# RHEOLOGICAL MODELS OF SUSPENSIONS

**Pierre M. Adler**

Laboratoire d'Aérothermique
Centre National de la Recherche
F-92190 Meudon, France

**Ali Nadim**

Department of Mathematics
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

**Howard Brenner**

Department of Chemical Engineering
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

## I. Introduction

Determination of the rheological and other dynamical properties of suspensions constitutes a field of fundamental importance to engineers, applied physicists, chemists, biologists, and industrial practitioners. From a practical standpoint, information on the macroscopic behavior of suspensions owes its importance to the many industrial processes that require the movement and processing of suspensions. Obvious examples occur in heavy industries such as the paint, pulp and paper, and concrete industries. Ferrofluids, for example, constitute a high technology suspension and possess novel properties useful in specialized industrial applications. Suspensions also occur naturally; examples are blood flow and the transportation of sediment in oceans and rivers. On the less pragmatic side, suspensions are of much theoretical interest. They provide an area of fundamental research, combining elements of fluid mechanics, statistical physics, and continuum theory, that focuses on the goal of describing the macroscopic properties of such



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"heterogeneous continua" starting with the exact laws that govern the interstitial fluid and particulate-phase properties at the microscale.

Until the early 1980's, studies of suspensions were largely confined to the engineering sciences. However, the interdisciplinary nature of suspension rheology has been recognized, and now, many significant contributions are being made by chemists and physicists as well as engineers and applied mathematicians. This chapter is intended to collect existing models of suspensions together within a unified framework that aims to bridge parochial disciplinary fragmentation of the subject.

Many review articles on suspension theories already exist. Some are listed chronologically in Table I together with a brief commentary attempting to capture the primary focus of each. Among other things, such a categorical listing provides a brief historical account of the growth of this technologically important field since the late 1960s. It also furnishes some insight into the more specialized subdivisions into which suspension theory has branched. The present review will focus mainly on theoretical results pertaining to the rheological properties of multiparticle suspensions. Single particle (i.e., dilute) results have been sufficiently reviewed in the past (cf. Table I for references) to render unnecessary detailed commentary here. Moreover, experimental results will not generally be reviewed, although some will be cited at appropriate junctures to provide comparison with existing theories.

Since this chapter is concerned mainly with reviewing existing models of suspensions, such complicating factors as nonNewtonian suspending fluids, inertia, and wall (i.e., noncontinuum) effects will be excluded for the most part. Neglect of inertial effects is tantamount to requiring the translational, rotary, and shear Reynolds numbers (based on particle size) to be small. In such circumstances, and for incompressible Newtonian suspending fluids, the microscale motion of the interstitial fluid is governed by the Stokes and continuity equations, each of which is linear. The latter property renders tractable the actual solutions of boundary-value problems and confers a convenient linear form upon important global quantities such as hydrodynamic forces and torques, as outlined in the next section. On the other hand (in the absence of Brownian motion), neglect of inertia may render indeterminate (Leal, 1980) the Stokes-flow problem thereby posed. Examples of this indeterminacy are provided by the lateral position of a neutrally buoyant sphere relative to the wall bounding a simple shear flow, or the terminal orientation of a non-spherical particle sedimenting in a quiescent fluid. Such indeterminacy has interesting implications regarding the often assumed ergodicity of purely mechanical multiphase transport processes. As a rule, the absence of inertia favors nonergodic states, whereas inclusion of inertial, nonNewtonian, and/or Brownian effects removes the configurational indeterminacy of the Stokes equations (Leal, 1979, 1980).

TABLE I

MAJOR REVIEWS OF SUSPENSION THEORIES

| Author | Content |
|---|---|
| Happel and Brenner (1965) | A theoretical overview; a comprehensive review of the literature prior to 1965. |
| Goldsmith and Mason 1967) | An account of experimental observations. |
| Brenner (1970) | General definitions and relations for the rheological properties of two-phase systems, mainly dilute. |
| Cox and Mason (1971) | Motions of single particles. |
| Brenner (1972a) | Suspension rheology; rigid and deformable particles. |
| Brenner (1972b) | Particle dynamics; wall effects; inertial effects; inhomogeneous shear fields; Brownian motion. |
| Sather and Lee (1972) | A statistical approach. |
| Batchelor (1974) | General properties of random two-phase materials; analogies; bounds, dilute suspensions at order $\phi$ and $\phi^2$. |
| Brenner (1974) | An exhaustive account of the rheology of dilute suspensions of axisymmetric Brownian particles. |
| Jinescu (1974) | Classification of the rheological behavior of suspensions. |
| Batchelor (1976a) | A review of consequences of various forces acting on suspensions; dilute suspensions at order $\phi$ and $\phi^2$. |
| Jeffrey and Acrivos (1976) | A discussion of major experimental and theoretical works. |
| Mewis and Spaull (1976) | Rheological behavior; main forces involved; structure. |
| Mason (1977) | An account of the work of Mason and co-workers. |
| Saville (1977) | Movement of ionic solutions near charged interfaces. |
| Buyevich and Shchelchkova (1978) | A statistical approach; phase averages. |
| Leal (1979) | NonNewtonian suspending fluids; cumulative effects of weak and strong viscoelasticity. |
| Brunn (1980) | NonNewtonian suspending fluids; their influence on the motion of an isolated particle and on particle–particle and particle–wall interactions. |
| Herczyński and Pieńkowska (1980) | A statistical approach; macroscopic equations; hierarchy closure. |
| Leal (1980) | The indeterminate character of some Stokes flow problems; influence of a nonNewtonian suspending fluid, inertia and deformability. |
| Mewis (1980) | An account of rheological behavior; flocculated suspensions. |
| Russel (1980) | Effects of colloidal forces (i.e. van der Waals, electrostatic, and Brownian forces). |
| Davis and Acrivos (1985) | Sedimentation in monodisperse and polydisperse suspensions; effect of wall inclination. |
| Feuillebois (1988) | Particle–particle and particle–wall interactions; inertial effects; unsteadiness. |
| Metzner (1985) | Suspensions in polymeric liquids. |
| Barnes *et al.*, (1987) | Applications of computer simulations to dense suspension rheology. |
| Bird *et al.*, (1987) | Suspensions of macromolecules from a statistical mechanical viewpoint. |
| Brady and Bossis (1988) | Molecular-dynamics-like simulation of suspensions ("Stokesian dynamics") |

This chapter will focus on infinitely-extended suspensions in which potential complications introduced by the presence of walls are avoided. The only wall-effect case that can be treated with relative ease is the interaction of a sphere with a plane wall (Goldman *et al.*, 1967a,b). The presence of walls can lead to relevant suspension rheological effects (Tözeren and Skalak, 1977; Brunn, 1981), which result from the existence of particle depeletion boundary layers (Cox and Brenner, 1971) in the proximity of the walls arising from the finite size of the suspended spheres. Going beyond the dilute and semidilute regions considered by the authors just mentioned is the ad hoc percolation approach, in which an infinite cluster—assumed to occur above some threshold particle concentration—necessarily interacts with the walls (cf. Section VI).

Other complicating effects arise from the presence of gravity, interparticle forces, and Brownian motion. Gravity (or some equivalent external force field) constitutes the driving force for sedimentation processes. Interparticle forces such as double-layer forces, important when the suspended particles are both small and charged (and the suspending fluid is an electrolyte), as well as London-van der Waals attractive forces, also important for small particles, have attracted the attention of colloid scientists for many years. Saville (1977) and Russel (1980) review many aspects of such colloidal forces in the context of suspensions. The influence of a macroscopic electric field on conducting particles in suspension may also be important. [See, e.g., Arp and Mason (1977a), and Adler (1981b) for two-sphere interactions.] However, such effects will be excluded from this chapter; a discussion of aggregable suspensions, which requires consideration of interparticle forces, will also be omitted, but since the latter field has important fundamental and practical prospects, a few contributions will be cited. Adler and Mills (1979) and Adler (1979) analyzed the rupture by hydrodynamic forces of particulate aggregates undergoing both simple shear and sedimentation. Subsequently, this topic was extended to fractal flocs by Sonntag and Russel (1986). van de Ven and Hunter (1979) introduced an elastic floc model that displayed general agreement with oscillating flow experiments, and van Diemen and Stein (1983) conducted experiments with aqueous quartz dispersions.

Brownian motion must be taken into account for suspensions of small (submicron-sized) particles. By their very nature, such stochastic Brownian forces favor the ergodicity of any configurational state. Although no completely general framework for the inclusion of Brownian motion will be presented here, its effects will be incorporated within specific contexts. Especially relevant, in the present rheological context, is the recent review by Felderhof (1988) of the contribution of Brownian motion to the viscosity of suspensions of spherical particles.

This chapter is organized as follows. Section II provides a general introduction to the theoretical models. Starting with the equations of motion,

valid locally, the grand-resistance matrix formulation of this multiparticle system is introduced. Various specific solutions of the many-body problem in low Reynolds-number hydrodynamics are discussed, followed by a statistical formulation of this multiparticle system. Empirical and so-called cell models are discussed in Section III. Historically, cell models were among the first to be employed to account for particle–particle hydrodynamic interactions. They have since proven valuable for correlation purposes and order-of-magnitude phenomenological coefficient estimates, though they lack a rational geometric basis. Section IV addresses dilute suspensions in which the particulate volumetric fraction $\phi$ is assumed sufficiently small such that only one-, or at most, two-body particle interactions with the fluid are important. Statistical models of suspensions are reviewed in Section V. Formal expansions are first described together with a number of proposed closure schemes for the resulting hierarchy of equations. Monte Carlo calculations, both with and without hydrodynamic interactions among particles, are briefly surveyed.

Section VI outlines percolation-theory approaches to the modeling of suspensions. Following a general introduction to percolation concepts, some theoretical and experimental developments are described. Above some threshold concentration, an infinite cluster of particles forms as a result of the nonzero time interval over which adjacent particles sensibly interact hydrodynamically. Section VII reviews contributions to the rheology of ordered models of suspensions. When a single particle is contained within the unit cell of a spatially periodic suspension, the kinematics of the flow are known a priori, at which point the dynamical problem can be solved completely. Novel concepts such as maximum kinematic concentration, self-reproducibility of the lattice in time, and time-averaged rheological properties are discussed. Finally, four "current research" areas are reviewed in Section VIII. The first, Stokesian dynamics, consists of a molecular-dynamics-type simulation technique applied to suspensions, highlighting hydrodynamic interactions among the suspended particles. The second is the application of generalized Taylor dispersion theory to the analysis of momentum transport processes in suspensions. (Included in this category is a discussion of the significant experimental contributions of Mondy, Graham and co-workers to the falling-ball viscometry of suspensions.) The third area addresses suspensions possessing fractal structure, which are important for concentrated or heterogeneous suspensions. Lastly, some novel aspects of magnetic fluid phenomena are discussed.

## Notation and Scope

To facilitate references to mathematical equations appearing in the original literature, we have in (almost) all cases retained the author's original notation

in preparing our review rather than attempting a premature standardization. While this results in minor notational inconsistencies in the text [e.g., the angular velocity of a rigid rotating particle is represented by $\omega$ in Eq. (2.4) but by $\boldsymbol{\Omega}$ in Eq. (7.11)], we believe any momentary confusion resulting from our convention will be more than offset by ease of access to the author's original equations.

The scope of this chapter is admittedly subjective, reflecting to a large extent the current individual and collective interests of its authors. Accordingly, no attempt is made to cover *all* technologically and scientifically important aspects of suspension rheology. For instance, our focus is geared more towards suspensions in general than towards the specific properties of, say, suspensions of colloidal and molecular particulates. As such, although some discussion of colloidal forces, Brownian motion, and "flexible" bodies appears, our review does not, in any sense, provide a comprehensive survey of so-called "colloidal" suspensions. The interested reader will find here, *inter alia*, an extended overview of spatially periodic and fractal models of suspensions as well as a description of momentum tracer schemes for probing suspension rheological properties—a new unsteady-state scheme wholly different from classical rheometric methods. In a periodical series of books bearing the name "*Advances in...*," such subjective choices of topics is both inevitable and, we hope, desirable.

## II. General Remarks

This section furnishes a brief overview of the general formulation of the hydrodynamics of suspensions. Basic kinematical and dynamical microscale equations are presented, and their main attributes are described. Solutions of the many-body problem in low Reynolds-number flows are then briefly exposed. Finally, the microscale equations are embedded in a statistical framework, and relevant volume and surface averages are defined, which is a prerequisite to describing the macroscale properties of the suspension.

### A. Basic Equations and Properties

Consider an unbounded, incompressible, Newtonian fluid undergoing a homogeneous shear flow characterized by the position-independent velocity gradient dyadic $\mathbf{G}$, which can be decomposed into symmetric and antisymmetric contributions $\mathbf{S}$ and $\ddot{\mathrm{A}}$, respectively, as

$$\mathbf{G} = \mathbf{S} + \ddot{\mathrm{A}}. \tag{2.1}$$

Let $\mu_0$ denote the fluid viscosity. Consider $N$ suspended particles, not necessarily identical, enumerated by the index $i = 1, 2, \ldots, N$. At each instant of time, the spatial and orientational geometric configuration of the particles, each assumed rigid, is completely determined upon specification of $3N$ independent spatial, scalar coordinates of designated locator points affixed to each particle, and $3N$ orientational coordinates (e.g., the three Eulerian angles of each of the $N$ particles) specifying their orientations. Allowing the 3-vectors $\mathbf{x}_i$ and (symbolically) $\mathbf{e}_i$ to denote the respective spatial and orientational coordinates of particle $i$, one can collectively denote the configurational coordinates of all the particles as $(\mathbf{x}^N, \mathbf{e}^N)$. The values of the spatial and orientational variables $\mathbf{x}^N$ and $\mathbf{e}^N$ together define a point in a $6N$-dimensional space, the phase space of the particulate phase, symbolized by $\Gamma_N$ (Hansen and McDonald, 1976).

When all relevant Reynolds numbers are sufficiently small to permit neglect of inertial effects, the interstitial fluid velocity and pressure fields $\mathbf{v}$ and $p$, respectively, satisfy the quasistatic Stokes and continuity equations,

$$\mu_0 \nabla^2 \mathbf{v} = \nabla p, \tag{2.2}$$

$$\nabla \cdot \mathbf{v} = 0. \tag{2.3}$$

Denote by $0_i$ the locator point of $i$, and denote by $\mathbf{r}_i$ a position vector drawn relative to $0_i$. Suppose $0_i$ to move with velocity $\mathbf{U}_i$ relative to a space-fixed coordinate system, and let the particle possess angular velocity $\boldsymbol{\omega}_i \equiv d\mathbf{e}_i/dt$ relative to the latter system. The no-slip condition on the surface $s_i$ of particle $i$ then takes the form

$$\mathbf{v} = \mathbf{U}_i + \boldsymbol{\omega}_i \times \mathbf{r}_i \quad \text{on } s_i \qquad (i = 1, \ldots, N). \tag{2.4}$$

Equations (2.2) and (2.3) are to be solved subject to Eq. (2.4), together with a condition imposed on the "average" velocity field (discussed in the following paragraphs) in order to obtain the fluid velocity and pressure fields. Furthermore, the translational and angular particle velocities $\mathbf{U}_i$ and $\boldsymbol{\omega}_i$ appearing in Eq. (2.4) are usually not specified a priori; more often, it is the external forces and torques acting on the particles that are assumed known. In such circumstances, force- and torque-free conditions imposed on the particles (consistent with neglect of particle inertia) are employed to calculate the velocities $\mathbf{U}_i$ and $\boldsymbol{\omega}_i$.

When $N$ is finite, although nevertheless possibly large, the particles are necessarily confined externally within a finite volume of the infinitely extended fluid. The velocity field must then asymptotically approach, far from the outermost particles, the undisturbed velocity field corresponding to $\mathbf{G}$; explicitly,

$$\mathbf{v} \to \mathbf{v}_\infty, \tag{2.5a}$$

in which

$$\mathbf{v}_\infty = \mathbf{U}_0 + \boldsymbol{\omega}_f \times \mathbf{r}_0 + \mathbf{S} \cdot \mathbf{r}_0, \tag{2.5b}$$

with $\mathbf{U}_0$ the translational velocity vector of the undisturbed fluid at a conveniently chosen reference point 0, $\mathbf{r}_0$ the position vector relative to 0, and $\boldsymbol{\omega}_f = -\frac{1}{2}\ddot{\boldsymbol{\varepsilon}}:\ddot{\boldsymbol{\Lambda}} \equiv \frac{1}{2}\nabla \times \mathbf{v}_\infty$, which is half the undisturbed vorticity vector ($\ddot{\boldsymbol{\varepsilon}} \equiv \varepsilon_{ijk}$, the unit isotropic triadic).

When $N$ is infinite, so that suspended particles are dispersed throughout the entire fluid domain, condition (2.5) is replaced by an equivalent one that prescribes the "average" fields $\mathbf{U}_0$ and $\mathbf{G}$. These are explicitly given for spatially periodic suspensions in Section VII. [See also the paragraph following Eq. (2.28).]

The detailed solution of Eqs. (2.2) and (2.3), subject to the given boundary and/or mean-field conditions, represents a formidable problem and has been solved only for a small number $N$ of particles. However, making use of the linear character of the governing equations, much can nonetheless be formally concluded regarding the functional dependence of the solution. In such context, we consider the formalism of Brenner and O'Neill (1972) in the following paragraph, albeit with minor modifications.

The hydrodynamic force $\mathbf{F}_i$ and torque $\mathbf{T}_i$ (about $0_i$) exerted by the fluid on particle $i$ are given respectively by the expressions

$$\mathbf{F}_i = \int_{s_i} d\mathbf{s} \cdot \mathbf{P}, \tag{2.6a}$$

$$\mathbf{T}_i = \int_{s_i} \mathbf{r}_i \times (d\mathbf{s} \cdot \mathbf{P}), \tag{2.6b}$$

in which $d\mathbf{s}$ is the outwardly-directed vector surface-element on the particle surface $s_i$ pointing into the fluid, and

$$\mathbf{P} = -\mathbf{I}p + \mu_0(\nabla\mathbf{v} + \nabla\mathbf{v}^\dagger) \tag{2.7}$$

is the stress tensor for the Newtonian fluid.

The particle stress $\mathbf{A}$, defined as the contribution to the bulk stress arising from the presence of the suspended particles in the fluid (Batchelor, 1970), possesses the symmetric and traceless deviatoric form

$$\mathbf{A} = \frac{1}{V}\sum_{i=1}^{N} \ddot{\mathscr{S}}_i, \tag{2.8a}$$

where

$$\ddot{\mathscr{S}}_i = \tfrac{1}{2}\int_{s_i} [d\mathbf{s} \cdot \mathbf{P}\mathbf{r}_i + \mathbf{r}_i d\mathbf{s} \cdot \mathbf{P} - \tfrac{2}{3}\mathbf{I}(d\mathbf{s} \cdot \mathbf{P} \cdot \mathbf{r}_i)]. \tag{2.8b}$$

Owing to the underlying linearity of the problem (including the assumed rigidity of the particles), the forces, torques, and particle stress are each necessarily linear functions of the kinematical quantities $\mathbf{U}_i - \mathbf{u}_i$, $\boldsymbol{\omega}_i - \boldsymbol{\omega}_f$ and $\mathbf{S}$ (where $\mathbf{u}_i$ denotes the velocity of the undisturbed flow $\mathbf{v}_\infty$ existing at point $0_i$ in the absence of particles). These linear relations may be written as the partitioned matrix relation

$$\begin{bmatrix} \mathbf{F}^N \\ \mathbf{T}^N \\ \mathbf{A} \end{bmatrix} = \mu_0 \mathbf{R}(\mathbf{x}^N, \mathbf{e}^N) \cdot \begin{bmatrix} \mathbf{U}^N - \mathbf{u}^N \\ \boldsymbol{\omega}^N - \boldsymbol{\omega}_f^N \\ \mathbf{S} \end{bmatrix}. \tag{2.9}$$

Notation similar to that introduced previously for $(\mathbf{x}^N, \mathbf{e}^N)$ has been used to collectively denote the forces $\mathbf{F}^N$, torques $\mathbf{T}^N$, velocities $\mathbf{U}^N$, etc., of all the $N$ particles. Relation (2.9) is similar to one of Brenner and O'Neill (1972) together with Hinch's (1972) adjunction of $\mathbf{A}$.

As a consequence of Lorentz' reciprocal theorem (see Happel and Brenner, 1965) the grand resistance matrix $\mathbf{R}(\mathbf{x}^N, \mathbf{e}^N)$ possesses many internal symmetries, greatly reducing the number of its independent elements. Another important feature of $\mathbf{R}$ is that it depends only on the instantaneous configuration $(\mathbf{x}^N, \mathbf{e}^N)$ of the particulate phase.

Denote by $\mathbf{F}_{i,\,\mathrm{ext}}$ and $\mathbf{T}_{i,\,\mathrm{ext}}$ the external force and torque (about $0_i$) acting on particle $i$. Neglect of particle inertia then leads to the equation

$$\begin{bmatrix} \mathbf{F}^N \\ \mathbf{T}^N \end{bmatrix} + \begin{bmatrix} \mathbf{F}_{\mathrm{ext}}^N \\ \mathbf{T}_{\mathrm{ext}}^N \end{bmatrix} = \mathbf{0}, \tag{2.10}$$

governing the instantaneous particle dynamics. Substitution of Eq. (2.9) into Eq. (2.10) yields a first-order system of differential equations governing the trajectory of the point $(\mathbf{x}^N, \mathbf{e}^N)$ in the phase space $\Gamma_N$. Consider, for instance, a suspension of $N$ force- and couple-free spheres. When the latter suspension is sheared, Eqs. (2.9) and (2.10) yield an equation of the structural form

$$d\mathbf{x}^N/dt = \mathbf{f}(\mathbf{x}^N), \tag{2.11}$$

with $\mathbf{f}$ as a nonlinear function of the particle positions (functionally dependent also on $\mathbf{S}$); its form can be deduced from the grand resistance matrix $\mathbf{R}$.

