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On viscous flow and effective viscosity of concentrated suspensions and emulsions

Effect of Particle Concentration and Surfactant Impurities

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With 1 figure and 4 tables

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Notation

a = radius of particle.
$A_n^m, \hat{A}_n^m, B_n^m, \hat{B}_n^m, \ldots, I_n^m, \hat{I}_n^m$ = general coefficients defined by [A1] to [A9].
c = concentration of surfactants in continuous phase.
C_1, C_2, C_3, C_4, C_5 = coefficients defined by [A14] to [A18].
D_b^s = diffusivity of surfactants in continuous phase.
D_i^s = surface diffusivity of surfactants.
E = rate of energy dissipation per unit volume.
$\boldsymbol{F}$ = frictional force.
$\boldsymbol{g}$ = acceleration due to gravity.
G = shear.
h = distance from center of particle to point of zero velocity.
$\boldsymbol{i}, \boldsymbol{j}, \boldsymbol{k}$ = *Cartesian* unit vectors.
J_n = surface flux of surfactants.
$\hat{K}$ = constant defined by [27].
$L_n^m, \hat{L}_n^m, M_n^m, \hat{M}_n^m, N_n^m, \hat{N}_n^m$ = parameters defined by [A11] to [A13].
m, n = integers.
p = pressure.
p_n = solid spherical harmonic of order n.
r = radius vector.
R_1, R_2 = radii of curvature.
s = surface area.
$S_n\{\theta, \varphi\}$ = surface spherical harmonic of order n.
$\boldsymbol{t}_r$ = unit vector in radial direction.
$\boldsymbol{T}_0$ = torque about center of particle.
U = velocity of uniform imposed field.
U_s = *Stokes* velocity of particle.
$\boldsymbol{v}$ = velocity vector.
$V_n^m, \hat{V}_n^m, X_n^m, \hat{X}_n^m, Y_n^m, \hat{Y}_n^m, Z_n^m, \hat{Z}_n^m$ = parameters defined by [66] to [69].
W_1, W_2, Y_1, Y_2 = parameters defined by [52] to [55].
x, y, z = *Cartesian* coordinates, z aligned with axis of particle.

Greek letters

α^* = overall adsorption rate constant.
β_n = viscosity parameter defined by [A19].
γ = ratio of radii of particle and cell.
$\hat{\gamma}_n$ = interfacial retardation viscosity defined by [A20].
Γ = surface concentration of surfactants.
Γ_0 = equilibrium surface concentration of surfactants.
Γ' = deviation of Γ from Γ_0.
$\Gamma_n^m, \hat{\Gamma}_n^m$ = coefficients defined by [31].
δ = thickness of *Nernst* diffusional layer.
Δ_n = parameter defined by [A10].
ε = parameter defined by [32]
ζ_n = general coefficient defined by [23].
η = dimensionless radius, $\eta = r/a$.
θ = cone angle.

λ	= viscosity ratio defined by [A21].
μ	= viscosity.
μ_{eff}	= effective viscosity.
$\xi_n(\theta, \varphi)$	= deviation from sphericity function.
ξ_n^m, ξ_n^m	= deviation parameters, defined by [61]
ϱ	= density.
σ	= surface tension.
τ_r	= surface shear force.
$\tau_{rr}, \tau_{r\theta}, \tau_{r\varphi}$	= components of stress tensor.
φ	= polar angle.
φ_n	= solid spherical harmonic of order n.
χ_n	= solid spherical harmonic of order n.
ψ	= parameter defined by [71].
$\omega_r, \omega_\theta, \omega_\varphi$	= components of vorticity.
Superscripts	
α	= pertains to phase in general.
c	= pertains to continuous phase.
d	= pertains to dispersed phase.
o	= pertains to imposed field.
Subscripts	
a	= at interface.
o	= equilibrium value.
r	= radial value.
θ	= tangential value.
Φ	= azimuthal value.
Special signs	
$\langle\,\rangle$	= expected value.

Introduction

In many practical situations one has to consider the motion of two-phase particulate systems within shear fields imposed by stationary or moving solid boundaries. In such cases the motion around spherical particles is not axi-symmetrical and the imposed shear fields may also cause deformation of fluid particles. This work deals with a general analysis of the motion around uniformly-sized particles of ensembles of both rigid and deformable particles moving at low particle *Reynolds* numbers in arbitrary imposed shear fields. Effects of surfactant impurities and volume concentration of fluid particles upon the motion and deformation are also considered. The general expressions derived here are employed to obtain specific relations for uniform, *Couette* and hyperbolic imposed flow fields. The velocity fields obtained here for both fluid phases can be used to evaluate interfacial convective rates of heat and mass transfer. For such applications one cannot treat the multiphase system as if composed of one equivalent phase.

Cell models and their statistical nature

Whenever a particulate system is composed of a very limited number of particles (dilute system) arranged in some fixed known geometrical array one may try to satisfy simultaneously all boundary conditions at the interfaces of all the particles, or at least some conditions alternatingly at the surfaces of the particles (e.g. method of reflection). However, for *concentrated* systems in which the particles positions cannot be prescribed, the complexity of the system dictates statistical approaches, one of which may be the cell model (2)[1]). This method is based on the assumption that the field properties around an arbitrary typical particle of the system (e.g. velocity components, shear stresses, temperature, heat fluxes, concentrations, mass fluxes, etc.) must attain extremal (maximum or minimum) values at some distance from the particle, because of the presence and mutual interactions of the neighbouring particles. We can thus envisage each particle to be enclosed by an imaginary enveloping surface, on which the field properties become extremal. Most particulate systems are composed of *randomly* dispersed particles. Therefore, the cell envelopes associated with the various particles are of different shapes and sizes. However in a concentrated system one expects any given particle to be, in a *statistical* sense, surrounded by a more or less unfixed, yet symmetrical cluster of particles. Upon superposition of the numerous cell envelopes of this cluster[2]) their statistically expected form tends to approach a spherical shape [in an ensemble of randomly moving particles (2)].

[1]) Cell models (of various shapes) have, so far, provided the only useful solutions, which agree with all experimental data for concentrated system (2, 10, 12, 19, 22) [but not necessarily for dilute ones as incorrectly implied in a recent paper (24)].

[2]) On a single center of a typical particle, whose size and shape represent the entire ensemble.

One must emphasize now that the velocity field determined by any boundary condition specified on this cell envelope is *not* the one that one can measure around a given particle, since it represents the expected statistical average velocity field of the entire assemblage. Therefore, the expressions derived in the present work become *properties* of the entire assemblage of particles. Similar assumptions are used frequently in statistical thermodynamics (20, 25).

The radius of the cell envelope is derived from the assumption that in randomly dispersed systems the ratio of the particle-to-cell volume must be equal to the ratio of the volume of the dispersed phase to the volume of the whole system. Accordingly, for a system composed of uniformly-sized spherical particles of radius a, the radius of the cell envelope is $a\Phi^{-1/3} = a\gamma^{-3}$, where Φ is the volume concentration of the dispersed phase (2).

