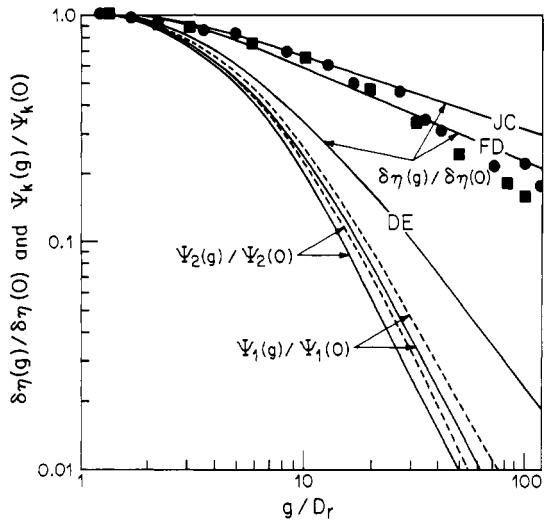

Figure 1. The three uppermost curves are ratios of the viscosity increments $[\delta\eta(g)/\delta\eta(0)] = (\eta(g) - \eta_s)/(\eta(0) - \eta_s)$ at finite shear to those at zero shear plotted vs. the dimensionless rate of shear g/D_r. The labels DE, JC, and FD, respectively, refer to the predictions of the Doi–Edwards theory, the theory of Jain and Cohen, and of our eq 19 with $cL^3 = 50$. The circles and squares indicate experimental results (for PBLG in *m*-cresol) taken from Figures 5 and 7, respectively, of ref 4. Finally, the pairs of curves labeled $\psi_k(g)/\psi_k(0)$ show how the normal stress coefficients vary with the shear rate. The dashed curves were computed according to the theory of Doi and Edwards and the solid curves are the predictions of the present theory for $cL^3 = 50$.

and JC were calculated by using the theories of Doi and Edwards and of Jain and Cohen, respectively.

Finally, we have included in Figure 1 theoretical predictions of the two coefficients $\psi_1(g)$ and $\psi_2(g)$, which are related to the normal stresses by the formulas

$$N_1 = \sigma_{zz} - \sigma_{xx} \equiv \psi_1(g)g^2$$
$$N_2 = \sigma_{yy} - \sigma_{zz} \equiv \psi_2(g)g^2 \qquad (20)$$

According to our theory

$$\psi_k(g) = \frac{1}{12}N^3c(\zeta a^2 D_r)\frac{1}{g^2}Y_k(g/D_r)F(g/D_r,c) \qquad (21)$$

with F defined by eq 9 and where $Y_1(g/D_r) = 3\langle u_z^2 - u_x^2\rangle$ and $Y_2(g/D_r) = 3\langle u_y^2 - u_z^2\rangle$. Here there are no contributions from the quartic (streaming) terms and so the ratio of a normal stress coefficient to its value at zero shear can be written as

$$\psi_k(g)/\psi_k(0) = [\psi_k(g)/\psi_k(0)]_{DE}\Phi(g/D_r) \qquad (22)$$

with $[\psi_k(g)/\psi_k(0)]_{DE}$ denoting the value of this ratio that is predicted by the theory of Doi and Edwards. The effects of hydrodynamic screening on these normal stresses can be extracted from the entries in Table II or seen by comparing the pairs of curves in Figure 1.

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Sedimentation of Asymmetric Elastic Dumbbells and the Rigid-Body Approximation in the Hydrodynamics of Chains

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ABSTRACT: The "rigid-body approximation", which has been used in much previous work on the hydrodynamics of flexible-chain molecules, is studied by the complete working out of a test case. The model used is that of the familiar elastic dumbbell, but here with the two beads having different Stokes radii. The diffusion equation of the internal coordinates of this model is solved numerically, and the coefficients of sedimentation and diffusion of the center of mass are calculated. It is found that the motions of the internal and external coordinates are coupled and that a circulation, similar to a vortex ring, occurs in the internal coordinates when translational forces are applied to the whole molecule. Thus the motion is not perfectly described as that of an ensemble of rigid bodies, although the deviations from this simplified description are small.

Introduction

The steady-state hydrodynamic behavior of long-chain molecules is an area in which outstanding unsolved problems remain in spite of some spectacular successes. A common model is the bead–spring chain with hydrodynamic interaction expressed by the Burgers–Oseen tensor; with this model hydrodynamic problems such as sedimentation or viscosity can be formulated rigorously as diffusion problems in the multidimensional space of the chain. The difficulty comes in solving the diffusion equation, since in this equation every coordinate is coupled to every other by hydrodynamic interaction if not by direct spring connections. The problem can be solved in closed form only after preaveraging the elements of the Burgers–Oseen tensor, an approximation originally introduced by Kirkwood and Riseman;[1] then a transformation to

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normal coordinates is frequently successful.[2] Perturbation developments[3,4] and dynamical simulation on a computer[5] have led to interesting but still somewhat inconclusive results.