The structure of the system in Eq. (2.11) is formally very simple, although apart from the kinematic reversibility of the individual particle motions, which is a consequence of the time invariance of the quasistatic Stokes and continuity equations (Slattery, 1964), very little else can be said explicitly. Equation (2.11) would appear to pose a fruitful future study within the more general framework of dynamical systems (Collet and Eckmann, 1980) whose temporal evolution is governed by a system of equations identical in structure

to Eq. (2.11). Although this interesting new field is still in its infancy (Aref and Balachandar, 1986), it appears that widely differing behaviors (i.e., 'chaos') may be exhibited by otherwise identical systems that differ only insignificantly in their initial configurations.

In this context, consider, for example, several existing results pertaining to the temporal behavior of multiparticle systems. Two-sphere systems are the only ones completely analyzed to date. In simple shear, the relative trajectory of two spheres may be either open or closed, depending on their initial separation (Batchelor and Green, 1972a); thus, the corresponding temporal behavior is either aperiodic or periodic. In elongational flows, the relative trajectories are always open. Other examples are provided by sedimenting spheres. Two identical spheres settle at the same velocity (Goldman *et al.*, 1966), thus maintaining their original configuration, whereas two unequal spheres settle at different speeds. Three or more equal, vertically-aligned spheres exhibit the phenomenon of "critical initial spacing" (Leichtberg *et al.*, 1976). Depending on the initial spacing, the gap between the two leading spheres in the chain may asymptote in time, either towards zero or to some finite separation distance. Ganatos *et al.* (1978) have further examined three-sphere configurations.

## B. Solutions of the Many-Body Problem in Low Reynolds-Number Hydrodynamics

Having exposed the general fluid-mechanical and particulate equations, attention is now directed towards reviewing the many-body problem as governed by Eqs. (2.2)–(2.5). Unless otherwise stated, our focus is exclusively on rigid-sphere suspensions. Historically, the earliest study is that of G. G. Stokes (1851), who calculated the drag force on a sphere translating through an otherwise quiescent viscous fluid. For the sake of completeness, and as one of the few analytical results that will be cited here, we also recall that the velocity and pressure fields about a sphere of radius $a$ suspended in a sheared fluid with the velocity at infinity given by Eq. (2.5) are, respectively

$$\begin{aligned}\mathbf{v} = \mathbf{U}_0 &+ (\mathbf{U} - \mathbf{U}_0) \cdot \left[\frac{3}{4}\frac{a}{r}(\mathbf{I} + \hat{\mathbf{r}}\hat{\mathbf{r}}) + \frac{1}{4}\left(\frac{a}{r}\right)^3(\mathbf{I} - 3\hat{\mathbf{r}}\hat{\mathbf{r}})\right] \\ &+ \boldsymbol{\omega}_f \times \mathbf{r} + \left(\frac{a}{r}\right)^3(\boldsymbol{\omega} - \boldsymbol{\omega}_f) \times \mathbf{r} \\ &+ \mathbf{S} \cdot \mathbf{r}\left[1 - \left(\frac{a}{r}\right)^5\right] - \frac{5}{2}\left(\frac{a}{r}\right)^3\left[1 - \left(\frac{a}{r}\right)^2\right] r\mathbf{S}:\hat{\mathbf{r}}\hat{\mathbf{r}}\hat{\mathbf{r}} \qquad (2.12a)\end{aligned}$$

and

$$p - p_\infty = \frac{3\mu_0 a}{2r^2}\hat{\mathbf{r}}\cdot(\mathbf{U}-\mathbf{U}_0) - 5\mu_0\left(\frac{a}{r}\right)^3 \mathbf{S}:\hat{\mathbf{r}}\hat{\mathbf{r}}. \tag{2.12b}$$

Here, the sphere center is instantaneously situated at point 0; the sphere center translates with velocity U, while it rotates with angular velocity $\omega$; r is measured relative to 0; its magnitude $|\mathbf{r}|$ is denoted by $r$. Moreover, $\hat{\mathbf{r}} = \mathbf{r}/r$ is a unit radial vector. The latter solution is derivable in a variety of ways; e.g., from Lamb's (1932) general solution (Brenner, 1970). [Equation (2.12) represents a superposition (Brenner, 1958) of three physically distinct solutions, corresponding, respectively, to (i) translation of a sphere through a fluid at rest at infinity; (ii) rotation of a sphere in a fluid at rest at infinity; (iii) motion of a neutrally buoyant sphere suspended in a linear shear flow. The latter was first obtained by Einstein (1906, 1911; cf. Einstein, 1956) in connection with his classic calculation of the viscosity of a dilute suspension of spheres, which formed part of his 1905 Ph.D. thesis.]

Passing beyond the isolated sphere case, two spheres pose the simplest "interaction" problem arising in low Reynolds-number flows. Studies of the these originated years ago (Stimson and Jeffery, 1926; Manley and Mason, 1952), although complete and systematic results for all separation distances and relative sphere sizes were obtained only much later. For equal spheres, these results were given by Batchelor and Green (1972a), Arp and Mason (1977b), Kim and Mifflin (1985), Yoon and Kim (1987), and Cichocki *et al.* (1988). Results for unequal spheres were tabulated by Adler (1981a) and, in a more complete form, by Jeffrey and Onishi (1984). Such two-sphere interaction calculations are important not only because they are directly relevant to dilute suspension analyses, but their existence also provides a criterion of the accuracy of numerical or computational schemes for the more general $N$-particle case.

In a series of papers, Felderhof has devised various methods to solve anew one- and two-sphere Stokes flow problems. First, the classical "method of reflections" (Happel and Brenner, 1965) was modified and employed to examine two-sphere interactions with mixed slip-stick boundary conditions (Felderhof, 1977; Renland *et al.*, 1978). A novel feature of the latter approach is the use of "superposition" of forces rather than of velocities; as such, the mobility matrix (rather than its inverse, the grand resistance matrix) was derived. Calculations based thereon proved easier, and convergence was more rapid; explicit results through terms of $0(\rho^{-7})$ were derived, where $\rho$ is the nondimensional center-to-center distance between spheres. In a related work, Schmitz and Felderhof (1978) solved Stokes equations around a sphere by the so-called Cartesian ansatz method, avoiding the use of spherical coordinates. They also devised a second method (Schmitz and Felderhof, 1982a), in which

this Cartesian problem is formulated as an expansion of scattered waves. Through use of the same scheme, as previously mentioned, this method was extended to include two-sphere interactions (Schmitz and Felderhof, 1982b,c) and obtained terms of $0(\rho^{-12})$. Efforts are underway (Kim, 1986) to extend these calculations to the interaction of ellipsoidal particles.

None of these two-body methods has yet been extended to the many-body problem. A contribution by Kynch (1959) applied a reflection scheme to the three-body problem, although explicit details were not provided.

A suspension composed of an infinitely-extended regular array of identical spheres was examined by Kapral and Bedeaux (1978) as an application of the scheme developed by Bedeaux *et al.* (1977) [and independently by Zuzovsky *et al.* (1983)] with similar results. This problem will be encountered again in Section VII. In a certain sense, the multiparticle problem is thereby reduced to a single particle problem (within a unit cell-boundary), since all of the particles exist in identical states. That is, each is kinematically and dynamically indistinguishable from the others.

Mazur (1982) and Mazur and van Saarloos (1982) developed the so-called method of "induced forces" in order to examine hydrodynamic interactions among many spheres. These forces are expanded in irreducible induced-force multipoles and in a hierarchy of equations obtained for these multipoles when the boundary conditions on each sphere were employed. Mobilities are subsequently derived as a power series-expansion in $\rho^{-1}$. In principle, calculations may be performed to any order, having been carried out by the above authors through terms of $0(\rho^{-7})$ for a suspension in a quiescent fluid. To that order, hydrodynamic interactions between two, three, and four spheres all contribute to the final result. This work is reviewed by Mazur (1987).

A numerical solution technique was developed by Leichtberg *et al.* (1976) and Ganatos *et al.* (1978) to investigate the coaxial settling of three or more spheres, as well as the motion of identical spheres in a horizontal plane; the fluid is assumed quiescent in all cases. A collocation technique was used in the latter problem to determine the coefficients appearing in the expansion of the general solution of Stokes equations by demanding the boundary conditions to be satisfied at a finite number of points lying on the sphere surfaces. The choice of these points is a delicate problem. No systematic extension of this method has yet been made. A recent analysis (Hassonjee *et al.*, 1988) extends the original Ganatos *et al.* (1978) treatment to asymmetric clusters of spherical particles.

In conclusion, much remains to be done in the field of many-body hydrodynamic interactions. Existing results need to be embedded into a unified and systematic framework and extended from quiescent to sheared suspensions. The methods of Mazur and co-workers can be used to derive far-

field approximations, numerical techniques (e.g., collocation) can supply the middle range, and "lubrication" approximations (see Section VII) can furnish limiting asymptotic results for two or more spheres in close proximity to one another.

## C. Statistical Formulation

This subsection attempts a statistical description of the multiparticle problem. Such developments closely follow those employed in the classical theory of liquids (Hansen and McDonald, 1976), together with the contribution of Batchelor (1970), as well as certain technical elements reviewed by Herczyński and Pieńkowska (1980).

Consider a statistically homogeneous dispersion of $N$ particles contained in a volume $V$. Although generalization to the case of dissimiliar particles is not difficult, the particles are assumed for simplicity to be identical spheres (radii $a$). For any given experimental realization, the configuration of the latter particulate system at time $t$ is completely determined by the values of the $3N$ coordinates $\mathbf{x}^N$ representing the particle locator points (chosen to lie at the sphere centers so as to preclude individual particle orientational issues) of the $N$ spheres. Note that the dynamical variables (i.e., momenta) need not be included in the phase space since inertia has been systematically neglected.

Suppose the particles are distinguished by numbering them from 1 to $N$; denote by

$$F^{(N)}(\mathbf{x}^N, t)\, d\mathbf{x}^N \tag{2.13}$$

the probability that at time $t$ in a given realization (the locator point for) particle 1 lies within the interval $(\mathbf{x}_1, \mathbf{x}_1 + d\mathbf{x}_1)$ while, simultaneously, particle 2 is located within the region $(\mathbf{x}_2, \mathbf{x}_2 + d\mathbf{x}_2)$, etc. In Eq. (2.13),

$$d\mathbf{x}^N = \prod_{i=1}^{N} d\mathbf{x}_i$$

constitutes the phase–space volume element centered at $\mathbf{x}^N$. The particle-specific probability density function $F^{(N)}$ represents the limiting value of the ratio of the number of times that such a configuration obtains to the total number of realizations in the limit as the latter number approaches infinity.

It is important to recognize that major theoretical difficulties arise in the limiting process $N \to \infty$. This highlights the important differences existing between the cases of finite (although very large) $N$ and infinite $N$. These issues are addressed in Section VII,D.

A series of lower-order particle-specific probability densities $F^{(n)}$ $(n \leq N)$ may be defined as

$$F^{(n)}(\mathbf{x}^n, t) = \int \cdots \int F^{(N)}(\mathbf{x}^N, t)\, d\mathbf{x}_{n+1}\, d\mathbf{x}_{n+2}, \ldots, d\mathbf{x}_N, \tag{2.14}$$

possessing a similar interpretation to that of Eq. (2.13) for the first $n$ particles, irrespective of where the remaining $N-n$ particles may be located. Probability densities in Eqs. (2.13) and (2.14) are to be regarded as normalized in the sense that

$$\int F^{(N)}(\mathbf{x}^N, t)\, d\mathbf{x}^N = 1. \tag{2.15}$$

Requisite integrations appearing in Eqs. (2.14) and (2.15) are to be performed over the entire volume available to the particles for each $d\mathbf{x}_i$. Given the indistinguishability of the (identical) particles, it is often more convenient to define the (generic) probability density $P^N(\mathbf{x}^N, t)$ that *any* particle is located in $(\mathbf{x}_1, \mathbf{x}_1 + d\mathbf{x}_1)$, any other in $(\mathbf{x}_2, \mathbf{x}_2 + d\mathbf{x}_2)$, etc. It is easily verified that

$$P^{(N)}(\mathbf{x}^N, t) = N!\, F^{(N)}(\mathbf{x}^N, t). \tag{2.16}$$

Similarly, the lower-order generic density $P^{(n)}(\mathbf{x}^n, t)$ can be demonstrated to be related to its particle-specific counterpart by the expression

$$P^{(n)}(\mathbf{x}^n, t) = \frac{N!}{(N-n)!} F^{(n)}(\mathbf{x}^n, t), \tag{2.17}$$

which reduces to Eq. (2.16) when $n = N$. Note the normalization requirement imposed on the latter generic density requires that

$$\int \cdots \int P^{(n)}(\mathbf{x}^n, t)\, d\mathbf{x}_1, \ldots, d\mathbf{x}_n = N!/(N-n)!, \tag{2.18}$$

in which the numerical factor must be accounted for in calculating the expected values of any configuration-dependent quantity.

Of particular importance in most theories are the first two densities $P^{(1)}$ and $P^{(2)}$. The first, $P^{(1)}(\mathbf{x}, t)$ represents the probability density for finding a particle at $\mathbf{x}$ at time $t$; it is equal to the average volumetric particulate number density $n$:

$$P^{(1)}(\mathbf{x}, t) = n. \tag{2.19}$$

For a stationary homogeneous system, $n$ is a constant given by $N/V$. (Note that $n$ here is not a counting index.) $P^{(2)}(\mathbf{x}_1, \mathbf{x}_2, t)$ represents the probability density for finding two particles at $\mathbf{x}_1$ and $\mathbf{x}_2$ simultaneously. For a homogeneous system it depends on the difference $\mathbf{x}_1 - \mathbf{x}_2$ rather than on $\mathbf{x}_1$ and $\mathbf{x}_2$

individually:

$$P^{(2)} \equiv P^{(2)}(\mathbf{x}_1 - \mathbf{x}_2, t). \tag{2.20}$$

Also of importance is the conditional probability density $F_c^{(N-1)}$ for finding particles 2–$N$, respectively, at $\mathbf{x}_2$–$\mathbf{x}_N$, given that particle 1 is located at $\mathbf{x}_1$. The relation

$$F^{(N)}(\mathbf{x}_1, \ldots, \mathbf{x}_N, t) = F^{(1)}(\mathbf{x}_1, t) F_c^{(N-1)}(\mathbf{x}_2, \ldots, \mathbf{x}_N, t \,|\, \mathbf{x}_1), \tag{2.21}$$

governing the latter conditional probability, may be written for its generic counterpart $P_c^{(N-1)}$ as

$$P^{(N)}(\mathbf{x}_1, \ldots, \mathbf{x}_N, t) = P^{(1)}(\mathbf{x}_1, t) P_c^{(N-1)}(\mathbf{x}_2, \ldots, \mathbf{x}_N, t \,|\, \mathbf{x}_1) \tag{2.22}$$

upon multiplication of Eq. (2.21) by $N!$, while observing that

$$P_c^{(N-1)} = (N-1)!\, F_c^{(N-1)}. \tag{2.23}$$

The temporal evolution of the probability density $F^{(N)}$ and, concomitantly, of $P^{(N)}$ is governed by the Liouville equation

$$\partial P^{(N)}(\mathbf{x}^N, t)/\partial t + \nabla_{\mathbf{x}^N} \cdot [\mathbf{U}^N P^{(N)}(\mathbf{x}^N, t)] = 0, \tag{2.24}$$

expressing the conservation of particles in phase space. Upon integration over $\mathbf{x}_N$, $\mathbf{x}_{N-1}$, ..., similar equations can be derived for each of the lower-order densities $P^{(n)}$, akin to the so-called BBGKY hierarchy (Hansen and McDonald, 1976; McQuarrie, 1976).

The statistical average of any configuration-dependent tensorial quantity $\mathbf{A}(\mathbf{x}^N, t)$ is defined as

$$\bar{\mathbf{A}} = \frac{1}{N!} \int \mathbf{A}(\mathbf{x}^N, t) P^{(N)}(\mathbf{x}^N, t)\, d\mathbf{x}^N. \tag{2.25}$$

Similar conditional averages may also be defined (cf. Section IV).

The incorporation of Brownian motion can be effected in a manner similar to that of Batchelor (1976b), who found the translational diffusion flux due to Brownian motion to be equivalent to one produced by steady forces acting on the particles. In this context, the force exerted on particle $i$ in an ensemble of $N$ particles is taken to be

$$\mathbf{F}_i = -kT\, \partial \ln P^{(N)}(\mathbf{x}^N, t)/\partial \mathbf{x}_i \qquad (1 \leq i \leq N). \tag{2.26}$$

The formal framework introduced in this subsection has been employed, for example, to study the sedimentation of suspensions (Batchelor, 1972).

## D. Volume Averages for Homogeneous Suspensions

From an experimental point of view, it is generally more convenient to employ "volumetric" rather than "statistical" [cf. Eq. (2.25)] averages to derive expressions for the bulk properties of suspensions. In order to effect a correspondence between these, an averaging volume $V$ must be selected that is large enough to contain a representative number of particles and yet sufficiently small (compared to the size of the experimental system) such that the local statistical properties of the suspension do not vary appreciably within $V$. A general multiple-scale analysis will not be introduced here but can be performed as by Brenner (1970) and by Lévy and Sanchez-Palencia (1983a). When such a volume can be found, the ergodicity property of (locally) statistically homogeneous suspensions allows one to equate volumetric and statistical averages.

The volume average of any quantity $\mathbf{A}$ is defined as

$$\langle \mathbf{A} \rangle = V^{-1} \int_V \mathbf{A}\, d^3\mathbf{x}, \tag{2.27}$$

in contrast with Eq. (2.25). Integration of Eq. (2.27) is to be performed over the entire volumetric domain contained within $V$, including the interior of the particulate phase. It is sometimes useful to replace the latter integral by an equivalent surface integral extended over the external areal domain $\partial V$ bounding $V$ (Brenner, 1970), so as to avoid dealing with possible ambiguities pertaining to the values of $\mathbf{A}$ existing within the particle interiors. When $\mathbf{A}$ is a divergence-free tensor of any order (other than zero), it is easy to show that

$$\langle \mathbf{A} \rangle = V^{-1} \int_{\partial V} \mathbf{x}\, d\mathbf{s} \cdot \mathbf{A}. \tag{2.28}$$

Necessary definitions now exist at this stage to permit continuing the discussion preceding and following Eq. (2.5) for the case of *infinitely* extended suspensions. When $N$ is infinite rather than finite, average macroscopic quantities must be prescribed in place of the prior asymptotic boundary condition (2.5). These must be defined as volume averages. For example, the macroscopic velocity gradient $\langle \mathbf{G} \rangle$ is defined as

$$\langle \mathbf{G} \rangle = V^{-1} \int_V \nabla \mathbf{v}\, d^3\mathbf{x}, \tag{2.29}$$

which is decomposable into respective symmetric $\langle \mathbf{S} \rangle$ and antisymmetric $\langle \ddot{\Lambda} \rangle$ contributions, as in Eq. (2.1).

Among possible macroscopic dynamical quantities of interest, the most useful is the macroscopic stress,

$$\langle \mathbf{P} \rangle = V^{-1} \int_V \mathbf{P}\, d^3\mathbf{x}. \tag{2.30}$$

As usual, its isotropic portion, corresponding to the average pressure, is first removed as being without consequence for the incompressible flows of interest to us here. Its antisymmetric part, which is related to any external-body couples exerted on the suspended particles, is also separated out. These operations result in the symmetric and traceless average deviatoric stress,

$$\langle \ddot{\tau} \rangle = \tfrac{1}{2}(\langle \mathbf{P} \rangle + \langle \mathbf{P}^\dagger \rangle - \tfrac{1}{3}\mathbf{I}(\mathbf{I} : \langle \mathbf{P} \rangle). \tag{2.31}$$

To identify the contribution to the latter stress arising from the presence of the particles in the fluid, we write [cf. Eq. (2.8)]

$$\langle \ddot{\tau} \rangle = 2\mu_0 \langle \mathbf{S} \rangle + \langle \mathbf{A} \rangle. \tag{2.32}$$

Elementary calculations (Batchelor, 1970) yield the following expression for $\langle \mathbf{A} \rangle$:

$$\langle \mathbf{A} \rangle = \frac{1}{V} \sum_{i \in V} \ddot{\mathscr{G}}_i, \tag{2.33a}$$

with

$$\ddot{\mathscr{G}}_i \overset{\text{def}}{=} \tfrac{1}{2} \int_{S_i} [d\mathbf{s} \cdot \mathbf{P}\mathbf{x} + \mathbf{x}\, d\mathbf{s} \cdot \mathbf{P} - \tfrac{2}{3}\mathbf{I}(d\mathbf{s} \cdot \mathbf{P} \cdot \mathbf{x})]. \tag{2.33b}$$

The so-called particle contribution $\langle \mathbf{A} \rangle$ to the mean stress may thus be evaluated by performing an integration over the surfaces of all particles contained within $V$.

Such a generic derivation was first effected by Landau and Lifshitz (1959) in the absence of any complicating factors. Included in these complicating factors are inertia, which necessitates the introduction of Reynolds stresses, as well as interfacial tension, present when the suspension is composed of droplets rather than rigid particles. Batchelor's (1970) analysis incorporates such factors.

## E. Concluding Remarks

The preceding paragraphs furnish the basic elements constituting the starting point for rheological investigations of suspensions. Subsequent analysis based thereon has a two-fold thrust: (i) Determination of the (statistical)

generic structure of the suspension and (ii) calculation of the hydrodynamic interaction forces. Of course, these are inseparably intertwined since the forces determine the structure, whereas the structure determines the forces. It is precisely this duality that makes the study of suspensions challenging.

In practice, progress occurs, or at least is deemed to have occurred, when one of these two reciprocal factors has been simplified. In most cases, a priori, ad hoc assumptions are made regarding the suspension's geometric microstructure. In cell models, the configurational problem is artificially eliminated upon replacing the suspension with an "equivalent" collection of space-filling cells, the bounding surfaces of which have kinematical and/or dynamical boundary conditions imposed on them. By their very nature, cell models, however, represent a mean-field treatment of suspension microstructure and, hence, cannot be extended to include interparticle forces, clustering, or other correlation effects. In dilute suspensions, the particulate concentration is assumed to be so low that only single-sphere interaction with the fluid needs to be considered. In statistical models the missing element is the many-body interaction, which is often crudely approximated either as a superposition of two-body interactions or as a power series expansion in inverse powers of the mean-separation distance, with the configuration obtained by a Monte Carlo-type calculation.