Since the cell represents the bounds of "influence" or "perturbation" due to a typical particle on the field around it, it is evident that the extremum field values which must be specified on the envelope must be those of the "unperturbed" field, i.e. to those field values of the continuous phase which would have been encountered, had one not introduced into it the particles of the dispersed phase. In the present analysis we adopt the "free surface spherical cell" model, which assumes that on the envelope the radial velocity component and the tangential shear stresses have the values of the unperturbed shear field, i.e. that tangential shear stresses cannot be transferred across the cell envelope. This model differs somewhat from the "zero-vorticity" model (2), which assumes that no vorticity diffuses from one cell to another.

Expected velocity and pressure fields

For steady motion with negligible inertia (i.e. Re $\ll 1$), the equations of motion and continuity for the expected velocity and pressure fields around and inside the fluid particles in the assemblage are

$$\mu^{\alpha}\nabla^2 \langle \boldsymbol{v}^{\alpha} \rangle = \boldsymbol{\nabla} \langle p^{\alpha} \rangle, \quad [1]$$

and

$$\boldsymbol{\nabla} \cdot \langle \boldsymbol{v}^{\alpha} \rangle = 0. \quad [2]$$

Dropping for simplicity the expected value sign ($\langle\rangle$), the general solutions to these equations in terms of solid spherical harmonics (5) is

$$\boldsymbol{v}^{\alpha} = \sum_{n=-\infty}^{\infty} \Big[\nabla \boldsymbol{x}(\boldsymbol{r}\chi_n^{\alpha}) + \nabla \varphi_n^{\alpha} + \frac{(n+3)}{2\mu^c(n+1)(2n+3)} \times r^2 \nabla p_n^{\alpha} - \frac{n}{\mu^c(n+1)(2n+3)} \boldsymbol{r} p_n^{\alpha} \Big] \quad [3]$$

and

$$p^{\alpha} = \sum_{n=-\infty}^{\infty} p_n^{\alpha} \,. \quad [4]$$

Placing the origin of the coordinate system at the center of a typical particle, the requirement that the velocity at the origin be finite restricts solid spherical harmonics in the dispersed phase ($\alpha \equiv d$) to positive values. The general solutions [3] and [4] are also applicable to the arbitrary imposed shear field ($\alpha \equiv 0$) in the absence of the dispersed particles.

To evaluate the various solid spherical harmonics involved, the following boundary conditions are employed:

At the surface of a particle

$$\boldsymbol{v}^d = \boldsymbol{v}^c, \quad [5]$$

$$v_r^d = v_r^c = 0, \quad [6]$$

$$\boldsymbol{\tau}_r^d = \boldsymbol{\tau}_r^c - \sigma(\Gamma)\left(\frac{1}{R_1} + \frac{1}{R_2}\right)\boldsymbol{t}_r + \nabla_s \sigma(\Gamma). \quad [7]$$

At the spherical cell envelope (i.e. at $r = \gamma^{-1}$)

$$v_r^c = v_r^0 \,, \quad [8]$$

$$\tau_{r\theta}^c = \tau_{r\theta}^0 \,, \quad [9]$$

$$\tau_{r\varphi}^c = \tau_{r\varphi}^0 \,. \quad [10]$$

Condition [7] states that the surface shear forces in both phases, when taken in components, show a difference due to the curvature of the surface (capillary effect on the normal component) and to the interfacial tension gradients set up by adsorbed surfactant impurities (1).

Using the approximate relation

$$\sigma(\Gamma) = \sigma(\Gamma_0 + \Gamma') \cong \sigma(\Gamma_0) + \left(\frac{\partial\sigma}{\partial\Gamma}\right)_0 \Gamma', \; \Gamma' \ll \Gamma_0, \quad [11]$$

whereby

$$\nabla_s \sigma(\Gamma) \cong \left(\frac{\partial\sigma}{\delta\Gamma}\right)_0 \nabla_s \Gamma', \quad [12]$$

we transform, following *Brenner* (8), boundary conditions [5] to [10] as follows:

At $r = a$:

$$\boldsymbol{v}^c \cdot \boldsymbol{t}_r = 0, \quad [13]$$

$$\boldsymbol{v}^d \cdot \boldsymbol{t}_r = 0, \quad [14]$$

$$r\frac{\partial v_r^d}{\partial r} = r\frac{\partial v_r^c}{\partial r}, \quad [15]$$

$$\boldsymbol{r} \cdot \nabla \boldsymbol{x} \boldsymbol{v}^d = \boldsymbol{r} \cdot \nabla \boldsymbol{x} \boldsymbol{v}^c, \quad [16]$$

$$\boldsymbol{r} \cdot \nabla \boldsymbol{x}(\boldsymbol{r x \tau}_r^d) = \boldsymbol{r} \cdot \nabla \boldsymbol{x}(\boldsymbol{r x \tau}_r^c) - \left(\frac{\partial\sigma}{\partial\Gamma}\right)_0 [\boldsymbol{r} \cdot \nabla \boldsymbol{x}(\boldsymbol{r x}\nabla_s\Gamma')], \quad [17]$$

$$\tau_r^c \cdot t_r - \tau_r^d \cdot t_r = \sigma(\Gamma)(1/R_1 + 1/R_2), \quad [18]$$

and

$$r \cdot \nabla x \tau_r^d = r \cdot \nabla x \tau_r^c \quad [19]$$

At $r = \gamma^{-1}$:
$$v^c \cdot t_r = v^0 \cdot t_r, \quad [20]$$

$$r \cdot \nabla x \tau_r^c = r \cdot \nabla x \tau_r^0, \quad [21]$$

$$r \cdot \nabla x (r x \tau_r^c) = r \cdot \nabla x (r x \tau_r^0). \quad [22]$$

To employ the transformed boundary conditions [13] to [22], one must specify the shape of the particle, which may be deformed by the external shear field. This shape is not *a priori* known. It is expedient to first approximate the particle by spherical shape, and later calculate the deviation of its shape from sphericity. This calculated deviation can then be utilized to initiate an iterative procedure for reformulation of the aforementioned boundary conditions.

We now express the boundary conditions in terms of the general solution [3], in which the solid spherical harmonics have been further expanded in terms of solid surface harmonics, and the latter in turn resolved in the general form

$$\zeta_n S_n(\theta, \varphi) = \sum_{m=0}^{n} (\zeta_n^m \cos m\varphi + \hat{\zeta}_n^m \sin m\varphi) P_n^m(\cos\theta) \quad [23]$$

where

$$\zeta_n^m = A_n^m, B_n^m, \ldots, I_n^m, \alpha_n^m, \alpha_{-n-1}^m, \ldots, \gamma_{-n-1}^m$$

and

$$\hat{\zeta}_n^m = \hat{A}_n^m, \hat{B}_n^m, \ldots, \hat{I}_n^m, \hat{\alpha}_n^m, \hat{\alpha}_{-n-1}, \ldots, \hat{\gamma}_{-n-1}$$

Surfactant impurities

The surface flux of surfactant impurities at steady state, neglecting coupling effects due to surface shear forces, is given by

$$J_n = \nabla_s \cdot [\Gamma(v)_a - D_i^s \nabla_s \Gamma) \cong \Gamma_0 \nabla_s \cdot (v)_a - D_i^s \nabla_s^2 \Gamma'. \quad [24]$$