In a recent paper[6] this author attempted to avoid solving the diffusion equation in the case of small flow rates by postulating that the motion of the chain in steady flow could be simulated by averaging over an ensemble of rigid chains, the ensemble having the same distribution of coordinates as the flexible chain. The hydrodynamic problem was solved numerically for each of the rigid bodies in the ensemble, and the results were then averaged. This postulate was based on previous work by Kramers,[7] who showed that the postulate was valid for the sedimentation and viscosity of a chain without hydrodynamic interactions, and by the author[6] and by Gotlib and Svetlov,[8] who all showed that the postulate remained valid when hydrodynamic interaction in the Kirkwood–Riseman preaveraged form was introduced.

However, in a recent paper Wilemski and Tanaka[9] have shown that the viscosity calculated in this way is in general only an upper bound, not the exact answer. Fixman[10] also has shown that the postulate is not valid for flexible chains in sedimentation if the hydrodynamic interactions are not preaveraged. Nevertheless, if it could be established that the postulate, even if not perfectly accurate, still gave better results than Kirkwood–Riseman preaveraging, there would be a strong incentive to use it because of the relative simplicity of methods based on it. A related approach, avoiding solution of the diffusion equation, has been used by Harvey[11] for models of biological molecules containing a few flexible joints. At the moment the experimental evidence on flexible chains is encouraging,[12] but Fixman's preliminary dynamical simulation[5] is not.

In this paper we examine the question for a simple model for which exact results can be obtained; the model is the elastic dumbbell consisting of two spheres connected by a spring and with hydrodynamic interaction. If the spring obeys Hooke's law and has zero equilibrium length, the diffusion equation for sedimentation can be reduced to a one-dimensional differential equation that can be solved numerically to any desired degree of accuracy. It turns out that the rigid-body postulate is valid as long as the Stokes radii of the two spheres are equal, but when they are unequal, a small error appears. Further, we find that the rigid-body postulate can be thought of as introducing preaveraging at a higher level, a preaveraging, not of the hydrodynamic interactions, but of the flows induced by them in the space of the molecule's internal coordinates.

Sedimentation and Diffusion of the Elastic Dumbbell

The model consists of two spherical beads, with radii a_1 and a_2 and with masses m_1 and m_2, connected by a Hooke's-law spring with force constant k. They are immersed in a fluid with viscosity η, so the beads have Stokes friction factors $\rho_1 = 6\pi\eta a_1$ and $\rho_2 = 6\pi\eta a_2$; the spring is assumed not to interact directly with the fluid. The centers of the spheres are located in space by the vectors $\mathbf{r}_1$ and $\mathbf{r}_2$; the probability distribution function of these centers is denoted by Ψ. There is a gravitational field, $\hat{\mathbf{k}}g$, where $\hat{\mathbf{k}}$ is a unit vector. The total forces that beads 1 and 2 exert on the fluid are denoted by $\mathbf{F}_1$ and $\mathbf{F}_2$.

To save work and to simplify the differential equations, we shall describe the hydrodynamic interaction between the beads by a simple formula originally introduced by Burgers;[13] this is perfectly accurate only in the limit of small bead radii. Since our purpose is to examine the consequences of the rigid-body postulate and since the elastic dumbbell is in no way an accurate model of any known real molecule, we see no need to go to a more refined (and complicated) formula.

We can now write down the equations for the average velocities, $\dot{\mathbf{r}}_1$ and $\dot{\mathbf{r}}_2$, neglecting inertia and assuming that the motions arise from diffusion or from the applied forces and are opposed only by viscous resistance:

$$\mathbf{F}_1 = k(\mathbf{r}_2 - \mathbf{r}_1) - k_BT\nabla_1 \ln \Psi + \hat{\mathbf{k}}gm_1 = \rho_1(\dot{\mathbf{r}}_1 - \mathbf{v}_1) \quad (1a)$$

$$\mathbf{F}_2 = k(\mathbf{r}_1 - \mathbf{r}_2) - k_BT\nabla_2 \ln \Psi + \hat{\mathbf{k}}gm_2 = \rho_2(\dot{\mathbf{r}}_2 - \mathbf{v}_2) \quad (1b)$$

Here $\mathbf{v}_1$ is the velocity that the fluid would have at $\mathbf{r}_1$ due to $\mathbf{F}_2$ if bead 1 were absent, and vice versa for $\mathbf{v}_2$. These velocities are given in terms of the Burgers–Oseen hydrodynamic-interaction tensor,[1,12] with $\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$:

$$\mathbf{v}_1 = \mathbf{T}\cdot\mathbf{F}_2 \quad (2)$$

$$\mathbf{T} = \frac{1}{8\pi\eta r}\left(1 + \frac{\mathbf{rr}}{r^2}\right) \quad (3)$$