Percolation approaches (Section VI) attempt to predict the gross structure of the suspension without, however, requiring detailed knowledge of the interaction forces. Beyond a critical concentration, the existence of an infinite cluster of particles can be expected to occur in shear flows. In spatially periodic models of suspensions (Section VII), one can avoid the problem of structure by assuming the instantaneous particle configuration as well as the kinematical motions of the particles (but not the fluid) to be known a priori, independently of the dynamics. The response of the suspension to the particle motion is studied with the important bonus that the many-body hydrodynamic interaction problem can be solved *exactly* for the spatially periodic configuration. As such, the spatially periodic configuration offers interesting possibilities towards obtaining a complete solution, even when a large number of unequal-size particles is contained within each unit cell of the periodic array.

In Stokesian dynamics (Section VIII), a direct simulation is made starting with a randomly chosen initial particle configuration. The structure is allowed to evolve as part of the detailed fluid-mechanical solution, and the hydrodynamic particle interactions are determined at least to the extent of assuming pairwise additivity of these interactions. The "momentum tracer" method (Section VIII) is characterized by the interesting feature that the particulate phase of the suspension is at rest. The static configuration of this suspension is

assumed given, and results are derived for the configuration-specific kinematic viscosity tetradic of the suspension, the latter being viewed as a macroscopic continum.

## III. Empirical and Cell Models

This brief section provides a historical and practical overview of useful empiricisms employed in suspension theories, including a few useful formulas. Early investigators were mainly concerned with the measurement and correlation of two fundamentally important, but apparently unrelated, quantities: (i) The "effective" viscosity $\mu$ of sheared suspensions of neutrally buoyant particles and (ii) the sedimentation speed $u_s$ of suspensions of non-neutrally buoyant particles. Upon appropriate normalization, both were regarded as being functions only of the volumetric solids concentration $\phi$:

$$\mu/\mu_0 \stackrel{\text{def}}{=} \mu_r(\phi), \tag{3.1a}$$

$$u_s/u_0 \stackrel{\text{def}}{=} u_r(\phi), \tag{3.1b}$$

with $\mu_r$, the so-called relative viscosity, and $u_0$, the settling velocity of an isolated particle. The forms in Eq. (3.1), where the indicated ratios depend only on $\phi$, are now recognized to be correct only in the absence of nonhydrodynamic forces. Subsequent experiments were primarily oriented towards determining the statistical structure of the suspensions (cf. Section V).

Many experimental results on viscosity were empirically correlated by Rutgers (1962a,b) and Thomas (1965). A useful semiempirical formula is that of Mooney (1951). Its derivation is based on an approximate functional argument together with the introduction of an ad hoc "crowding factor" $k$. Upon contemplating two possible ways of reaching the same total concentration $\phi_1 + \phi_2$, Mooney proposed the formula

$$\mu_r = \exp[\beta\phi(1 - k\phi)^{-1}], \tag{3.2}$$

where $\beta$ and $k$ are constants. To achieve asymptotic agreement with Einstein's limiting result [see Eq. (4.1)], $\beta$ is set equal to 2.5. The factor $k$ is usually taken as the reciprocal of the maximum attainable concentration $\phi_{\max}$, namely

$$k = \phi_{\max}^{-1}. \tag{3.3}$$

The infinite viscosity prediction of Eq. (3.2) as $\phi$ approaches its maximum value is not necessarily correct. In the case of a spatially periodic lattice (Section VII), a rigorous analysis incorporating the time dependence of the relative positions of adjacent spheres in a shear flow provides results counter

to the infinite viscosity prediction. [This same conclusion is reached independently by Marrucci and Denn (1985) by heuristic reasoning not limited to spatially periodic model systems.] Furthermore, at least for spatially periodic systems, the actual value of $\phi_{max}$ depends explicitly on the type of flow under consideration, as discussed in Section VII.

Krieger and Dougherty (1959) proposed the closely-related formula

$$\mu_r = (1 - k\phi)^{-\beta/k}, \tag{3.4}$$

to which similar criticisms may be addressed.

Recent macroscopic rheological experiments shed light on the microrheology of suspensions. Gadala-Maria and Acrivos (1980) observed the behavior of concentrated suspensions of spheres under several flow conditions. Longtime drift was observed to occur in the value of the shear viscosity, ultimately yielding a reproducible asymptotic value. Under unsteady shear conditions, the macroscopic stress exhibited memory. These phenomena were originally attributed to the development of structure in the suspension for long periods of time; however, Leighton and Acrivos (1987) have recently shown this effect to be due to so-called shear-induced particle diffusion.

Pätzold (1980) compared the viscosities of suspensions of spheres in simple shear and extensional flows and obtained significant differences, which were qualitatively explained by invoking various flow-dependent sphere arrangements. Goto and Kuno (1982) measured the apparent relative viscosities of carefully controlled bidisperse particle mixtures. The larger particles, however, possessed a diameter nearly one-fourth that of the tube through which they flowed, suggesting the inadvertant intrusion of unwanted wall effects.

Similar experiments have been performed with settling suspensions, which leads to comparable empirical correlations. Early experiments are reviewed by Happel and Brenner (1965). Reviews by Fitch (1979) and by Davis and Acrivos (1985) provide the state of the art.

Two formulas widely used to correlate experimental sedimentation data are

$$u_r = (1 - \phi)^{\beta} \tag{3.5a}$$

and

$$u_r = \frac{1 - 1.88\phi}{1 + 5\phi}. \tag{3.5b}$$

The former was devised by Maude and Whitmore (1958) to fit experimental results available at the time, whereas the latter was theoretically derived by Reed and Anderson (1980) upon assuming pairwise additivity of the hydro-

dynamic particle–particle interactions and by preaveraging such interactions among all particles save the test one. Although not entirely satisfactory from a theoretical viewpoint, Eq. (3.5b) is found to be in good agreement with data (Kops-Werkhoven and Fijnaut, 1982). Buscall *et al.* (1982) correlated their carefully obtained experimental data by analogy with the Krieger and Dougherty (1959) relative viscosity formula in Eq. (3.4) to obtain

$$u_r = (1 - k\phi)^{-\beta/k}. \tag{3.5c}$$

Estimates of $u_r$ based on pairwise additivity by Glendinning and Russel (1982) may also be cited. These authors find, however, that the approximate, pairwise-additive treatment of hydrodynamic interactions fails to be adequate for all but very dilute suspensions. Their theoretical formalism can nonetheless be systematically improved by including three- (or more) particle interaction effects.

Cell models constitute a second major class of empirical developments. Among these, only two will be mentioned here as constituting the most successful and widely used. The first, due to Happel (1957, 1958), is useful for estimating the effective viscosity and settling velocity of suspensions. Here, the suspension is envisioned as being composed of fictitious identical cells, each containing a single spherical particle of radius $a$ surrounded by a concentric spherical envelope of fluid. The radius $b$ of the cell is chosen to reproduce the suspension's volume fraction $\phi$ via application of the formula

$$\phi = (a/b)^3. \tag{3.6}$$

Stokes equations are solved within the cell, satisfying stick boundary conditions imposed at the particle surface $r = a$ together with vanishing tangential stress on the outer boundary $r = b$ (along with additional kinematical boundary conditions imposed there on the velocity field, serving to isolate the cell from the remainder of the suspension). Theoretical results, containing no adjustable parameters, are in fair agreement with much experimental data.

Cell-type models are still in use (Adler, 1979; Russel and Benzing, 1981) because of their simplicity. Predicted results are often quite reasonable, exhibiting features intuitively anticipated. On the other hand, such models fail to provide definitive answers to many of the fundamental issues encountered in suspension rheology. Moreover, because of their strictly ad hoc geometric nature, no obvious way exists for their rational improvement.

Frankel and Acrivos (1967) introduced a rather different type of cell model based on lubrication-theory-type arguments. First, the rate of mechanical energy dissipation in the small gap between adjacent sphere pairs is calculated,

based on two spheres approaching (or receding from) one another along their line of centers. (Dissipation, arising from the relative "sliding motion" occurring between two spheres moving along different streamlines in a simple shear flow, is negligible when compared to that caused by the normal component of the relative motion.) The relative velocity of the two spheres, as well as the time-averaged gap distance between them, is deduced from average values of the shear rate and the particle concentration. All line-of-centers orientations are assumed equally likely, while the average interparticle gap width is inferred from the specified mean-particle concentration (assuming a cubic arrangement of spheres). The relative viscosity thereby obtained (Frankel and Acrivos, 1967) is

$$\mu_r = \frac{9\chi^{1/3}}{8(1-\chi^{1/3})} \quad \text{as} \quad \chi \overset{\text{def}}{=} \frac{\phi}{\phi_{\max}} \to 1. \tag{3.7}$$

Though Eq. (3.7) compares well with some experimental data, it does not agree with the analysis of Section VII, where it is shown for time- and spatially-periodic models of sheared suspensions that, although the *instantaneous* contribution to the stress tensor is indeed singular, its *time average* is not! Stated alternatively, the contribution arising from the inner "lubrication" zone is of the same order of magnitude as that of the outer nonsingular region. This conclusion can be compared to that of Batchelor and Green (1972b), as commented on by Batchelor (1974), to the effect that the dissipation in the inner zone (arbitrarily defined as a nondimensional gap of less than $0.0025a$ between adjacent sphere surfaces) contributes only about 20% of the effective viscosity to the $\phi^2$ term in dilute suspensions. Here again, the contribution arising from the lubrication layer is important but not predominant. Similar remarks relating to Eq. (3.7) have been made by Marrucci and Denn (1985). Further comments on Eq. (3.7) are given in Section VIII,A, where the two-dimensional counterpart of Eq. (3.7) is found to agree with dynamic simulations by Brady and Bossis (1985), although for reasons unrelated to those underlying the Frankel and Acrivos (1967) derivation.

Indirectly related to the cell models of this section is the work of Davis and Brenner (1981) on the rheological and shear stability properties of *three-phase* systems, which consist of an emulsion formed from two immiscible liquid phases (one, a discrete phase wholly dispersed in the other continuous phase) together with a third, solid, particulate phase dispersed within the interior of the discontinuous liquid phase. An elementary analysis of droplet breakup modes that arise during the shear of such three-phase systems reveals that the destabilizing presence of the solid particles may allow the technological production of smaller size emulsion droplets than could otherwise be produced (at the same shear rate).

## IV. Dilute Suspensions

As is well known, Einstein (1906, 1911) calculated the additional rate of mechanical energy dissipation engendered by the introduction of a single sphere into a homogeneous shear flow and ultimately obtained

$$\mu/\mu_0 = 1 + \tfrac{5}{2}\phi \qquad (\phi \ll 1) \tag{4.1}$$

for the effective viscosity $\mu$ of a dilute suspension. (Interestingly, the existence of two dates associated with this result stems from an algebraic slip committed by Einstein in his original 1906 paper and subsequently corrected in 1911.)

Later, Landau and Lifshitz (1959) obtained the same result by averaging the stress tensor over the entire space, thereby initiating one of the first dynamical (i.e., nonenergetic) approaches to calculating the rheological properties of suspensions. Attempts to extend Eq. (4.1) to higher concentrations are legion. Most propose a power series expansion of the form

$$\mu/\mu_0 = 1 + 2.5\phi + k_1\phi^2 + k_2\phi^3, \ldots . \tag{4.2}$$

The long-range, purely hydrodynamic interaction between two suspended spheres in a shear flow was first calculated by Guth and Simha (1936), yielding a value of $k_1 = 14.1$ via a reflection method. Saito (1950, 1952) proposed two alternative modifications, obtaining $k_1 = 12.6$ and 2.5, respectively; the latter value is obtained upon supposing a spatially uniform distribution of particles.

Vand's (1948) analysis considered the effect of adding an incremental volume fraction $\delta\phi$ of spheres to an existing suspension of spheres of concentration $\phi$. Also included was the contribution arising from doublets. His value of $k_1 = 7.35$ was later corrected by Manley and Mason (1954) to $k_1 = 10.05$. In a pioneering, often overlooked, investigation, Peterson and Fixman (1963) obtained $k_1 = 4.31784$, correctly identifying and properly posing many of the underlying questions later addressed and resolved more rigorously by others. Their approximate result was obtained by assuming a uniform density for the two-particle probability density and using an inaccurate far-field approximation for the hydrodynamic interaction.

In a systematic study of particle–particle interactions that also has often been overlooked, Cox and Brenner (1971) developed a comprehensive general theory for calculating the rheological properties of a suspension of particles of arbitrary shape to $0(\phi^2)$, including wall effects. They did not, however, attempt an explicit numerical calculation of $k_1$, and it is perhaps for this reason that their work has not received the thoughtful attention it deserves.

Finally, Batchelor and Green (1972b) furnished a rigorous calculation of the coefficient $k_1$. In a subsequent series of papers, Batchelor also examined the sedimentation of a dilute suspension (Batchelor, 1972), the effects of Brownian

motion (Batchelor, 1976b, 1977), and polydispersity effects (Batchelor, 1982, 1983; Batchelor and Wen, 1982). In what follows, Batchelor and Green's (1972b) derivation of the bulk stress to order $\phi^2$ will be examined, emphasizing the key point of their arguments. Subsequently, other relevant results, as well as other derivations, will be quoted and extensions thereof will be cited.

Consider a suspension of identical, spherical (radii $a$), force- and couple-free particles. Upon neglect of both inertia and Brownian movement, the proper rheological starting point is Eq. (2.33) for the particle stress. As in Eq. (4.1), the contribution arising when particle–particle interactions are absent is known. Its explicit inclusion in $\langle \mathbf{A} \rangle$ yields

$$\langle \mathbf{A} \rangle = 5\phi\mu_0 \langle \mathbf{S} \rangle + 5\phi\mu_0 \left( \frac{\langle \mathbf{A} \rangle}{5\phi\mu_0} - \langle \mathbf{S} \rangle \right). \tag{4.3}$$

The second term reflects interaction effects. The parenthetical contribution appearing in the latter term may be alternatively expressed as

$$\frac{\ddot{\mathscr{S}}}{20\pi a^3 \mu_0/3} - \langle \mathbf{S} \rangle, \tag{4.4}$$

with $\ddot{\mathscr{S}}$ as the statistical average of $\ddot{\mathscr{S}}_i$ [cf. Eq. (2.33b)] for the averaging volume $V$ containing $N$ particles. As such, Eq. (4.4) is equivalent to

$$\frac{1}{N!} \int \left( \frac{\ddot{\mathscr{S}}}{20\pi a^3 \mu_0/3} - \langle \mathbf{S} \rangle \right) P^{(N)}(\mathbf{x}^N)\, d\mathbf{x}^N, \tag{4.5a}$$

which may be transformed to the form

$$\frac{1}{(N-1)!} \int \left( \frac{\ddot{\mathscr{S}}}{20\pi a^3 \mu_0/3} - \langle \mathbf{S} \rangle \right) P_c^{(N-1)}(\mathbf{x}^{N-1} \mid \mathbf{x}_0)\, d\mathbf{x}^{N-1} \tag{4.5b}$$

with the aid of Eq. (2.2). Here, $\ddot{\mathscr{S}}$ is to be regarded as the particle stress, functionally dependent on the geometric arrangement of the $N-1$ remaining particles, given that the designated particle is located at $\mathbf{x}_0$.

A number of difficulties arise in attempting to exploit Eq. (4.5b). First, the conditional density $P_c^{(N-1)}$ is as yet unknown, apart from being difficult to obtain. This may be circumvented by supposing that interaction with one particle constitutes the dominant contribution to Eq. (4.5b), allowing the averaging to be performed by replacing the weighting function,

$$[(N-1)!]^{-1} P_c^{(N-1)}\, d\mathbf{x}^{N-1},$$

in Eq. (4.5b) by the simpler, two-particle conditional probability, $P(\mathbf{x}_0 + \mathbf{R} \mid \mathbf{x}_0) d^3\mathbf{R}$. However, this probability tends to the position-independent

value $N/V$ for large $|\mathbf{R}|$. The concomitant $0(|\mathbf{R}|^{-3})$ integrand results in a non-absolutely convergent integral. To deal with this difficulty, Batchelor and Green (1972b) proposed finding a quantity whose mean value is known and which for large $|\mathbf{R}|$ possesses the same functional dependence as does the integrand. By its subtraction from and addition to the integrand, proper evaluation of the integral can be effected.

The required conditional probability density $P(\mathbf{x}_0 + \mathbf{R}\,|\,\mathbf{x}_0)$ for finding a second particle at $\mathbf{x}_0 + \mathbf{R}$ (given the existence of the reference sphere at $\mathbf{x}_0$) can be obtained by solving the Liouville equation,

$$\frac{\partial}{\partial t} P(\mathbf{x}_0 + \mathbf{R}\,|\,\mathbf{x}_0) + \frac{\partial}{\partial \mathbf{R}} \cdot [\mathbf{V}(\mathbf{R}) P(\mathbf{x}_0 + \mathbf{R}\,|\,\mathbf{x}_0)] = 0 \tag{4.6}$$

[with $\mathbf{V}(\mathbf{R})$ the relative velocity of the centers of two spheres], subject to the boundary conditions

$$P = 0 \quad \text{at } R = 2a \tag{4.7a}$$

and

$$P \to N/V \equiv 3\phi/4\pi a^3 \quad \text{as } R \to \infty, \tag{4.7b}$$

applicable for systems without long-range order. Despite their widespread use, both of the above boundary conditions are of a tentative hypothetical nature; different results would, of course, arise from the choice of other conditions (Yoshida, 1988). Furthermore, Eq. (4.6) shows the probability to be simply convected with the velocity $\mathbf{V}$. It is therefore possible that some domains of the flow are not reached by the streamlines coming from infinity. This phenomenon occurs, for instance, in simple shear flow (Darabaner and Mason, 1967). Hence, in such circumstances, only particular probability densities are obtained, without any universal meaning.

To obtain $\ddot{\mathscr{S}}$, it is further necessary to solve the Stokes problem for two spheres. In the case of a purely straining motion, where only open trajectories obtain the result of the complete analysis, as outlined above, eventually yields (Batchelor and Green, 1972b)

$$\mu/\mu_0 = 1 + \tfrac{5}{2}\phi + 7.6\phi^2. \tag{4.8}$$

This can be compared to the previously cited results pertaining to Eq. (4.2). Yoon and Kim (1987) have more accurately recalculated the last coefficient in Eq. (4.8) to be 6.95.

Similar methods have been applied by Batchelor (1972, 1982; Batchelor and Wen, 1982) to a number of other problems. A sedimenting suspension of equal spheres was examined first. Since no relative motion exists between two identical settling spheres, the probability density cannot be determined from

Eq. (4.6); rather, the distribution was assumed uniform, and the mean sedimentation velocity $u_s$ of a settling sphere found to be related to the velocity $u_0$ of an isolated sphere by the expression

$$u_s/u_0 \simeq 1 - 6.55\phi. \tag{4.9}$$

This result has been generalized (Batchelor, 1982; Batchelor and Wen, 1982) to a polydisperse suspension of settling spheres, obtaining for the average settling velocity $u_{s,i}$ of species $i$,

$$u_{s,i}/u_{0,i} = 1 + \sum_{j=1}^{m} s_{ij}\phi_j, \tag{4.10}$$

with $m$, the total number of species; $u_{0,i}$, the settling speed of a particle of species $i$ in isolation; and $\phi_j$, the volume fraction of species $j$. Calculated values of the coefficients $s_{ij}$ are displayed in the previous reference for a variety of circumstances. For spherical particles, there is no influence manifested of translational Brownian motion on the first-order Einstein coefficient in Eq. (4.1)*. Such effects do, however, arise at $0(\phi^2)$ as a consequence of the particle–particle interactions.

In a sheared suspension, the effects are two-fold. First, the expression for bulk stress itself must be modified. Second, the probability density is affected since the continuity equation for the latter must be replaced by a convection–diffusion equation. As a consequence, the distinction between open and closed trajectories loses some of its meaning. Batchelor (1977) gives the equivalent viscosity of a sheared suspension subject to strong Brownian motion as

$$\mu/\mu_0 = 1 + \tfrac{5}{2}\phi + 6.2\phi^2, \tag{4.11}$$

independently of the explicit form adopted for the bulk flow. The current status of the contribution of Brownian motion to the viscosity of suspensions of spherical particles is reviewed by Felderhof (1989).

Finally, the mean flux of particles of various sizes in the presence of bulk concentration gradients was calculated (Batchelor, 1976b, 1983), and the corresponding Fickian diffusion tensors systematically obtained. With no interparticle forces, the numerical results may be represented by the approx-

* However, for nonspherical particles, rotational Brownian motion effects already arise at $0(\phi)$. In the case of ellipsoidal particles, such calculations have a long history, dating back to early polymer-solution rheologists such as Simha and Kirkwood. Some of the history of early incorrect attempts to include such rotary Brownian effects is documented by Haber and Brenner (1984) in a paper addressed to calculating the $0(\phi)$ coefficient and normal stress coefficients for general triaxial ellipsoidal particles in the case where the rotary Brownian motion is dominant over the shear (small rotary Peclet numbers)—a problem first resolved by Rallison (1978).

imate interpolation formulas

$$D_{ii}/D_i^{(0)} = 1 + 1.45\phi_i - \sum_{k(\neq i)} \frac{2.5\phi_k}{1 + 0.6\lambda_{ik}} \tag{4.12a}$$

$$D_{ij}/D_i^{(0)} = \phi_i(\lambda_{ij}^3 + 2\lambda_{ij}^2) \qquad (j \neq i), \tag{4.12b}$$

in which $\lambda_{ij} = a_j/a_i$. The effect of colloidal forces was also explored in the cited references, and numerical results were obtained for a few representative cases.

Transcending the central body of knowledge for dilute suspensions described in the preceding paragraphs, Russel (1976, 1978) analyzed the rheological properties of electrostatically stabilized colloidal suspensions, including Brownian motion. Details are provided in limiting cases. Haber and Hetsroni (1981) investigated the sedimentation of liquid spheres of different sizes, whose density and viscosity differed from that of the suspending fluid. Feuillebois (1984) derived the average sedimentation velocity of monodisperse solid spheres in the presence of vertical concentration inhomogeneities. Caflish and Luke (1985) calculated the variance of the sedimentation speed; in the infinite particle number limit, it was found to be infinite, a conclusion whose physical significance is unclear.