Relating this flux to the kinetics of diffusion from the continuous phase to the interface (6)

$$J_n = \frac{D_b^s}{\delta} (\Gamma_0 - \Gamma_i) / \left(\frac{\partial \Gamma}{\partial c}\right)_{eq}, \quad [25]$$

and the kinetics of adsorption-desorption mechanism on the interface

$$J_n = -\alpha^*(\Gamma - \Gamma_i), \quad [26]$$

we obtain

$$J_n = -\alpha^* \left[1 + \alpha^* \frac{\delta}{D_b^s} \left(\frac{\partial \Gamma}{\partial c}\right)_{eq}\right]^{-1} \Gamma' = -\hat{K}\Gamma'. \quad [27]$$

Introducing expressions [27] into [24], expressing $\nabla_{\hat{s}} \cdot (v)_a$ in terms of solid spherical harmonics, expanding the latter according to Eqn. [23], assuming that Γ' is also expandable in the form

$$\Gamma' = \sum_{n=1}^{\infty} \Gamma_n^{\hat{}\prime} S_n^{\hat{}}(\theta, \varphi), \quad [28]$$

whereby

$$D_i^s \nabla_s^2 \Gamma' = D_i^s \sum_{n=1}^{\infty} \Gamma' \nabla_s^2 S_n(\theta, \varphi), \quad [29]$$

and noting, that from the theory of surface spherical harmonics (7),

$$\nabla_s^2 S_n(\theta, \varphi) = -n(n+1) S_n(\theta, \varphi) \quad [30]$$

we find, applying orthogonality properties of spherical harmonics and *Legendre*'s polynomials, that

$$\Gamma_n^m = \frac{a\Gamma_0}{D_i^s} \frac{1}{(n^2 + n + \varepsilon)} \times \left[\frac{n(n+2)}{2(2n+3)} A_n^m + n(n-1) B_n^m\right], \quad [31]$$

where

$$\varepsilon = \frac{\hat{K} a^2}{D_i^s}. \quad [32]$$

Note, that an expression similar to [31] is obtained for $\hat{\Gamma}_n^m$ in which $\hat{A}_n^m$ and $\hat{B}_n^m$ exchange A_n^m and B_n^m, respectively.

General expressions

Introduction of relation [31] into boundary condition [17], and utilization of the orthogonality properties of solid surface harmonics and *Legendre* polynomials, gives a set of nine equations, the simultaneous solution of which results in a set of nine coefficients A_n^m, B_n^m, ..., I_n^m, listed in the Appendix. With their aid one may describe the flow fields in the dispersed and continuous phases of the ensemble in terms of the given coefficients α_n^m, α_{-n-1}^m, ..., γ_{-n-1}^m of the unperturbed field. The latter can be derived from the examination of suitable expressions for specific flow conditions. Note that another set of nine coefficients $\hat{A}_n^m$, $\hat{B}_n^m$, ..., $\hat{I}_n^m$ is obtained in terms of the coefficients $\hat{\alpha}_n^m$, $\hat{\alpha}_{-n-1}^m$, ..., $\hat{\gamma}_{-n-1}^m$ of the unperturbed field. The two sets of coefficients are identical, except for the supersign $\hat{}$.

General expressions for velocity components, pressure distributions, shear stresses and vorticity distribution in both phases of the assemblage have been derived from Eqns. [3] and [4] and are reported elsewhere (19). For the sake of brevity we present in this work only expressions for specific imposed shear fields.

Characteristic parameters of imposed flow fields

a) Uniform flow

Uniform imposed flow fields may be encountered in nature, e.g. atmospheric sedimentation of dust or fallout, aerosols, fog, etc., and in sedimentation of suspensions and the like in large diameter vessels. For such a flow[1])

$$\boldsymbol{v}^0 = -U\,\boldsymbol{k}, \qquad [33]$$

$$\boldsymbol{v}^0 \cdot \boldsymbol{t}_r = -U\cos\theta = -U P_1(\cos\theta), \qquad [34]$$

and

$$\boldsymbol{r} \cdot \nabla \boldsymbol{x}\, \boldsymbol{v}^0 = 0. \qquad [35]$$

It follows from the general solution [3] and the expansions of the solid spherical harmonics that for this case

$$\beta_1^0 = -U, \qquad [36]$$

and that all other coefficients are equal to zero.

b) Couette flow

This uniform shear field is encountered in coaxial cylinders *rotational viscometry*. Here

$$\boldsymbol{v}^0 = G(y+h)\,\boldsymbol{i} - U\,\boldsymbol{i}, \qquad [37]$$

$$\boldsymbol{v}^0 \cdot \boldsymbol{t}_r = (Gh - U)\cos\varphi P_1^1(\cos\theta)$$

$$+ \frac{Ga}{6}\,\eta \sin 2\varphi P_2^2(\cos\theta) \qquad [38]$$

$$\boldsymbol{r} \cdot \nabla \boldsymbol{x}\, \boldsymbol{v}^0 = -Ga\eta\cos\theta, \qquad [39]$$

whereby we find

$$\beta_1^1 = Gh - U, \qquad [40]$$

$$\hat{\beta}_2^2 = \frac{Ga}{6}, \qquad [41]$$

and

$$\gamma_1^0 = -Ga. \qquad [42]$$

c) Hyperbolic flow

A hyperbolic flow field is set up by the motion of four rotating cylinders. For such a field

$$\boldsymbol{v}^0 = G(x\,\boldsymbol{i} + y\,\boldsymbol{j}) - U_x\,\boldsymbol{i} - U_y\,\boldsymbol{j} \qquad [43]$$

$$\boldsymbol{v}^0 \cdot \boldsymbol{t}_r = \frac{Ga}{3}\,\eta\cos 2\varphi P_2^2(\cos\theta) - U_x\cos\varphi P_1^1(\cos\theta)$$

$$- U_y \sin\varphi P_1^1(\cos\theta). \qquad [44]$$

and

$$\boldsymbol{r} \cdot \nabla \boldsymbol{x}\, \boldsymbol{v}^0 = 0. \qquad [45]$$

Using these relations one obtains

$$\beta_1^1 = -U_x, \qquad [46]$$

$$\hat{\beta}_1^1 = -U_y, \qquad [47]$$

and

$$\beta_2^2 = \frac{Ga}{3}. \qquad [48]$$

Frictional force, torque and force balance on particles of ensemble

Using *Brenner's* (8) expression for the frictional force acting upon a particle of the ensemble

$$\boldsymbol{F} = -4\pi\nabla(r^3 p_{-2}),$$

we obtain in terms of the coefficient G_n^m

$$\boldsymbol{F} = -4\pi\,\mu^c a(G_1^0\,\boldsymbol{k} + G_1^1\,\boldsymbol{j} + G_1^1\,\boldsymbol{i}). \qquad [49]$$

Similarly, from the expression for the torque (8), experienced by a particle of the ensemble about its origin

$$\boldsymbol{T}_0 = -8\pi\,\mu^c\,\nabla(r^3\chi_{-2}) \qquad [50]$$

we find

$$\boldsymbol{T}_0 = -8\pi\,\mu^c a(I_1^0\,\boldsymbol{k} + I_1^1\,\boldsymbol{j} + I_1^1\,\boldsymbol{i}).$$

A force balance on a particle gives

$$\boldsymbol{F} + \frac{4}{3}\pi a^3(\varrho^d - \varrho^c)(1-\gamma^3)\,\boldsymbol{g} = 0. \qquad [51]$$

When directions of vectors $\boldsymbol{k}$ and $\boldsymbol{g}$ coincide, using the characteristic parameters of the imposed flow fields derived in the previous section, and the general expression for the coefficients (A1) to (A9), we obtain the following specific expressions for frictional force and torque on particles of ensembles in uniform, *Couette*, and hyperbolic imposed fields:

	Frictional force	Torque
Uniform	$6\pi\,\mu^c a\,U_s\,\boldsymbol{k}$	0
Couette	0(1)	0
Hyperbolic	0(2)	0

Note: (1) A force balance for this case gives $U = Gh$, whereby $\beta_1^1 = 0$.
(2) A force balance for this case gives $U_x = U_y = 0$, whereby $\beta_1^1 = \hat{\beta}_1^1 = 0$.

