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Rheological properties of nondilute suspensions of deformable particles

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The creeping flow equations have been solved to account for effects of shear on drop shape when the influence of neighboring drops is considered. A cell model is used to account for finite concentrations of the dispersed phase. From these results a constitutive equation is derived and implications for several flows are discussed. The shape and orientation of drops are computed and compared with existing data. Finally, dynamic viscosity and rigidity are obtained for nondilute suspensions of viscoelastic particles in an oscillatory shear flow.

INTRODUCTION

The case for suspensions as worthy models of rheological behavior has been convincingly made on several occasions.[1,2] Conceptual advantages which obtain from a specific model for which essentially exact hydrodynamic calculations can be made are evident in the early work of Einstein[3] and the later extensions of Taylor,[4] Frölich and Sack,[5] and others.

A serious problem arises, however, when one attempts to include effects of particle interactions. In all of the examples cited above, particle concentrations were sufficiently low so that flow in the region of an isolated particle could be analyzed, and the bulk effect determined by scaling linearly with concentration. For purposes of nomenclature we shall refer to any system for which this approach is valid as "dilute." Any system for which the presence of one particle affects the flow near another particle is called "nondilute." Rigorous analyses of rheological characteristics of suspensions have been limited almost exclusively to dilute systems. An exception is the recent work of Batchelor and Green.[6] From their results one can recognize the considerable difficulty which attends calculation of specific rheological properties in nondilute systems when mutual interactions of trajectories of particles are considered. Computational difficulties can be reduced by describing the complications of particle interactions through the simplification of one or another of several types of cell models. The model is certainly not an exact picture of particle behavior in nondilute systems. Nevertheless, it has some appeal as a technique for combining the rigor of a dilute system model with the practicality of real systems in which particle interactions almost surely occur. In this spirit Simha[7] and others[8,9] were able to extend the results of Einstein to finite concentrations with some success.

Early work with the cell model was confined to extensions of elementary suspension models (e.g., Einstein's rigid spheres) and to elementary rheological characteristics (e.g., shear viscosity). In the work reported here we show how a cell model can be applied to deformable particles, viscoelastic particles, and a variety of flows. When the work was begun, we were not aware of any other similar attempts to model suspensions. However, Yaron and Gal-Or[10] and Brennen[11] have recently used cell models to obtain predictions, by means of an energy dissipation method, of suspension viscosity.

In the work presented here we draw heavily upon the results of Frankel and Acrivos[2] and of Cox.[12] A constitutive equation is obtained for a cell model consisting of an emulsion of deformable Newtonian drops contained in a second Newtonian phase. Responses for several specific flows are presented, and predictions of drop shape and orientation are compared with earlier theories and with previously published experimental data. The results for Newtonian fluids are then extended to nondilute suspensions of viscoelastic particles and to shear flow.

EMULSION OF NEWTONIAN FLUIDS: VELOCITY AND PRESSURE FIELDS

We consider two immiscible incompressible Newtonian fluids of equal density. Drops of viscosity μ^* are suspended uniformly throughout a second continuous Newtonian phase of viscosity μ_0. It is assumed, at present, that the drops are uniform in size and, when undeformed, are spheres with radius a. We first consider a basic flow of the continuous phase in the limit of a dilute system. Apparatus geometry and operation are taken to be such that the basic (i.e., unperturbed) flow relevant to a single particle can be described by

$$\mathbf{u}^\infty = \mathbf{\Gamma}^{(\infty)}(t)\cdot\mathbf{r} = \mathbf{E}\cdot\mathbf{r} + \tfrac{1}{2}\boldsymbol{\omega}\times\mathbf{r} \ ,$$
$$= \nabla\chi_1\times\mathbf{r} + \nabla\phi_2 \ . \tag{1}$$

Here, $\mathbf{\Gamma}^{(\infty)}(t)$ is the velocity gradient tensor, $\mathbf{E}$ is the corresponding rate of deformation tensor, $\boldsymbol{\omega}$ is the vorticity, and $\mathbf{r}$ is the position vector with respect to an origin at the center of the undeformed drop. It is well known that such a flow can be described by two solid spherical harmonics of order one and two. Define a characteristic shear rate $G\sim(\mathbf{E}:\mathbf{E})^{1/2}$, and let γ be the interfacial tension between the two phases. All velocities are made dimensionless by Ga, stresses within the drop by $G\mu^*$ and outside the drop by $G\mu_0$, distances by a, and time by G^{-1}. With respect to a rectangular Cartesian coordinate system, the equation of the drop surface is given by

$$r = 1 + \epsilon f\left(\frac{x_1}{r},\ \frac{x_2}{r},\ \frac{x_3}{r},\ t\right) \ , \tag{2}$$

where $f = O(1)$ and $\epsilon \ll 1$.

The particle Reynolds number in each phase is taken to be small enough so that the creeping motion equations are valid. Then, the system is described by

$$\nabla^2\bar{\mathbf{u}}=\nabla\bar{p}\,;\qquad \nabla\cdot\bar{\mathbf{u}}=0\,,\qquad \text{for } r>1+\epsilon f \tag{3}$$

$$\nabla^2\mathbf{u}^*=\nabla p^*;\quad \nabla\cdot\mathbf{u}^*=0\,,\quad 0\le r<1+\epsilon f\ . \tag{4}$$

Boundary conditions are

$$\bar{\mathbf{u}}=\mathbf{u}^*,\qquad \text{on } r=1+\epsilon f \tag{5}$$

$$(\bar{\mathbf{P}}-s\,\mathbf{P}^*)\cdot\mathbf{n}=k\left(\frac{1}{R_1}+\frac{1}{R_2}\right)\mathbf{n},\quad \text{on } r=1+\epsilon f \tag{6}$$

$$\bar{\mathbf{u}}\to\mathbf{u}_c\qquad \text{on}\quad r=\frac{b}{a}=\phi^{-1/3} \tag{7}$$

$$\bar{\mathbf{u}}\cdot\mathbf{n}=\mathbf{u}^*\cdot\mathbf{n}=K^*\epsilon\frac{\partial f}{\partial t},\qquad \text{on } r=1+\epsilon f \tag{8}$$

$$\mathbf{u}^* \text{ is finite at } \mathbf{r}=0\ . \tag{9}$$

Here, $\bar{\mathbf{u}}$, $\bar{p}$, and $\bar{\mathbf{P}}$ denote velocity, pressure, and the stress tensor in the continuous phase, and $\mathbf{u}^*$, p^*, and $\mathbf{P}^*$ the corresponding variables in the discontinuous phase. $\mathbf{n}$ is the outer unit normal and R_1 and R_2 are the principal radii of curvature of the drop surface. Also,

$$s=\mu^*/\mu_0,\quad k=\gamma/\mu_0 Ga\,,\quad K^*=\left|\nabla(r-\epsilon f)\right|^{-1}\ .$$