Comparisons with experimental data have been effected by Batchelor. In careful experiments, Kops-Werkhoven and Fijnaut (1981) obtained $-6 \pm 1$ for the coefficient of the first-order volume fraction term in the sedimentation velocity [cf. Eq. (4.9)] and $1.3 \pm 0.2$ for the corresponding term in the diffusion coefficient [cf. Eq. (4.12)]. The latter term is derived from light-scattering experiments. For monodisperse suspensions, these results agree reasonably well with Batchelor's predictions.

In related contributions, Felderhof (1978) arrived at this same diffusion coefficient, except for a numerical difference due to his use of a different far-field expression for the hydrodynamic interaction. Several investigators proposed schemes for circumventing the difficulty that arises from the existence of nonabsolutely convergent integrals in the theory. Thus, Jeffrey (1974) employed a group expansion method; Hinch (1977) statistically averaged the conservation and constitutive relations, obtaining an infinite hierarchy of equations which then had to be truncated; O'Brien (1979) used an integral representation of the solution to the basic equations; Feuillebois (1984) devised a novel method based on decoupling the treatment of the divergent integrals from the calculation of hydrodynamic interactions, while keeping the reference volume finite.

Another related field of interest—but one beyond the scope of our review—is the concentration dependence of the self and collective diffusivities, including distinctions between short- and long-term self diffusivities. The interested reader is referred to the careful discussions by Batchelor (1983), Rallison and Hinch (1986) and Yoshida (1988) in this context.

## V. Statistical Models

Theoretical trends in the study of suspensions employ concepts and techniques originally developed in connection with theories of liquids, for example, equation hierarchies, closure problems, and Monte Carlo methods. In marked contrast with the definitive achievements reviewed in the previous section, the present section outlines a field currently under active development.

Knowledge of basic molecular–theoretic (Hansen and McDonald, 1976) concepts and properties, such as those of hard-sphere models of liquids, constitutes a prerequisite for admission to the present field. While relevant experimental techniques in this field will not be reviewed here, it is difficult to avoid mentioning light scattering. The review by Pusey and Tough (1982) shows how dynamic light scattering can provide data on both collective and self-diffusion coefficients. Moreover, the static structure factor, which is the spatial Fourier transform of the radial distribution function, can be obtained by static light-scattering experiments. Discovery of many enlightening results relating to suspension structures can be anticipated with further development of this experimental technique. A paper by Rallison and Hinch (1986) provides an illuminating discussion of dynamic light-scattering phenomena, with emphasis on particle-interaction effects.

Various formal expansions are outlined below, followed by a summary of numerical calculations employing Monte Carlo techniques and major conclusions derived from these techniques.

### A. Formal Expansions

The review by Herczyński and Pieńkowska (1980) of these expansions provides an excellent entrée to the major theories analyzed in the literature on the subject, most of which address determination of the permeability of random arrays of spheres. In this context, it is useful to define the so-called phase function,

$$H(\mathbf{r}, t) = \begin{cases} 1 & \text{in the fluid,} \\ 0 & \text{in the particles,} \end{cases} \tag{5.1}$$

which may be used, for example, to calculate averages restricted to the fluid phase alone.

As before, let $\mathbf{P}$ be the local stress tensor, and denote by an overbar the statistical average of any quantity. The definition of the fluid-velocity field may be analytically extended to the solid-particle interiors and the pressure therein assumed to vanish. As such, taking the statistical average of the

Stokes equations and using the phase function $H(\mathbf{r}, t)$, it may be shown formally that

$$-\nabla\overline{p(\mathbf{r})} + \mu_0\nabla^2\overline{\mathbf{v}(\mathbf{r})} = n(\mathbf{r})\int_{s_1} d\mathbf{s}\cdot\overline{\mathbf{P}(\mathbf{r}\,|\,\mathbf{R}_1)}, \tag{5.2a}$$

with $n(\mathbf{r}, t)$, the particle-number density function; $\mathbf{P}(\mathbf{r}\,|\,\mathbf{R}_1)$, the stress tensor existing when a sphere is centered at $\mathbf{R}_1$; and $s_1$, the surface of the latter sphere. Complementing this equation is the averaged continuity equation,

$$\nabla\cdot\overline{\mathbf{v}(\mathbf{r})} = 0. \tag{5.2b}$$

Appearing in the integrand of Eq. (5.2a) is the averaged stress,

$$\overline{\mathbf{P}(\mathbf{r}\,|\,\mathbf{R}_1)} = \overline{p(\mathbf{r}\,|\,\mathbf{R}_1)}\mathbf{I} + \mu_0[\overline{\nabla\mathbf{v}(\mathbf{r}\,|\,\mathbf{R}_1)} + \overline{\nabla\mathbf{v}^\dagger(\mathbf{r}\,|\,\mathbf{R}_1)}]. \tag{5.3}$$

The required equations for $\overline{p(\mathbf{r}\,|\,\mathbf{R}_1)}$ and $\overline{\mathbf{v}(\mathbf{r}\,|\,\mathbf{R}_1)}$ are derived by conditionally averaging the Stokes equations, thereby obtaining

$$-\nabla\overline{p(\mathbf{r}\,|\,\mathbf{R}_1)} + \mu_0\nabla^2\overline{\mathbf{v}(\mathbf{r}\,|\,\mathbf{R}_1)} = n(\mathbf{r}\,|\,\mathbf{R}_1)\int_{s_2} d\mathbf{s}\cdot\overline{\mathbf{P}(\mathbf{r}\,|\,\mathbf{R}_1, \mathbf{R}_2)}, \tag{5.4a}$$

$$\nabla\cdot\overline{\mathbf{v}(\mathbf{r}\,|\,\mathbf{R}_1)} = 0. \tag{5.4b}$$

Equations (5.4a,b) are similar to Eqs. (5.2) except for the additional conditioning with respect to $\mathbf{R}_1$. To evaluate the RHS one must obtain equations for $P(\mathbf{r}\,|\,\mathbf{R}_1, \mathbf{R}_2)$ and $\mathbf{v}(\mathbf{r}\,|\,\mathbf{R}_1, \mathbf{R}_2)$ by twice conditionally averaging the Stokes equations.

The hierarchy of equations thereby obtained can be closed by truncating the system at some arbitrary level of approximation. The results eventually obtained by various authors depend on the implicit or explicit hypotheses made in effecting this closure—a clearly unsatisfactory state of affairs. Most contributions in this context aim at calculating the permeability (or, equivalently, the drag) of a porous medium composed of a random array of spheres. The earliest contribution here is due to Brinkman (1947), who empirically added a Darcy term to the Stokes equation in an attempt to represent the hydrodynamic effects of the porous medium. The so-called Brinkman equation thereby obtained was used to calculate the drag exerted on one sphere of the array, as if it were embedded in the porous medium continuum. Tam (1969) considered the same problem, treating the particles as point forces; he further assumed, in essence, that the RHS of Eq. (5.2a) was proportional to the average velocity and hence was of the explicit form

$$-\alpha^2\mu_0\overline{\mathbf{v}(\mathbf{r})}. \tag{5.5}$$

The phenomenological constant $\alpha$ is calculated by Brinkman's self-consistent argument. In circumstances where the particles are identical, the drag computed in this manner reduces to Brinkman's formula.

Lundgren (1972) treated the case of a suspension of spheres. He assumed the RHS of Eq. (5.2a) to be a linear functional of $\overline{\mathbf{v}(\mathbf{r})}$, choosing this functional dependence to be of the form

$$A\overline{\mathbf{v}(\mathbf{r})} + B\nabla^2\overline{\mathbf{v}(\mathbf{r})}. \tag{5.6}$$

The first term is, of course, equivalent to that considered by the previous authors, whereas the second combines with the Stokes term to yield an effective viscosity. Coefficients $A$ and $B$ were determined through a self-consistent scheme.

Howells (1974) restricted his attention to fixed particles, extending the method of Childress (1972) by considering a given number of particles chosen from an infinite set. This partly self-consistent scheme furnishes terms valid in the small-solids concentration limit. In a very readable paper, Hinch (1977) combined some of the above procedures in formulating an "averaged-equation" approach to particle interactions, providing expressions for the bulk stress, average sedimentation velocity, and effective permeability in suspensions and fixed beds.

In the same vein, Itoh (1983) employed Eq. (5.5) to calculate $\alpha$ using the same self-consistent argument, but with the inclusion of an intermediate fluid layer around the test sphere. Theoretical results compared well with experimental results.

Another series of related papers includes those of Herczyński and Pieńkowska (1980), who reinterpreted the derivation of Bedeaux *et al.* (1977) in terms of grand-canonical averages. Buyevich and coworkers developed yet another scheme by spatially averaging the equations in each phase of the suspension; a complete account of this can be found in Buyevich and Shchelchkova (1978). Contributions by Freed and Muthukumar provide yet another perspective. As their first entrée (Freed and Muthukumar, 1978), they considered the Stokes problem for the velocity disturbance and friction coefficient arising from the motion of a single sphere moving with constant velocity **U** through a stationary suspension of spheres at finite concentration. They obtained a formal solution given in terms of the so-called Oseen tensor. These authors were not concerned with the velocity field per se, but rather only with its statistical average. Divergent integrals were encountered and summed, and the average velocity field was shown to be a solution of the Brinkman equation. A number of applications exist for these results; however, in view of the formidable nature of the expansion, calculations are generally restricted to second-order terms, corresponding to binary particle–particle interactions.

Freed and Muthukumar (1982) and Muthukumar and Freed (1982) applied a similar scheme to suspensions of hard spheres. Results resembling those of Batchelor and Green (1972b) were obtained upon assuming a spatially uniform distribution of spheres.

Beenakker (1984) and Beenakker and Mazur (1983, 1984) used their method of induced forces (cf. Section II) to calculate particle diffusivity and effective viscosity in concentrated suspensions. Beenakker's (1984) paper introduces a novel wave vector-dependent viscosity $\mu(\mathbf{k})$ by considering the average response of the suspension to an externally applied force. The usual viscosity is obtained by considering the limit of zero wave-number, from which an explicit expression for $\mu$ (as a double summation of propagators) is obtained. This general formula was used in various ways. For dilute suspensions, the viscosity was expanded in terms of the concentration, yielding the same results as those of Freed and Muthukumar (cf. the previous paragraph). Another original feature entails the procedure used at high concentrations: $\mu(k)$ is expressed in terms of renormalized connectors in order to account for spheres interacting with one another via the intervening suspension. The effective viscosity is then expanded with the help of density-fluctuation correlation functions of increasing order, wherein the first two terms of the expansion are evaluated via the equilibrium pair distribution function $g(r)$ (i.e., the classical Percus-Yevick distribution for hard spheres). Agreement between numerical and experimental results is satisfactory for solids concentrations of up to 30% (see de Kruif *et al.*, 1985). It must be stressed, however, that the above treatments account only for the viscous contribution to the stress, while neglecting the effect on the bulk stress tensor of the nonequilibrium structures formed in sheared suspensions.

## B. Numerical Calculations

Monte Carlo techniques were first applied to colloidal dispersions by van Megen and Snook (1975). Included in their analysis was Brownian motion as well as van der Waals and double-layer forces, although hydrodynamic interactions were not incorporated in this first study. Order–disorder transitions, arising from the existence of these forces, were calculated. Approximate methods, such as first-order perturbation theory for the disordered state and the so-called cell model for the ordered state, were used to calculate the latter transition, exhibiting relatively good agreement with the "exact" Monte Carlo computations. Other quantities of interest, such as the radial distribution function and the excess pressure, were also calculated. This type of approach appears attractive for future studies of suspension properties.

van Megan *et al.*, (1983) and Pusey and van Megan (1983) employed the expansion proposed by Mazur and van Saarloos (1982) to obtain diffusion coefficients in concentrated, hard-sphere dispersions. Comparison of these predictions with experimental data for relatively concentrated suspensions revealed that two- and three-particle interactions were of the same orders of magnitude. Inclusion of two-body terms, however, made the agreement with experiments worse, whereas the further addition of three-body terms improved the comparison. This result is intriguing since Beenakker and Mazur (1982) have recently shown that three-body contributions change the algebraic sign of the second-order term in the expression for the concentration-dependence of the self-diffusion coefficient. They conclude that "... two-sphere hydrodynamic interactions do not suffice to describe the properties of suspensions at higher densities." Of course, this statement also casts a shadow on the validity of analyses where pairwise additivity is assumed.

Other review articles relating to colloidal suspensions and containing discussions of numerical calculations (Monte Carlo simulations) include contributions by van Megen and Snook (1984) and Castillo *et al.* (1984). The scope of these articles is not, however, limited to numerical techniques; they also provide general reviews of the statistical mechanics of colloidal suspensions.

## VI. Percolation Models

Application of percolation theory concepts to the study of suspensions has attracted much interest. Major aspects of the general theory are briefly recounted in the following subsection, after which, an analogy between percolation and suspension flows is detailed together with its main predictions. We conclude with a discussion of supporting experimental results obtained for "two-dimensional" suspensions.

### A. Percolation Theory

Percolation theory is reviewed by Stauffer (1985). The so-called "site" percolation problem may be posed as in the pioneering analysis by Broadbent and Hammersley (1957), who initiated the subject. If "atoms" are distributed randomly at the sites of a regular lattice in such a way that any given site has probability $p$ of being occupied, what is the probability $P(p)$ that a given atom belongs to an infinite cluster? By an infinite cluster, a connected collection of atom-containing neighboring sites extending to infinity without interruption is meant. The "bond" percolation problem is rather similar to the previous

one. Consider a regular lattice and let $p$ now denote the fraction of bonds between two sites which are "favorable" (e.g., not blocked, open, etc., depending on the particular problem being studied). What is the probability $P(p)$ that a favorable bond is part of an infinite cluster linked by such bonds?

Both problems share the common property that $P(p)$ is of measure zero for $p < p_c$, with the critical threshold value $p_c$ as a function of the type of lattice considered. Few exact formulas exist for $P(p)$ or even $p_c$. There are, however, a number of empirical rules. For instance, for the bond percolation problem,

$$zp_c \approx \frac{d}{d-1}, \tag{6.1}$$

where $z$ is the coordination number and $d$ is the dimensionality of the space in which the lattice is embedded. Near the critical concentration $p_c$, the probability $P(p)$ adopts the power-law form

$$P(p) = \text{const}|p - p_c|^{\beta}. \tag{6.2}$$

In two dimensions (d = 2), the so-called "critical exponent" is $\beta \approx 0.14$. Considerably more details (cf. Stauffer, 1985; Havlin and Ben-Arraham, 1983) are known about the geometry of random networks.

Conductance of such a random network constitutes the simplest transport problem that can be studied by percolation ideas. A crude effective-medium theory shows that the bulk conductance is proportional to the number of active bonds:

$$\sigma(p) = \text{const}(p - p_c)^{+1} \qquad (p > p_c). \tag{6.3}$$

This expression is confirmed by computer simulations except near the critical value, where it is found that

$$\sigma(p) = \text{const}(p - p_c)^{s} \qquad (p \gtrsim p_c). \tag{6.4}$$

Values ascribed to the critical exponent $s$ in the literature are somewhat controversial. Results (Derrida and Vannimenus, 1982) indicate that $s$ is close to 1.28. Below $p_c$ the bulk conductance is zero, since the network fails to form an infinite cluster whose existence would permit current to be conducted through the system.

According to Stauffer (1979), "A complete understanding of percolation would require [one] to calculate these exponents exactly and rigorously. This aim has not yet been accomplished, even in general for other phase transitions. The aim of a scaling theory as reviewed here is more modest than complete understanding: We want merely to derive relations between critical exponents." Three principal methods currently employed to derive critical exponents are (i) series expansions, (ii) Monte Carlo simulation, and

(iii) renormalization-group theory. Stauffer (1979) outlines the scope, possibilities, and limitations of each. Many (computer generated) results in this area are either empirical or semiempirical; some are obtained under rather delicate conditions. Consequently, knowledge of the existence of past failures, as well as successes, plays an important role in advancing the subject.

### B. Application to Suspensions

DeGennes (1979, 1981) was the first to apply percolation concepts to suspensions during an examination of the mechanisms of "collision" occurring between two neutrally buoyant spheres in a simple shear flow—a subject earlier investigated exhaustively by Mason and co-workers (Arp and Mason, 1977b). Compared to molecular collisions occurring in gases, the distinguishing feature of such shear-induced collisions is its finite duration (the time interval being inversely proportional to the shear rate $\gamma$). Of course, this gross attribute does not differentiate between the significant differences distinguishing equatorial and polar collision times. Furthermore, from a hydrodynamic viewpoint, no real physical contact occurs between the spheres, whence the precise meaning of the term "collision" is elusive. Nevertheless, the average collision time is reckoned to be of the order of $2.5\gamma^{-1}$. As such, a finite probability $p$ exists for a given sphere to be in "contact" with one (or more) of the others. This probability is independent of $\gamma$ and is obviously a monotone increasing function of the solid-phase concentration $\phi$. Thus, as $\phi$ and $p$ increase, each sphere becomes progressively more likely to exist as part of a cluster than in isolation.

By analogy to percolation arguments, a critical concentration $\phi_c$ is assumed to exist, beyond which value an infinite cluster forms. With $\phi_\infty$ the fraction of spheres belonging to an infinite cluster, the percolation analogy with Eq. (6.2) suggests that

$$\phi_\infty = \text{const}(\phi - \phi_c)^{\beta_3}. \tag{6.5}$$

Formation of such an infinite cluster appears likely to change the suspension hydrodynamics drastically. For example, the classical parabolic Poiseuille velocity profile existing within a circular tube is likely to be severely blunted, a phenomenon observed experimentally by Karnis *et al.* (1966).

In parallel with conductive transport [cf. Eq. (6.4)], momentum transport, as quantified by the shear viscosity, is expected to obey the scaling law

$$\mu/\mu_0 = \text{const}|\phi - \phi_c|^{-s_3}. \tag{6.6}$$

As emphasized by DeGennes (1979), none of the quantitative "predictions" of this percolation model agree with known experimental results other than the

apparent formation of an infinite cluster. For instance, both the detailed velocity profile and concentration dependence of the suspension viscosity are at odds with the above predictions, as evidenced by comparison with the early experiments of Karnis *et al.* (1966).

DeGennes' suggestions were later implemented by the Marseille group. Their experiments were aimed at verifying both the formation of an infinite cluster and the scaling law in Eq. (6.6). The most representative of these contributions is embodied in the work of Bouillot *et al.* (1982). Ease of observation was achieved by shearing a "two-dimensional" suspension in a macro-couette apparatus. This configuration was achieved by pouring a thin layer of light liquid onto a denser immiscible liquid, following which, equal-sized spheres were inserted into that layer. Admittedly, such experiments suffer a number of drawbacks, including "end effects" arising from the finite thickness of the upper layer and an insufficiency of sphere numbers to assure statistical reliability. Nevertheless, interesting features appear to be present in the experiments.

Here again, as in the three-dimensional "touching" configuration referred to previously, no remarkable "kink" or discontinuity was observed in the viscosity–concentration curve; the results could be correlated by an empirical Eilers (1941) -like law. However, statistical evaluation of the clusters proved interesting. Clusters were defined arbitrarily by supposing that any two spheres closer than $\frac{1}{10}$ of their common radius (corresponding to the resolution of the photographic device) belong to the same cluster. As a function of the "two-dimensional" surface concentration $\phi^s$ (defined as the areal fraction of the projected area of the spheres to the total area of the Couette apparatus), experiments revealed the appearance of a cluster at about $\phi_c^s \approx 0.65$. The latter embodied a large fraction ($\approx 75\%$) of the total sphere population. The cluster completely surrounded the inner cylinder. Thus, the existence of infinite clusters appears to have been experimentally verified, although other statistical characterizations, such as measurement of the radial distribution function $g(r)$, have yet to be performed.

The foregoing results may be discussed in terms of spatially periodic suspensions, which represent the only exactly analyzable suspension models currently available for concentrated systems. Since spatially periodic models are discussed in the next section, the remainder of this section may be omitted at first reading.

First, the observed critical concentration $\phi_c^s \approx 0.65$ may be compared with the maximum kinematic concentration ($\phi_{max} = \pi/4 \simeq 0.785$) possible for a two-dimensional suspension of circular disks undergoing simple shear. That the actual $\phi_c^s$ value is lower than the theoretically predicted one may be rationalized in terms of spatially periodic packings allowing the existence of more concentrated systems than disordered packings. According to Berryman

(1983), random close packing (rcp) is predicted to occur at a concentration $\phi^{rcp} \approx 0.82$ in two dimensions. The theoretical value corresponding to ordered close packing (ocp) in the static case is $\phi^{ocp} = 0.9069$. The assumption that the randomness causes the same fractional decrease to occur in the dynamic packing case leads to the estimate

$$\phi_c^s = (\phi^{rcp}/\phi^{ocp})\phi_{max} \approx 0.71, \tag{6.7}$$

which lies within 10% of the observed 0.65 value. A further distinction between random-loose and random-close packing may yet improve the estimate further.

Second, the spatially periodic model suggests further interpretations and experiments. That no "kink" exists in the viscosity vs. concentration curve may be related to the fact that the average dissipation rate remains finite at the maximum kinematic concentration limit, $\phi_{max}$. Infinite strings of particles are formed at this limit. It may thus be said that although the geometry "percolates," the resulting fields themselves do not, at least not within the context of the spatially periodic suspension model.

Systematic four-roller (Bentley and Leal, 1986a,b) experiments suggest themselves as candidates to investigate more completely the entire class of two-dimensional shear flows, these being distinguished by a single scalar parameter $\lambda$ [cf. Eq. (7.8) and Fig. 1]. Measurement of $\phi_c^s$ as a function of $\lambda$, and its subsequent comparison with the predicted $\phi_{max}(\lambda)$ values, would prove equally interesting. It may also be instructive to exceed $\phi_{max}(\lambda)$ by changing the flow parameter $\lambda$ at a fixed concentration $\phi$. This would permit the singular case of simple shear flow to be embedded into the more general class of two-dimensional incompressible flows.