The same results are obtained for neutrally buoyant particles.

[1]) In the *Cartes*ian coordinate system the direction of unit vector $\boldsymbol{k}$ coincides with the axis $\theta = 0$, $\theta = \pi$.

Velocity profiles in the dispersed and continuous phases

Employing the general expressions from reference (19), the velocity components for some specific imposed fields are summarized in table 1, where the following parameters are defined:

$$W_1 = 3(1 + 2/3\beta_1) + 2\gamma^5(1 - \beta_1), \quad [52]$$

$$Y_1 = 2(1 + \beta_1) + 3\gamma^5(1 - 2/3\beta_1), \quad [53]$$

$$W_2 = 5(1 + 2/5\beta_2) + 2\gamma^7(1 - \beta_2), \quad [54]$$

$$Y_2 = 2(1 + \beta_2) + 5\gamma^7(1 - 2/5\beta_2). \quad [55]$$

Pressure distribution

The general expressions of reference (19) are also employed to arrive at specific expressions for pressure distributions in various imposed fields as given in table 2. The total pressure distribution should include, in addition to the terms of table 2, the reference p_0 and the static pressure $\varrho g r \cos\theta$ terms.

Distribution of shear stress components

The specific expressions for stress tensor components in the dispersed and continuous phases of two-phase particulate systems in uniform, *Couette* and hyperbolic imposed fields are presented in table 3. (General expressions are given in reference [(19)].

Distribution of vorticity components

The general vorticity components can be reduced (19) to specific cases which are presented in table 4.

Deviation of shape of a particle from sphericity

Boundary condition [18] is now utilized to find the deviation of shape of a typical particle from sphericity.

It is assumed that the shape of a typical particle's interface can be represented by

$$r = a[1 + \xi(\theta, \varphi)], \quad [56]$$

such that

$$|\xi(\theta, \varphi)| \ll 1. \quad [57]$$

According to *Landau* and *Lifshitz* (14)

$$\frac{1}{R_1} + \frac{1}{R_2} = \frac{2}{a} - \frac{2\xi}{a} - \frac{1}{a}\left[\frac{1}{\sin^2\theta}\frac{\partial^2\xi}{\partial\varphi^2} + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\xi}{\partial\theta}\right)\right] + 0(\xi)^2. \quad [58]$$

Assuming that the deviation $\xi(\theta, \varphi)$ from sphericity can be expanded into surface spherical harmonics according to

$$\xi(\theta, \varphi) = \sum_{n=0}^{\infty} \xi_n S_n(\theta, \varphi),$$

that the volume of the deformed particle remains constant and that the origin of the coordinate system remains always coincident with the center of gravity of the particle, *Hetsroni* et al. (9) have shown, using the properties of surface spherical harmonics, and neglecting the term of $0(\xi)^2$, that

$$\frac{1}{R_1} + \frac{1}{R_2} = \frac{1}{a}\left[2 + \sum_{n=0}^{\infty} (n^2 + n - 2)\xi_n S_n(\theta, \varphi)\right]. \quad [59]$$

Introducing this expression into boundary condition [18], expressing the radial components of the surface shear force in terms of spherical harmonics, eliminating harmonics of order zero and one, which represent the reference pressure and force balance terms, one obtains, after some manipulation, for the shape of the particle's interface

$$r = a\left\{1 + \sum_{n=0}^{\infty}\sum_{m=0}^{n} [\xi_n^m \cos m\varphi + \hat{\xi} \sin m\varphi]\, P_n^m(\cos\theta)\right\} \quad [60]$$

where

$$\xi_n^m = \frac{1}{(n^2 + n + 2)}\frac{\mu^d}{\sigma}\left\{2n(n-1)\left(B_n^m - \beta_n E_n^m\right) + \frac{(n^2 - n - 3)}{(2n+3)}\left(A_n^m - \beta_n D_n^m\right) - 2\beta_n(n+1) \times (n+2)H_n^m - \beta_n\frac{(n^2 + 3n - 1)}{(2n-1)}G_n^m\right\}. \quad [61]$$

Expression [61] can be used to reformulate boundary conditions [13] to [22]. Such a reformulation has been recently employed by *Haber* and *Hetsroni* (13) for the case of a single particle in an unbounded infinite fluid. However, because of the complexity of the expressions involved, the reformulative procedure was not carried beyond the second iteration.

In the present analysis we have restricted ourselves to the first iteration. The deviations of the shape of a typical particle from sphericity for the various imposed fields considered are given as follows

Uniform

$$r = a.$$

Table 1. Velocity components in dispersed and continuous phases of ensembles in various imposed fields