With the exception of (7), this is identical to the problem formulation of Frankel and Acrivos.[2] Boundary condition (7) accounts for the characteristics of the cell model. ϕ is the volume fraction of discontinuous phase in the system, and b, as defined in Eq. (7), represents a characteristic length of a "cell" of continuous fluid surrounding each drop. Then, $\mathbf{u}_c$ is the continuous-phase velocity on the boundary of the cell. A weakness of the model is the unspecified parameter $\mathbf{u}_c$. Since the volume-average velocity gradient for a suspension can be shown to be equal to the velocity gradient of the unperturbed flow, one might argue that it is reasonable to set $\mathbf{u}_c=\mathbf{u}^\infty$; i.e.,

$$\mathbf{u}_c=\langle\mathbf{\Gamma}\rangle\cdot\mathbf{r}=\mathbf{\Gamma}^\infty\cdot\mathbf{r}=\mathbf{E}\cdot\mathbf{r}+\tfrac{1}{2}\omega\times\mathbf{r}\,,\ \text{at } r=y^{-1} \tag{10}$$

where $y=a/b=\phi^{1/3}$. This was done by Simha[7] in his analysis of rigid-sphere suspensions. On the other hand, Happel[8] chose a different boundary condition, but his result fails to reduce to Einstein's formula in the limit of a dilute solution. For this reason we follow Simha's approach and use Eq. (10).

Solution of the system of Eq. (3)–(10) is effected by the techniques used by Frankel and Acrivos[2] and by Cox,[12] although significant differences in the results arise because of the boundary conditions (7) and (10). Since both phases are Newtonian fluids and since nonlinear inertial effects are neglected, Lamb's general solution of the creeping motion equations can be used. Then, inside of the drop one writes

$$\mathbf{u}^*=\sum_{n=0}^{\infty}\left(\nabla\chi_n^*\times\mathbf{r}+\nabla\phi_n^*+\frac{n+3}{2(n+1)(2n+3)}r^2\nabla p_n^*-\frac{n}{(n+1)(2n+3)}\mathbf{r}p_n^*\right), \tag{11}$$

$$p^*=\sum_{n=0}^{\infty}p_n^*,$$

while outside of the drop,

$$\bar{\mathbf{u}}=\mathbf{u}_c+\sum_{n=0}^{\infty}\left(\nabla\bar{\chi}_{-n-1}\times\mathbf{r}+\nabla\bar{\phi}_{-n-1}-\frac{(n-2)}{2n(2n-1)}r^2\nabla\bar{p}_{-n-1}+\frac{(n+1)}{n(2n-1)}\mathbf{r}\bar{p}_{-n-1}\right)+\sum_{n=0}^{\infty}\left(\nabla\bar{\bar{\chi}}_n\times\mathbf{r}+\nabla\bar{\bar{\phi}}_n+\frac{n+3}{2(n+1)(2n+3)}r^2\nabla\bar{\bar{p}}_n-\frac{n}{(n+1)(2n+3)}\mathbf{r}\bar{\bar{p}}_n\right), \tag{12}$$

$$\bar{p}=\sum_{n=0}^{\infty}(\bar{p}_{-n-1}+\bar{\bar{p}}_n)\ ,\ \text{and}\ \bar{p}_{-1}=0\ .$$

Here, χ_n^*, ϕ_n^*, p_n^*, $\bar{\bar{\chi}}_n$, $\bar{\bar{\phi}}_n$, $\bar{\bar{p}}_n$, $\bar{\chi}_n$, $\bar{\phi}_n$, and $\bar{p}_n$ are solid spherical harmonics of order n. Note that, in contrast to problems without a finite outer boundary, harmonic functions of order n appear in the expressions for velocity and pressure outside of the drop. Properties of spherical harmonics (see Lamb[13] or Cox[12]) permit one to express χ_n^*, etc., in terms of surface spherical harmonics Q_n^*, S_n^*, etc. Thus,

$$(\chi_n^*,\ \phi_n^*,\ p_n^*,\ \bar{\bar{\chi}}_n,\ \bar{\bar{\phi}}_n,\ \bar{\bar{p}}_n)=r^n(Q_n^*,\ S_n^*,\ T_n^*,\ \bar{\bar{Q}}_n,\ \bar{\bar{S}}_n,\ \bar{\bar{T}}_n),$$
$$(\bar{\chi}_{-n-1},\ \bar{\phi}_{-n-1},\ \bar{p}_{-n-1})=r^{-n-1}(\bar{Q}_n,\ \bar{S}_n,\ \bar{T}_n), \tag{13}$$

where any surface spherical harmonic, e.g., $S_n^*(\theta,\Phi,t)$, is given by

$$S_n^*(\theta,\Phi,t)=S^*_{p_1p_2\cdots p_n}(t)\left(\frac{\partial^n(1/r)}{\partial x_{p_1}\partial x_{p_2}\cdots\partial x_{p_n}}\right)r^{n+1}\ . \tag{14}$$

The quantity $S^*_{p_1p_2\cdots p_n}(t)$ is an nth order tensor which is a function of time only, and is symmetric with respect to interchanges of any pair of indices.

Cox's study of the motion of a single drop in the special form of Eq. (1) for laminar shear flow confirmed Taylor's earlier results; viz., that if the drop is only slightly deformed from a spherical shape; i.e., $\epsilon\ll 1$ [see Eq. (2)], then the parameter ϵ is either $O(k^{-1})$ for $k\gg 1$ and $s=O(1)$ or ϵ is $O(s^{-1})$ if $k=O(1)$ and $s\gg 1$. We will show that the same conditions hold for our case.