An experiment by Camoin and Blanc (1985), performed in the same apparatus, allowed the structure of the resulting clusters to be analyzed in the presence of attractive forces existing between the suspended particles. The resulting structure was found to be fractal in nature for circumstances wherein the attractive forces dominated over hydrodynamics forces.

## VII. Spatially Periodic Suspensions

Spatially periodic models of suspensions (Adler and Brenner, 1985a,b; Adler *et al.*, 1985; Zuzovsky *et al.*, 1983; Adler, 1984; Nunan and Keller, 1984) constitute an attractive subject for theoretical treatment since their geometrical simplicity permits rigorous analysis, even in highly concentrated systems. In particular, when a unit cell of the spatially periodic arrangement contains but a single particle, the underlying kinematical problems can be

readily identified and solved. Dynamical properties, such as interstitial velocity, pressure, and stress fields, can be derived from these kinematical results using classical tools such as the grand resistance matrix (Brenner and O'Neill, 1972). Formally, the single particle ("perfect crystal") problem has been completely solved, as seen shortly. An immediate application of the single particle problem is to the study of colloidal crystals, which are thought to mimic the microscopic structures and phases observed in atomic crystalline systems. The existence of various length scales provides for easy experimental observation of some spectacular macroscopic phenomena. Overbeek (1982) provides a general view of the physicochemical and colloidal aspects of monodisperse suspensions; Pieranski (1983) emphasizes the solid-state physics of such "crystals." Also of interest in this context is the treatise edited by Pieranski and Rothen (1985).

When more than one particle is contained within a unit cell, the fundamental conceptual problems are essentially the same, though the detailed analyses are considerably more difficult because of the intrusion of nontrivial dynamical features into what were previously purely kinematical ones. Nonetheless, some of the interstitial fluid field-properties, as well as the existence of a grand resistance matrix formulation governing the configurational evolution of the particulate phase, continue to remain valid. The scope of applications is, moreover, greatly enhanced. Some motions of so-called colloidal crystals can only be addressed by assigning more than one particle per cell. Moreover, such multi-particle analyses provide the basis for further suspension-simulation studies via methods similar to those employed in molecular dynamics. In particular, these involve temporal evolutionary studies of the instantaneous spatial distribution of $N$ particles moving within a unit cell and are subject to periodic boundary conditions [see Hansen and McDonald (1976) as well as Section VIII of this chapter]. For the most part this section focuses on our own work on this subject (Adler and Brenner, 1985a,b; Adler *et al.*, 1985; Zuzovsky *et al.*, 1983; Adler, 1984). An independent approach, substantially different in scope, has been developed using so-called homogenization methods (Bensoussan *et al.*, 1978; Sanchez-Palencia, 1980), whose applications have been directed primarily towards immobile particulate systems (such as porous media). Such homogenization methods employ a multiple length-scale analysis, with the spatial period furnishing one of the characteristic length scales. An analysis of suspension behavior has been made via such techniques by Lévy and Sanchez-Palencia (1983a,b) for dilute suspensions of particles and droplets, as well as for concentrated suspensions of solid particles. Nguetseng (1982) analyzed the behavior of phase mixtures subjected to vibrations.

This section begins with an account of spatially periodic suspension models embodying a single particle (a solid sphere in most cases) per unit cell. Rigidity

of the suspended particles results in the existence of a maximum possible kinematic concentration whose numerical value is shown to depend explicitly on the macroscopic flow field being considered. Instantaneous, configuration-specific, suspension-scale rheological properties, amounting to a spatial average of the comparable microscale properties, follow from computation of the local interstitial dynamical fields. Time averages of these dynamical fields can be meaningfully performed when, in addition to the instantaneous spatial periodicity, the motion of the lattice is simultaneously time periodic. In such circumstances, the particulate microscale configuration of the suspension reproduces itself in time; it is over one such period of the self-reproducing lattice that the time average is to be performed. Several results are given for both dilute and concentrated suspensions. Finally, a unit cell containing $N$ particles (with $N$ possibly large) is considered, and some preliminary results for such systems are outlined.

## A. Description and Kinematics of Spatially Periodic Suspensions

This subsection, which finds its genesis in the work of Adler and Brenner (1985a), is organized as follows: Following a brief introduction to the physical system under study, the kinematical possibility of the existence of a microscale interstitial fluid motion, consistent with a prescribed macroscale shearing motion of the suspension as a whole, is analyzed in the context of the mutual impenetrability of the suspended particles. This allows the concept of a "maximal kinematic concentration" to be defined. Next, the reproducibility (or, more generally, "near reproducibility") of the lattice in time is studied. Such temporal configurational periodicity is critical when time averaging of instantaneous quasistatic states needs to be performed to obtain the effective properties of the suspension.

Consider a suspension composed of an ordered, repetitive, three-dimensional array of identical, rigid spheres immersed in an otherwise homogeneous fluid continuum and extending indefinitely in every direction. From a formal point of view, the lattice $\Lambda$, representing the group of translational self-coincidence symmetry operations of this spatially periodic medium, consists of the set of points

$$\mathbf{R}_{\mathbf{n}} = n_1\mathbf{l}_1 + n_2\mathbf{l}_2 + n_3\mathbf{l}_3 \qquad (n_j = 0, \pm 1, \pm 2, \ldots) \qquad (j = 1, 2, 3). \quad (7.1)$$

Here, $(\mathbf{l}_1, \mathbf{l}_2, \mathbf{l}_3)$ denote three linearly independent vectors of $\mathbb{R}^3$, serving as a basis of $\Lambda$, whereas $\{n_1, n_2, n_3\} \equiv \mathbf{n}$, say, is a triad of integers. The symbol $\mathbf{0} \equiv \{0, 0, 0\}$ will be arbitrarily chosen to designate the lattice origin.

Equivalently, the lattice $\Lambda$ may be represented by the second-order tensor

$$\mathbf{L} = \mathbf{l}_1\mathbf{e}_1 + \mathbf{l}_2\mathbf{e}_2 + \mathbf{l}_3\mathbf{e}_3, \tag{7.2}$$

with the trio of unit vectors $(\mathbf{e}_1, \mathbf{e}_2, \mathbf{e}_3)$ denoting an orthonormal basis of the vector space $\mathbb{R}^3$. The determinant $d(\Lambda)$ of the lattice, corresponding to the superficial volume of a unit cell, is defined as

$$d(\Lambda) = |\det \mathbf{L}|. \tag{7.3}$$

Consider the centers of the identical spherical particles of radii $a$ to be instantaneously located at the lattice points $\mathbf{R}_n$. As such, the simplest geometric state exists, in which only one particle is contained within each unit cell. When the latter suspension is sheared, the three basic lattice vectors $\mathbf{l}_i$ $(i = 1, 2, 3)$ (or, equivalently, the dyadic $\mathbf{L}$) become functions of time $t$. Under a homogeneous deformation, the lattice composed of the sphere centers remains spatially periodic, although its instantaneous spatially periodic configuration necessarily changes with time.

In the present rheological context, lattice deformation may be regarded as arising from the transport of neutrally buoyant lattice points suspended within a macroscopically homogeneous linear shear flow. The *local* vector velocity field $\mathbf{v}$ at a general (interstitial or particle interior) point $\mathbf{R}$ of such a spatially periodic suspension can be shown to be of the form

$$\mathbf{v}(\mathbf{R} + \mathbf{R}_n) - \mathbf{v}(\mathbf{R}) = \mathbf{R}_n \cdot \mathbf{G}, \tag{7.4}$$

with $\mathbf{G}$ as the constant macroscopic velocity gradient dyadic. $\mathbf{G}$ is assumed to be independent of both position and time. Hence, the local velocity gradient $\nabla\mathbf{v}$ is instantaneously spatially periodic for all time. For the applications that follow, it is further supposed that the strain rate $\mathbf{G}$ is traceless:

$$\operatorname{tr} \mathbf{G} = 0, \tag{7.5}$$

corresponding to the combination of an incompressible fluid, $\nabla \cdot \mathbf{v} = 0$, and rigid particles. The foregoing considerations, together with an assumed no-slip condition on the sphere surfaces, define the state of the system.

Since rigid spheres are nondeformable, it is known that in a *static* system, $d(\Lambda)$ possesses a minimum value (over all possible lattices) to which corresponds a maximal solids concentration

$$\delta = 4\pi a^3/3d_{\min}(\Lambda). \tag{7.6}$$

This yields $\delta \approx 0.74$, a value first calculated by Gauss in 1831. Similar considerations can be extended to nonspherical (e.g., convex) particles; the corresponding mathematical framework constitutes a portion of the so-called geometry of numbers (Lekkerkerker, 1969).

Equivalent considerations for nonstatic, sheared systems demonstrate the kinematical possibility of such shearing motions. This requires, *inter alia*, that the distance between any two sphere centers remains larger than $2a$. The static viewpoint can be generalized to such circumstances as follows: Rather than considering the lattice deformation, it suffices to examine the deformed "collision sphere." The latter body $\mathfrak{S}$ is defined as the set of points

$$\mathfrak{S} = \{\mathbf{x}:\mathbf{x} = (\exp \mathbf{G}^{\dagger} t) \cdot \mathbf{x}_0, \quad \forall \|\mathbf{x}_0\| \leq 2a, \quad \forall t \in (-\infty, \infty)\}. \tag{7.7}$$

When the lattice points initially lie entirely outside $\mathfrak{S}$ (except $\mathbf{0}$, which lies at the center of $\mathfrak{S}$), it can be shown (Adler and Brenner, 1985a) that macroscopic shearing motion is possible for all times.

A minimal value of the determinant $d(\Lambda)$ corresponds to the body $\mathfrak{S}$, and thus, also corresponds to a maximum kinematic concentration, a quantity of some practical importance. Determination of the maximum kinematic concentration for a flow characterized by a given velocity gradient $\mathbf{G}$ requires the corresponding configuration of $\mathfrak{S}$ to be calculated and its minimal determinant to be deduced (generally from geometric number theory). Calculations have been performed for both two- and three-dimensional shearing motions (Adler, 1984). The most general two-dimensional incompressible linear flow can be written parametrically as (Kao *et al.*, 1977)

$$u = Gy, \qquad v = \lambda Gx, \qquad w = 0, \tag{7.8}$$

with $(u, v, w)$ the respective $(x, y, z)$ components of the velocity field, $G$ the magnitude of the shear rate, and $\lambda$ a nondimensional parameter lying in the

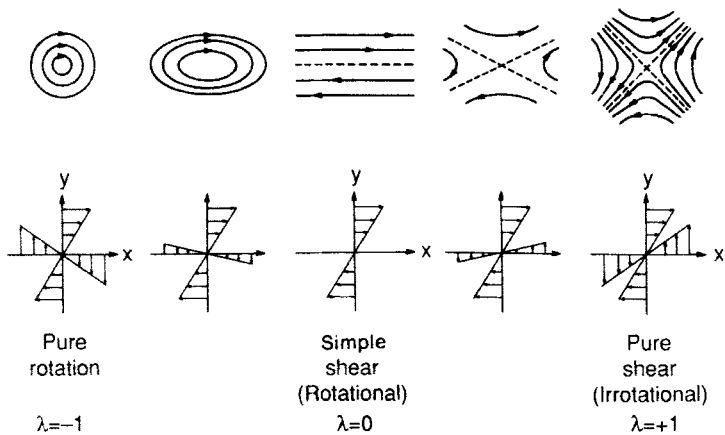



FIG. 1. Schematic of a family of two-dimensional steady incompressible shear flows showing the streamline patterns at the top and the corresponding velocity components at the bottom. By varying $\lambda$ continuously from $-1$ to $+1$, the flow can be varied from pure rotation (without strain) to pure strain (without rotation).

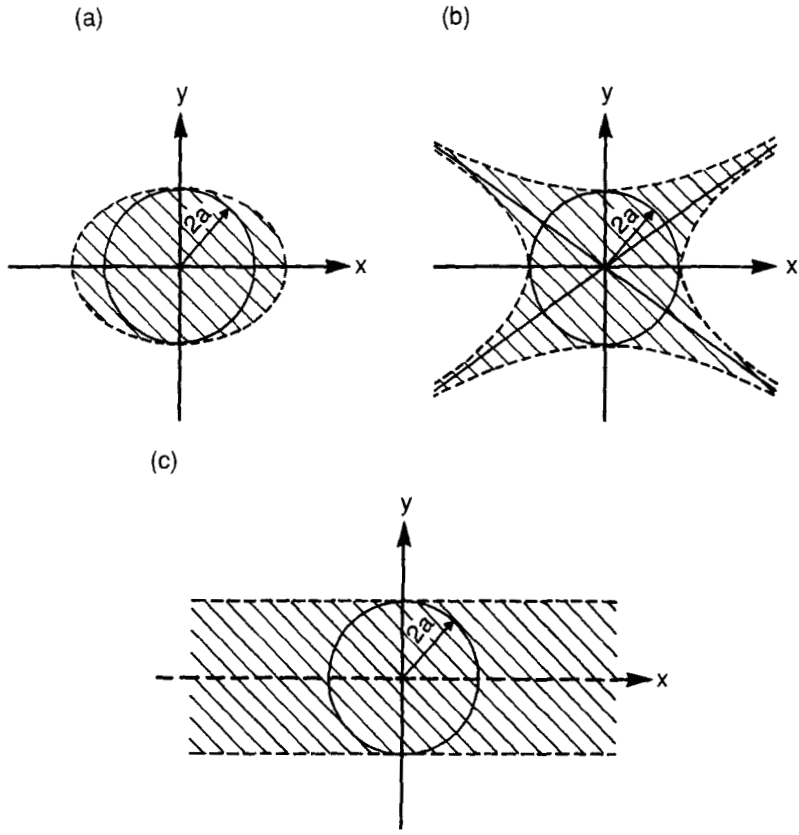



FIG. 2. The star body $\mathscr{S}$ for a two-dimensional lattice subjected to a two-dimensional shear flow. (a) Elliptic streamlines, $\lambda < 0$; (b) hyperbolic streamlines, $\lambda > 0$; (c) simple shear flow, $\lambda = 0$.

range $-1 \leq \lambda \leq 1$, encompassing all possible flow variants. Figure 1 (Kao *et al.*, 1977) summarizes the entire family of trajectories.

The body $\mathfrak{S}$ is illustrated in Fig. 2 for the simple case of a spatially periodic suspension of circular disks subjected to the flow given by Eq. (7.8). It is evident from the figure that any point lying within the body $\mathfrak{S}$ will later be found within the collision disk, contradicting the specified impenetrability condition imposed on these rigid bodies.

A similar analysis can be performed for three-dimensional lattices subjected to the same flow. The corresponding maximum concentration curve in three dimensions is shown in Fig. 3 as a function of the flow parameter $\lambda$. This curve displays a discontinuous dependence on $\lambda$ in the neighborhood of $\lambda = 0$, revealing a very special feature of simple shear flow. The "saw-tooth" property characterizing hyperbolic flows ($\lambda > 0$) is derived from the best estimates

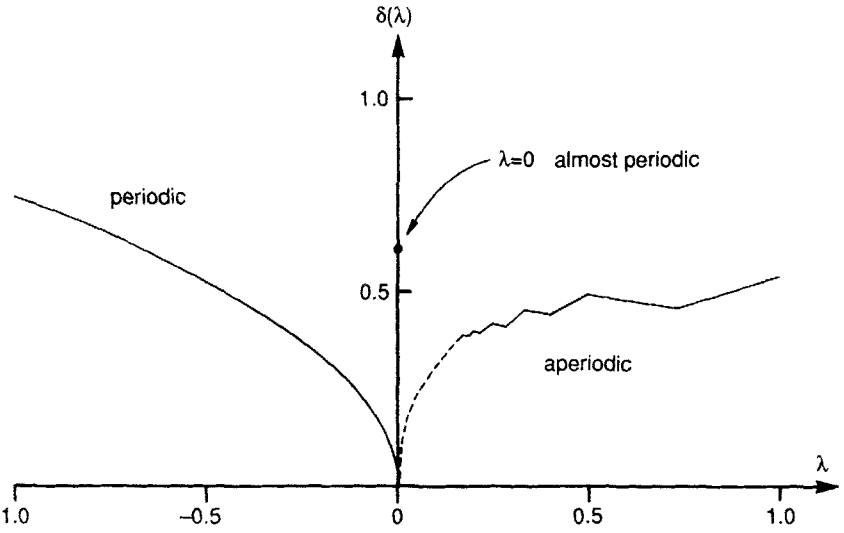



FIG. 3. The maximum density $\delta(\lambda)$ as a function of the flow parameter $\lambda$ for a three-dimensional lattice.

currently available for the minimum value of $d(\Lambda)$, obtained from the geometry of numbers. Such estimates are not definitive in any absolute sense.

In summary, the key point of the foregoing analysis is the existence of a maximum particulate-phase concentration whose value depends explicitly on the specified shear flow in which the particles are suspended.

Finally, the self-reproducibility in time of the lattice configuration (for two-dimensional flows) must be addressed. In the elliptic streamline region ($\lambda < 0$), the lattice necessarily replicates itself periodically in time owing to closure of the streamlines. For hyperbolic flows ($\lambda > 0$), the lattice is not generally reproduced; however, in connection with research on spatially periodic models of foams (Aubert *et al.*, 1986; Kraynik, 1988), Kraynik and Hansen (1986, 1987) found a finite set of reproducible hexagonal lattices for the extensional flow case $\lambda = 1$. It is not clear how this unique discovery can be extended, if at all.

The most interesting case arises for simple shear flows ($\lambda = 0$). It can be proven mathematically that time-periodic motion is possible only when the direction of the flow is parallel to either a lattice plane or a lattice line. These are respectively termed "slide" and "tube" flows; the origin of such terminology is evident from Fig. 4. Very similar configurations have been experimentally observed by Ackerson and Clark (1983).

For simplicity of presentation, and since no novel results are furnished by tube flows, subsequent attention is restricted to slide flows. As in Fig. 4(a), the

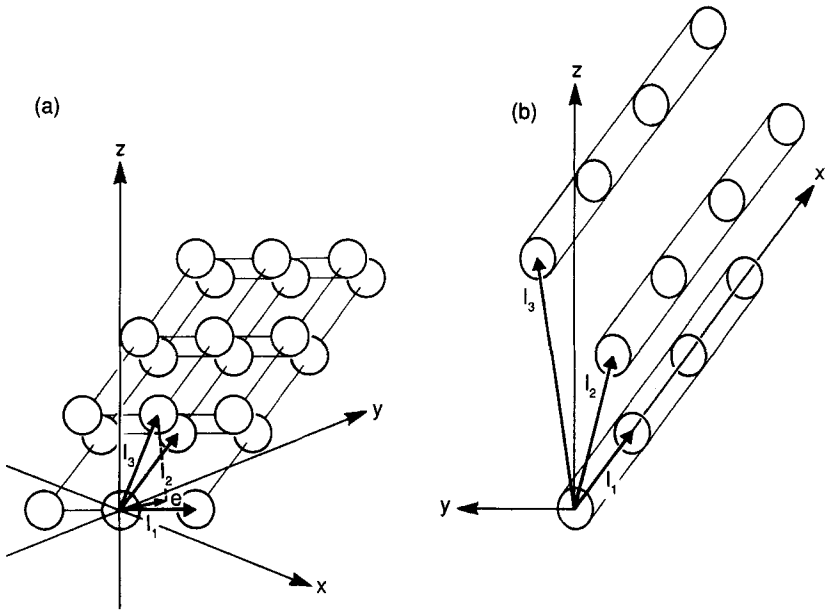



FIG. 4. The two possible configurations for a three-dimensional lattice in a simple shear flow. The velocity field is given by $u = Gz$; **e** is the projection of $\mathbf{l}_3$ onto the $x-y$ plane: (a) slide flow, (b) tube flow.

relative positions of two slide planes are determined by $\mathbf{l}_3$. Since the projection of $\mathbf{l}_3$ onto the $z$-axis remains constant in time, only its temporal projection **e** onto the $x$-$y$ plane needs to be known. Inasmuch as that projection is a straight line, and since $\mathbf{l}_3$ is only required modulo the spatial periods $\mathbf{l}_1$ and $\mathbf{l}_2$, determination of the reproducibility (or lack thereof) gives rise to a classical problem in the theory of numbers (Fig. 5). Thus, depending on the rational or

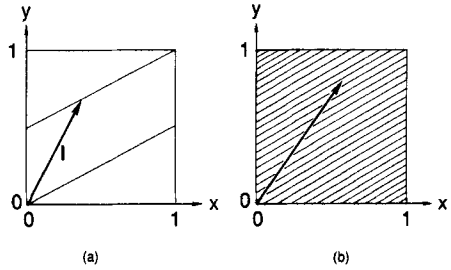



FIG. 5. Illustration of the interaction of the vector **e**($t$) with the unit square. (a) The slope is rational and equal to $\frac{1}{2}$; **e** visits the two segments in a periodic manner. (b) The slope is irrational; **e** visits the whole square with a uniform probability.

irrational character of the slope (cf. Fig. 5), the temporal lattice behavior will either be periodic or "almost periodic" in simple shear flow. For a rational slope, the terminus of the vector $\mathbf{e}$ visits a finite number of segments; otherwise, $\mathbf{e}$ visits the entire unit square $[0, 1]^2$ with uniform probability. Such knowledge proves essential when time averaging is to be performed.

## B. Rheology

This subsection describes general dynamical properties of the interstitial velocity and pressure fields, from which the instantaneous rheological properties of the spatially periodic suspension are deduced, followed by the requisite time averaging for self-reproducing structures (Adler *et al.*, 1985). As a consequence of Eq. (7.4), the velocity field may be decomposed into respective linear ($\mathbf{R} \cdot \mathbf{G}$) and spatially periodic ($\tilde{\mathbf{v}}(\mathbf{R})$) contributions. With account taken of the interstitial velocity vector $\bar{\mathbf{v}}^*$, the velocity field may be written as

$$\mathbf{v}(\mathbf{R}) = \mathbf{R} \cdot \mathbf{G} + \tilde{\mathbf{v}}(\mathbf{R}) + \bar{\mathbf{v}}^*, \tag{7.9}$$

where the spatially periodic field $\tilde{\mathbf{v}}(\mathbf{R})$ is assigned zero mean when averaged over the unit cell. The translational velocity $\mathbf{U}_\mathbf{n}$ of particle $\mathbf{n}$ may be similarly decomposed as

$$\mathbf{U}_\mathbf{n} = \mathbf{U}_\mathbf{0} + \mathbf{R}_\mathbf{n} \cdot \mathbf{G}, \tag{7.10}$$

with $\mathbf{U}_\mathbf{0}$ the translational velocity of particle $\mathbf{0}$.