Velocity components	Uniform	*Couette*	Hyperbolic
V_r^d	$\frac{3}{2}\frac{U_s}{W_1}\beta_1(1-\gamma^5)(1-\eta^2)\cos\theta$	$\frac{3}{2}\frac{Ga}{(Y_2-W_2\gamma^3)}\beta_2\eta(\gamma^7-1)(1-\eta^2)\sin 2\varphi\sin^2\theta$	$\frac{3\,Ga}{(Y_2-W_2\gamma^3)}\beta_2\eta(\gamma^7-1)(1-\eta^2)\cos 2\varphi\sin^2\theta$
V_θ^d	$\frac{3}{2}\frac{U_s}{W_1}\beta_1(1-\gamma^5)(2\eta^2-1)\sin\theta$	$\frac{3}{2}\frac{Ga}{(Y_2-W_2\gamma^3)}\beta_2\eta(\gamma^7-1)\left(1-\frac{5}{3}\eta^2\right)\sin 2\varphi\sin\theta\cos\theta$	$\frac{3Ga}{(Y_2-W_2\gamma^3)}\beta_2\eta(\gamma^7-1)\left(1-\frac{5}{3}\eta^2\right)\cos 2\varphi\sin\theta\cos\theta$
V_φ^d	0	$\frac{3}{2}\frac{Ga}{(Y_2-W_2\gamma^3)}\beta_2\eta(\gamma^7-1)\left(1-\frac{5}{3}\eta^2\right)\cos 2\varphi\sin\theta$	$-\frac{3Ga}{(Y_2-W_2\gamma^3)}\beta_2\eta(\gamma^7-1)\left(1-\frac{5}{3}\eta^2\right)\sin 2\varphi\sin\theta$
V_r^c	$\frac{3}{2}\frac{U_s}{W_1}\left(\eta^2\gamma^5-Y_1+\frac{W_1}{\eta}-\frac{1}{\eta^3}\right)\cos\theta$	$\frac{1}{2}\frac{Ga}{(Y_2-W_2\gamma^3)}\left(-3\eta^3\gamma^7+\eta Y_2-\frac{W_2}{\eta^2}+\frac{3}{\eta^4}\right)\sin 2\varphi\sin^2\theta$	$\frac{Ga}{(Y_2-W_2\gamma^3)}\left(-3\eta^3\gamma^7+\eta Y_2-\frac{W_2}{\eta^2}+\frac{3}{\eta^4}\right)\cos 2\varphi\sin^2\theta$
V_θ^c	$\frac{3}{2}\frac{U_s}{W_1}\left(-\frac{1}{2\eta^3}-\frac{W_1}{2\eta}+Y_1-\eta^2\gamma^5\right)\times\sin\theta$	$\frac{Ga}{2(Y_2-W_2\gamma^3)}\left(-5\eta^3\gamma^7+\eta Y_2-\frac{2}{\eta^4}\right)\sin 2\varphi\sin\theta\cos\theta$	$\frac{Ga}{(Y_2-W_2\gamma^3)}\left(\eta Y_2-5\eta^3\gamma^7-\frac{2}{\eta^4}\right)\cos 2\varphi\sin\theta\cos\theta$
V_φ^c	0	$\frac{Ga}{2(Y_2-W_2\gamma^3)}\left(-5\eta^3\gamma^7+\eta Y_2-\frac{2}{\eta^4}\right)\cos 2\varphi\sin\theta$	$\frac{-Ga}{(Y_2-W_2\gamma^3)}\left(\eta Y_2-5\eta^3\gamma^7-\frac{2}{\eta^4}\right)\sin 2\varphi\sin\theta$

Table 2. Pressure distribution in ensembles of particles in various imposed fields

Flow Field	p^d	p^c
Uniform	$10\frac{\mu^d}{a}\eta\beta_1(1-\gamma^5)\cdot\frac{3}{2}\frac{U_s}{W_1}\cos\theta$	$-\frac{3}{2}\mu^c\frac{U_s}{W_1}\left(\frac{W_1}{\eta^2}+10\eta\gamma^5\right)\cos\theta$
Couette	$\frac{21}{2}\mu^d\frac{G}{(Y_2-W_2\gamma^3)}\eta^2\beta_2(1-\gamma^7)\sin 2\varphi\sin^2\theta$	$-\frac{\mu^c}{2}\frac{G}{(Y_2-W_2\gamma^3)}\left(21\eta^2\gamma^7+\frac{W_2}{\eta^3}\right)\sin 2\varphi\sin^2\theta$
Hyperbolic	$21\mu^d\frac{G}{(Y_2-W_2\gamma^3)}\eta^2\beta_2(1-\gamma^7)\cos 2\varphi\sin^2\theta$	$-\mu^c\frac{G}{(Y_2-W_2\gamma^3)}\left(21\eta^2\gamma^7+\frac{W_2}{\eta^3}\right)\cos 2\varphi\sin^2\theta$

Table 3. Stress tensor components in dispersed and continuous phases of ensembles of particles in various imposed fields

Stress tensor component	Uniform	*Couette*	Hyperbolic
τ_{rr}^{d}	$-9\frac{\mu^d}{r}\frac{U_s}{W_1}\beta_1(1-\gamma^5)\eta^2\cos\theta$	$\frac{3}{2}\frac{\mu^d G\beta_2(\gamma^7-1)}{(Y_2-W_2\gamma^3)}(2+\eta^2)\sin 2\varphi\sin^2\theta$	$\frac{3\mu^d G\beta_2(\gamma^7-1)}{(Y_2-W_2\gamma^3)}(2+\eta^2)\cos 2\varphi\sin^2\theta$
$\tau_{r\theta}^{d}$	$-\frac{9}{2}\frac{\mu^d}{r}\frac{U_s}{W_1}\eta^2\beta_1(1-\gamma^5)\sin\theta$	$\mu^d G\beta_2\frac{(\gamma^7-1)}{(Y_2-W_2\gamma^3)}(3-8\eta^2)\sin 2\varphi\sin\theta\cos\theta$	$2\mu^d G\beta_2\frac{(\gamma^7-1)}{(Y_2-W_2\gamma^3)}(3-8\eta^2)\cos 2\varphi\sin\theta\cos\theta$
$\tau_{r\varphi}^{d}$	0	$\mu^d G\beta_2\frac{(\gamma^7-1)}{(Y_2-W_2\gamma^3)}(3-8\eta^2)\cos 2\varphi\sin\theta$	$-2\mu^d G\beta_2\frac{(\gamma^7-1)}{(Y_2-W_2\gamma^3)}(3-8\eta^2)\sin 2\varphi\sin\theta$
τ_{rr}^{c}	$\frac{9}{2}\frac{\mu^c}{r}\frac{U_s}{W_1}(-2\eta^2\gamma^5+2\eta^{-3}$ $+\eta^{-1}W_1)\cos\theta$	$\frac{\mu^c G}{(Y_2-W_2\gamma^3)}\left(Y_2-\frac{3}{2}\gamma^7\eta^2-12\eta^{-5}+\frac{1}{3}W_2\eta^{-3}\right)$ $\times\sin 2\varphi\sin^2\theta$	$\frac{2\mu^c G}{(Y_2-W_2\gamma^3)}\left(Y_2-3\gamma^7\eta^2-12\eta^{-5}+\frac{1}{3}W_2\eta^{-3}\right)$ $\times\cos 2\varphi\sin^2\theta$
$\tau_{r\theta}^{c}$	$-\frac{9}{2}\frac{\mu^c}{r}\frac{U_s}{W_1}(\eta^2\gamma^5-\eta^{-3})\sin\theta$	$\mu^c\frac{G}{(Y_2-W_2\gamma^3)}(Y_2-8\gamma^7\eta^2+8\eta^{-5}-W_2\eta^{-3})$ $\times\sin 2\varphi\sin\theta\cos\theta$	$2\mu^c\frac{G}{(Y_2-W_2\gamma^3)}(Y_2-8\gamma^7\eta^2+8\eta^{-5}-W_2\eta^{-3})$ $\times\cos 2\varphi\cdot\sin\theta\cos\theta$
$\tau_{r\varphi}^{c}$	0	$\mu^c\frac{G}{(Y_2-W_2\gamma^3)}(Y_2-8\gamma^7\eta^2+8\eta^{-5}-W_2\eta^{-3})\cos 2\varphi\sin\theta$	$-2\mu^c\frac{G}{(Y_2-W_2\gamma^3)}(Y_2-8\gamma^7\eta^2+8\eta^{-5}-W_2\eta^{-3})\sin 2\varphi\sin\theta$

Table 4. Vorticity components in dispersed and continuous phases of ensembles of particles in various imposed flow fields