All unknown functions are assumed to be expressible as power-series expansions in terms of the parameter ϵ. Thus, for example,

$$\mathbf{u}^*=\mathbf{u}^{(0)*}+\epsilon\mathbf{u}^{(1)*}+\dots\ ,$$
$$\bar{\mathbf{u}}=\bar{\mathbf{u}}^{(0)}+\epsilon\bar{\mathbf{u}}^{(1)}+\dots\ , \tag{15}$$

etc. Similarly, the function f of Eq. (2) is written as a power series of surface spherical harmonics of order n,

$$f=\sum_{n=0}^{\infty}F_n(\theta,\Phi,t)=\sum_{n=0}^{\infty}(F_n^{(0)}+\epsilon F_n^{(1)}+\dots)\ . \tag{16}$$

The equation for the drop surface is related to the principal radii of curvature[14]

$$\frac{1}{R_1}+\frac{1}{R_2}=2+\epsilon\sum_{n=0}^{\infty}(n^2+n-2)F_n-2\epsilon^2\left(\sum_{n=0}^{\infty}F_n\right)\times\sum_{n=0}^{\infty}(n^2+n-1)F_n+O(\epsilon^3)\ . \tag{17}$$

Equations describing the zeroth-order motion of the drop are found by substitution of (15) into (3) and (4) and isolation of coefficients of ϵ^0. The resulting equations are solved in accord with boundary conditions for an undeformed drop surface ($r=1$). From these results a first estimate of drop deformation is found from evaluation of $F_n^{(0)}$ with boundary condition (8) and Eq. (16). The procedure is standard,[2,12] although details are different in the present case because of the positive-order harmonics present in (12). It should be noted that we have taken $\epsilon(\partial f/\partial t)$ in (8) to be $O(1)$, following Frankel and Acrivos,[2] rather than $O(\epsilon)$, which was the choice of Cox.[12] The zeroth-order solution involves the surface spherical harmonics $S_2^{(0)*}$, $T_2^{(0)*}$, $\bar{S}_2^{(0)}$, $\bar{T}_2^{(0)}$, $\bar{\bar{S}}_2^{(0)}$, $\bar{\bar{T}}_2^{(0)}$, $F_2^{(0)}$, $Q_1^{(0)*}$, $T_0^{(0)*}$, and $\bar{T}_0^{(0)}$. Explicit expressions for them are lengthy and are not included here. Of particular interest is the coefficient for the harmonic describing the surface deformation. From (8),

$$\epsilon\frac{\partial F_{ik}^{(0)}}{\partial t}=\frac{20}{z}\{[(19s+16)+21(s-1)y^5-40(s-1)y^7]S_{ik}$$
$$-[4(s+1)-5(5s+2)y^3+42sy^5-5(5s-2)y^7$$
$$+4(s-1)y^{10}]k\epsilon F_{ik}^{(0)}\}, \tag{18}$$

where $y=\phi^{1/3}$, $S_{ik}=\frac{1}{6}E_{ik}$ (see Cox[12]),

$$z=2(19s+16)(2s+3)-(s-1)[25(19s+16)y^3$$
$$-42(19s+16)y^5+25(19s+18)y^7-76(s-1)y^{10}] \ .$$

In the limit $y\to 0$, the expressions for the harmonics as well as (18) reduce to the known results for a dilute system.

An analogous procedure is next used to obtain a first-order solution, except that boundary conditions are now applied at $r=1+\epsilon f$. The procedure has been outlined in some detail by Cox.[12] Here again, algebraic details have not been included.

FORMULATION OF CONSTITUTIVE EQUATION

The chief purpose of the work described here is to provide knowledge of the flow field within a single cell, from which one can derive an expression relating bulk stress in the suspension model to bulk motion of the suspension. We follow the procedure given by Batchelor,[15] and discussed in some detail by Brenner.[16] When inertial effects are neglected and Brownian motion is not considered, bulk stress is related to bulk motion by

$$\langle P_{ij}\rangle=-\frac{1}{V}\int_{V-\Sigma V_n}p\delta_{ij}dV+2\langle E_{ij}\rangle+\frac{1}{V}$$
$$\times\sum_{n=1}^{N}\int_{A_n}[P_{ik}x_jn_k-(u_in_j+u_jn_i)]dA \ ,$$
$$=2\langle E_{ij}\rangle+\frac{1}{V}\sum_{n=1}^{N}\int_{A_n^{(c)}}[P_{ik}x_jn_k-(u_in_j+u_jn_i)]dA \tag{19}$$

where the angular brackets $\langle\,\rangle$ denote a volume average and V is a control volume large enough to contain a statistically significant number of particles (N particles) yet small with respect to a length scale over which macroscopic variables, such as shear rate, change appreciably. V_n and A_n are the volume and surface, respectively, of the nth particle, and $A_n^{(c)}$ is the surface of the cell associated with the nth particle. Inserting results obtained in the previous section, one can reduce (19) to the same form as that applicable to dilute systems:[2]

$$\langle P_{ij}\rangle=-P\delta_{ij}+2\mu_0\langle E_{ij}\rangle-3\mu_0G\phi\bar{T}_{ij}+O(\mu_0\phi G\epsilon^2), \tag{20}$$

where from this point on, all quantities are dimensional except $\bar{T}_{ij}=\bar{T}_{ij}^{(0)}+\epsilon\bar{T}_{ij}^{(1)}+\dots$. Equation (20) has been written for a homogeneous suspension. If there is a distribution over M different particle sizes, one merely replaces ϕ in Eq. (20) by $\sum_{m=1}^{M}\phi_m$. Thus to find the constitutive equation, the only necessary harmonic coefficient is $\bar{T}_{ij}$. It in turn is related in a complicated way to the surface coefficients F_{ij}. Eliminating $\bar{T}_{ij}$, one eventually obtains

$$P_{ij}=-P\delta_{ij}+2\mu_0E_{ij}+\mu_0\phi\Bigg\{\frac{20(s-1)}{z}[(19s+16)-19(s-1)y^7]E_{ij}+\frac{48}{z}[(19s+16)+21(s-1)y^5$$
$$-40(s-1)y^7]\beta^{-1}\epsilon F_{ij}+M(s,y)\,\epsilon\,\mathcal{L}d[F_{ik}E_{kj}]+N(s,y)\,\beta^{-1}\epsilon^2\mathcal{L}d[F_{ik}F_{kj}]+O(G\epsilon^2)\Bigg\} \ , \tag{21}$$

where ϵF_{ij} satisfies the equation

$$\epsilon F_{ij}+C(s,y)\beta\epsilon\frac{\mathfrak{D}F_{ij}}{\mathfrak{D}t}$$
$$=K(s,y)\beta E_{ij}+A(s,y)C(s,y)\beta\epsilon\mathcal{L}d(F_{ik}E_{kj})$$
$$+B(s,y)C(s,y)\epsilon^2\mathcal{L}d(F_{ik}F_{kj})+O(\beta G\epsilon^2) \tag{22}$$

and $\beta=(kG)^{-1}=\mu_0a/\gamma$. We have removed the average symbols $\langle\ \rangle$ in (21) to indicate that a constitutive equation is implied for the suspension now considered as a continuum.

