right] \frac{\exp(-z^2)}{\sqrt{\pi}} + C_2 \quad (59)$$

where

$$C_2 = \frac{1}{\sqrt{\pi}} \left[\frac{1}{6a} + \frac{1}{5a^2} \right] + \left[\frac{a}{15} - \frac{17}{60a} - \frac{1}{5a^3} \right] \frac{\exp(-a^2)}{\sqrt{\pi}} - \frac{2\lambda}{3} \left\{ \left[\frac{a^2}{6} + \frac{1}{4}\right] \operatorname{erf}(a) + \left[\frac{a}{6} + \frac{1}{6a}\right] \frac{\exp(-a^2)}{\sqrt{\pi}} \right\} - \frac{1}{\sqrt{\pi}} \left[\frac{1}{6a} + \frac{a}{2} \right] + \left[\frac{a^2}{15} - \frac{1}{4} - \frac{3}{8a^2} \right] \operatorname{erf}(a) \quad (60)$$

Then the dispersion coefficient is

$$\begin{aligned} \left(\frac{K_{xc}}{D} - 1\right)/\beta^2 &= C_1 \left\{ \left(\frac{2\lambda}{3}\right) \left[\left(\frac{13}{45} - \frac{1}{16a^2}\right) \operatorname{erf}(a) \right. \right. \\ &+ \left. \left. \left(\frac{13}{45a} - \frac{7}{350a^3} - \frac{1}{30a^5}\right) \frac{\exp(-a^2)}{\sqrt{\pi}} + \left(\frac{1}{9a^2} - \frac{1}{3a} \right. \right. \right. \\ & \left. \left. \left. - \frac{1}{32a^5}\right) \frac{1}{\sqrt{\pi}} \right] + \left[\frac{58}{315} - \frac{1}{6a^2} - \frac{1}{8a^4} - \frac{5}{32a^6} \right] \operatorname{erf}(a) \right. \\ &+ \left. \left[\frac{1}{14a^7} + \frac{2}{5a^5} - \frac{1}{9a^3} \right] \frac{1}{\sqrt{\pi}} + \left[-\frac{58}{315a} + \frac{337}{2520a^3} \right. \right. \\ & \left. \left. - \frac{89}{560a^5} - \frac{1}{14a^7} \right] \frac{\exp(-a^2)}{\sqrt{\pi}} \right\} \quad (61) \end{aligned}$$

However, this dispersion coefficient is only valid up to $0(\sqrt{\epsilon})$ since this is the relative size of the dumbbell to the channel gap. Upon retaining terms of that order in the above equations we have:

$$\left(\frac{K_{xc}}{D} - 1\right)/\beta^2 = \frac{8}{945} \left[1 - \frac{17\sqrt{\epsilon}}{2\sqrt{\pi}} \right] \quad (62)$$

As in the case of a linear shear flow, the above result for Poiseuille flow tends to the single Brownian particle result (in this case $8/945$) when ϵ tends to zero.

DISCUSSION AND CONCLUSIONS

The results obtained above are summarized in

Table 1. Boundary effects on dispersion coefficients for simple shear flow.

Solute	Infinite domain	Between two plates
S. B.	$\frac{K_{xc}}{D} = 1$	$\frac{K_{xc}}{D} = \frac{1}{3} + 4 \sum_{n=1}^{\infty} \frac{(-1)^n}{\lambda_n^2} e^{-\lambda_n^2 t} \rightarrow 0$ $(\frac{K_{xc}}{D} - 1)/\beta^2 = t^2$ $(\frac{K_{xc}}{D} - 1)/\beta^2 = \sum_{n=0}^{\infty} \frac{(-1)^n}{\mu_n^2} T \rightarrow \frac{2}{15}$
E. D.	$\frac{K_{xc}}{D} = 1$	$\frac{K_{xc}}{D} \rightarrow 0$ $(\frac{K_{xc}}{D} - 1)/\beta^2 = t^2$ $(\frac{K_{xc}}{D} - 1)/\beta^2 \rightarrow \frac{2}{15} \left[1 + \frac{3\sqrt{\epsilon}}{\sqrt{\pi}} + \dots \right]$ for small ϵ

* \rightarrow means the approaching quantities as time goes to infinity,

** S. B. and E. D. denote the single Brownian and the elastic dumbbell models respectively.

*** λ_n and μ_m are defined in Appendix A.

Tables 1 and 2. The predictions found for the elastic dumbbell model are compared against the corresponding results for a single Brownian particle. As indicated in Table 1, both particles have the same dispersion characteristics in unbounded flow but differ when placed between the confines of parallel, solid boundaries. In that case the parameter ϵ , the ratio of the time scale for diffusion across the gap to the relaxation time of the

Table 2. Flow effects on steady taylor dispersion value of $(K_{xc}/D - 1)/\beta^2$.