Vorticity components	Uniform	*Couette*	Hyperbolic
ω_{θ}^{d}	0	$\frac{7}{2}\frac{G\beta_2\eta^2}{(Y_2-W_2\gamma^3)}(\gamma^7-1)\cos 2\varphi\sin\theta$	$-\frac{7G\beta_2\eta^2}{(Y_2-W_2\gamma^3)}(\gamma^7-1)\sin 2\varphi\sin\theta$
ω_{φ}^{d}	$\frac{15}{4}\frac{U_s}{W_1}\beta_1\eta^2(\gamma^5-1)\sin\theta$	$-\frac{7}{2}\frac{G\beta_2\eta^2}{(Y_2-W_2\gamma^3)}(\gamma^7-1)\sin 2\varphi\sin\theta\cos\theta$	$-\frac{7G\beta_2\eta^2}{(Y_2-W_2\gamma^3)}(\gamma^7-1)\cos 2\varphi\sin\theta\cos\theta$
ω_{θ}^{c}	0	$\frac{1}{2}\frac{GW_2\eta^{-3}}{(Y_2-W_2\gamma^3)}\left(7\frac{\gamma^7\eta^5}{W_2}-1\right)\cos 2\varphi\sin\theta$	$-\frac{GW_2\eta}{(Y_2-W_2\gamma^3)}\left(7\frac{\gamma^7\eta^5}{W_2}-1\right)\sin 2\varphi\sin\theta$
ω_{φ}^{c}	$\frac{3}{4}\frac{U_s}{W_1}\frac{\eta^{-1}}{r}(5\gamma^5\eta^3-W_1)\sin\theta$	$-\frac{1}{2}\frac{GW_2\eta^{-3}}{(Y_2-W_2\gamma^3)}\left(7\frac{\gamma^7\eta^5}{W_2}-1\right)\sin 2\varphi\sin\theta\cos\theta$	$-\frac{GW_2\eta}{(Y_2-W_2\gamma^3)}\left(7\frac{\gamma^7\eta^5}{W_2}-1\right)\cos 2\varphi\sin\theta\cos\theta$

Couette

$$\begin{aligned} r = a\Big[1 &+ \frac{3}{16}\,\frac{G a \beta_2 \mu^d}{\sigma(Y_2 - W_2\gamma^3)} \\ &\times \left(2\gamma^7 - \frac{2}{3}\,Y_2 + 2\,W_2 + 5\right)\sin 2\varphi \sin^2\theta\Big]. \end{aligned}$$

Hyperbolic

$$\begin{aligned} r = a\Big[1 &+ \frac{3}{8}\,\frac{G a \beta_2 \mu^d}{\sigma(Y_2 - W_2\gamma^3)} \\ &\times \left(2\,\gamma^7 - \frac{2}{3}\,Y_2 + 2\,W_2 + 5\right)\cos 2\varphi \sin^2\theta\Big]. \end{aligned}$$

Effective viscosity of two-phase multiparticle systems

Happel (3), and more extensively *Happel* and *Brenner* (10), have shown on the basis of energy dissipation considerations, and the spherical cell concept, that the effective viscosity of an ensemble of particles in slow viscous motion can be expressed by

$$\mu_{\mathrm{eff}} = \frac{E^c}{E^0}\,. \qquad [62]$$

Here the rate of energy dissipation per unit volume of the fluid, in the continuous phase, on a spherical surface of radius $b = a\gamma^{-1}$, in the absence of the dispersed phase, is

$$E^0 = \int_{S_b} \boldsymbol{ds}\cdot\boldsymbol{\tau}^0\cdot\boldsymbol{v}^0, \qquad [63]$$

and when the dispersed particles are present

$$E^c = \int_{S_b} \boldsymbol{ds}\cdot\boldsymbol{\tau}^c\cdot\boldsymbol{v}^c\,. \qquad [64]$$

Utilizing boundary conditions [8] to [10], and the expressions for velocity components, and for radial component of the stress force, we obtain

$$\begin{aligned} E^0 = \mu^c\, b \int_0^{2\pi}\!\!\int_0^{\pi} &\Big\{\sum_{n=1}^{\infty}\sum_{m=0}^{n}\left[\left(V_n^m \cos m\varphi + \hat V_n^m \sin m\varphi\right)\right. \\ &\times P_n^m(\cos\theta)\Big]\cdot\sum_{n=1}^{\infty}\sum_{m=0}^{n}\left[\left(L_n^m \cos m\varphi + \hat L_n^m \sin m\varphi\right)\right. \\ &\times P_n^m(\cos\theta)\Big]\Big\}\sin\theta\, d\theta\, d\varphi + \mu^c\, b \int_0^{2\pi}\!\!\int_0^{\pi}\sum_{n=1}^{\infty}\sum_{m=0}^{n} \\ &\times \frac{1}{(n+1)\,n}\left[\left(N_n^m \frac{d\cos m\varphi}{d\varphi} + \hat N_n^m \frac{d\sin m\varphi}{d\varphi}\right)\right. \\ &\times \frac{P_n^m(\cos\theta)}{\sin\theta} + \left(M_n^m \cos m\varphi + \hat M_n^m \sin m\,\varphi\right) \\ &\times \frac{dP_n^m(\cos\theta)}{d\theta}\Big]\sum_{n=1}^{\infty}\sum_{m=0}^{n}\Big[\left(Z_n^m \cos m\varphi + \hat Z_n^m \sin m\varphi\right) \\ &\times \frac{dP_n^m(\cos\theta)}{d\theta}\Big]\sin\theta\, d\theta\, d\varphi + \mu^c\, b\int_0^{2\pi}\!\!\int_0^{\pi}\sum_{n=1}^{\infty}\sum_{m=0}^{n} \\ &\times \frac{1}{n(n+1)}\left[\left(N_n^m \cos m\varphi + \hat N_n^m \sin m\,\varphi\right)\frac{dP_n^m(\cos\theta)}{d\theta}\right. \\ &+ \left(M_n^m \frac{d\cos m\varphi}{d\varphi} + \hat M_n^m \frac{d\sin\varphi}{d\varphi}\right)\frac{P_n^m(\cos\theta)}{\sin\theta}\Big] \\ &\times \sum_{n=1}^{\infty}\sum_{m=0}^{n}\left[\left(Z_n^m \frac{d\cos m\varphi}{d\varphi} + \hat Z_n^m \frac{d\sin m\varphi}{d\varphi}\right)\right. \\ &\times \frac{P_n^m(\cos\theta)}{\sin\theta}\Big]\sin\theta\, d\theta\, d\varphi. \end{aligned} \qquad [65]$$

where

$$\begin{aligned} V_n^m = {}& \frac{(n^2 - n - 3)}{n}\,\gamma^{-n-1}\,\alpha_n^m + 2(n-1)\gamma^{-n+1}\,\beta_n^m \\ &+ \frac{2(n^2 + 3n - 1)}{(n+1)}\,\gamma^n\,\alpha_{-n-1}^m - 2(n+2)\gamma^{n+2}\,\beta_{-n-1}^m \end{aligned} \qquad [66]$$

and

$$\begin{aligned} Z_n^m = {}& \frac{1}{n(n+1)}\left[(n+3)\gamma^{-n-1}\,\alpha_n^m + (n+1)\gamma^{-n-1}\,\beta_n^m\right. \\ &\left. - (n-2)\gamma^n\,\alpha_{-n-1}^m - n\gamma^{n+2}\,\beta_{-n-1}^m\right]. \end{aligned} \qquad [67]$$