Adherence of fluid to the particle surfaces requires satisfaction of the no-slip boundary conditions

$$\tilde{\mathbf{v}}(\mathbf{R}_\mathbf{n} + \mathbf{r}) = (\mathbf{U}_\mathbf{0} - \bar{\mathbf{v}}^*) + (\boldsymbol{\Omega} - \bar{\boldsymbol{\omega}}) \times \mathbf{r} - \mathbf{r} \cdot \bar{\mathbf{S}} \quad \text{when } |\mathbf{r}| = a \tag{7.11}$$

with $\boldsymbol{\Omega}$ as the common angular velocity of each of the particles. Additionally, $\bar{\boldsymbol{\omega}} = -\bar{\boldsymbol{\varepsilon}} : \mathbf{G}/2 \, (\equiv -\varepsilon_{ijk} G_{kj}/2)$ is the pseudovector of the antisymmetric portion of $\mathbf{G}$, and $\bar{\mathbf{S}} = (\mathbf{G} + \mathbf{G}^\dagger)/2$ is its corresponding symmetric portion.

Stokes Eqs. (2.2) and (2.3), in conjunction with Eq. (7.9), imply the spatial periodicity of the pressure gradient. As such, the pressure field may be decomposed as

$$p(\mathbf{R}) = \tilde{p}(\mathbf{R}) - \mathbf{R} \cdot \bar{\mathbf{F}}, \tag{7.12}$$

with $\tilde{p}(\mathbf{R})$ a spatially periodic field, and $\bar{\mathbf{F}}$ a constant vector equal to the force per unit volume exerted by the fluid on the particles.

Arguments much the same as those presented in Section II, together with

the linear nature of the Stokes equations, yield the dynamical relationship

$$\begin{bmatrix} \mathbf{F} \\ \mathbf{N} \\ \mathbf{A} \end{bmatrix} = \mu_0 \begin{bmatrix} {}^{t}\mathbf{K} & \mathbf{C} & \dddot{\phi} \\ (\tau_f/\tau_0)\mathbf{C}^{\dagger} & {}^{r}\mathbf{K} & \ddot{\tau} \\ (\tau_f/\tau_0)\dddot{\mathbf{M}} & \ddot{\mathbf{N}}^{*} & \ddot{\mathbf{Q}} \end{bmatrix} \begin{bmatrix} \bar{\mathbf{v}}^{*} - \mathbf{U}_0 \\ \bar{\omega} - \boldsymbol{\Omega} \\ \bar{\mathbf{S}} \end{bmatrix}, \tag{7.13}$$

relating the hydrodynamic force **F**, torque **N** (about the particle center), and particle stress **A** to the kinematical forcing terms appearing on the RHS. As a consequence of the Lorentz reciprocal theorem (Happel and Brenner, 1965), a number of dynamic symmetry relations (Adler *et al.*, 1985) also apply to the coefficient matrix appearing in Eq. (7.13).

The partitioned "grand resistance matrix" in Eq. (7.13) is a function only of the instantaneous geometrical configuration of the particulate phase. This consists of the fixed particle shapes together with the variable relative particle positions and orientations. As such, geometrical symmetry arguments (where such symmetry exists) may be used to reduce the number of independent, nonzero scalar components of the coefficient tensors in Eq. (7.13) for particular choices of coordinate axes (e.g., "principal axis" systems).

Of special interest in applications is the important case of centrosymmetric particles, including spheres, ellipsoids, circular disks, and rods [cf. Brenner (1974) for a comprehensive account of the ensuing geometric symmetry simplifications]. Including the translational symmetry of the lattice, a suspension composed of individually centrosymmetric particles possessing identical orientations is itself centrally symmetric since an "empty" (i.e., particle-free) lattice necessarily possesses this point-group symmetry element. In such circumstances, geometric symmetry arguments (Brenner, 1974) reduce Eq. (7.13) to the form

$$\begin{bmatrix} \mathbf{F} \\ \mathbf{N} \\ \mathbf{A} \end{bmatrix} = \mu_0 \begin{bmatrix} {}^{t}\mathbf{K} & \mathbf{0} & \mathbf{0} \\ \mathbf{0} & {}^{r}\mathbf{K} & \ddot{\tau} \\ \mathbf{0} & \ddot{\mathbf{N}}^{*} & \ddot{\mathbf{Q}} \end{bmatrix} \begin{bmatrix} \bar{\mathbf{v}}^{*} - \mathbf{U}_0 \\ \bar{\omega} - \boldsymbol{\Omega} \\ \bar{\mathbf{S}} \end{bmatrix}. \tag{7.14}$$

This form significantly simplifies the algebraic structure of the kinetic problem. In particular, no direct coupling now exists between the translational motion and the angular and shearing motions, suggesting the possibility of treating the translational motion independently of the latter two.

In principle at least, Eq. (7.14) provides the basis for a complete calculation of the configuration-specific rheological properties of the suspension at each given instant of time $t$. In order to calculate therefrom the time-averaged properties of the suspension, consider the macroscopic simple shear flow discussed previously in connection with Fig. 4.

Consider a function $f$ (of any tensorial rank) that is functionally dependent only on the geometry of the suspension—for example, in the case of spheres,

on the geometry of the lattice $\Lambda(t)$. For simple shear flow, $f$ will generally depend on both the static (time independent) and kinematic (time dependent) elements of the lattice. In order to simplify the representation, the static components will not appear explicitly among the arguments of $f$. Thus, notationally we write

$$f[\mathbf{L}(t)] = f[\mathbf{e}(t)], \tag{7.15}$$

with $\mathbf{e}(t)$ as the projected lattice vector previously defined. Of course, when specific lattice calculations are actually performed, the static elements play a role too and need be incorporated.

The quantity of physical interest in applications normally proves to be not the instantaneous value of the function $f$ itself, but rather its time average, defined as

$$\langle f \rangle = \lim_{T \to \infty} \frac{1}{T} \int_0^T f[\mathbf{e}(t)]\, dt. \tag{7.16}$$

In order to effect this integration, the behavior of $\mathbf{e}(t)$ within the unit square must be known. In accordance with the preceding development, a distinction must be made between the respective two cases of rational and irrational values of the slope of $\mathbf{e}$.

When the slope $\xi$ is rational [cf. Fig. 5(a)], $\mathbf{e}$ possesses a time-periodic trajectory $\mathscr{L}$ within the unit square of total length $L$. The required average [Eq. (7.16)] can then be computed as

$$\langle f \rangle = \frac{1}{L} \int_{\mathbf{e} \in \mathscr{L}} f(\mathbf{e})\, dl, \tag{7.17}$$

whose computation now appears in the guise of a purely geometric time-independent problem, where $dl$ is a differential line element along the trajectory $\mathscr{L}$.

For irrational values of $\xi$, the terminus of the $\mathbf{e}$ vector visits all accessible positions in the unit square with uniform probability. Hence, the time average $\langle f \rangle$ can be shown (Adler *et al.*, 1985) to be equivalent to the integral

$$\langle f \rangle = \int_{[0,1]^2} f(\mathbf{e})\, dx\, dy \tag{7.18}$$

over the unit square.

This generic formula permits averages to be calculated for any pertinent suspension property $f$. When time-independent external forces $\mathbf{F}^{(e)}$ and torques $\mathbf{N}^{(e)}$ act on each of the suspended particles, Eq. (7.14), together with the net force- and torque-free conditions characterizing the neutrally buoyant

particles, yields

$$\begin{aligned}\langle \mathbf{U}_0 - \bar{\mathbf{v}}^* \rangle &= \mu_0^{-1} \langle {}^t\mathbf{K}^{-1} \rangle \cdot \mathbf{F}^{(e)} \\ \langle \boldsymbol{\Omega} - \bar{\boldsymbol{\omega}} \rangle &= \langle {}^r\mathbf{K}^{-1} \cdot \dddot{\tau} \rangle : \bar{\mathbf{S}} + \mu_0^{-1} \langle {}^r\mathbf{K}^{-1} \rangle \cdot \mathbf{N}^{(e)} \\ \langle \mathbf{A} \rangle &= -\langle \ddot{\mathbf{N}}^* \cdot {}^r\mathbf{K}^{-1} \rangle \cdot \mathbf{N}^{(e)} - \mu_0 \langle \ddot{\mathbf{N}}^* \cdot {}^r\mathbf{K}^{-1} \cdot \dddot{\tau} - \dddot{\mathbf{Q}} \rangle : \bar{\mathbf{S}}.\end{aligned} \tag{7.19}$$

Preceding results for the simple shear case are potentially relevant for a variety of applications in the sense that all stationary suspension-scale rheological properties of interest may now be derived in a rigorous straightforward (albeit tedious) manner. The essentially geometric character of these dynamical results again bears emphasis. This is, perhaps, not surprising in retrospect since the particle kinematics have been reduced to a geometric quadrature, while the efficacy of the grand resistance matrix (which now embodies the dynamical elements of the problem) stems from its dependence on only the geometrical configuration of the particulate phase. Obviously, this pair of independent geometrical elements supplement one another nicely; together they constitute a potent combination useful, perhaps, in even more general circumstances.

A second prominent feature here is the ergodic character (or lack thereof) of the process, depending on the rationality or irrationality of $\xi$. This leads inevitably to the fascinating question, "Does a real system choose between these values of $\xi$, and if so, how?" The boundaries themselves remain neutral with respect to the choice of $\xi$ whenever they are compatible with the flow. Thus, for a slide flow, the walls must be parallel to the slides, whereas for a tube flow, they must be parallel to the tube. In both cases there remains an additional degree of freedom, which is precisely the choice of $\xi$. Other examples of indeterminancy arise from the neglect of fluid and particle inertia, as already discussed in Section I (see also the review in Leal, 1980). Whether or not inclusion of nonlinear inertial effects can remove the above indeterminacy, as it often does for the purely hydrodynamic portion of the problem, is a question that lies beyond the scope of the present (linear) Stokesian context.

Finally, hyperbolic and elliptic flows deserve at least a few comments. A suspension undergoing a hyperbolic flow does not generally reproduce itself in time. Accordingly, its time average is not physically meaningful, even if it is assumed to exist. Elliptic flow represents perhaps the simplest case among the class of two-dimensional flows since it is always self-reproducing as a consequence of the closed streamlines. However, its very simplicity is itself a source of disappointment since it is a relatively straightforward matter to determine the configurations explored by the suspension during each period and perform the requisite time integrations along these configurations. Thus, our geometric scheme offers no advantages over this direct temporal approach.

## C. Cubic Arrays

This subsection summarizes available numerical results for the rheological properties of cubic arrays of neutrally buoyant spherical particles suspended in shear flows. [Comparable porous media calculations for seepage flows through fixed spatially periodic rectangular arrays of cylinders and cubic arrangements of spheres, encompassing the complete range of particle concentrations, are presented by Sangani and Acrivos (1982).]

A general solution of Stokes equations can be obtained by analytic continuation of the interstitial velocity and pressure fields into the interior of the regions occupied by the spheres, replacing the particle interiors by singular multipole force distributions located at the sphere centers $\mathbf{R}_n$ (Zuzovsky *et al.*, 1983). Explicitly, $(\mathbf{v}, p)$ satisfies the dynamical equation

$$\mu_0 \nabla^2 \mathbf{v} = \nabla p - \sum_{\alpha=0}^{\infty} \sum_{\mathbf{n}} \nabla^\alpha \delta(\mathbf{R} - \mathbf{R}_n)(\cdot)^\alpha \mathbf{F}_{\alpha+1}, \tag{7.20}$$

where $\nabla^\alpha = \nabla, \ldots, \nabla$ denotes $\alpha$ successive applications of the gradient operator; $\delta(\mathbf{R} - \mathbf{R}_n)$ is the Dirac delta function, whereas $\mathbf{F}_{\alpha+1}$ is a completely symmetric constant tensor of rank $\alpha + 1$ to be determined. The symbol $(\cdot)^\alpha$ represents $\alpha$ successive dot multiplications; additionally,

$$\sum_{\mathbf{n}} \equiv \sum_{n_1=-\infty}^{\infty} \sum_{n_2=-\infty}^{\infty} \sum_{n_3=-\infty}^{\infty}. \tag{7.21}$$

Equation (7.20) is to be regarded as applying throughout all of space, including the particle interiors. Boundary conditions imposed at the sphere surfaces implicitly furnish the relations determining the $\mathbf{F}$'s, these being related to the forces, torques, etc., exerted on the fluid by the particles. For instance, the vector $\mathbf{F}_1$ is related to the external force acting on each particle via the expression

$$\mathbf{F}_1 = -\mathbf{F}_{\text{ext}}, \tag{7.22}$$

whereas $\mathbf{F}_2$ is expressible as

$$\mathbf{F}_2 = \mathbf{A} + \tau_0 \bar{\mathbf{P}}^a, \tag{7.23}$$

with $\mathbf{A}$ the so-called particle stress, $\bar{\mathbf{P}}^a$, the antisymmetric portion of the macroscopic stress tensor $\bar{\mathbf{P}}$, and $\tau_0$ the superficial volume of a unit cell.

Calculations have thus far been performed for the three standard cubic arrays, namely simple cubic (sc), body-centered cubic (bcc), and face-centered cubic (fcc). As a result of this geometric symmetry, the couple $\mathbf{N}$ and particle stress dyadic $\mathbf{A}$ are given by the configuration-specific relations

$$\begin{aligned} \mathbf{N} &= \mu_0 \xi^{(r)}(\boldsymbol{\Omega}) - \bar{\boldsymbol{\omega}}) \\ \mathbf{A} &= \mu_0 \overset{\cdots}{\psi}{}^{(s)} : \bar{\mathbf{S}}. \end{aligned} \tag{7.24}$$

TABLE II

COEFFICIENTS FOR USE IN EQS. (7.26)

| Lattice type | $n$ | $\tilde{a}_{20}$ | $\tilde{b}_{20}$ |
|---|---|---|---|
| sc | 1 | 0.2857 | −0.04655 |
| bcc | 2 | −0.0897 | 0.01432 |
| fcc | 4 | −0.0685 | 0.01271 |

Upon appropriate reduction in the number and nature of the independent tensorial components of $\dddot{\psi}^{(s)}$ ($\equiv \psi^{(s)}_{ijkl}$), resulting from the common point-group symmetry elements of the sphere and cube (applied to fourth-rank tensors), the material tensor can be shown quite generally to be of the form (Zuzovsky *et al.*, 1983)

$$\begin{aligned}\dddot{\psi}^{s}/\tau_0 = {} & \alpha(\mathbf{e}_1\mathbf{e}_1\mathbf{e}_1\mathbf{e}_1 + \mathbf{e}_2\mathbf{e}_2\mathbf{e}_2\mathbf{e}_2 + \mathbf{e}_3\mathbf{e}_3\mathbf{e}_3\mathbf{e}_3) \\ & + \beta[(\mathbf{e}_1\mathbf{e}_2 + \mathbf{e}_2\mathbf{e}_1)(\mathbf{e}_1\mathbf{e}_2 + \mathbf{e}_2\mathbf{e}_1) \\ & + (\mathbf{e}_2\mathbf{e}_3 + \mathbf{e}_3\mathbf{e}_2)(\mathbf{e}_2\mathbf{e}_3 + \mathbf{e}_3\mathbf{e}_2) \\ & + (\mathbf{e}_3\mathbf{e}_1 + \mathbf{e}_1\mathbf{e}_3)(\mathbf{e}_3\mathbf{e}_1 + (\mathbf{e}_1\mathbf{e}_3)]. \end{aligned} \tag{7.25}$$

Coefficients $\alpha$, $\beta$, and $\xi^{(r)}$ are determined by solving Stokes equations.

For dilute arrays these coefficients are given by the expressions

$$\begin{aligned}\alpha &= (5/2)\phi[1 - (1 - 60\tilde{b}_{20})\phi + 12\tilde{a}_{20}\phi^{5/3} + 0(\phi^{7/3})]^{-1} \\ \beta &= (5/2)\phi[1 - (1 + 40\tilde{b}_{20})\phi - 8\tilde{a}_{20}\phi^{5/3} + 0(\phi^{7/3})]^{-1} \\ \xi^{(r)} &= 6\phi[1 - \phi + 12\tilde{a}_{20}^2\phi^{10/3} + 0(\phi^{14/3})]^{-1}. \end{aligned} \tag{7.26}$$

Requisite coefficients $\tilde{a}_{20}$ and $\tilde{b}_{20}$ are tabulated in Table II for each of the three cubic lattices. These values agree well with those independently derived by Kapral and Bedeaux (1978).

For highly concentrated suspensions where the spheres almost touch, these coefficients adopt the asymptotic forms (Zuzovsky *et al.*, 1983)

$$\begin{aligned}\alpha &= (3\pi/16)\chi^{1/3}(1 - \chi^{1/3})^{-1}, \\ \beta &= (\pi/4)\ln(\chi^{-1/3} - 1)^{-1}, \\ \xi^{(r)} &= \pi\ln(\chi^{-1/3} - 1)^{-1}, \end{aligned} \tag{7.27}$$

for simple cubic arrays. Here, $\chi = \phi/\phi_{\max}$, with $\phi_{\max} = \pi/6$ for a simple cubic array.

Equations (7.26) and (7.27) furnish limiting results for both dilute and concentrated systems. Nunan and Keller (1984) subsequently extended these numerical calculations to intermediate concentrations as well, simultaneously

confirming the dilute and concentrated sphere suspension asymptotes in Eqs. (7.26) and (7.27).

The foregoing configuration-specific rheological results are valid only instantaneously at the instant the sheared suspension momentarily possesses the specified cubic arrangement. As such, the configuration-specific rheological results will not be compared to formulas previously cited in Section II. In order to derive stationary values for the macroscopic rheological properties of suspensions, a large number of ordered structures must be analyzed and time averages [or the equivalent averages in Eq. (7.17) or (7.18)] computed therefrom. Thus, the average of any desired interstitial field property can clearly be derived or (more practically) estimated by interpolation. [This is reminiscent of the determination of the relative trajectories of two spheres in linear shear flows (Adler, 1981a,b).]

To conclude this subsection, we expose an interesting paradox arising from the time dependence of the particle configuration. As discussed in Section III, Frankel and Acrivos (1967) developed a time-independent "lubrication" model for treating concentrated suspensions. Their result, given by Eq. (3.7), predicts singular behavior of the shear viscosity in the maximum concentration limit where the spheres touch. Within the spatially periodic framework, the instantaneous macroscopic stress tensor may be calculated for the lubrication limit, $\varepsilon \to 0$. The symmetric portion of its deviatoric component takes the form (Zuzovsky *et al.*, 1983)

$$\frac{\mu_0 \pi a}{2\tau_0 \varepsilon} \mathbf{mm} : \bar{\mathbf{S}} \left( 3 \frac{\mathbf{mm}}{|\mathbf{m}|^2} - \mathbf{I} \right) \tag{7.28}$$

for the configuration shown in Fig. 6. Here, $\varepsilon$ denotes the gap width made dimensionless with the sphere radius. The time integral in Eq. (7.17) resulting from integration of Eq. (7.28) can be shown (Zuzovsky *et al.*, 1983) to be nonsingular! That is, terms of 0(1) result upon integration rather than terms that tend to infinity in the $\varepsilon \to 0$ limit. Thus, although the instantaneous stress tends to infinity in the touching-sphere limit, the time-average stress nevertheless remains finite—a fact that contradicts Eq. (3.7). These conclusions regarding the nonsingular nature of the touching-sphere limit are supported by the scaling arguments of Marrucci and Denn (1985) with respect to the important role played by the time-dependence of the relative sphere positions, in which arguments are not limited to periodic arrays.

Of course, in this limit, nonhydrodynamic factors may dominate the suspension's rheological properties. Included in this class are such potentially relevant features as surface roughness, interstitial fluid cavitation (Goldman *et al.*, 1967a), particle elasticity and lattice disorder, any of which, when incorporated into the analysis, might give rise to singular behavior in the $\varepsilon \to 0$

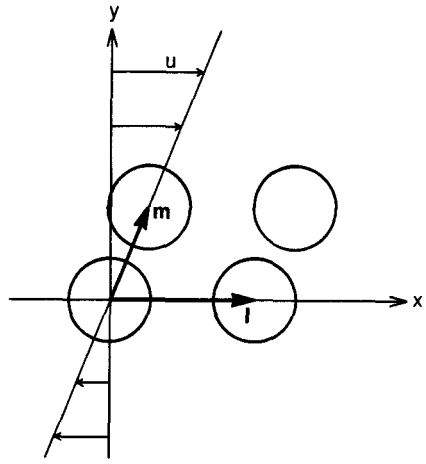



FIG. 6. Two-dimensional array in a simple shear flow; $u = Gy$, $v = 0$ are the velocity components.

limit. However, a detailed discussion of the relative importance of such phenomena in the interpretation and rationalization of experimental results appears premature at this stage. Comments advanced in Section VI regarding the possible formation of infinite clusters may also be relevant to the resolution of this paradox.

## D. Extension to $N$ Particles in a Unit Cell

The previous analysis may be extended to spatially periodic suspensions whose basic unit cell contains not one, but many particles. Such models would parallel those employed in liquid-state theories, which are widely used in computer simulations of molecular behavior (Hansen and McDonald, 1976). This subsection briefly addresses this extension, showing how the trajectories of each of the particles (modulo the unit cell) can be calculated and time-average particle stresses derived subsequently therefrom. This provides a natural entrée into recent dynamic simulations of suspensions, which are reviewed later in Section VIII.

Consider a spatially periodic suspension whose basic unit cell contains $N$ particles, all of whose sizes, shapes, and orientations may be different. The particulate phase of the system is completely specified geometrically by the values of the $3N$ spatial coordinates $\mathbf{r}^N$, and $3N$ orientational coordinates $\mathbf{e}^N$ of the (generally nonspherical) particles, as in Section II,A. A particle is identified by the pair of scalar and "vector" indices $i$ ($i = 1, \ldots, N$) and $\mathbf{n}$,

respectively, the latter of which indicates the particular unit cell to which particle $i$ is assigned.