Several remarks are in order concerning Eqs. (21) and (22). The symbol $\mathcal{L}d[\,]$ is defined by

$$\mathcal{L}d[b_{ik}]\overset{\text{def}}{=}\tfrac{1}{2}(b_{ik}+b_{ki}-\tfrac{2}{3}b_{mm}\delta_{ik})$$

and the functions A, B, C, K, M, and N are defined in terms of their arguments in Table I. Note the appearance in Eq. (22) of the Jaumann derivative

$$\frac{\mathfrak{D}F_{ij}}{\mathfrak{D}t}=\frac{\partial F_{ij}}{\partial t}+u_k\frac{\partial F_{ij}}{\partial x_k}+\tfrac{1}{2}\omega_k(\epsilon_{kim}F_{mj}+\epsilon_{kjm}F_{mi}) \ .$$

This arises from consideration of the fact that the analysis of a single particle was carried out with respect to a coordinate system with origin fixed in the particle. Naturally, the constitutive equation is to be written with respect to a laboratory-fixed coordinate system. Thus, the transformation

$$\frac{\partial}{\partial t}\to\frac{D}{Dt}=\frac{\partial}{\partial t}+u_k\frac{\partial}{\partial x_k}$$

is applied to time derivatives which arise from Eq. (8). Combination of D/Dt with other terms permits the reduction in (22) to $\mathfrak{D}/\mathfrak{D}t$. Equations (21) and (22) are the new results of this section. Substitution of ϕ_m and

TABLE I. Coefficients in Eqs. (21), (22), and (23).

$$A(s,y)=\frac{1}{7z^2}[40(19s+16)^2(4s-9)+500(19s+16)^2(s-1)y^3-840(s-1)(1027s^2+1801s+672)y^5+100(s-1)(5317s^2+12706s+5952)y^7$$
$$+10500(s-1)^2(29s-64)y^8-20(s-1)^2(11771s-149776)y^{10}+2100(s-1)^2(191s-1456)y^{12}-2500(s-1)^2(137s-282)y^{14}$$
$$-272160(s-1)^3y^{15}+237200(s-1)^3y^{17}],$$

$$B(s,y)=\frac{6}{7z^2}[192(137s^3+624s^2+741s+248)-600(548s^3+765s^2-24s-64)y^3+336(1644s^3+1533s^2-1598s-704)y^5+7500(s-1)$$
$$\times(137s^2+76s+32)y^6-600(548s^3+557s^2-788s-492)y^7-8400(s-1)(411s^2+161s+128)y^8+24(s-1)(208651s^2+66588s+81586)y^{10}$$
$$-8400(s-1)(411s^2+75s+134)y^{12}-2400(s-1)^2(137s-11)y^{13}+7500(s-1)(137s^2+12s+4)y^{14}+1344(s-1)^2(411s-191)y^{15}$$
$$-2400(s-1)^2(137s-58)y^{17}+26304(s-1)^3y^{20}],$$

$$C(s,y)=\frac{z}{20\{4(s+1)-5(5s+2)y^3+42sy^5-5(5s-2)y^7+4(s-1)y^{10}\}},$$

$$K(s,y)=\frac{(19s+16)+21(s-1)y^5-40(s-1)y^7}{6\{4(s+1)-5(5s+2)y^3+42sy^5-5(5s-2)y^7+4(s-1)y^{10}\}},$$

$$M(s,y)=\frac{360(s-1)^2}{7z^2}[4(19s+16)^2-28(19s+16)^2y^5+20(19s+16)(19s+30)y^7+49(s-1)(361s+544)y^{10}-70(s-1)(361s+640)y^{12}+25(s-1)$$
$$\times(361s+668)y^{14}],$$

$$N(s,y)=\frac{288}{7z^2}[4(19s+16)^2(s-6)+50(19s+16)^2(s-1)y^3-84(s-1)(713s^2+1249s+488)y^5+50(s-1)(773s^2+1736s+816)y^7+25200(s-1)^3y^8$$
$$-(s-1)^2(48973s-118448)y^{10}+1050(s-1)^2(59s-111)y^{12}-125(s-1)^2(289s-138)y^{14}-15204(s-1)^3y^{15}+14900(s-1)^3y^{17}],$$

where $z=2(19s+16)(2s+3)-25(19s+16)(s-1)y^3+42(19s+16)(s-1)y^5-25(19s+18)(s-1)y^7+76(s-1)^2y^{10}$

y_m for ϕ and y, respectively, permits application of these results to polydisperse systems.

If we define the inverse Jaumann operator[17] by

$$\mathfrak{L} \triangleq \left(1+h\frac{\mathfrak{D}}{\mathfrak{D}t}\right)^{-1},$$

where $h(s,y)=C(s,y)\beta$, then the system of equations (21) and (22) can be combined to give

$$P_{ij}=-P\delta_{ij}+2\mu(s,y)E_{ij}+\beta\mu_0\phi\Big\{-m_1(s,y)\mathfrak{L}\left(\frac{\mathfrak{D}E_{ij}}{\mathfrak{D}t}\right)+m_2(s,y)\mathfrak{L}\{\mathfrak{L}d[\mathfrak{L}(E_{ik})E_{kj}]\}$$
$$+m_3(s,y)\mathfrak{L}\{\mathfrak{L}d[\mathfrak{L}(E_{ik})\mathfrak{L}(E_{kj})]\}+m_4(s,y)\mathfrak{L}d[\mathfrak{L}(E_{ik})E_{kj}]+m_5(s,y)\mathfrak{L}d[\mathfrak{L}(E_{ik})\mathfrak{L}(E_{kj})]+O(G\beta^{-1}\epsilon^2)\Big\}, \tag{23}$$

where

$$\frac{\mu(s,y)}{\mu_0}=1+\phi\,\frac{2[(5s+2)-5(s-1)y^7]}{4(s+1)-5(5s+2)y^3+42sy^5-5(5s-2)y^7+4(s-1)y^{10}},$$

$$m_1(s,y)=\frac{2}{5}\left[\frac{(19s+16)+21(s-1)y^5-40(s-1)y^7}{4(s+1)-5(5s+2)y^3+42sy^5-5(5s-2)y^7+4(s-1)y^{10}}\right]^2,$$

$$m_2(s,y)=\frac{48}{z}[(19s+16)+21(s-1)y^5-40(s-1)y^7]A(s,y)C(s,y)K(s,y),$$

$$m_3(s,y)=\frac{48}{z}[(19s+16)+21(s-1)y^5-40(s-1)y^7]B(s,y)C(s,y)[K(s,y)]^2,$$

$$m_4(s,y)=M(s,y)K(s,y),$$

$$m_5(s,y)=N(s,y)[K(s,y)]^2.$$

Equation (23) can be cast into a special case of the familiar form of Oldroyd's eight-constant model[18] by operating on both sides of (23) with $(1+h\mathfrak{D}/\mathfrak{D}t)$. Also, Eq. (23) can be simplified to provide a comparison with the 1953 analysis of Oldroyd for moderately concentrated suspensions.[9] If one operates on (23) with $(1+h\mathfrak{D}/\mathfrak{D}t)$, neglects nonlinear terms in E_{ij}, and defines $p_{ij}=P_{ij}+p\delta_{ij}$, there results

$$\left(1+h_1\frac{\mathfrak{D}}{\mathfrak{D}t}\right)P_{ij}=2\mu\left(1+h_2\frac{\mathfrak{D}}{\mathfrak{D}t}\right)E_{ij}. \tag{24}$$

Oldroyd's equation of 1953 had the same form. A comparison of coefficients is shown in Table II. To $O(\phi)$ both methods yield the same dependence of μ/μ_0 on cell size. The value of the coefficient of ϕ^2 in the expression for relative viscosity derived here however, approaches 15.6 as $s\to\infty$, while Oldroyd obtained 2.5. Oldroyd had noted that 2.5 was too small. He cites 14.1 as a satisfactory value.