Solute	Simple shear flow	Rectilinear poiseuille flow	Poiseuille flow in a tube
S. B.*	$\frac{2}{15}$	$\frac{8.8}{945}$	$\frac{9}{3072}$
E. D. (small ϵ)	$\frac{2}{15} \left[1 - \frac{2\sqrt{\epsilon}}{\sqrt{\pi}} \right]$	$\frac{8}{945} \left[1 - \frac{17\sqrt{\epsilon}}{2\sqrt{\pi}} \right]^{**}$	$\left[0.0635 \right]$

* S. B. and E. D. mean the single Brownian and elastic dumbbell models respectively.

** To take into account the decrease in average velocity gradient exerted to molecule due to the concentration distribution by using $\beta' = k_g \beta$ where

$$k_g = \left[1 + \frac{1}{2a^2} \right] \operatorname{erf}(a) + \frac{1}{\sqrt{\pi}a} \left[e^{-a^2} - 2 \right]$$

then it becomes

$$\frac{8}{945} \left[1 - \frac{9\sqrt{\epsilon}}{2\sqrt{\pi}} \right]$$

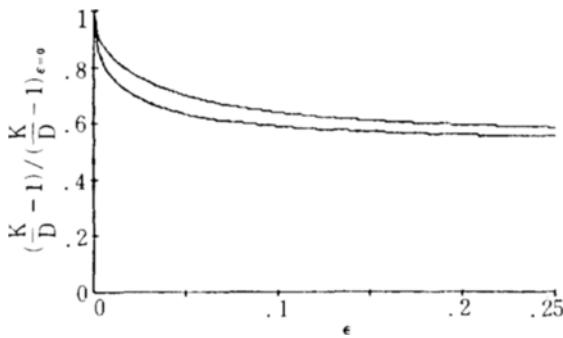


Fig. 4. Steady x_c dispersion of Elastic Dumbbell normalized by that of Spherical Brownian model as a function of ϵ (Upper one is for simple shear flow based on equation (52) and lower one is for Poiseuille flow based on (61)).

dumbbell, becomes important. As previously mentioned, this parameter is also proportional to the square of the dumbbell's radius of gyration to the channel gap.

For the time-dependent development of dispersion characteristics, there are three different regions, of which the first two are shown in Figure 3. For very short times, the dispersion coefficient will respond as it would for an infinite domain and the elastic dumbbell will disperse in a fashion similar to a single Brownian particle. Very quickly, however, the effects of finite values of the parameter ϵ become important.

In the final stage, where steady Taylor dispersion is approached, an exact solution for the elastic dumbbell model in a simple shear flow was obtained and the results are given in Figure 4. Here the dispersion coefficient is plotted against the parameter ϵ and the intercept at $\epsilon = 0$ represents the case of a single Brownian particle. As ϵ increases, the dispersion coefficient eventually

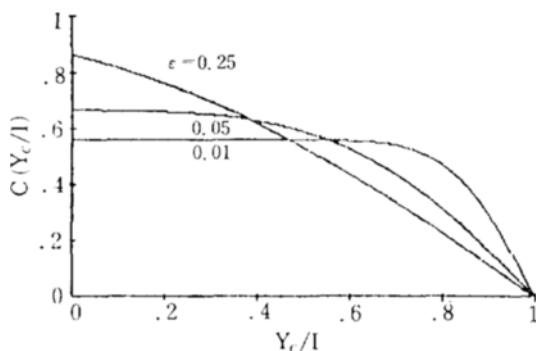


Fig. 5. Steady center of mass distribution of Elastic Dumbbell model as a function of y_c for various of ϵ .