Stokes Eqs. (2.2) and (2.3) are again assumed to describe the interstitial fluid dynamics and kinematics, while the adherence condition at the particle surfaces now requires that

$$\mathbf{v} = \mathbf{U}_{i,\mathbf{n}} + \boldsymbol{\Omega}_i \times \mathbf{r}_i \quad \text{on } s_i, \tag{7.29}$$

with $\mathbf{U}_{i,\mathbf{n}}$ and $\boldsymbol{\Omega}_i$ the respective translational and rotational velocities of particle $\{i, \mathbf{n}\}$. Note that $\boldsymbol{\Omega}_i$ does not depend on the cell number $\mathbf{n}$ for the homogeneous macroscopic shear flows being considered. The velocity of the particle $\{i, \mathbf{n}\}$ can be decomposed, as in Eq. (7.13), into the sum

$$\mathbf{U}_{i,\mathbf{n}} = \mathbf{U}_i + \mathbf{R}_\mathbf{n} \cdot \mathbf{G}, \tag{7.30}$$

with $\mathbf{U}_i$ the velocity of particle $i$ in cell $\mathbf{0}$. Upon employing the decomposition in Eq. (7.9), which continues to be valid in present circumstances, the counterpart of Eq. (7.11) here adopts the form

$$\tilde{\mathbf{v}} = (\mathbf{U}_i - \bar{\mathbf{v}}^*) + (\boldsymbol{\Omega}_i - \bar{\boldsymbol{\omega}}) \times \mathbf{r}_i - \mathbf{r}_i \cdot \bar{\mathbf{S}}, \qquad \text{on } s_i. \tag{7.31}$$

As a consequence of the linearity of the governing equations, the grand resistance matrix formulation is again applicable, yielding

$$\begin{bmatrix} \mathbf{F}^N \\ \mathbf{N}^N \\ \mathbf{A} \end{bmatrix} = \mu_0 \mathbf{R}(\mathbf{r}^N, \mathbf{e}^N, \mathbf{L}) \begin{bmatrix} \bar{\mathbf{v}}^{*N} - \mathbf{U}^N \\ \bar{\boldsymbol{\omega}}^N - \boldsymbol{\Omega}^N \\ \bar{\mathbf{S}} \end{bmatrix}, \tag{7.32}$$

where the partitioned matrix $\mathbf{R}$ is a material property dependent only on the configuration $(\mathbf{r}^N, \mathbf{e}^N)$ of the particles and the configuration of the time-dependent lattice $\mathbf{L}$.

Upon neglecting particle inertial effects, the dynamics of the individual particle motions is governed by the force/torque balance

$$\begin{bmatrix} \mathbf{F}^N \\ \mathbf{N}^N \end{bmatrix} + \begin{bmatrix} \mathbf{F}^N_{\text{ext}} \\ \mathbf{N}^N_{\text{ext}} \end{bmatrix} = \begin{bmatrix} \mathbf{0} \\ \mathbf{0} \end{bmatrix}, \tag{7.33}$$

where $\mathbf{F}^N_{\text{ext}}$ and $\mathbf{N}^N_{\text{ext}}$ are each $3N$ vectors composed of the external three-dimensional force and torque vectors, if any, acting on the particles. Equation (7.33) together with Eq. (7.32) provides a first-order evolution system for $(\mathbf{r}^N, \mathbf{e}^N)$. Thus, as in Section II,A, for a suspension of spheres, a trajectory equation of the form

$$d\mathbf{r}^N/dt = \mathbf{f}(\mathbf{r}^N, \mathbf{L}) \tag{7.34}$$

can be obtained, with **f** as a nonlinear vector function. The trajectories $\mathbf{r}^N(t)$ of the $N$ spheres may thus be determined, at least in principle, by solving Eq. (7.34).

Computation of the grand resistance matrix **R** for each possible particle configuration provides a major numerical challenge (see Section VIII). The various methods cited in Section II for dealing with the many-body problem are potentially useful in this context. Detailed calculations must be performed for a number of accessible configurations, and the configurational evolution determined by interpolation in order to effect the requisite time averaging.

Determination of the maximum particle concentration is also of interest since it no longer constitutes a purely kinematical problem. Rather, the suspension contained within the unit cell is now a mixed "object" possessing both solid-like and liquid-like features. In particular, it behaves like a solid insofar as mutual impenetrability demands are concerned, whereas it behaves like a liquid in its ability to change its configuration (i.e., it can "flow").

The question of ergodicity of the dynamical system in Eq. (7.34) remains. When the lattice exactly reproduces itself in time (as was the case for rational simple shear flow), **L**, and hence $\mathbf{r}^N$, are periodic functions of time, whence the process is nonergodic. When **L** is almost periodic in time, so is $\mathbf{r}^N$. But it is not known whether $\mathbf{r}^N$ visits the entire available space or just some subspace thereof. This question must be answered before meaningful averages can be performed.

Another remaining problem arises when the results obtained for a finite cell are extrapolated to an infinite suspension. This necessitates the cell size to be much larger than any other length scales characterizing the suspension. While this is usually the case, it fails to be true near the "percolation threshold." Possible existence of the latter critical point is discussed by DeGennes (1979); if it does exist, a special technique called finite-size scaling (Stauffer, 1985) may be used to extract the asymptotic limit from numerical data gleaned on finite cells. This is equivalent to extracting the limiting behavior of an infinite suspension from the corresponding results derived for a finite suspension of $N$ particles.

In conclusion, we note that the formulation of Eqs. (7.32) and (7.33) is formally complete, encompassing the possibilities of dissimilar nonspherical particles within a unit cell, interparticle forces, Brownian motion, etc. At the same time, the scheme is rigorous, at least within the formal constrained geometric framework adopted. Just as "one particle per cell" results have contributed to the identification of the key features of the suspension problem, so it is to be expected that $N$-particle dynamical analyses will provide more general answers to comparable long-standing questions pertaining to the rheological properties of concentrated suspensions.

## VIII. Current Research Topics

Four novel approaches to contemporary studies of suspensions are briefly reviewed in this final section. Addressed first is Stokesian dynamics, a newly developed simulation technique. Surveyed next is a recent application of generalized Taylor dispersion theory (Brenner, 1980a, 1982) to the study of momentum transport in suspensions. Third, a synopsis is provided of recent studies in the general area of fractal suspensions. Finally, some novel properties (e.g., the existence of antisymmetric stresses) of dipolar suspensions are reviewed in relation to their applications to magnetic and electrorheological fluid properties.

### A. Stokesian Dynamics

The extension to multiparticle unit cells alluded to in Section VII,E has, in some sense, already been achieved. Contributions by Bossis and Brady (1984) and Brady and Bossis (1985) provide a general technique for simulating the temporal evolution of sheared suspensions. These authors subsequently applied their technique to calculating the rheological properties of nondilute suspensions. This periodic boundary-condition scheme for simulating unbounded suspensions is closely related to that of Section VII,E, though we retain here the original notation of Bossis and Brady for ease of reference. In the paragraphs that follow, we content ourselves with merely reviewing the rudiments of this new simulation technique. A much more comprehensive survey has been provided by Brady and Bossis (1988), who present examples, of Stokesian dynamics applications to suspension rheology, porous media, diffusion of interacting particles, and bounded suspensions.

In the absence of inertia and Brownian motion, the quasistatic dynamics of $N$ rigid suspended particles contained within a unit cell is governed by the composite force and torque balance

$$\mathbf{F}_H + \mathbf{F}_P = \mathbf{0}, \tag{8.1}$$

in which $\mathbf{F}_H$ and $\mathbf{F}_P$ are $6N$ force–torque vectors of hydrodynamic and nonhydrodynamic origins, respectively. The equivalent grand resistance formulation [cf. Eq. (7.32)] for the hydrodynamic force–torque vector is given as

$$\mathbf{F}_H = \mathbf{R} \cdot \mathbf{U}^* + \dddot{\Phi} : \mathbf{E}, \tag{8.2}$$

with the particulate material entities $\mathbf{R}$ and $\Phi$ respectively referred to by Brady and Bossis (following Brenner and O'Neill, 1972) as the grand resistance and shear resistance matrices. $\mathbf{U}^*$ denotes the translational-angular velocity "vector" of the particles relative to the bulk, and $\mathbf{E}$ denotes the symmetric

portion of the bulk rate of strain tensor (corresponding to $\bar{\mathbf{S}}$ in Section VII). Substitution of Eq. (8.2) into Eq. (8.1) and subsequent multiplication by $\mathbf{R}^{-1}$ yields the evolution equation

$$\mathbf{U}^* = -\mathbf{R}^{-1} \cdot \{\dddot{\Phi}:\mathbf{E} + \mathbf{F}_P\}. \tag{8.3}$$

The simulation technique involves temporal integration of Eq. (8.3) to find the instantaneous positions and orientations of the suspended particles. Since $\mathbf{R}$ and $\ddot{\Phi}$ are configuration dependent, they must be updated at each time step as the configuration evolves in time. (Allowance can also be made for the externally imposed rate-of-strain dyadic $\mathbf{E}$ to depend on time if desired, e.g., time periodicity.) Integration is continued beyond the time at which a "stationary" particle state is achieved, as characterized by monitoring the average of the square of the particle velocities relative to the bulk. (Note that questions of reproducibility of the structure or of its ergodicity are not addressed, although the computational results are themselves reproducible beginning from different initial configuration.)

This general technique was employed to simulate the motion of a monolayer of identical spherical particles subjected to a simple shear. Confinement to a monolayer represents tremendous economies of computer time compared with a three-dimensional simulation. Hopefully, these highly specialized monolayer results will provide comparable insights into the physics of three-dimensional suspensions. Periodic boundary conditions were used in the simulation, and the method of Evans (1979) was incorporated to reproduce the imposed shear.

In order to account for hydrodynamic interactions among the suspended particles, Bossis and Brady (1984) used both pairwise additivity of velocities (mobilities) and forces (resistances), discussing the advantages and disadvantages of each method. While their original work did not take explicit account of three- (or more) body effects, the recent formulation of Durlofsky, Brady, and Bossis (1988) does provide a useful procedure for incorporating both the far-field, many-body interactions and near-field, "lubrication" forces into the grand resistance and mobility matrices.

Simulations were carried out with and without the presence of additional nonhydrodynamic, interparticle forces. When included, the latter were assumed to be repulsive in nature and given pairwise for spheres by the DLVO-type expression

$$\mathbf{F}_{\text{rep}} = \mathbf{F}_0 \frac{\tau e^{-\tau h}}{1 - e^{-\tau h}}, \tag{8.4}$$

with $\mathbf{F}_0$, the amplitude of the force; $\tau$, the inverse of the Debye length (made dimensionless with the sphere radius); and $h$, the dimensionless separation distance between adjacent sphere surfaces (Takamura *et al.*, 1981; Bossis and Brady, 1984). Important parameters were the volumetric solids fraction $\phi$,

characteristic interaction length $\tau^{-1}$, and shear rate $\dot{\gamma}$ (which is made dimensionless with $|\mathbf{F}_0|/6\pi\mu a^2$).

Principal results pertaining to the long-time mean structure of the suspension calculated by Bossis and Brady (1984) are embodied in the pair distribution function $g(\mathbf{r}) = g(r, \vartheta)$, defined as the conditional probability density for finding a particle at $\mathbf{r}$, given the existence of another particle at the origin (and normalized by dividing by the particle number density). Angular structure is found to exist only in the presence of repulsive forces where a larger particle density exists on the upstream side of the sphere situated at the origin. (On the downstream side, both the repulsive forces and shear tend to separate the particles.) Radial structure is also found (mainly due to excluded volume effects), possessing classical nearest neighbor peaks, second nearest-neighbor peaks, etc. Both the angular and radial structures were found to be functionally dependent on the particle-number density, shear rate, and repulsive-force range. Increasing the areal fraction $\phi$ of the particles and/or the length range $\tau^{-1}$ of the DLVO-type repulsive forces causes a transition to a layered structure, in which lines of particles "slide" relative to one another. As densities approaching the maximum possible for flow are achieved, cluster formation is observed to occur. Experiments by Husband and Gadala-Maria (1987) have verified the formation of anisotropic structures in noncolloidal suspensions.

In addition to the microstructural geometrical features described above, macroscopic, dynamical, rheological properties of the suspensions are derived by Brady and Bossis (1985). Dual calculations are again performed, respectively with and without DLVO-type forces. When such forces are present, an additional contribution (the so-called "elastic" stress) to the bulk stress tensor exists. In such circumstances, the term (Batchelor, 1977; Brady and Bossis, 1985)

$$\frac{1}{V}\sum_{i=2}^{N}\sum_{j<i}\mathbf{r}^{ij}\mathbf{F}^{ij}, \tag{8.5}$$

must be added to the RHS of Eq. (2.3a), where $\mathbf{r}^{ij}$ is the center-to-center separation of particles $i$ and $j$, and $\mathbf{F}^{ij}$ is the pairwise interparticle force acting between them.

With the bulk, deviatoric stress tensor denoted by $\boldsymbol{\sigma}$, Bossis and Brady define the relative viscosity $\eta_r$ of the suspension as

$$\langle\sigma_{xy}\rangle = \eta_r\eta_0\dot{\gamma}. \tag{8.6}$$

Additionally, primary and secondary normal stress coefficients $\psi_1$ and $\psi_2$ are defined by the respective relations

$$\begin{aligned}\langle\sigma_{xx}\rangle - \langle\sigma_{yy}\rangle &= -\psi_1\dot{\gamma}^2,\\ \langle\sigma_{yy}\rangle - \langle\sigma_{zz}\rangle &= -\psi_2\dot{\gamma}^2.\end{aligned} \tag{8.7}$$

Expressions are derived for these coefficients in terms of dynamical quantities (such as the relative radial and tangential velocities of pairs of spheres) directly calculable by the simulation scheme.

Normal stress differences do not exist in the absence of interparticle forces. Moreover, the relative viscosity of the suspension is a function of only $\phi$. At particle densities approaching the maximum possible that still allow the suspension to flow, cluster size (and, as a result, the viscosity of the two-dimensional monolayer) appears to scale as

$$[1 - (\phi/\phi_{max})^{1/2}]^{-1}, \tag{8.8}$$

with the $\frac{1}{2}$ exponent replaced by $\frac{1}{3}$ in three dimensions. However, since the density range investigated was limited, the possible emergence of a different mode of behavior at densities close to the "percolation threshold," $\phi_{max}$, is not ruled out. Comments are also offered by Bossis and Brady on the finite limit obtained for the viscosity of a spatially periodic suspension (cf. Section VI and VII,B). Comparison of their results with experiments has been found to be satisfactory (Brady and Bossis, 1985), although this comparison involves an ad hoc rescaling to convert their areal fraction to the comparable volumetric fraction prevailing in the three-dimensional experiments.

Repulsive interparticle forces cause the suspension to manifest non-Newtonian behavior. Detailed calculations reveal that the primary normal stress coefficient $\psi_1$ [cf. Eq. (8.7)] decreases like $\dot{\gamma}^{-1}$. In contrast, the suspension viscosity displays shear-thickening behavior. This feature is again attributed to the enhanced formation of clusters at higher shear rates.

Similar methods were employed by Schonberg *et al.* (1986) to investigate the multiparticle motions of a finite collection of neutrally buoyant spheres suspended in a Poiseuille flow. They were also used by Ansell and Dickinson (1986) to simulate the fragmentation of a large colloidal floc in a simple shear flow.

Finally, we direct attention to Barnes *et al.* (1987), for their extensive review of applications of computer simulations to dense suspension rheology, and also to Hassonjee *et al.* (1988), for their numerical scheme for dealing with large clusters of spherical particles.

## B. Momentum Tracer Methods

In a companion pair of contributions, Mauri and Brenner (1991a,b) introduce a novel scheme for determining the rheological properties of suspensions. Their approach extends generalized Taylor–Aris dispersion-theory moment techniques (Brenner, 1980a, 1982)—particularly as earlier addressed to the study of tracer dispersion in immobile, spatially periodic media (Brenner, 1980b; Brenner and Adler, 1982)—from the realm of *material*

tracer transport in suspensions to that of *momentum* tracer transport. Among other things, the configuration-specific viscosity of a suspension *at rest* (i.e., at zero shear rate) is shown by Mauri and Brenner to be the same as that for a *flowing* suspension possessing the same instantaneous particle configuration, at least in the limit of small Reynolds numbers.

The underlying *ansatz* consists of deliberately introducing a weak*, low-intensity, impulsive source of momentum (a so-called momentum "tracer") into the interstices of an otherwise quiescent suspension and monitoring the temporal spread of this momentum tracer from its initial point of introduction as it "diffuses" throughout the suspension in consequence of the kinematic viscosity of the interstitial fluid. Central to interpreting the instantaneous moments of the resulting momentum density-distribution is the fact that the momentum originally introduced impulsively into the system is conserved, since no external (or inertial) forces act on the neutrally buoyant suspension. In an abstract sense, momental diffusion of this conserved momentum tracer occurs by a mechanism conceptually no different from that underlying the mass diffusion of a conserved material tracer, except that the rate of momental diffusion is governed by the kinematic viscosity $\nu = \mu_0/\rho$ of the interstitial fluid, whereas the rate of mass diffusion is governed by the molecular diffusivity $D$ of the material tracer through the interstitial fluid. (Indeed, this is the basis for all analogies between mass and momentum transport in *homogeneous* fluids.) Consequently, by analogy, just as the long-time mean-square displacement of a Brownian material tracer, through the interstices of the suspension, provides the suspension-scale (mean) dispersivity dyadic $\bar{D}_{ij}$ (Brenner, 1980b; Brenner and Adler, 1982) in terms of the interstitial molecular diffusivity $D$ and particulate-phase configuration, so too does the long-time spread of the "Brownian" momentum tracer in Mauri and Brenner's (1991a,b) theory furnish the suspension-scale kinematic viscosity tetradic $\bar{\nu}_{ijkl}$ in terms of the kinematic viscosity $\nu$ of the interstitial fluid and this same particulate configuration.

Specifics of this approach are outlined in the next few paragraphs. Consider a spatially periodic "suspension," one whose density $\rho$ is everywhere constant and whose kinematic viscosity $\nu(\mathbf{r})$ is everywhere a spatially periodic function of position, albeit perhaps discontinuous. (Generalization to the case of

* Such "weakness" assures that the initial arrangement of particles prior to introduction of the tracer is not sensibly disturbed by the impulse as it "diffuses" throughout the suspension. Thus, in contrast with *flowing* systems, the mode of particle arrangement is decoupled from the hydrodynamics of the momentum transport process (as well as being time independent). Hence, the geometry of the particulate phase may be arbitrarily specified, leading to the unambiguous concept of configuration-specific rheological properties as experimentally realizable, macroscopic, dynamic attributes of such configurations.

spatially periodic distributions of *rigid* particles is addressed subsequently.) The vector $\mathbf{r}$ arises upon decomposition of the position vector $\mathbf{R}$ into the sum

$$\mathbf{R} = \mathbf{R}_n + \mathbf{r} \tag{8.9}$$

of discrete [cf. Eq. (7.1)] and continuous vectors. In particular, the vector $\mathbf{r}$ is "local" (Brenner, 1980b) in nature, being defined only within the interior domain $\tau_0$ of a unit cell (the magnitude of whose superficial volume is also denoted by the same symbol $\tau_0$).

After introduction of an impulsive source $\mathbf{U}\,\delta(\mathbf{R} - \mathbf{R}')\,\delta(t)$ of momentum into the suspension at position $\mathbf{R} = \mathbf{R}'$ (with $\mathbf{R}' = \mathbf{R}_{n'} + \mathbf{r}'$), at time $t = 0$ and vector strength $\mathbf{U}$, subsequent transport of this momentum tracer through the suspension (the latter assumed to be initially at rest) is governed by the system of equations (Mauri and Brenner, 1991a,b)

$$\partial \mathbf{P}/\partial t + \nabla \cdot \dddot{\mathbf{J}} = \mathbf{I}\,\delta_{\mathbf{m}0}\,\delta(\mathbf{r} - \mathbf{r}')\,\delta(t), \tag{8.10}$$

$$\nabla \cdot \mathbf{P} = \mathbf{0}, \tag{8.11}$$

with

$$\dddot{\mathbf{J}} = \mathbf{I}\boldsymbol{\Pi} - \nu(\mathbf{r})(\nabla \mathbf{P} + {}^{\dagger}\nabla \mathbf{P}). \tag{8.12}$$

Here, $\mathbf{I}$ is the dyadic idemfactor and $\mathbf{m} = \mathbf{n} - \mathbf{n}'$; moreover, $\nabla \equiv \partial/\partial \mathbf{r}$ is the local gradient operator defined only within a unit cell ($\mathbf{r} \in \tau_0$). The "material" functions $\mathbf{P}$, $\dddot{\mathbf{J}}$, and $\boldsymbol{\Pi}$ are the respective dyadic, triadic, and vector fields defined by the linear transformations

$$\mathbf{p} = \mathbf{P}(\mathbf{m}, \mathbf{r}, t\,|\,\mathbf{r}') \cdot \mathbf{U} \qquad (p_i = P_{ij}U_j), \tag{8.13a}$$

$$\pi = \boldsymbol{\Pi}(\mathbf{m}, \mathbf{r}, t\,|\,\mathbf{r}') \cdot \mathbf{U} \qquad (\pi = \Pi_j U_j), \tag{8.13b}$$

$$\mathbf{T} = -\dddot{\mathbf{J}}(\mathbf{m}, \mathbf{r}, t\,|\,\mathbf{r}') \cdot \mathbf{U} \qquad (T_{ij} = -J_{ijk}U_k), \tag{8.13c}$$

as the respective "propagators" for the momentum density $\mathbf{p} \equiv \rho\mathbf{v}$, the pressure $\pi$, and the total stress tensor $\mathbf{T}$, each of which arise from the introduction of the impulse of strength $\mathbf{U}$ at position $\mathbf{R}'$ at time $t = 0$. That these are indeed material functions follows from the fact that these fields depend only on the prescribed kinematic viscosity field $\nu(\mathbf{r})$ and spatially periodic configuration—which functional dependence follows from the uniquely posed system of Eqs. (8.10)–(8.13) and (8.14) that define these fields.