APPLICATION TO SPECIFIC FLOW FIELDS

Steady shearing flow

In this case Eq. (1) becomes

$$\mathbf{u}^\infty = \mathbf{E}\cdot\mathbf{r} + \tfrac{1}{2}\boldsymbol{\omega}\times\mathbf{r} = \{Gx_2, 0, 0\} \tag{25}$$

so that $G=$ const, $E_{12}=E_{21}=G/2$, and $\omega_3=-G$. All other $E_{ij}=\omega_i=0$. Application of Eq. (23) to this flow ultimately leads to

$$\frac{\mu}{\mu_0} = 1+\phi\,\frac{2(5s+2)-10(s-1)y^7}{4(s+1)-5(5s+2)y^3+42sy^5-5(5s-2)y^7+4(s-1)y^{10}} + O(\mu_0\phi G\epsilon^2)\,, \tag{26}$$

$$N_1 = P_{11}-P_{22} = \beta\mu_0\phi G^2\,\frac{m_1(s,y)}{1+(hG)^2} + O(\mu_0\phi G\epsilon^2)\,, \tag{27}$$

$$N_2 = P_{22}-P_{33} = -\tfrac{1}{4}\beta\mu_0\phi G^2\left(\frac{2m_1(s,y)-L(s,y)}{1+(hG)^2}\right) + O(\mu_0\phi G\epsilon^2)\,, \tag{28}$$

where $L(s,y)=m_2(s,y)+m_3(s,y)+m_4(s,y)+m_5(s,y)$.

Expressions of the form of (26) have been obtained previously for suspension models. Keller *et al.*[19] reached the result by means of an energy dissipation method for two concentric liquid spheres. Brennen[11] has recently found this result from consideration of a model for blood flow in which properties of the red-cell membrane are included. Yaron and Gal-Or[10] have also achieved a similar result from a free-surface cell model in which allowance is made for surfactant effects. None of these authors, however, has included the effect of drop deformation. It is this additional physical phenomenon that gives rise to the normal stress differences of (27) and (28). By evaluating the various functions of s and y to $O(y^3)$ (recall $\phi=y^3$), one obtains

$$\frac{\mu}{\mu_0} = 1+\phi\,\frac{(5s+2)}{2(s+1)}\left[1+\phi\,\frac{5(5s+2)}{4(s+1)}+O(\phi^{5/3})\right], \tag{29}$$

$$N_1 = \frac{2}{5}\,\frac{\beta\mu_0\phi G^2}{1+Z^2}\left\{\frac{19s+16}{4(s+1)}\left[1+\phi\,\frac{5(5s+2)}{4(s+1)}+O(\phi^{5/3})\right]\right\}^2, \tag{30}$$

$$N_2 = -\frac{1}{280}\,\frac{\beta\mu_0\phi G^2}{1+Z^2}\,\frac{(19s+16)(29s^2+61s+50)}{(s+1)^3} \times\left[1+\phi\,\frac{5(5s+2)(41s^2+121s+188)}{8(s+1)(29s^2+61s+50)}+O(\phi^{5/3})\right], \tag{31}$$

where

$$Z = \frac{(19s+16)(2s+3)}{40(s+1)k}\left[1+\phi\,\frac{5(19s+16)}{4(s+1)(2s+3)}+O(\phi^{5/3})\right].$$

Experimental data of sufficient accuracy to permit a clear test of (29)–(31) do not appear to exist. The general tendencies of emulsion viscosity as predicted, for example, from Taylor's theory,[4] have been confirmed. However, effects of emulsifier and surfactant properties, as discussed by Nawab and Mason[20] and by Yaron and Gal-Or,[10] can be sufficient to render experimental uncertainties as large as the incremental effects predicted from (29)–(31).

The predictions contain some interesting ingredients, however. For example, the ratio $N_1/N_2<0$ for small values of ϕ is in accord with currently accepted measurements of polymer solutions. The shear viscosity is constant because terms of $O(\mu_0\phi G\epsilon^2)$ have been neglected. The condition of small drop deformation is valid under the three conditions

(1) $k\gg 1$ and $s=O(1)$,

(2) $k=O(1)$ and $s\gg 1$,

or

(3) $k\gg 1$ and $s\gg 1$,

as shown by Cox[12] and also in the next section. In the first case $Z=O(\epsilon)$ and N_1 and N_2 are proportional to $\beta\mu_0G^2$. As $\phi\to 0$, N_1 and N_2 reduce to the predictions of Schowalter *et al.*[21] In the second case, however, N_1 and N_2 are $O(\mu_0\phi G\epsilon^2)$. In case (3) $Z=O(sk^{-1})$. N_1 and N_2 increase with increasing G, but more slowly than in case (1). To be applicable to this situation the results of Schowalter *et al.* [their Eqs. (38) and (39)] need to be multiplied by $[1+(19s/20k)^2]^{-1}$.

Irrotational flows

Since the vorticity is zero, we have $\mathcal{D}/\mathcal{D}t=D/Dt$ in Eq. (23). As an example, consider the case of a fluid started impulsively from rest:

$$E_{ij}(t)=\begin{cases}0, & t\le 0\\ E_{ij}=\text{const}, & t>0.\end{cases} \tag{32}$$

From Eq. (23) one obtains

TABLE II. Comparison of coefficients for Eq. (24).