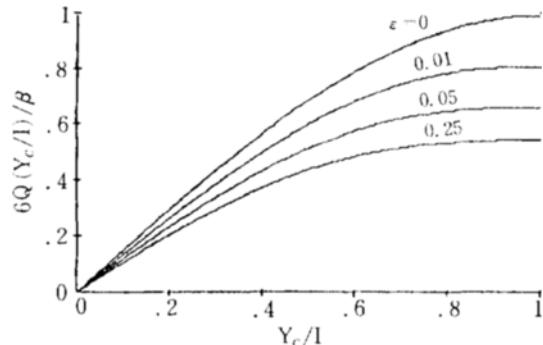


Fig. 6. The x_c dispersion of Spherical Brownian model as a function of dimensionless time scaled by τ_c (Upper is for Poiseuille flow based on (B9) and lower is for simple shear flow based on (A23)).

decreases to approximately one half of the value for the single Brownian particle. This decrease is simply a reflection of the fact that increasing the size of the dumbbell relative to the channel gap causes the particle to sample a restricted range of the velocity field across the gap. The coupling between convection and Brownian diffusion is thereby decreased. This point can be made clear by consideration of the concentration profile of Fig. 3-5, which indicates that the dumbbell is unable to approach to the solid walls and sample the velocity field in that region. Another important finding is that the decrease in the dispersion coefficient with increasing ϵ occurs rather quickly and has approached its final value to within a few percent after ϵ is raised to 0.1.

Dispersion depends on not only the vertical distribution of solute, but also on the vertical velocity distribution. The transient behavior of a single Brownian particle is shown in Figure 6, and it takes a much longer time in case of simple shear flow than in Poiseuille flow to achieve steady Taylor dispersion. The reason is that in Poiseuille flow there is a region of larger velocity gradients near the walls where the concentration is comparably low. This allows the approach to steady Taylor dispersion to occur sooner and to also have a somewhat lower dispersion coefficient than for simple shear flow. The other factor governing the level of quasi-steady dispersion is the geometry of the boundary. As shown in the first row in Table 2, the effects of flow and geometry are tremendous when one considers the differences between flow between parallel plates and down circular tubes. Simple shear flow is by far the most effective dispersing flow when compared with Poiseuille flow. On the other hand, the difference in the dependence on the parameter ϵ between simple shear and Poiseuille flow is only slight when one considers the elastic dumbbell

model.

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NOMENCLATURE

$A(A_I, A_R)$: pre-exponential factor of ray expansion, I and R refer to incident and reflected rays
b	: radius of tube
D	: translational diffusivity
H	: Spring constant of dumbbells
J	: Jacobian defined in (36)
kT	: Boltzman energy
$K(K_{xc}, K_{yc})$: Dispersion coefficient, x_c and y_c refer to x_c and y_c directions.
l	: Characteristic length
\hat{n}	: Outer normal unit vector
t	: Time
p^k	: k th moment of x_c defined in (14)
\bar{p}^k	: Averaged k th moment of x_c defined in (16)
Q	: Dimensionless centroid function
$\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_c, \mathbf{r}$: position vector
$S(S_I, S_R)$: Exponential factor in ray expansion, I and R refer to incident and reflected ray
U	: Mean velocity
$\mathbf{U}_1, \mathbf{U}_2$: velocity vector
x_1, x_2, x_c	: x components of position vectors
y_1, y_2, y_c	: y components of position vectors
z_1, z_2, z_c	: z components of position vectors
x_{c0}, y_{10}, y_{20}	: Initial value of x_c, y_1, y_2

Greek Letters

α	: Characteristic velocity gradient
δ	: Kronecker delta
ϵ	: Ratio of characteristic times
ζ	: Friction coefficient
λ	: constant
λ_n, μ_m	: Eigenvalues
τ_c	: Characteristic time l^2/D
τ_p	: Characteristic time for dumbbells
Φ	: Integrated distribution function defined in (9)
ψ	: Distribution function defined in ()
$\langle \rangle_B$: Averaged quantities defined in (25)
$\langle \rangle_C$: Averaged quantities defined in (26)

Appendix A. Spherical Brownian in Simple Shear Flow

Dimensionless governing equation and its auxilliary

conditions are:

$$\frac{\partial \Phi}{\partial t} + \beta y_c \frac{\partial \Phi}{\partial x_c} - \frac{\partial^2 \Phi}{\partial x_c^2} - \frac{\partial^2 \Phi}{\partial y_c^2} = 0 \quad (A1)$$

$$\Phi(x_c, y_c) = \delta(x_c) \delta(y_c) \text{ at } t=0 \quad (A2)$$

$$\frac{\partial \Phi}{\partial y_c} = 0 \quad \text{at } y_c = \pm 1 \quad (A3)$$