Equations (8.10)–(8.13) are merely Stokes equations rewritten in a suggestive form chosen to emphasize transport of the momentum tracer density $\rho\mathbf{v}$, as well as to exploit the analogy between Eq. (8.10) for momentum transport and the comparable equation (Brenner, 1980b) for transport of the scalar probability density $P$, which is equivalent to the material tracer density. The absence of a convective term $\mathbf{vp}$ from the flux expression in Eq. (8.12)

reflects the neglect of inertial effects (valid at small, unit-cell Reynolds numbers), where transport occurs purely by the "molecular diffusion" of momentum. Explicitly, the dyadic $P_{ij}(\mathbf{R}, t \mid \mathbf{R}')$ [note the equivalence of the arguments $(\mathbf{R}, t \mid \mathbf{R}')$ and $(\mathbf{m}, \mathbf{r}, t \mid \mathbf{r}')$] may be regarded as the dyadic "probability density" (more conventionally, the Green's function) for finding the momentum tracer at position $\mathbf{R}$ at time $t$ pointing in the $x_i$ direction ($i = 1, 2, 3$), given that initially ($t = 0$) it was located at $\mathbf{R}'$ and had direction $x_j$ ($j = 1, 2, 3$). The triadic $\dddot{\mathbf{J}}$ may be similarly interpreted as the flux of the momental probability density arising in joint consequence of momental "Brownian" motion (whose intensity is measured by the kinematic viscosity) together with the action of the pressure stresses $\mathbf{\Pi}$ [cf. Eq. (8.12)].

Equations (8.10)–(8.12) are to be solved within each unit cell subject to the conditions

$$(\mathbf{P}, \hat{\mathbf{n}} \cdot \dddot{\mathbf{J}}) \qquad \text{continuous across } S_p, \tag{8.14a}$$

$$|\mathbf{R}_m|^n \mathbf{h} \to \mathbf{0} \text{ as } |\mathbf{m}| \to \infty \qquad (n = 0, 1, 2, \ldots), \tag{8.14b}$$

and

$$\mathbf{h}(\mathbf{m}^*, \mathbf{r} + \mathbf{l}_j) = \mathbf{h}(\mathbf{m}^*, \mathbf{r} + \mathbf{l}_j) = \mathbf{h}(\mathbf{m}, \mathbf{r}) \quad \text{on } \partial\tau_0. \tag{8.15}$$

Here, $\hat{\mathbf{n}}$ is a unit normal vector at the interstitial phase boundary $S_p$, if any, across which the kinematic viscosity $\nu(\mathbf{r})$ is possibly discontinuous, whereas the generic symbol $\mathbf{h}$ denotes either $\mathbf{P}$ or $\dddot{\mathbf{J}}$. Equation (8.15) expresses continuity of the pertinent fields across the unit cell faces $\partial\tau_0$. In Eq. (8.15), $\mathbf{m}^*$ is to be chosen such that $\mathbf{R}_{m^*} = \mathbf{R}_m - \mathbf{l}_j$ is a basic lattice vector [cf. Eq. (7.1)].

Equations (8.10)–(8.12), tensorial ranks and boundary conditions (8.14)–(8.15) notwithstanding, embody a structure similar in format and symbolism to their counterparts for the transport of passive scalars, e.g., the material transport of the scalar probability density $P$ (Brenner, 1980b; Brenner and Adler, 1982), at least in the absence of convective transport. As such, by analogy to the case of nonconvective material transport, the effective kinematic viscosity $\bar{\nu}_{ijkl}$ of the suspension may be obtained by matching the total spatial moments of the probability density $P_{ij}$ to those of an equivalent coarse-grained dyadic probability density $\bar{P}_{ij}$, valid on the suspension scale, using a scheme (Brenner and Adler, 1982) identical in conception to that used to determine the effective diffusivity for material transport at the Darcy scale from the analogous scalar material probability density $P$. In particular, the second-order total moment $\ddddot{\mathbf{M}}^{(2)}$ ($\equiv \mathbf{M}^{(2)}_{ijkl}$) of the probability density $\mathbf{P}$, defined as

$$\ddddot{\mathbf{M}}^{(2)}(t \mid \mathbf{r}') = \int_{\tau_0} d\mathbf{r} \sum_{\mathbf{m}} \mathbf{P}(\mathbf{m}, \mathbf{r}, t \mid \mathbf{r}') \mathbf{R}_m \mathbf{R}_m, \tag{8.16}$$

is found to be governed in the asymptotic long-time limit by the expression

$$d\overset{\cdots\cdots}{\mathbf{M}}^{(2)}/dt \simeq \tau_0^{-1} \int_{\partial\tau_0} d\mathbf{s} \cdot [\overset{\cdots\cdots}{\mathscr{J}}\mathbf{r} + (\overset{\cdots\cdots}{\mathscr{J}}\mathbf{r})^{\dagger}]. \tag{8.17}$$

In Eq. (8.17), $\overset{\cdots\cdots}{\mathscr{J}}\ (\equiv \mathscr{J}_{ijkl})$ is found by solving the steady-state unit cell equations (Mauri and Brenner, 1991a)

$$\nabla \cdot \overset{\cdots\cdots}{\mathscr{J}} = \mathbf{0}, \tag{8.18a}$$

$$\nabla \cdot \overset{\cdots}{\mathscr{P}} = \mathbf{0}, \tag{8.18b}$$

$$\overset{\cdots\cdots}{\mathscr{J}} = \mathbf{I}\ddot{\mathscr{p}} - \nu(\nabla\overset{\cdots}{\mathscr{P}} + {}^{\dagger}\nabla\overset{\cdots}{\mathscr{P}}), \tag{8.18c}$$

$$(\overset{\cdots}{\mathscr{P}}, \hat{\mathbf{n}} \cdot \overset{\cdots\cdots}{\mathscr{J}}) \text{ continuous across } S_p. \tag{8.18d}$$

The three tensor fields $\ddot{\mathscr{p}}(\equiv \mathscr{p}_{ij})$, $\overset{\cdots}{\mathscr{P}} \equiv (\mathscr{P}_{ijk})$ and $\overset{\cdots\cdots}{\mathscr{J}}(\equiv \mathscr{J}_{ijkl})$ appearing in these equations are further required to satisfy the "jump" boundary conditions

$$[\![\overset{\cdots}{\mathscr{P}}]\!] = -[\![\mathbf{Ir}]\!], \tag{8.19a}$$

$$[\![\ddot{\mathscr{p}}]\!] = \mathbf{0}, \tag{8.19b}$$

$$[\![\overset{\cdots\cdots}{\mathscr{J}}]\!] = \mathbf{0}, \tag{8.19c}$$

imposed across the cell boundaries $\partial\tau_0$. The double-bracketed operator $[\![\ ]\!]$ appearing in Eq. (8.19) denotes the jump in the value of its argument across "equivalent" points symmetrically situated on opposite faces of the unit cell.

The suspension-scale momentum transport equation, whose moments need to be matched with those of Eq. (8.17), is adopted (Mauri and Brenner, 1991a) in the general form

$$\partial\bar{\mathbf{P}}/\partial t + \nabla_{\mathbf{R}} \cdot \overset{\cdots}{\mathbf{J}} = \mathbf{I}\,\delta(\mathbf{R} - \mathbf{R}')\,\delta(t) \tag{8.20a}$$

$$\nabla_{\mathbf{R}} \cdot \bar{\mathbf{P}} = \mathbf{0}, \tag{8.20b}$$

with

$$\overset{\cdots}{\mathbf{J}} = \mathbf{I}\bar{\Pi} - 2\overset{\cdots\cdots}{\bar{v}} : \nabla_{\mathbf{R}}\bar{\mathbf{P}}. \tag{8.20c}$$

An overbar denotes coarse-grained quantities. The Newtonian constitutive Eq. (8.20c), in effect, defines the configuration-specific, anisotropic, kinematic viscosity-tetradic $\overset{\cdots\cdots}{\bar{v}}\ (\equiv \bar{v}_{ijkl})$ of the spatially periodic suspension. Subject to the attenuation conditions,

$$|\mathbf{R} - \mathbf{R}'|^n(\bar{\mathbf{P}}, \overset{\cdots}{\mathbf{J}}) \to \mathbf{0} \quad \text{as } |\mathbf{R} - \mathbf{R}'| \to \infty \qquad (n = 0, 1, 2, \ldots), \tag{8.20d}$$

the set of Eq. (8.20) is used to derive evolution equations for the total moments of the suspension-scale probability dyadic $\bar{\mathbf{P}}$. The second-order moment of $\bar{\mathbf{P}}$

is found to adopt the asymptotic form

$$d\overline{\overline{\overline{\overline{\mathbf{M}}}}}^{(2)}/dt \simeq 4\overline{\overline{\overline{\overline{v}}}}. \tag{8.21}$$

Mauri and Brenner (1991a) show the lower-order moments to be properly matched; furthermore, the asymptotic correspondence of Eq. (8.21) with Eq. (8.17) requires that

$$\bar{v}_{ijkl} = \tfrac{1}{2}(N_{ijkl} + N_{ljki}), \tag{8.22}$$

where

$$\overline{\overline{\overline{\overline{\mathbf{N}}}}} = \frac{1}{2\tau_0}\int_{\partial\tau_0} \mathbf{r}\, d\mathbf{s} \cdot \overline{\overline{\overline{\overline{\mathscr{J}}}}} \tag{8.23}$$

with $\overline{\overline{\overline{\overline{\mathscr{J}}}}}$ to be found by solving Eq. (8.18) and (8.19).

Equation (8.22) constitutes the means whereby the configuration-specific kinematic viscosity of the suspension may be computed from the prescribed spatially periodic, microscale, kinematic viscosity data $\nu(\mathbf{r})$ by first solving an appropriate microscale unit-cell problem. Its "Lagrangian" derivation differs significantly from volume-average Eulerian approaches (Zuzovsky *et al.*, 1983; Nunan and Keller, 1984) usually employed in deriving such suspension-scale properties.

Results for the rigid-particle case can be extracted (Mauri and Brenner, 1991a) from the analysis presented here by formally setting

$$\nu(\mathbf{r}) = \nu_0 \equiv \text{const} \qquad (\mathbf{r} \in \tau_f) \tag{8.24}$$

in Eq. (8.18c) and solving Eqs. (8.18) and (8.19) in the interstitial fluid region $\tau_f$ external to the rigid-particle surfaces $S_p$ so as to satisfy the "no-slip" boundary condition

$$\mathbf{P} = \rho(\mathbf{V} + \boldsymbol{\Omega} \times \mathbf{r}) \quad \text{on } S_p. \tag{8.25}$$

Here, the vector constants $\mathbf{V}$ and $\boldsymbol{\Omega}$ are to be determined so as to satisfy the respective pair of dyadic and triadic particle–surface boundary conditions

$$\int_{S_p} d\mathbf{s} \cdot \overline{\overline{\overline{\mathscr{J}}}} = \mathbf{0}, \tag{8.26a}$$

$$\int_{S_p} \mathbf{r} \times (d\mathbf{s} \cdot \overline{\overline{\overline{\overline{\mathscr{J}}}}}) = \mathbf{0}, \tag{8.26b}$$

which express the force- and torque-free properties of the suspended bodies (and hence of the suspension as a whole).

To recapitulate, the momental "Brownian" motion of the conserved momentum tracer allows it to sample all portions of the suspension's intracell kinematic viscosity field $\nu(\mathbf{r})$, $(\mathbf{r} \in \tau_0)$, thereby furnishing the proper effective

viscosity of the suspension *without* the necessity for defining any arbitary averages of the microscale stresses or velocity gradients. Such ad hoc averages have heretofore constituted an essential element of virtually all suspension rheology schemes. Appearing in its stead is an Einstein-type diffusion formula for the temporal spread of the second moment of the momentum density, which provides the basis for the scheme. Equally novel is that the suspension is macroscopically at rest during the momentum diffusion process, rather than undergoing steady shear. This essentially Lagrangian approach furnishes the configuration-specific kinematic viscosity of concentrated suspensions. The configuration-specific values obtained by this scheme can be shown (Mauri and Brenner, 1991b) to be identical to values derived from the scheme described in Section VII.

*Falling-Ball Suspension Viscometry*

Closely related to the preceding momentum tracer scheme, which utilizes (tracer) motion through an otherwise quiescent suspension to establish the suspension's rheological properties, is the experimental work of Mondy, Graham and co-workers (1986a,b, 1987). Regarding each of their suspensions of neutrally buoyant particles as being a fluid continum possessing an effective Newtonian scalar viscosity $\mu$, they used experimental observations of the mean (i.e., time average) sedimentation speed of a heavy ball falling through the suspension, together with an assumed applicability of Stokes law to this mean ball velocity, to determine $\mu$ (after extrapolating their results to eliminate wall effects). Results obtained in this manner agreed well, over the entire concentration range studied ($0 < \phi < 0.5$), with standard nonquiescent suspension viscosity data (Thomas, 1965; Gadala-Maria and Acrivos, 1980) derived from Couette and capillary flow experiments, during which, the suspension was, of course, sheared.

What is remarkable about the Mondy-Graham results is that for each suspension investigated, the observed viscosity was independent of the relative diameter of the sedimenting ball ($d_f$) to that of the suspended spheres ($d_s$) over the entire size range studied ($0.75 \leq d_f/d_s \leq 12.0$). This despite the fact that, because of collisions with the suspended spheres, the instantaneous trajectory of the falling ball was observed to deviate significantly from a simple, uniform-speed, purely vertical trajectory at the smaller ball sizes. In the words of Mondy *et al.*, (1986a),

> Passage of a ball of the same or smaller diameter than the suspended balls is extremely discontinuous. Periods of almost no motion, as the falling ball approaches and 'rolls off' suspended spheres, alternate with periods of almost free fall in the interstices between suspended particles. A statistical analysis reveals that falling-ball terminal velocities averaged over a distance of approximately 100 suspended-ball diameters are reproducible.

It appears to us that this apparently "random" motion, superposed on the steady mean-settling velocity, is analogous to that of Brownian motion in the sense that it arises from the fact that the continuum is not structureless.

Subsequent falling-ball experiments performed with suspended rods (Graham *et al.*, 1987; Milliken *et al.*, 1989) replacing the spheres revealed significant and systematic differences between quiescent values of the suspension viscosity and those derived from Couette and capillary viscometer flow measurements. This is attributed by Graham, Mondy, and co-workers to fundamental differences in the distributions of rod orientations characterizing the quiescent and sheared suspensions.

### C. Fractal Suspensions

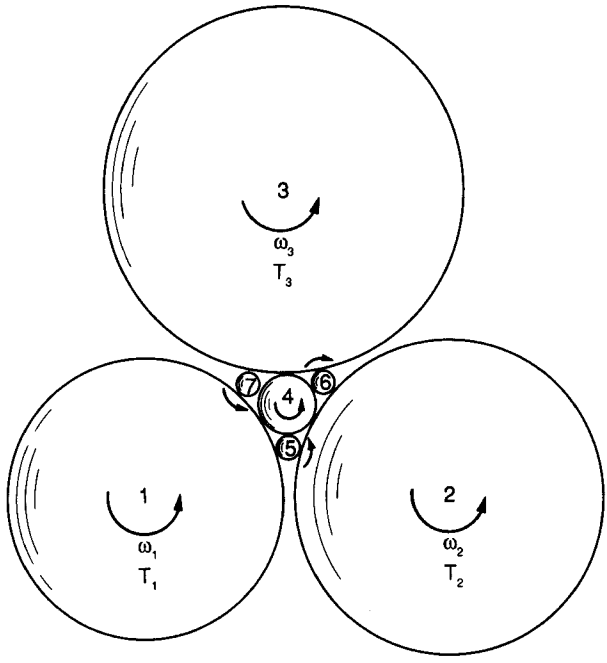
Another contemporary research thrust described here pertains to the hydrodynamic properties of fractal suspensions. The potential importance of such structures stems from the close analogy existing between percolation and suspension rheology near the critical concentration, as outlined in Section VI. Since the infinite cluster formed near the percolation threshold is fractal, the suspension itself may be expected to be fractal in that limit. A second potential area of application is to the rheology of highly polydisperse suspensions, involving a multiplicity of length scales and hence, suggesting the existence of fractal structures. Such structures may be expected to arise here from the presence of the large variety of particle sizes rather than from formation of infinite clusters, which was previously the case in the percolation analog.

Aggregable suspensions were shown (Weitz and Oliveria, 1984; Schaefer *et al.*, 1984) to yield fractal flocs, a result which sheds new light on the old subject of coagulation and flocculation.

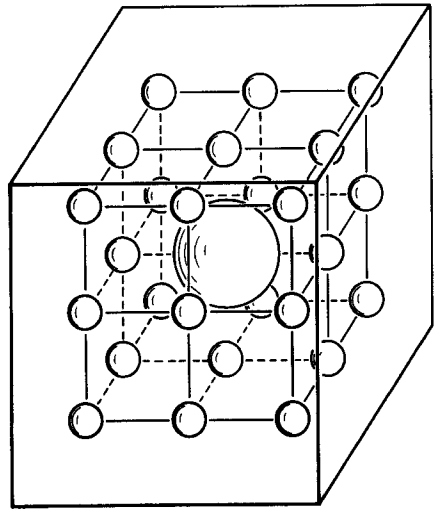
Available results pertinent to the hydrodynamics of fractal suspensions are sparse thus far, encompassing only three physical situations. Gilbert and Adler (1986) determined the Stokes rotation-resistance dyadic for spheres arranged in a Leibniz packing [Fig. 7(a)]. With the gap between any two spheres assumed small compared with their radii, lubrication-type approximations suffice. In this analysis, the inner spheres are assumed to rotate freely, whereas external torques $\mathbf{T}_i$ ($i = 1, 2, 3$) are applied to the three other spheres. For Stokes flow, these torques are linearly related to the sphere angular velocities by the expression

$$(\mathbf{T}_1, \mathbf{T}_2, \mathbf{T}_3) = \mathbf{M}_n \cdot (\omega_1, \omega_2, \omega_3), \tag{8.27}$$

with $\mathbf{M}_n$ as the rotational resistance dyadic whose numerical value is dependent on the generation number $n$ of the packing. Approximate formulas exist for $\mathbf{M}_n$; moreover, its asymptotic behavior for large $n$ has been studied.




(a)



(b)

FIG. 7. Two examples of fractal suspensions (a) The spheres are arranged in a Leibnitz packing with the construction process illustrated to $n = 2$; sphere 4 is created during the generation $n = 1$, while spheres 5, 6 and 7 are created during step $n = 2$. (b) The spheres are arranged according to a modified Menger sponge, again the contruction stage is shown to $n = 2$.

Another fractal structure of interest is considered by Adler (1986). A three-dimensional fractal suspension may be constructed from a modified Menger sponge, as shown in Fig. 7(b). A scaling argument permitted calculating the effective viscosity of such a suspension; however, this viscosity should be compared with numerical results for the solution of Stokes equations in such a geometry before this rheological result is accepted unequivocally.

Finally, in a related dynamical, though nonrheological context, Adler (1987) determined the drag exerted on fractal two-dimensional flocs possessing various fractal dimensions. He found a very weak effect (if indeed any effect) of this particular parameter on the drag for spatial dimensions ranging from 1.5 to 2.0.

### D. Antisymmetric Stresses, Internal Spin Fields, and Vortex Viscosity in Magnetic Fluids

Suspended spherical particles, each containing a permanently embedded dipole (e.g., magnetic), are unable to freely rotate (Brenner, 1984; Sellers and Brenner, 1989) in response to the shear and/or vorticity field that they are subjected to whenever a complementary external (e.g., magnetic) field acts on them. This hindered rotation results from the tendency of the dipole to align itself parallel to the external field because of the creation of a couple arising from any orientational misalignment between the directions of the dipole and external field. In accordance with Cauchy's moment-of-momentum equation for continua, these couples in turn give rise to an antisymmetric state of stress in the dipolar suspension, representable as the pseudovector $\mathbf{T}_\times = -\vec{\varepsilon}:\mathbf{T}^a$ of the antisymmetric portion $\mathbf{T}^a = \frac{1}{2}(\mathbf{T} - \mathbf{T}^\dagger)$ of the deviatoric stress $\mathbf{T} = \mathbf{P} + \mathbf{I}p$.

Accompanying the impeded particle rotation is the (kinematical) existence of an internal spin field $\boldsymbol{\Omega}$ within the suspension, which is different from one-half the vorticity $\boldsymbol{\omega} = (\frac{1}{2})\nabla \times \mathbf{v}$ of the suspension. The disparity $\boldsymbol{\omega} - \boldsymbol{\Omega}$ between the latter two fields serves as a reference-frame invariant pseudovector in the constitutive relation $\mathbf{T}_\times = \zeta(\boldsymbol{\omega} - \boldsymbol{\Omega})$, which defines the so-called "vortex viscosity" $\zeta$ of the suspension. Expressions for $\zeta(\phi)$ as a function of the volume $\phi$ of suspended spheres are available (Brenner, 1984) over the entire particle concentration range and are derived from the prior calculations of Zuzovsky *et al.* (1983) for cubic, spatially-periodic suspension models.

These suspension viscosity concepts are of growing technological importance in rationalizing and quantifying the behavior and properties of so-called magnetic fluids (Rosensweig, 1982, 1985, 1987). In a novel proposal, Brenner (1984) outlined a potentially useful scheme to use the apparently rigid-body rotation of a dipolar suspension to measure its vortex viscosity

(independently of its shear viscosity). Closely related to vortex viscosity is the heat- and mass-transfer study by Nadim *et al.* (1986) of enhanced, effective-conductivity transport properties in such dipolar suspensions when undergoing apparently rigid-body rotations. The so-called continuum-mechanical principle of material-frame indifference (Ryskin and Rallison, 1980) would, in such circumstances, incorrectly suggest the impossibility of affecting the transport rate by a rigid-body rotation of the apparatus housing the suspension.

Intimately related to these magnetic-field suspension rheology developments is the growing field of electrorheology, which involves comparable electric fields and was the subject of an international symposium (Carlson and Conrad, 1987).

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