We can solve for the velocities of the two beads:

$$\begin{aligned}\dot{\mathbf{r}}_1 &= (1/\rho_1)\mathbf{F}_1 + \mathbf{T}\cdot\mathbf{F}_2 \\ &= (k/\rho_1)(\mathbf{r}_2 - \mathbf{r}_1) + k\mathbf{T}\cdot(\mathbf{r}_1 - \mathbf{r}_2) - \\ &\quad k_BT[(1/\rho_1)\nabla_1 + \mathbf{T}\cdot\nabla_2] \ln \Psi + g(m_1/\rho_1 + m_2\mathbf{T}\cdot)\hat{\mathbf{k}}\end{aligned} \quad (4a)$$

$$\begin{aligned}\dot{\mathbf{r}}_2 &= (1/\rho_2)\mathbf{F}_2 + \mathbf{T}\cdot\mathbf{F}_1 \\ &= (k/\rho_2)(\mathbf{r}_1 - \mathbf{r}_2) + k\mathbf{T}\cdot(\mathbf{r}_2 - \mathbf{r}_1) - \\ &\quad k_BT[(1/\rho_2)\nabla_2 + \mathbf{T}\cdot\nabla_1] \ln \Psi + g(m_2/\rho_2 + m_1\mathbf{T}\cdot)\hat{\mathbf{k}}\end{aligned} \quad (4b)$$

When we add and subtract these, we get equations for the velocities of the center-of-mass coordinate, $\mathbf{R} = (\mathbf{r}_1 + \mathbf{r}_2)/2$, and of the interbead vector, $\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$:

$$\dot{\mathbf{R}} = -\frac{k_BT}{2}\left(\frac{1}{2\rho_1} + \frac{1}{2\rho_2} + \mathbf{T}\cdot\right)\nabla_R \ln \Psi - \frac{1}{2}\left(\frac{1}{\rho_1} - \frac{1}{\rho_2}\right) \times (k\mathbf{r} + k_BT\nabla_r \ln \Psi) + \frac{g}{2}\left[\frac{m_1}{\rho_1} + \frac{m_2}{\rho_2} + (m_1 + m_2)\mathbf{T}\cdot\right]\hat{\mathbf{k}} \quad (5)$$

$$\begin{aligned}\dot{\mathbf{r}} = &-k\left(\frac{1}{\rho_1} + \frac{1}{\rho_2} - 2\mathbf{T}\cdot\right)\mathbf{r} - k_BT\left[\left(\frac{1}{2\rho_1} - \frac{1}{2\rho_2}\right)\nabla_R + \left(\frac{1}{\rho_1} + \right.\right. \\ &\left.\left.\frac{1}{\rho_2} - 2\mathbf{T}\cdot\right)\nabla_r\right] \ln \Psi + g\left[\frac{m_1}{\rho_1} - \frac{m_2}{\rho_2} - (m_1 - m_2)\mathbf{T}\cdot\right]\hat{\mathbf{k}}\end{aligned} \quad (6)$$

In these equations ∇_R and ∇_r are the gradients with respect to R and r, respectively; from the usual formulas for converting partial derivatives from one coordinate system to another we get

$$\nabla_R = \nabla_1 + \nabla_2 \quad (7)$$

$$\nabla_r = (1/2)(\nabla_1 - \nabla_2) \quad (8)$$

In eq 5 the first term is the contribution from diffusion down a gradient in the concentration of the center of mass, and the last term is the contribution arising directly from external forces. Both of these terms are conventional. The middle term, however, is a contribution to the motion of the center of mass arising from forces and gradients in the internal coordinate, r. Hence we cannot in general find the diffusion or sedimentation coefficients without first obtaining the dependence of Ψ on the internal coordinates; the only exception comes when $\rho_1 = \rho_2$, that is, when the two spheres are of equal size, in which case the middle term

vanishes. We therefore must form a partial differential equation in the usual way to describe the diffusion of the internal coordinates.

As a preliminary, we resolve $\dot{\mathbf{r}}$ into components along the radial and tangential directions. We define unit vectors $\hat{\mathbf{r}}$ and $\hat{\theta}$ in the r and θ directions of a spherical coordinate system r,θ,ϕ; the polar axis is oriented in the direction $\hat{\mathbf{k}}$ of the external force. The components of the various operators follow:

$$\hat{\mathbf{k}} = \hat{\mathbf{r}} \cos\theta - \hat{\theta} \sin\theta \tag{9}$$

$$T_{rr} = (1/4\pi\eta r)\hat{\mathbf{r}}\hat{\mathbf{r}}; \qquad T_{\theta\theta} = (1/8\pi\eta r)\hat{\theta}\hat{\theta} \tag{10}$$

$$T_{r\theta} = 0 = T_{\theta r} \tag{11}$$

$$\mathbf{T}\cdot\hat{\mathbf{k}} = \frac{\hat{\mathbf{r}}\cos\theta}{4\pi\eta r} - \frac{\hat{\theta}\sin\theta}{8\pi\eta r} \tag{12}$$

$$\nabla_r = \hat{\mathbf{r}}\partial/\partial r + (\hat{\theta}/r)\partial/\partial\theta \tag{13}$$