An expression for E^c, similar to [65], is obtained if Y_n^m and $\hat Y_n^m$ are substituted for V_n^m and $\hat V_n^m$, respectively, and X_n^m and $\hat X_n^m$, for Z_n^m and $\hat Z_n^m$, respectively, where

$$\begin{aligned} Y_n^m = {}& 2n(n-1)\gamma^{-n+1}\,E_n^m + \frac{(n^2 - n - 3)}{(2n+3)}\,\gamma^{-n-1}\,D_n^m \\ &+ 2(n+1)(n+2)\gamma^{n+2}\,H_n^m + \frac{(n^2 + n - 1)}{(2n-1)}\,\gamma^n\,G_n^m \end{aligned} \qquad [68]$$

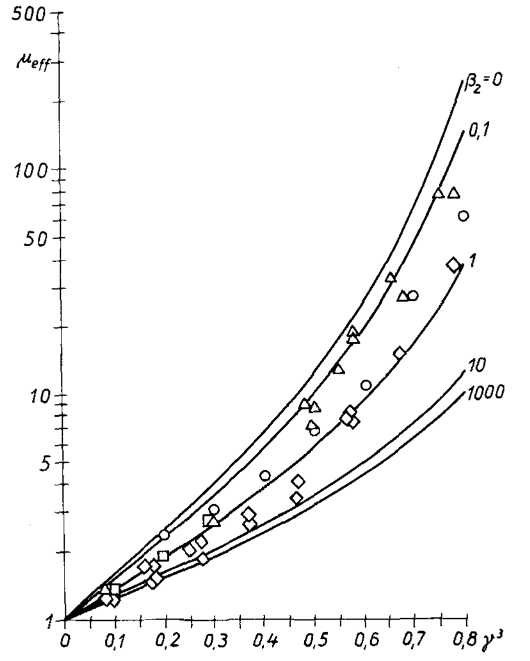

Fig. 1. Effective viscosity of emulsion. (Data: ○ = *Neogy* and *Ghosh* (18) (xylene-in-water and water-in-benzene emulsions); △ = *Sibree* (15) (limpid and viscous paraffin in water); ◇ = *Sherman* (17) (water-in-oil emulsion); □ = *Broughton* and *Windebank* (16) (model emulsion). Solid lines represent our model (Eq. 70).

and

$$X_n^m = \frac{(n+3)}{2(n+1)(2n+3)} \gamma^{-n-1} D_n^m + \gamma^{-n+1} E_n^m - \frac{(n-2)}{2n(2n-1)} \gamma^n G_n^m + \gamma^{n+2} H_n^m . \quad [69]$$

On the basis of the above expressions we find that for two-phase multiparticle systems, in a uniform imposed field, the effective viscosity of the ensemble $\mu_{\text{eff}} = 0$, whereas for both the *Couette* and the hyperbolic imposed fields

$$\mu_{\text{eff}} = 1 + 5 \cdot 5\gamma^3 \psi \quad [70]$$

where

$$\psi = \frac{4\gamma^7 + 10 - 84/11\gamma^2 + 4\beta_2(1-\gamma^7)}{10(1-\gamma^{10}) - 25\gamma^3(1-\gamma^4) + 10\beta_2(1-\gamma^3)(1-\gamma^7)} . \quad [71]$$

Discussion

The formulations which have been derived here reflect the effect of the volume concentration of the dispersed phase through the parameter γ, and of the presence of surfactant contaminations through the "interfacial retardation viscosity" $\tilde{\gamma}_n$. The latter does not have a unique value, but depends on the character of the imposed field, as shown by eq. [A 21]. Thus, when the imposed field is represented by spherical harmonics of several orders, we find here that there will be more than one "retardation viscosity".

a) Reduction of theory to specific solutions

The specific expressions derived from the general theory for the case of a uniform imposed field are identical with those previously derived by *Gal-Or* and *Waslo* (1) from different considerations. The expressions for *Couette* and hyperbolic imposed fields reduce in the limit $\gamma \to 0$ and $\beta_2 \to \infty$ to those of *Taylor* (11). The present results indicate clearly that contamination of the interface by surfactant impurities retards the circulatory motion within fluid particles and reduces their deformability. This effect is even more pronounced in concentrated systems (large γ value), as compared to infinitely diluted ones ($\gamma \to 0$).

b) Comparison with experiment

The representation of the behavior of two-phase multiparticle systems by "spheroid cell" models, even bearing in mind their statistical nature, has been open to criticism. It is, therefore, instructive to analyse the predictions of theories, based on these models, in relation to empirical data. *Yaron* and *Gal-Or* (12)[1]) have already demonstrated the satisfactory agreement between relative velocities of ensembles in uniform fields, predicted from the "free-surface spherical cell" model, and experimental values. In the present work we evaluate the realism of predictions of the cell model in the case of effective viscosities of both suspensions of solid particles and of liquid emulsions. It should be noted, that expressions [70] and [71] for coaxial cylinders rotational viscometry (*Couette* field) reduce to those of *Wacholder* and *Hetsroni* (4)[2]) for emulsions of absolutely pure systems ($\gamma_n = 0$) and of *Happel* (3) for a dispersion of solid particles ($\tilde{\gamma}_n \to \infty$). For the latter case the predicted effective viscosity as a function of volume concentration of the dispersed phase in the range $0 < \gamma^3 < 0.5$ was already compared with the experimental data by *Happel* and *Brenner* (10). In view of the familiar large scatter of experimental results in rotational viscosimetry, due to a variety of factors not all of which are directly accountable for by simple theory based on energy dissipation considerations, one may consider the extent of agreement to be at least fair[3]).

It is even more difficult to obtain reliable data for effective viscosity of liquid emulsions, since surfactant contamination by even minute, undetectable quantities of surfactant impurities, can substantially effect the measurements. In fig. 1 we compare some experimental results with theoretical curves derived from eq. [70]. It is shown that the theoretical lines and the empirical data both follow the same trend.

Apparently, a considerable amount of very careful viscometric measurements with controlled levels of contamination is yet necessary before one can definitely derive conclusions regarding the relative merits of cell models for predicting effective viscosities.

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[1]) In a most recent study, *Barnea* (22) has demonstrated, that our model gives the best agreement with experimental data for about one hundred different two-phase systems.

[2]) Their solution, however, erroneously contains a slightly different numerical coefficient as compared to our Eqn. [71].

[3]) q. v. also, a recent paper by *Sather* and *Lee* (21).

Summary

Previous analysis by *Happel* (3) of viscous flow in concentrated solid suspensions has been extended to include concentrated emulsions of slightly deformable fluid particles in the presence or absence of surfactant impurities.

General expressions were obtained for viscous flow in multi-particle systems when arbitrary shear fields are imposed. Specific relations were then derived for uniform, *Couette* and hyperbolic fields. The behavior is found to be strongly dependent upon particle concentration and surfactant concentration. The theoretical expressions obtained for effective viscosity of emulsions compare favorably with experimental data of *Neogy* and *Ghosh* (18), *Sibree* (15), *Sherman* (17), and *Broughton* and *Windebank* (16). These results support other studies on ensemble velocities [(10), (12), and in particular (22)], which strongly indicate the practical value and factual reliability of cell models in predicting the behavior of suspensions and emulsions.

