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球狀粒子의 懸濁液에 관한 流動變形論

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Rheology of Concentrated Suspensions of Spherical Particles

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Abstract

This paper presents a statistical mechanical description of the random motion of particles in suspension and some results derived there-from for the viscosity of concentrated suspensions of solid spherical particles. In statistical mechanics the information about the probability of dynamical states of the particles of a fluid (i.e., their positions, translational velocities and rotational velocities) is embedded in a particle distribution function, and all of the macroscopic properties of the fluid are specified as integral moments of the distribution function. In particular, the local stress in a suspension is defined as the integral over all particle states of the distribution weighted with the stress at a point for a given instantaneous total particle state. Thus, the calculation of the rheological properties of the suspension comes down to a determination of the distribution function and this local stress function.

If the overall shear rate in the suspension is steady and not too large and the particles are neutrally buoyant solid spheres, the net forces and torques on the particles are zero and the local fluid motion is governed by the Stokes equations. It is shown that under these conditions 1) the particle distribution function is independent of the linear and angular velocities of the particles and so is uniquely determined by the particle positions, 2) the viscosity of the suspension must be independent of the shear rate for all concentrations, and 3) the viscosity can be written in a power series in the concentration of particles in which the term of the nth power is the incremental contribution to the viscosity from interactions involving particles. In order to calculate the coefficients of these terms the fluid velocity near the surface of a sphere moving with its neighbors in a shear field is required. Since an exact determination of the flow field is impractical to obtain for groups of more than two particles, an approximate solution of the Stokes equations obtained by the method of weighted residuals is used in the calculations of the suspension viscosity reported here. The particle configuration is assumed to be simple cubic, and the distribution of interparticle distances is obtained from an approximate statistical model. The viscosity-concentration relationship calculated under these assumptions is found to agree closely with the compilations of experimental data reported by Rutgers and Thomas.

I. Introduction

Suspensions of solid particles in liquids typically exhibit viscosities which are strongly dependent on the particle concentration. Since the pioneering study of Einstein there have been many investigations of the theoretical basis for the viscosity-concentration relationship, which can be determined,

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at least in principle, from an analysis of the coupled motions of the liquid and the particles. Considerable progress in this direction has been made for very dilute suspensions, for which the particles are sufficiently far apart on the average that they can be presumed to move independently of one another. In more concentrated suspensions interactions among pairs, triples and larger groups of particles become more frequent with increasing particle density until, at concentrations near the maximum packing fraction, multiple interactions completely dominate the particle motion. The determination of the fluid and particle motions in concentrated suspensions is thus complicated by two fundamentally different, though related, problems: the calculation of the fluid velocity field for given particle configurations and statistical analysis of the probabilities of instantaneous particle positions and velocities.

Of the numerous theoretical studies of suspension rheology there have been four [1-4] which have proposed specific models for treating the fluid-particle dynamics of concentrated suspensions. In each of these studies the suspension considered consists of a dispersion of neutrally buoyant, equal-sized, rigid spherical particles in an incompressible newtonian liquid. Inertial forces are assumed negligible, and the macroscopic flow is taken to be a steady, simple shearing motion. The first model used to represent particle interactions in concentrated suspensions was the cell model, in which the effect of the neighbors on the motion of the liquid around each particle is approximated by requiring that the motion of the liquid satisfy some prescribed boundary conditions on a spherical surface of radius b concentric with the particle. The local fluid velocity in the spherical annulus surrounding the particle is then the solution of the Stokes equations which satisfies the prescribed cell-surface boundary condition on $r=b$ and the no-slip condition on the particle surface $r=a$. Simha [1], in his specification of the model, argued that b should be proportional to R, the average interparticle distance, for dilute suspensions, and proportional to R-a for higher concentrations. The velocity at each point on the surface of the cell is assumed to equal the local value of the macroscopic shear flow. In the calculation by Happel [2] the cell volume is chosen such that the fraction of it occupied by the particle equals ϕ, the volume fraction of particles in the suspension as a whole, i.e. $b=a/\phi^{1/3}$. He also used a different boundary condition on the cell surface, requiring that the normal component of the fluid velocity and the tangential stress be the same at each point on $r=b$ as those of the macroscopic flow.

The method of Kynch [3] is based on the similarity of the flow field around freely-suspended particles to the potential field owing to point charges at the centers of grounded conducting spheres having the same configuration as the particles. The contribution of each source to the local potential is assumed to be independent of the locations of the other spheres, and the position distribution is assumed to be uniform and random except for a small spherical shell about each sphere from which neighboring spheres are excluded. Both of these assumptions, as well as that of point sources, are evidently most appropriate for very dilute suspensions, although the calculated viscosities agree well with measured values for concentrations up to 25 volume per cent solids.