	Oldroyd[9]	Present work
$\frac{\mu}{\mu_0}$	$1+\phi\frac{(5s+2)}{2(s+1)}\left[1+\phi\frac{(5s+2)}{5(s+1)}\right]$	$1+\phi\frac{(5s+2)}{2(s+1)}\left[1+\phi\frac{5(5s+2)}{4(s+1)}\right]$
h_1	$h_0\left[1+\phi\frac{(19s+16)}{5(s+1)(2s+3)}\right]$	$h_0\left[1+\phi\frac{5(19s+16)}{4(s+1)(2s+3)}\right]$
h_2	$h_0\left[1-\phi\frac{3(19s+16)}{10(s+1)(2s+3)}\right]$	$h_0\left[1+\phi\frac{3(19s+16)}{4(s+1)(2s+3)}\right]$
	$h_0=\frac{(19s+16)(2s+3)}{40(s+1)}\beta$	

$$P_{ij} = -P\delta_{ij} + \left[2\mu(s,y) - \beta\mu_0\phi \frac{m_1(s,y)}{h(s,y)} \exp(-t/h)\right] E_{ij} + \beta\mu_0\phi\,\mathcal{L}d(E_{ik}E_{kj})\{m_2(s,y)[1-\exp(-t/h)$$

$$-(t/h)\exp(-t/h)] + m_3(s,y)[1-\exp(-2t/h) - (2t/h)\exp(-t/h)] + m_4(s,y)[1-\exp(-t/h)]$$

$$+ m_5(s,y)[1-\exp(-t/h)]^2 + O(k\epsilon^2)\}\ . \tag{33}$$

Equation (33) displays several interesting properties which show some correspondence with experiment. For example, when $t/h \ll 1$, stress in the direction of positive stretching increases linearly with t/h, the initial slope depending on E_{ij}. As time increases, the stress, depending on the coefficients of (33), may exhibit overshoot phenomena before reaching a steady-state value. These phenomena are in qualitative agreement with the observations of biaxial stretching reported by Maerker and Schowalter.[22]

At steady state Eq. (33) reduces to an equation of the Reiner–Rivlin type

$$P_{ij} = -P\delta_{ij} + 2\mu(s,y)E_{ij} + \beta\mu_0\phi[L(s,y) + O(k\epsilon^2)]\mathcal{L}d(E_{ik}E_{kj})\ . \tag{34}$$

As Cox[12] has pointed out, this result is valid only when $k \gg 1$, in contrast to the case of laminar shear flow discussed earlier.

Finally, if we characterize uniaxial and biaxial extension, respectively, by

$$[E_{ij}]_{ue} = \begin{bmatrix} G & 0 & 0 \\ 0 & -\frac{G}{2} & 0 \\ 0 & 0 & -\frac{G}{2} \end{bmatrix};\quad [E_{ij}]_{be} = \begin{bmatrix} G & 0 & 0 \\ 0 & G & 0 \\ 0 & 0 & -2G \end{bmatrix} \tag{35}$$

and define elongational viscosities by

$$\eta_{ue} = \frac{(P_{11} - P_{33})_{ue}}{G};\quad \eta_{be} = \frac{(P_{11} - P_{33})_{be}}{G},$$

then

$$\eta_{ue} = 3\mu_0\left(\frac{\mu(s,y)}{\mu_0} + \phi\frac{L(s,y)}{4k}\right)\ ,$$

$$\eta_{be} = 6\mu_0\left(\frac{\mu(s,y)}{\mu_0} - \phi\frac{L(s,y)}{2k}\right)\ .$$

Substitution of the indicated functions leads to

$$\frac{\eta_{ue}}{3\mu_0} = 1 + \phi\left[\frac{2(5s+2)}{4(s+1) - 5(5s+2)\phi} + \frac{12}{35k}\,\frac{(19s+16)(25s^2+41s+4)}{4(s+1) - 5(5s+2)\phi} + O(\phi^{5/3})\right]\ , \tag{36}$$

$$\frac{\eta_{be}}{6\mu_0} = 1 + \phi\left[\frac{2(5s+2)}{4(s+1) - 5(5s+2)\phi} - \frac{24}{35k}\,\frac{(19s+16)(25s^2+41s+4)}{4(s+1) - 5(5s+2)\phi} + O(\phi^{5/3})\right]\ , \tag{37}$$

where $k = \gamma/(\mu_0 aG)$. Thus, the equations predict a linearly increasing viscosity with increasing stretch rate in uniaxial extension and a linearly decreasing viscosity in biaxial extension. This behavior is in qualitative agreement with experimental data at sufficiently small stretch rates.[22,23] It is interesting that the model predicts a shear independent viscosity for laminar shearing flow (to the order considered), but a stretch-dependent extensional viscosity.

DROP DEFORMATION

The primary purpose of this paper is to note the rheological properties of a nondilute suspension model. However, a by-product of the computations is a prediction of drop deformation in shearing fields, and we include some of these results.

Taylor[24] found that drop behavior depends on the two dimensionless groups k and s. Taylor's work has been extended by numerous authors, but we focus our attention on that of Cox[12] and of Cerf.[25] For steady laminar shear flow Cox, following Taylor, described drop behavior by the two parameters

$$D \triangleq \frac{L-B}{L+B} = \frac{19s+16}{16(s+1)k}\left[1 + \left(\frac{19s}{20k}\right)^2\right]^{-1/2}\ , \tag{38}$$

$$\alpha = \frac{\pi}{4} - \tfrac{1}{2}\tan^{-1}\left(\frac{19s}{20k}\right)\ . \tag{39}$$

Here, D is a deformation parameter, defined in terms of L and B, the longest and shortest axes, respectively, of the drop, and α is the angle between the major axis of the drop and the flow direction (see Fig. 1).

Recent data of Torza *et al.*[26] indicate that (38) describes actual drop behavior rather well for either $s \gg 1$ or $s \ll 1$, but (39) is a good approximation to the data only for $s \gg 1$. In the opposite extreme, $s \ll 1$, an equation due to Cerf[25,26] and subsequently corrected by Roscoe[1]

$$\alpha = \frac{\pi}{4} - \frac{(19s+16)(2s+3)}{80(s+1)k} \tag{40}$$

provides better agreement. We shall show that application of our model leads to an expression for α which reduces to both Cox's and Cerf's forms in limiting cases.

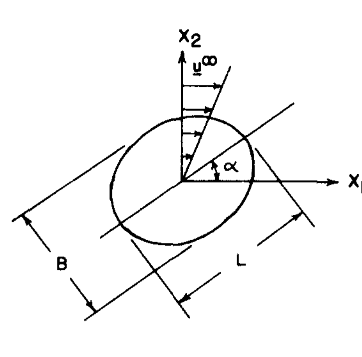

FIG. 1. Definition of parameters for drop deformation.