We limit ourselves now to situations in which the currents in the space of the external coordinates are constant, as, for example, in a sedimentation-velocity experiment with uniform concentration in a constant gravitational field or in a diffusion experiment with a spatially constant gradient. Further, we assume that the gradient of Ψ with respect to the external coordinates is parallel to $\hat{\mathbf{k}}$ and has a magnitude F/k_BT, so that

$$\hat{\mathbf{k}}F = -k_BT\nabla_R \ln\Psi \tag{14}$$

At last we can write out the two components of $\dot{\mathbf{r}}$:

$$\dot{r}_r = -\left(\frac{1}{\rho_1} + \frac{1}{\rho_2} - \frac{1}{2\pi\eta r}\right)\left(kr + k_BT\frac{\partial \ln\Psi}{\partial r}\right) + \left[g\left(\frac{m_1}{\rho_1} - \frac{m_2}{\rho_2} - \frac{m_1 - m_2}{4\pi\eta r}\right) + \frac{1}{2}\left(\frac{1}{\rho_1} - \frac{1}{\rho_2}\right)F\right]\cos\theta \tag{15}$$

$$\dot{r}_\theta = -\left(\frac{1}{\rho_1} + \frac{1}{\rho_2} - \frac{1}{4\pi\eta r}\right)\frac{k_BT}{r}\frac{\partial \ln\Psi}{\partial\theta} - \left[g\left(\frac{m_1}{\rho_1} - \frac{m_2}{\rho_2} - \frac{m_1 - m_2}{8\pi\eta r}\right) - \frac{1}{2}\left(\frac{1}{\rho_1} + \frac{1}{\rho_2}\right)F\right]\sin\theta \tag{16}$$

These equations can be simplified if we define a length γ which is related to the mean extension of the spring

$$\gamma = (k_BT/k)^{1/2} \tag{17}$$

We now introduce a dimensionless coordinate x

$$x = r/\gamma \tag{18}$$

and two dimensionless coefficients

$$\alpha = \frac{1}{2\pi\eta(1/\rho_1 + 1/\rho_2)} = \frac{3a_1a_2}{a_1 + a_2} \tag{19}$$

$$\beta = \frac{m_1 - m_2}{4\pi\eta(m_1/\rho_1 - m_2/\rho_2)} = \frac{3a_1a_2(m_1 - m_2)}{2(m_1a_2 - m_2a_1)} \tag{20}$$

We also introduce two dimensionless forces, F' and G

$$F' = \frac{1/\rho_1 - 1/\rho_2}{2k\gamma(1/\rho_1 + 1/\rho_2)}F \tag{21}$$

$$G = \frac{g(m_1/\rho_1 - m_2/\rho_2)}{(1/\rho_1 + 1/\rho_2)(kk_BT)^{1/2}} = \frac{g(m_1a_2 - m_2a_1)}{k\gamma(a_1 + a_2)} \tag{22}$$

and a harmonic mean resistance coefficient, ρ

$$\rho = 2/(1/\rho_1 + 1/\rho_2) \tag{23}$$

With these new quantities eq 15 and 16 can be rewritten:

$$\dot{r}_r = \frac{2k\gamma}{\rho}\left\{\left(\frac{\alpha}{x} - 1\right)\left(x + \frac{\partial \ln\Psi}{\partial x}\right) + \left[G\left(1 - \frac{\beta}{x}\right) + F'\right]\cos\theta\right\} \tag{24}$$

$$\dot{r}_\theta = \frac{2k\gamma}{\rho}\left\{\left(\frac{\alpha}{2x} - 1\right)\frac{1}{x}\frac{\partial \ln\Psi}{\partial\theta} - \left[G\left(1 - \frac{\beta}{2x}\right) + F'\right]\sin\theta\right\} \tag{25}$$

To simplify matters we set F' equal to zero for a while; we shall generalize later.

It is instructive to consider what these equations can tell us about the rigid-body postulate. In this postulate it is explicitly assumed that the only internal motions are rigid-body rotations of constant angular velocity; in other words, $\dot{r}_r$ is assumed to be zero and $\dot{r}_\theta$ is assumed to be constant. If we adopt these assumptions, we can integrate eq 24 and 25 with respect to dr and $d\theta$, respectively, to get

$$\ln\Psi = G[x + (\alpha - \beta)\ln(x - \alpha)]\cos\theta - x^2/2 + F_1(\theta,\mathbf{R}) \tag{26}$$

$$\ln\Psi = Gx[(1 - \beta/2x)/(1 - \alpha/2x)]\cos\theta + C\theta + F_2(x,\mathbf{R}) \tag{27}$$

where C is an arbitrary constant and $F_1(\theta,\mathbf{R})$, $F_2(x,\mathbf{R})$ are arbitrary functions of integration. These two equations are inconsistent if $G \neq 0$ unless $\alpha = \beta$, which is only true if $\rho_1 = \rho_2$. Thus the rigid-body assumptions must be incorrect except when $\rho_1 = \rho_2$, and there is in general no function Ψ whose gradients produce diffusion currents that exactly cancel the currents produced in the space of the internal coordinates $\mathbf{r}$ by either sedimentation or diffusion in the space of the external coordinates $\mathbf{R}$; such cancellation can occur only in the special case that the Stokes resistances of the two beads are equal. The rigid-body postulate is thus correct only in special cases.