If we define

$$P^k(y_c; t) = \int_{-\infty}^{\infty} dx_c x_c^k \Phi(x_c, y_c; t) \quad (A4)$$

then

$$\frac{\partial P^k}{\partial t} - \frac{\partial^2 P^k}{\partial y_c^2} = \beta k y_c P^{k-1} + k(k-1) P^{k-2} \quad (A5)$$

$$P^k(y_c; t) = \delta_{k,0} \delta(y_c) \text{ at } t=0 \quad (A6)$$

$$\frac{\partial P^k}{\partial y_c} = 0 \quad \text{at } y_c = \pm 1 \quad (A7)$$

$$\frac{d\bar{P}^k}{dt} = \beta k y_c \bar{P}^{k-1} + k(k-1) \bar{P}^{k-2} \quad (A8)$$

$$\bar{P}^k(t) = \delta_{k,0} \text{ at } t=0 \quad (A9)$$

where

$$\bar{P}^k(t) = \int_{-1}^1 dy_c P^k(y_c; t) \quad (A10)$$

If we try the separation of variables in $P^k(y_c; t)$ or put $P^k(y_c; t) = Y(y_c)T(t)$, then we obtain two series of eigenvalues and corresponding eigenvectors for $Y(y_c)$. One is $\lambda_n = n\pi$ and $Y_n(y_c) = \cos(\lambda_n y_c)$ and the other is $\mu_m = (m+1/2)\pi$ and $Y_m(y_c) = \sin(\mu_m y_c)$. The first one is even with respect to y_c , and the latter is odd. We know that $P^0(y_c; t)$ is even with respect to y_c , so we have

$$P^0(y_c; t) = \frac{1}{2} + \sum_{n=1}^{\infty} \cos(\lambda_n y_c) \exp(-\lambda_n^2 t) \quad (A11)$$

In case of $P^1(y_c; t)$, we have

$$\frac{\partial P^1}{\partial t} - \frac{\partial^2 P^1}{\partial y_c^2} = \beta y_c P^0(y_c; t) \quad (A12)$$

$$P^1(y_c; 0) = 0 \quad (A13)$$

$$\frac{\partial P^1}{\partial y_c} = 0 \quad \text{at } y_c = \pm 1 \quad (A14)$$

It is obvious there is no homogeneous solution except zero to satisfy the initial and boundary conditions so that we can have an unique solution for $P^1(y_c; t)$. Let us use the method of eigenfunction expansions by putting:

$$P^1(y_c; t) = \sum_{m=0}^{\infty} \sin(\mu_m y_c) T_m(t) \quad (A15)$$

$$y_c P^0(y_c; t) = \sum_{m=0}^{\infty} \sin(\mu_m y_c) C_m(t) \quad (A16)$$

Then $C_m(t)$ can be obtained from the orthogonality of eigenfunctions.

$$C_m(t) = \frac{(-1)^m}{\mu_m^2} + \sum_{k=1}^{\infty} e^{-\lambda k^2 t} (-1)^{m+k} \left[\frac{1}{\mu_m^2 + \lambda_k^2} - \frac{1}{\mu_m^2 - \lambda_k^2} \right] \quad (A17)$$

Then equation for $T_m(t)$ is

$$\frac{dT_m}{dt} + \mu_m^2 T_m(t) = \beta C_m(t) \quad (A18)$$

$$T_m(t) = 0 \quad \text{at} \quad t = 0 \quad (A19)$$

Then we have

$$T_m(t) = \beta \frac{(-1)^m}{\mu_m^4} [1 - e^{-\mu_m^2 t}] + \sum_{k=1}^{\infty} \frac{(-1)^{m+k}}{\mu_m^2 - \lambda_k^2} \left[\frac{1}{(\mu_m + \lambda_k)^2} + \frac{1}{(\mu_m - \lambda_k)^2} \right] [e^{-\lambda_k^2 t} - e^{-\mu_m^2 t}] \quad (A20)$$

So we have

$$P^1(y_c; t) = \sum_{m=0}^{\infty} \sin(\mu_m y_c) T_m(t) \quad (A21)$$

$$\frac{K_{yc}}{D} = \frac{1}{3} + \sum_{k=1}^{\infty} \frac{(-1)^k}{\lambda_k^2} \exp(-\lambda_k^2 t) \quad (A22)$$

$$\frac{K_{xc}}{D} = 1 + 2\beta^2 \sum_{m=0}^{\infty} \frac{(-1)^m}{\mu_m^2} T_m(t) \quad (A23)$$