We consider drop deformation only to $O(\epsilon)$. Then, the equation of the drop surface becomes

$$r = 1 + \epsilon F_{ij}\left(\frac{\partial^2 r^{-1}}{\partial x_i \partial x_j}\right) r^3 + O(\epsilon^2) \quad , \tag{41}$$

where F_{ij}, which is associated with F_2, can be found from Eq. (22). The solution follows along the lines given by Cox.[12] One obtains

$$D = \frac{3K(s,y)}{2\sqrt{1+(hG)^2}}\,\frac{1}{k} \to \frac{19s+16}{16(s+1)\sqrt{1+Z^2}}\,\frac{1}{k} \times \left[1 + \phi\,\frac{5(5s+2)}{4(s+1)} + O(\phi^{5/3})\right] \quad , \tag{42}$$

$$\alpha = \frac{\pi}{4} - \tfrac{1}{2}\tan^{-1}(hG) \to \frac{\pi}{4} - \tfrac{1}{2}\tan^{-1}(Z),$$

where Z is defined following Eq. (31). Ignoring terms beyond those shown in (42) one obtains these limiting cases:

(1) $k \gg 1$ and $s = O(1)$:

$$D = \frac{19s+16}{16(s+1)k}\left(1 + \phi\,\frac{5(5s+2)}{4(s+1)}\right) \quad , \tag{43}$$

$$\alpha = \frac{\pi}{4} - \frac{(19s+16)(2s+3)}{80(s+1)k}\left(1 + \phi\,\frac{5(19s+16)}{4(s+1)(2s+3)}\right) . \tag{44}$$

(2) $k = O(1)$ and $s \gg 1$:

$$D = \frac{5}{4s}\left(1 + \frac{25}{4}\phi\right) \quad , \tag{45}$$

$$\alpha = \frac{\pi}{4} - \tfrac{1}{2}\tan^{-1}\left(\frac{19s}{20k}\right) \to 0 \quad . \tag{46}$$

(3) $k \gg 1$ and $s \gg 1$:

$$D = \frac{5(19s+16)}{4(s+1)\sqrt{(20k)^2 + (19s)^2}}\left(1 + \phi\,\frac{5(5s+2)}{4(s+1)}\right) \quad , \tag{47}$$

$$\alpha = \frac{\pi}{4} - \tfrac{1}{2}\tan^{-1}\left(\frac{19s}{20k}\right) \quad . \tag{48}$$

One notes that as $\phi \to 0$, Eq. (38) is approached for all three cases. However, Cox's prediction for α [Eq. (39)] is found only when $s \gg 1$ (cases 2 and 3). When $k \gg 1$ and $s = O(1)$, Eq. (44) reduces to the result of Cerf,[25] Eq. (40).

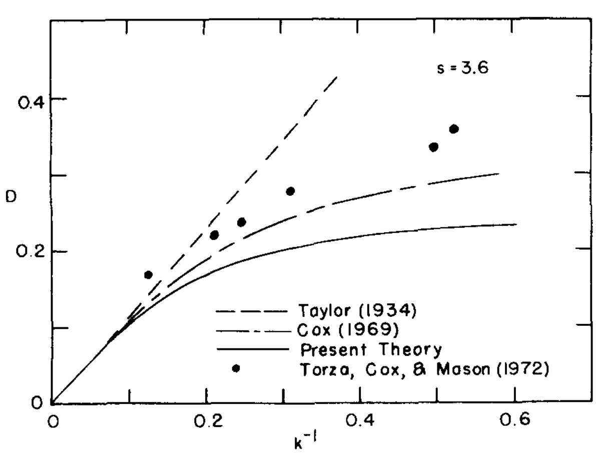

FIG. 2. Drop deformation. Comparison of theory and experiment for $s = 3.6$.

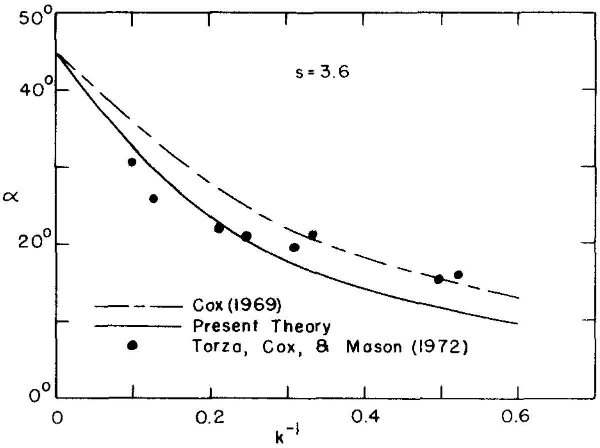

FIG. 3. Drop orientation. Comparison of theory and experiment for $s = 3.6$.

Data of Torza, *et al.*[26] for drop deformation and orientation of drops of two different silicone oils in oxidized castor oil [$\mu_0 = 65$ poise, $\gamma = 4.1$ dyn/cm] are shown in Figs. 2–5. When $s = 3.6$ and when one moves out of the regime $k \gg 1$, the theory of Cox shows better agreement of the deformation parameter D with the data than does our theory. However, it is interesting to note that, particularly at high values of k, the prediction of orientation angle α from Eq. (44) is more successful. This is especially true as s becomes small with respect to unity (Fig. 5).

We note in passing that for plane hyperbolic flow [$u^\infty = (\tfrac{1}{2}Gx_1, -\tfrac{1}{2}Gx_2, 0)$] one obtains the results of Taylor as $\phi \to 0$, with deformation increasing as ϕ increases. However, the condition of small deformation holds only if $k \gg 1$, in contrast to the case of laminar shear flow, where deformation is predicted to be small for all three of the cases considered.

VISCOELASTIC PARTICLES

Other authors have shown how similar results can be obtained with two-phase rheological models which in

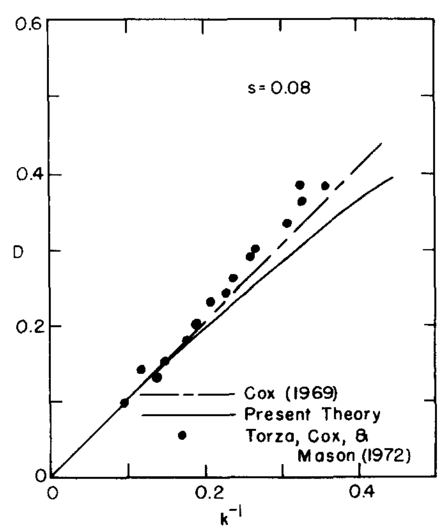

FIG. 4. Drop deformation. Comparison of theory and experiment for $s = 0.08$.