Since the rigid-body postulate does not apply in general, it is then necessary to solve for $\Psi(r)$ in order to proceed. We do this in the usual way by setting up the conservation equation for $\mathbf{j}$, the current of probability density. Since we have already assumed that the currents in $\mathbf{R}$ space are constant, these currents will contribute nothing to the divergence of $\mathbf{j}$, and the latter then contains only terms arising from differentiation with respect to the internal coordinates $\mathbf{r}$. Thus we have

$$0 = \text{div}\,\mathbf{j} = (1/r^2)(\partial/\partial r)(r^2j_r) + (1/r\sin\theta)(\partial/\partial\theta)(j_\theta\sin\theta) \tag{28}$$

with $j_r = \dot{r}_r\Psi(r)$ and $j_\theta = \dot{\mathbf{r}}_\theta\Psi(r)$. Working out the details of eq 28 leads to

$$\left(1 - \frac{\alpha}{x}\right)\frac{\partial^2\Psi}{\partial x^2} + \left[\frac{2}{x}\left(1 - \frac{\alpha}{2x}\right) + \left(1 - \frac{\alpha}{x}\right)\right]\frac{\partial\Psi}{\partial x} + \frac{1}{x^2}\left(1 - \frac{\alpha}{2x}\right)\frac{\partial^2\Psi}{\partial\theta^2} + \frac{\cos\theta}{x^2\sin\theta}\left(1 - \frac{\alpha}{2x}\right)\frac{\partial\Psi}{\partial\theta} + \left(3 - \frac{2\alpha}{x}\right)\Psi + G\left[\left(\frac{\beta}{x} - 1\right)\cos\theta\frac{\partial\Psi}{\partial x} + \left(1 - \frac{\beta}{2x}\right)\frac{\sin\theta}{x}\frac{\partial\Psi}{\partial\theta}\right] = 0 \tag{29}$$

Since there are no differentiations with respect to the components of $\mathbf{R}$ in eq 29, we note that a product of functions of $\mathbf{R}$ and $\mathbf{r}$ is a possible solution of this equation. Writing Ψ in this way, we have

$$\Psi(\mathbf{R},\mathbf{r}) = \Xi(\mathbf{R})\psi(\mathbf{r}) \tag{30}$$

Table I
Results of Various Ways of Calculating the Ratio of the Sedimentation Velocity of the Dumbbell with Hydrodynamic Interaction to That of the Dumbbell without Hydrodynamic Interaction

		m_1/m_2							
a_2/a_1	γ	1/8	1	4	8	16	preav [a]	diag [b]	rigid body [c]
1	20				1.0397		1.0397	1.0397	1.0397
2	5	1.1804	1.1804	1.1804	1.1804		1.1820	1.1796	1.1784
2	20		1.0522		1.0522		1.0523	1.0521	1.0520
8	9		1.0901	1.0901		1.0901	1.0946	1.0899	1.0869
8	20		1.0574			1.0574	1.0585	1.0560	1.0551

[a] Preaveraged approximation. [b] Diagonal approximation. [c] Rigid-body approximation.

The equilibrium form of ψ should be just the Boltzmann factor

$$\psi_0(\mathbf{r}) = \exp(-kr^2/2k_BT) = \exp(-x^2/2) \quad (31)$$

This does satisfy eq 29 if G is set equal to zero; it also causes the components of $\dot{\mathbf{r}}$, eq 24 and 25, to vanish, as they should. We now seek a first-order perturbation solution for eq 29, writing ψ as

$$\psi = \psi_0[1 + GQ(x) \cos\theta + ...] \quad (32)$$

thereby assuming that the first perturbation term has the angular dependence of a first-order spherical harmonic, an assumption that is justified by the results. We now substitute this in eq 29, collect the terms that are first-order in G, and divide by $\psi_0 G \cos\theta$ to get

$$\left(1 - \frac{\alpha}{x}\right)\frac{d^2Q}{dx^2} + \left[\frac{2}{x}\left(1 - \frac{\alpha}{2x}\right) - x\left(1 - \frac{\alpha}{x}\right)\right]\frac{dQ}{dx} - \frac{2}{x^2}\left(1 - \frac{\alpha}{2x}\right)Q = -x + \beta \quad (33)$$

This equation is to be solved subject to the boundary condition that the radial current, $\psi\dot{r}_r$, vanish at the surface of contact of the two beads, $x_0 = (a_1 + a_2)/\gamma$, since the beads are assumed to be impenetrable. With eq 24 and 32 this leads to the condition

$$\left(\frac{dQ}{dx}\right)_{x=x_0} = \frac{a_1 + a_2 - \beta\gamma}{a_1 + a_2 - \alpha\gamma} \quad (34)$$

Since eq 33 is of the second order, there must be two boundary conditions. The nature of the second boundary condition is indicated by the following. We examine the asymptotic form of eq 33 for large x; that is, we drop all the terms that tend toward zero as $x \to \infty$:

$$\frac{d^2Q}{dx^2} - \frac{dQ}{dx} \approx -x \quad (35)$$

One class of solutions of this which are asymptotically satisfactory, with the exception of terms that are of order x^{-2} in comparison to the larger terms, is $Q = A \exp(x^2/2)$, where A is an arbitrary constant. Such solutions are unacceptable as probability densities, however, since they do not have finite integrals, even when multiplied by ψ_0. We must therefore exclude such solutions and require that $Q(x)$ not increase as the exponential of $x^2/2$ when x gets large; this is the second boundary condition.