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Appendix

Characteristic general coefficients of the flow fields in the dispersed and continuous phase of the ensemble are:

$$A_n^m = 2(2n+3)\left\{\frac{(n+1)}{4(2n+3)}D_n^m + \frac{(n-1)}{2}E_n^m - \frac{(n+1)}{4(2n-1)}G_n^m + \frac{(n+1)(n+2)}{2n}H_n^m\right\}. \quad [A1]$$

$$B_n^m = -\frac{1}{2(2n+3)}A_n^m \quad [A2]$$

$$C_n^m = (2n+1)\lambda C_1 N_n^m \quad [A3]$$

$$\begin{aligned} D_n^m = \frac{1}{\Delta_n}\frac{(n+1)^2}{2(2n-1)}&\left[(n-1)C_2\left\{M_n^m\left(\gamma^{n+2}-\gamma^n\right) - 2L_n^m\left[(n+2)n\gamma^{n+2} - (n-1)(n+1)\gamma^n\right]\right\}\right.\\ &+ nC_3\left\{M_n^m\left(\gamma^{n+2}-\gamma^{-n+1}\right) - 2L_n^m\left[(n+2)n\gamma^{n+2} - (n-1)(n+1)\gamma^{-n+1}\right]\right\}\\ &\left.+ n(n+2)C_4\left[M_n^m - 2(n-1)(n+1)L_n^m\right]\left(\gamma^{-n+1}-\gamma^n\right)\right]. \end{aligned} \quad [A4]$$

$$\begin{aligned} E_n^m = \frac{1}{\Delta_n}\cdot\frac{(n+1)^2}{4(2n+3)(2n-1)}&\left[C_5\left\{M_n^m\left(\gamma^n-\gamma^{n+2}\right) - 2L_n^m\left[(n-1)(n+1)\gamma^n - (n+2)n\gamma^{n+2}\right]\right\}\right.\\ &+ n(n+2)C_4\left\{M_n^m\left(\gamma^n-\gamma^{-n-1}\right) - 2L_n^m\left[(n-1)(n+1)\gamma^n - (n+2)n\gamma^{-n-1}\right]\right\}\\ &\left.+ nC_3\left[M_n^m - 2(n+2)nL_n^m\right]\left(\gamma^{-n-1}-\gamma^{n+2}\right)\right], \end{aligned} \quad [A5]$$

$$F_n^m = [(n-1) + \lambda(n+2)]C_1 N_n^m, \quad [A6]$$

$$\begin{aligned} G_n^m = \frac{1}{\Delta_n}\frac{n(n+1)}{2(2n+3)}&\left[C_5\left\{M_n^m\left(\gamma^{n+2}-\gamma^{-n+1}\right) - 2L_n^m\left[n(n+2)\gamma^{n+2} - (n-1)(n+1)\gamma^{-n+1}\right]\right\}\right.\\ &+ n(n+2)C_4\left\{M_n^m\left(\gamma^{-n-1}-\gamma^{-n+1}\right) - 2L_n^m\left[n(n+2)\gamma^{-n-1} - (n-1)(n+1)\gamma^{-n+1}\right]\right\}\\ &\left.+ (n-1)C_2\left[M_n^m - 2n(n+2)L_n^m\right]\left(\gamma^{-n-1}-\gamma^{n+2}\right)\right], \end{aligned} \quad [A7]$$

$$H_n^m = \frac{1}{\Delta_n}\frac{n(n+1)}{4(2n+3)(2n-1)}\left[(n-1)C_2\left\{M_n^m\left(\gamma^{-n-1}-\gamma^n\right)-2L_n^m\left[n(n+2)\gamma^{-n-1}-(n-1)(n+1)\gamma^n\right]\right\}\right.$$
$$+\,nC_3\left\{M_n^m\left(\gamma^{-n-1}-\gamma^{-n+1}\right)-2L_n^m\left[n(n+2)\gamma^{-n-1}-(n-1)(n+1)\gamma^{-n+1}\right]\right\}$$
$$\left.+\,C_5\left[M_n^m-2(n-1)(n+1)L_n^m\right]\left(\gamma^n-\gamma^{-n-1}\right)\right], \qquad [A8]$$

$$I_n^m = (n-1)(\lambda-1)C_1N_n^m, \qquad [A9]$$

where

$$\Delta_n = \frac{n(n+1)^2(2n+1)}{2(2n+3)(2n-1)}\left\{C_5\left(\gamma^3-\gamma^{2n+2}\right)+(n-1)C_2\left(\gamma^{2n+2}-\gamma^{-1}\right)+nC_3\left(\gamma^3-\gamma^{-2n}\right)\right.$$
$$\left.+\,n(n+2)C_4\left(\gamma^{-2n}-\gamma^{-1}\right)\right\}, \qquad [A10]$$

$$L_n^m = \gamma^{-n-1}\alpha_n^m+\gamma^{-n+1}\beta_n^m+\gamma^n\alpha_{-n-1}^m-\gamma^{n+2}\beta_{-n-1}^m, \qquad [A11]$$

$$N_n^m = (n-1)\gamma^{-n}\gamma_n^m-(n+2)\gamma^{n+2}\gamma_{-n-1}^m, \qquad [A12]$$

$$M_n^m = 2n(n+2)\gamma^{-n-1}\alpha_n^m+2(n-1)(n+1)\gamma^{-n+1}\beta_n^m+2(n-1)(n+1)\gamma^n\alpha_{-n-1}^m+2n(n+2)\gamma^{n+2}\beta_{-n-1}^m. \qquad [A13]$$

$$1/C_1 = (n-1)n(n+1)\left\{[(n-1)+\lambda(n+2)]\gamma^{-n}-(\lambda-1)(n+2)\gamma^{n+1}\right\}. \qquad [A14]$$

$$C_2 = \left[\frac{1}{2}-\frac{\beta_n(n+1)}{(2n+1)}\right], \qquad [A15]$$

$$C_3 = \left[\frac{1}{2}+\frac{\beta_n(n+1)(n-1)}{n(2n+1)}\right], \qquad [A16]$$

$$C_4 = \left[\frac{1}{2n}+\frac{\beta_n}{(2n+1)}\right], \qquad [A17]$$

$$C_5 = \left[\frac{(n+1)}{2}-\frac{\beta_n n(n+2)}{(2n+1)}\right], \qquad [A18]$$

$$\beta_n = \frac{\mu^c}{\mu^d+\tilde{\gamma}_n}, \qquad [A19]$$

$$\tilde{\gamma}_n = -\frac{n}{(2n+1)}\left(\frac{\partial\sigma}{\partial\Gamma}\right)_0\frac{(n+1)}{(n^2+n+\varepsilon)}\frac{a\Gamma_0}{D_i^s} = -\frac{n}{(2n+1)}K_n\left(\frac{\partial\sigma}{\partial\Gamma}\right)_0.$$

and

$$\lambda = \mu^c/\mu^d. \qquad [A21]$$

Note that $\tilde{\gamma}_n$ has dimensions of viscosity. It may be regarded as a sort of "interfacial retardation viscosity" factor and represents the effects due to adsorbed surfactant impurities.

A set of coefficients, identical to those given by expression [A1] to [A9] but bearing the supersign $\wedge$, can also be obtained.

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