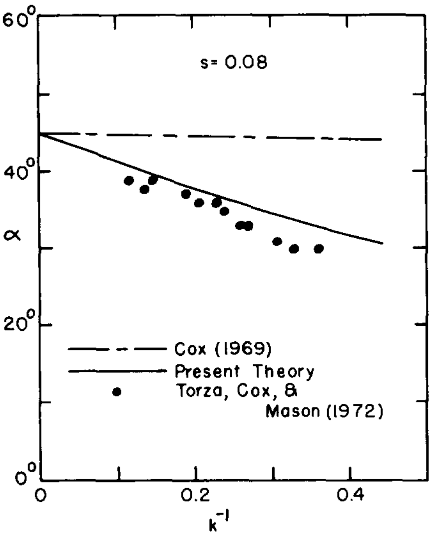

FIG. 5. Drop orientation. Comparison of theory and experiment for $s = 0.08$.

one case utilize a force due to interfacial tension between phases and in the other account explicitly for viscoelasticity by introducing it into the constitutive model of the discontinuous phase. We close by showing how one can use this latter approach for the cell model developed in the present paper. For purposes of illustration we consider a simple oscillatory flow with frequency ω in which the deformation is small enough to be considered infinitesimal. Then one can show[27] that the governing differential equations can be written

$$\mu_0\nabla^2\bar{\mathbf{u}} = \nabla\bar{p}, \quad \nabla\cdot\bar{\mathbf{u}} = 0, \tag{49}$$

$$\mu'\nabla^2\mathbf{u}^* = \nabla p^*, \quad \nabla\cdot\mathbf{u}^* = 0, \tag{50}$$

where $\mu' = \mu^* - ik^*/\omega$. The coefficients k^* and μ^* are constants which derive from the constitutive equation for quasilinear viscoelasticity

$$P^*_{ij} = -p^*\delta_{ij} + 2k^*C^*_{ij} + 2\mu^*(\mathfrak{D}C^*_{ij}/\mathfrak{D}t). \tag{51}$$

C^*_{ij} is the Eulerian strain tensor of the particle, defined by[28]

$$2C^*_{ij}(\mathbf{x}, t) = \delta_{ij} - \delta_{IJ}\frac{\partial X^I}{\partial x^i}\frac{\partial X^J}{\partial x^j},$$

where $\mathbf{X}$ and $\mathbf{x}$ are position vectors associated with reference time t_0 and present time t, respectively.

It is noteworthy and convenient that (49) and (50) are of the same form as (3) and (4). Thus, the solutions reported earlier can be used immediately with $k = 0$ and s replaced by $s' = \mu'/\mu_0$. We consider only zeroth-order solutions in terms of the deformation. After some computation results are obtained for the real and imaginary parts of the bulk-average viscosity $\eta = \eta' - i\eta''$.

$$\frac{\eta' - \mu_0}{\mu_0\phi} = \frac{10}{4 - 25\phi}\left(1 - \frac{\sigma^*\tau^*\omega^2}{1 + (\omega\tau^*)^2}\right), \tag{52}$$

$$\frac{\eta''}{k^*\phi} = \frac{(\sigma^*)^2\omega}{1 + (\omega\tau^*)^2}, \tag{53}$$

where

$$\tau^* = \frac{2(2s+3) - 25(s-1)\phi}{4 - 25\phi}\,\frac{\mu_0}{k^*},$$

$$\sigma^* = \frac{10}{4 - 25\phi}\,\frac{\mu_0}{k^*}, \quad s = \mu^*/\mu_0.$$

As $\phi \to 0$, these equations reduce to Cerf's results, as given in Eqs. (69) and (70) of Roscoe.[1] The condition $\epsilon \ll 1$ is satisfied when $G\tau \ll 1$ or when $\omega\tau \gg 1$ (or $s\omega\tau \gg 1$ if $s \gg 1$), where $\tau = 3\mu_0/(2k^*)$. The dynamic viscosity follows a familiar pattern. When ω is small, the dynamic viscosity (η') decreases and rigidity ($k' = \omega\eta''$) increases quadratically with ω. However, when ω is large and $s \gg 1$, both dynamic viscosity and rigidity reach saturation values, which are dependent on s and ϕ, but not on ω and k.

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[1] R. Roscoe, J. Fluid Mech. 28, 273 (1967).
[2] N. A. Frankel and A. Acrivos, J. Fluid Mech. 44, 65 (1970).
[3] A. Einstein, Ann. Phys. (Leipz.) 19, 289 (1906); 34, 591 (1911).
[4] G. I. Taylor, Proc. R. Soc. A 138, 41 (1932).
[5] H. Fröhlich and R. Sack, Proc. R. Soc. A 185, 415 (1946).
[6] G. K. Batchelor and J. T. Green, J. Fluid Mech. 56, 401 (1972).
[7] R. Simha, J. Appl. Phys. 23, 1020 (1952).
[8] J. Happel, J. Appl. Phys. 28, 1288 (1957).
[9] J. G. Oldroyd, Proc. R. Soc. A 218, 122 (1953).
[10] I. Yaron and B. Gal-Or, Rheol. Acta 11, 241 (1972).
[11] C. Brennen, (to be published).
[12] R. G. Cox, J. Fluid Mech. 37, 601 (1969).
[13] H. Lamb, *Hydrodynamics* (Dover, New York, 1945), 6th ed., p. 110 *et seq.*
[14] J. W. Gibbs and E. B. Wilson, *Vector Analysis* (Dover, New York, 1960), p. 411 *et seq.*
[15] G. K. Batchelor, J. Fluid Mech. 41, 545 (1970).
[16] H. Brenner, in *Progress in Heat and Mass Transfer*, edited by W. R. Schowalter, A. V. Luikov, W. J. Minkowicz, and N. H. Afgan (Pergamon, New York, 1972), Vol. 5, p. 89.
[17] J. D. Goddard and C. Miller, Rheol. Acta 5, 177 (1966).
[18] J. G. Oldroyd, Proc. R. Soc. A 245, 278 (1958).
[19] J. B. Keller, L. A. Rubenfeld, and J. E. Molyneux, J. Fluid Mech. 30, 97 (1967).
[20] M. A. Nawab and S. G. Mason, Trans. Faraday Soc. 54, 1712 (1958).
[21] W. R. Schowalter, C. E. Chaffey, and H. Brenner, J. Colloid Interface Sci. 26, 152 (1968).
[22] J. Maerker and W. R. Schowalter, Rheol. Acta 13, 627 (1974).
[23] D. D. Joye, G. W. Poehlein, and C. D. Denson, Trans. Soc. Rheol. 17, 287 (1973).
[24] G. I. Taylor, Proc. R. Soc. A 146, 501 (1934).
[25] R. Cerf, J. Chim. Phys. 48, 59 (1951).
[26] S. Torza, R. G. Cox, and S. G. Mason, J. Colloid Interface Sci. 38, 395 (1972).
[27] S. J. Choi, Ph.D. dissertation, Princeton University (1972).
[28] A. C. Eringen, *Nonlinear Theory of Continuous Media* (McGraw-Hill, New York, 1962), p. 13.