Equation 33 can be solved by any of several well-known methods of numerical integration, starting at x_0 and integrating outward; we used the extrapolation method of Bulirsch and Stoer.[14] The initial slope is given by eq 34, while the initial value of Q is adjusted by trial until the solution becomes well behaved at large x. Since the equation is linear, the solutions are linear in the initial value, so it is not difficult to find the latter.

We can now insert these results in eq 5 for the velocity of the center of mass, $\dot{\mathbf{R}}$. If we select the component in the direction of the external force, $\dot{R}_z$, and perform considerable algebra on the equation, we can get

$$\frac{\dot{R}_z}{\left(\frac{g(m_1 + m_2)}{\rho_1 + \rho_2}\right)} = 1 + \left(\frac{m_2}{m_1} - \frac{a_2}{a_1} - \frac{m_2a_1}{m_1a_2} + 1\right) \times \left(Q'(x) \cos^2\theta + \frac{Q(x) \sin^2\theta}{x} - 1\right) \Big/ 2\left(1 + \frac{m_2}{m_1}\right) + \frac{3(1 + a_2/a_1)[\cos^2\theta + (\sin^2\theta)/2]}{(4\gamma/a_1)x} \quad (36)$$

The left-hand side of this equation is the ratio of the center-of-mass velocity to the same quantity calculated without hydrodynamic interaction, and thus its deviation from unity measures the effect of the hydrodynamic interaction. The average velocity, $\langle\dot{R}_z\rangle$, is obtained by numerical integration, according to the formula

$$\langle\dot{R}_z\rangle = \frac{\int\int \dot{R}_z\psi x^2 \, dx \, d(\cos\theta)}{\int\int \psi x^2 \, dx \, d(\cos\theta)} \quad (37)$$

In the numerical integration over $\cos\theta$ we used the Gauss method with eight values of θ; in the integration over x we used the Romberg method of successive division of the interval[15] with 16 steps of 0.05 from x_0 to $x_0 + 0.8$ and a further 16 steps of 0.25 to $x_0 + 4.8$, at which point ψ_0 is 10^{-5} or less.

For comparison, we also need $\dot{R}_z$ calculated with the rigid-body assumption. We use eq 3–6 from ref 6, where $\dot{\mathbf{R}}$ was called $\mathbf{u}$; averaging is done in the same way as above. Other approximations of interest are the Kirkwood–Riseman preaveraging of the hydrodynamic interaction, from eq 37 of ref 6, and the diagonal approximation of Garcia de la Torre and Bloomfield,[16] in which only the zz components of the rigid-body formulas are retained.[6,16] (The other preaveraging method, the "preaveraged matrix-sum method", eq 31 in ref 6, gives ridiculously bad results with this model; for example, $\langle\dot{R}_z\rangle \geq 2.71$ for the case of $a_2 = 8a_1$ and $\gamma = 20a_1$; compare the numbers in Table I.) The results were averaged (with eq 37), numerically in the rigid-body and diagonal cases and analytically in the preaveraged case. The resulting formula for the latter case follows:

$$\langle\dot{R}_z\rangle = \frac{(1/\rho_1\rho_2 - T^2)g(m_1 + m_2)}{(1/\rho_1 + 1/\rho_2 - 2T)} \quad (38)$$

where T, the preaveraged zz component of the Burgers–Oseen tensor, is

$$T = a_1\{\gamma\rho_1[x_0 + (\pi/2)^{1/2} \exp({x_0}^2/2) \operatorname{erfc}(x_0/2^{1/2})]\}^{-1} \quad (39)$$

In the above from eq 26 on we have assumed that the gradient of the concentration of the center of mass, as

measured by F, was zero. In fact, however, the F-containing terms in the equations are of exactly the same form as those containing G when $m_2 = m_1$. (The F-containing terms do not depend on m_2/m_1.) The correspondence can be made exact when $m_2 = m_1$ by replacing $g(m_1 + m_2)$ by F; see eq 21–25.

Further, the ratio of the sedimentation velocity to the diffusion velocity should depend only on the ratio

$$\frac{g(m_1 + m_2)}{F} = \frac{g(m_1 + m_2)}{-k_B T \nabla_R \ln \psi} \tag{40}$$

At equilibrium, these two velocities should be equal and opposite, so their ratio should be −1; this gives $\nabla_R \ln \psi = g(m_1 + m_2)/k_B T$, or $\Psi = C \exp[g(m_1 + m_2)R/k_B T]$, which is the Boltzmann relation. Thus our results for the sedimentation velocity must depend on the total mass $m_1 + m_2$ but not on the ratio m_2/m_1 to be in accord with equilibrium statistical mechanics, since F does not depend on m_2/m_1.