Appendix B. Spherical Brownian in Poiseuille Flow

In this case $P^0(y_c; t)$ is exactly same as before, but for $P^1(y_c; t)$ we have

$$\frac{\partial P^1}{\partial t} - \frac{\partial^2 P^1}{\partial y_c^2} = \beta (1 - y_c^2) P^0(y_c; t) \quad (B1)$$

with same conditions as before. Let us try

$$P^1(y_c; t) = \beta [S_0(t) - \sum_{n=1}^{\infty} \cos(\lambda_n y_c) S_n(t)] \quad (B2)$$

$$(1 - y_c^2) P^0(y_c; t) = D_0(t) - \sum_{n=1}^{\infty} \cos(\lambda_n y_c) D_n(t) \quad (B3)$$

Then we get

$$D_0(t) = \frac{1}{3} - 2 \sum_{n=1}^{\infty} \frac{(-1)^n}{\lambda_n^2} \exp(-\lambda_n^2 t) \quad (B4)$$

$$D_n(t) = \frac{2(-1)^n}{\lambda_n^2} + \left[\frac{2}{3} - \frac{1}{2\lambda_n^2} \right] \exp(-\lambda_n^2 t)$$

$$+ 2 \sum_{k=1}^{\infty} \frac{(-1)^{k+n}}{\lambda_{n+k}^2} \left(\frac{1}{\lambda_{n+k}^2} + \frac{1}{\lambda_{n-k}^2} \right) \exp(-\lambda_k^2 t) \quad (B5)$$

Then we have

$$S_0(t) = \frac{t}{3} + 2 \sum_{n=1}^{\infty} \frac{(-1)^n}{\lambda_n^4} [\exp(-\lambda_n^2 t) - 1] \quad (B6)$$

$$S_n(t) = \left[\frac{2}{3} - \frac{(-1)^n}{2\lambda_n^2} \right] t \exp(-\lambda_n^2 t) + \frac{2(-1)^n}{\lambda_n^4} [1 - \exp(-\lambda_n^2 t)] + \sum_{k=1}^{\infty} 2(-1)^{k+n} \left\{ \frac{1}{\lambda_{n+k}^2} + \frac{1}{\lambda_{n-k}^2} \right\} \left[\frac{1}{\lambda_n^2 - \lambda_k^2} \right] [e^{-\lambda_k^2 t} - e^{-\lambda_n^2 t}] \quad (B7)$$

In order to get K_{xc}/D , we should know P^{-1} and dP^{-1}/dt .

$$\frac{K_{xc}}{D} = \frac{1}{2} \frac{d\bar{P}^2}{dt} - \bar{P}^1 \frac{d\bar{P}^1}{dt} \quad (B8)$$

After tedious calculation, we finally obtain

$$\left[\frac{K_{xc}}{D} - 1 \right] / \beta^2 = S_0 \sum_{n=1}^{\infty} \frac{(-1)^n}{\lambda_n^2} e^{-\lambda_n^2 t} + 4 \sum_{n=1}^{\infty} \frac{(-1)^n}{\lambda_n^2} S_n [e^{-\lambda_n^2 t} - 1] \quad (B9)$$

REFERENCES

1. Taylor, G.I.: *Proc. Roy. Soc.*, **219**, 186 (1953).
2. Aris, R.: *Proc. Roy. Soc.*, **235**, 67 (1956).
3. Brenner, H.: *Chem. Eng. Sci.*, **16**, 240 (1961).
4. Foister, R.T. and Van De Ven, T.G.M.: *J. Fluid Mech.*, **96**, 105 (1980).
5. Lighthill, M.J.: *J. Inst. Math. Appl.*, **2**, 97 (1966).
6. Smith, R.: *J. Fluid Mech.*, **111**, 107 (1981).
7. Cohen, J.K. and Lewis, R.M.: *J. Inst. Math. Appl.*, **3**, 266 (1967).
8. Cohen, J.K., Hagin, F.G. and Keller, J.B.: *J. Math. Anal. Appl.*, **38**, 83 (1972).
9. Dill, L.H. and Brenner, H.: *J. Coll. Int. Sci.*, **93**, 343 (1983).
10. Dill, L.H. and Brenner, H.: *J. Coll. Int. Sci.*, **94**, 430 (1983).
11. Dill, L.H. and Brenner, H.: *Physicochem. Hydrodyn.*, **4**, 279 (1983).
12. Bird, R.B., Hassager, O., Armstrong, R.C. and Curtiss, C.F.: "Dynamics of Polymeric Liquids Vol 2 'Kinetic Theory'", Wiley, N.Y. (1977).
13. Aubert, J.H. and Tirrell, M.: *J. Chem. Phys.*, **77**, 553 (1982).