Results

The functions $Q(x)$ that satisfy the two boundary conditions turn out to be curves of rather uninteresting appearance, tending asymptotically toward straight lines of unit slope at large x, though with pronounced curvature near x_0. Very small changes from the proper initial value at x_0 cause any one of these curves to diverge rapidly toward either plus or minus infinity as x increases, so there is no difficulty in locating the proper initial value. When $m_1 = m_2$, $Q(x)$ is exactly equal to x, as can be seen from eq 26 and 27. In other cases the shape of the curve seems to be determined by the necessity of satisfying eq 34 at x_0 combined with the tendency to approach unit slope at large x.

Table I gives results for the sedimentation rate $\langle \dot{R}_z \rangle$, expressed in units of the sedimentation rate of the dumbbell without hydrodynamic interaction. The rates are all near unity, since the average strength of the hydrodynamic interaction between two beads alone is not very large. Of interest are the differences between the rates calculated in various ways.

As expected, all $\langle \dot{R}_z \rangle$ are equal when $a_2 = a_1$, since eq 24 and 25 are then consistent, showing that the rigid-body postulate leads to exact results in this case. Preaveraging and the diagonal method also happen to be exact when $a_2 = a_1$, as can easily be shown algebraically. Again as expected, $\langle \dot{R}_z \rangle$ is independent of m_2/m_1; this provides a valuable check on the accuracy of the numerical integration, since the values of $Q(x)$ are indeed quite different for different m_2/m_1.

When the two beads are unequal in radius the different methods of calculation do not give the same answers. The rigid-body sedimentation rate is always less than the rate with diffusion taken properly into account. We conjecture that this may indicate the existence of a theorem similar to that proved by Wilemski and Tanaka[9] for viscosity; they showed that the rigid-body viscosity was an upper bound to the true viscosity. In the case of sedimentation it appears that the rigid-body value may be a lower bound.[17] The preaveraged rate, on the other hand, is higher than the true value by about as much as the rigid-body rate is lower. It is noteworthy that the results of the diagonal approximation are in three cases out of four closer to the true value than any of the others are.

Concluding Remarks

The rigid-body postulate is attractive, not only for its simplicity, avoiding as it does the solution of the diffusion equation, but also because of its similarity to the situation in equilibrium statistical mechanics. From the principle of detailed balancing one can conclude that there are no net currents in the configuration space of an equilibrium system, every flow induced by forces being exactly canceled by an opposite diffusional flow induced by a gradient of probability density. The rigid-body postulate attempts to extend this condition from equilibrium systems to steady-state systems close to equilibrium, though it is necessary to admit rigid-body rotations in the treatment of viscosity. Kramers[7] was thus able to calculate the viscosity of flexible chains without hydrodynamic interactions. Saito[18] showed that the same postulate, thus extended, gave a successful calculation of the viscosity number of rigid ellipsoids; he showed that the ellipsoids rotated at a constant net rate, although the hydrodynamically induced rotation varied with the angle of inclination of the ellipsoid to the streamlines; diffusion forced the net rate to be constant, independent of angle. Kirkwood and Riseman[1] assumed the same thing to be true for flexible chains with preaveraged hydrodynamic interaction; this was in fact correct in this case.[2,8]

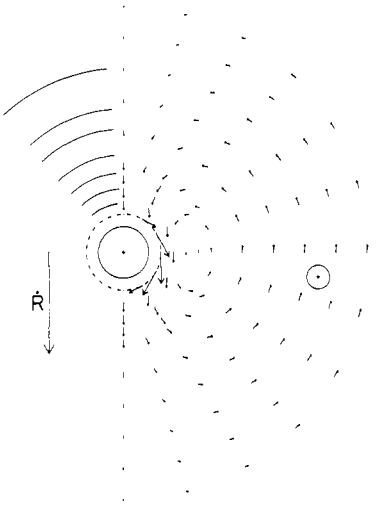

Figure 1. Dumbbell with $a_2 = 2a_1$, $\gamma = 5$, showing the flow produced in the internal coordinate, $\dot{\mathbf{r}}$, by an external sedimenting force. The average velocity of the whole dumbbell, $\langle \dot{\mathbf{R}} \rangle$, is shown by the large arrow; the small arrows show to the same scale $\dot{\mathbf{r}}$, the motion of the small bead with respect to the large one. The dashed circle is the locus of contact of the two beads. The circular arcs in the left quadrant are contours of probability density, ψ_0, at levels of 0.05, 0.04, 0.03, 0.02, 0.01, 0.005, 0.001, successively outward. This diagram is independent of the mass ratio m_2/m_1.

However, the present calculation, which was stimulated by parallel work by Wilemski and Tanaka,[9] shows that the rigid-body postulate fails when hydrodynamic interaction is taken into account as a function of distance and not preaveraged. The net currents in this case are not zero in general, even for simple sedimentation.

Figure 1 shows the flow pattern induced in the internal coordinates by an external sedimenting force. Since the internal velocity is $\dot{\mathbf{r}} = \dot{\mathbf{r}}_1 - \dot{\mathbf{r}}_2$, this flow is the motion of bead one, the small bead, with respect to the center of bead two, the large bead. We see that the flow is a circulation, with the small bead moving faster than the large bead when the two are close together and nearly in line vertically, and slower than the large bead when they are far apart in the equatorial plane. In Figure 2 are plotted the values of $\dot{r}$ as a function of x in the equatorial plane, as well as the hydrodynamic component of $\dot{r}$ for several values of the ratio m_2/m_1 ($\dot{r}$ itself, like $\dot{R}$, is independent of the mass ratio). By hydrodynamic component we mean the value from eq 6 with the diffusion terms omitted. We see

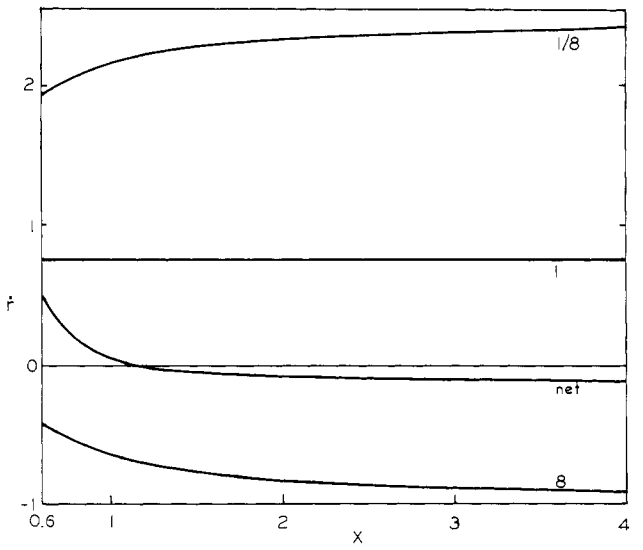

Figure 2. Magnitude of $\dot{r}$ as a function of the distance x between the beads in the equatorial plane, $\theta = \pi/2$. Same parameters as Figure 1. Magnitudes of flow are given relative to the sedimentation rate of the dumbbell without hydrodynamic interaction, $g(m_1 + m_2)/(\rho_1 + \rho_2)$. The curve marked "net" is the net flow rate, the sum of all components, from eq 16; this is independent of the mass ratio. For comparison are shown the curves marked with mass ratios m_2/m_1; these are the flow rates that would occur if only the hydrodynamic terms, the terms in eq 6 that are explicitly multiplied by g, were considered with no spring-force term and no diffusion terms.

that the hydrodynamic component is largely, but in general not completely, canceled by the diffusion terms in the total. The rigid-body approximation, of course, amounts to assuming that the diffusion terms always exactly cancel the hydrodynamic terms, except for steady rotations, which latter do not appear in the present model. Thus the rigid-body approximation appears to be a reasonable, but not perfect, approximation to the truth.

The major potential application of the rigid-body approximation is to long-chain molecules with many interacting segments. These have usually been treated by preaveraging the hydrodynamic interactions. In contrast to preaveraging, the rigid-body approximation has the advantage of setting a definite bound to the viscosity number[9] and apparently to the sedimentatation and diffusion coefficients as well. Moreover, we have found in the case of asymmetric dumbbells with a variety of size ratios that the rigid model gives results that are at least as good as the preaveraged ones. It is interesting that the diagonal approximation, which is actually a simplified version of the rigid-body approximation, gives the best results of all the approximate methods for the dumbbells. However, it must still be recognized that a dumbbell is not an accurate model of a long chain, so more work needs to be done before the situation is clear for such chains.

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Rotational Isomeric Modeling of a Polyethylene-like Polymer between Two Plates: Connection to "Gambler's Ruin" Problem

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ABSTRACT: A Monte Carlo simulation of a polyethylene-like polymer chain between two plates has been performed. This continuum treatment augments previous analytical lattice treatments of completely flexible chains between plates. The Monte Carlo results show that the simple concept of statistical length appropriate to unconfined bulk polymer is also appropriate to chain portions residing in the amorphous regions of lamellar semicrystalline polymer. Thus, the "gambler's ruin" method, with the statistical length of the polymer used as the fundamental step length, is a valid method to obtain quantitative estimates of quantities such as length of loops, length of ties, and fraction of loops or ties for moderately stiff polymers. Previous estimates of the amount of chain folding in polyethylene are thus shown to retain their validity for the more realistic isomeric state model.

I. Introduction

Two papers have recently been published in which analytical models for the properties for a homopolymer in the amorphous phase of a lamellar semicrystalline polymer were developed based on the mathematics of the "gambler's ruin" problem of mathematical statistics.[1,2] The conclusion of these works was that gambler's ruin methods correctly model the amorphous region of lamellar semi-