An approach which stresses the asymptotic aspects of the viscosity-concentration relationship was advanced by Frankel and Acrivos [4]. They examined the flow in the small gap between two closely spaced spheres to obtain the limiting form for the viscous energy dissipation in the fluid as the gap between the spheres goes to zero. A specific sphere configuration is used, namely simple cubic, with the axes aligned parallel to the principal directions of strain. The energy dissipation is calculated for a spherical shell of the same size as that used by Happel, i.e., the outer radius $b=a/\phi^{1/3}$. The calculation leads to an asymptotic expression for the relative viscosity of the suspension of the form

$$\mu/\mu_0 \sim C_1[1-(\phi/\phi_{max})^{1/3}]^{-1}$$

as $\phi \to \phi_m$ (whence $b \to a$), where μ_0 is the viscosity of the liquid and C_1 is a numerical constant equal to 9/8. This is in contrast to the asymptotic forms obtained from Simha's and Happel's results, wkich give

$$\mu/\mu_0 \sim C_2 \ [1-(\phi/\phi_{max})^{1/3}]^{-3}$$

where $C_2=1/20$ for the Simha model and $C_2=1/80$ for Happel's.

From these studies it has seemed evident to us that significant advances in the analysis of suspension rheology might be made if a statistical mechanical description of the random motion of the particles were available. Statistical mechanics has proven to be of immense value in relating the macroscopic properties of ordinary fluids to the parameters of their molecular structure. The purpose of the investigation reported here is to extend our earlier work [5] on the statistical mechanics of dilute suspensions ($\phi \gtrsim 15$ %) to higher concentrations. In the next section the principles of the statistical mechanics of particles in suspension are summarized. There the definitions are given for the macroscopic stress and shear rate tensors for suspensions of rigid spherical particles. These macroscopic quantities have the form of integral moments of the instantaneous local stress and shear rate for all possible particular configurations of particles weighted by the probability for finding the particles in those configurations. Next the calculations of the macroscopic stress and shear rate tensors for an approximate statistical model of the distribution of particle configurations in concentrated suspensions are described, and the results for the dependence of the viscosity on concentration are given. Finally, a comparison is made of these results with experimental viscosity-concentration data and with the results of the four studies described above.

II. Statistical mechanics of suspensions of spheres

The suspension to be considered consisits of N identical neutrally buoyant, rigid spherical particles dispersed in an incompressible newtonian liquid, the whole system occupying a total volume V. The overall flow $\boldsymbol{u}_0(\boldsymbol{x})$ is presumed to be a steady simple shearing motion, $\boldsymbol{u}_0=\boldsymbol{i}\ \kappa\ z$, where κ is the constant shear rate. There are no external forces or torques that act on the particles, and the flow is assumed sufficiently slow that local inertial forces in both the particle and liquid phases are everywhere negligible compared to the viscous and/or pressure forces.

During a shearing motion of the suspension the particles move relative to one another in a random manner along intricately coupled trajectories, which can be described only in statistical terms. Let us denote the instantaneous positions of the centers of the particles by $\boldsymbol{x}^N \equiv \{\boldsymbol{x}_i\}$, $i=1$ to N, and their translational and rotational velocities by $\boldsymbol{c}^N=\{\boldsymbol{c}_i\}$ and $\omega^N=\{\boldsymbol{\omega}_i\}$. Because the macroscopic flow is steady and inertial forces are negligible, conservation of linear and angular momentum in the particles requires that instantaneous forces and torques on the particles vanish. Hence the velocities $\boldsymbol{c}_i$ and $\boldsymbol{\omega}_i$ of each particle are uniquely determined functions of its position $\boldsymbol{x}_i$. As a consequence of this, the complete statistical description of the dynamical states of the particles is contained in the N-particle position distribution function $f^{(N)}(\boldsymbol{x}^N)$. This function is defined such that

$$f^{(N)}(\boldsymbol{x}^N)d\boldsymbol{x}_1 d\boldsymbol{x}_2 \cdots d\boldsymbol{x}_N \equiv f^{(N)} d\boldsymbol{x}^N$$

is the probability that the N particles are to be found in the N differential volumes(one in each) $d\boldsymbol{x}_1$ at $\boldsymbol{x}_1$, $d\boldsymbol{x}_2$ at $\boldsymbol{x}_2, \cdots$, and $d\boldsymbol{x}_N$ at $\boldsymbol{x}_N$. Since the particles are indistinguishable, $f^{(N)}$ carries the normalization.

$$\int \cdots \int f^{(N)} d\boldsymbol{x}^N = N!$$

Since the entire velocity and pressure fields in the liquid phase are uniquely determined for a given instantaneous particle configuration by the Stokes and continuity equations and the condition of the continuity of velocity across the solid-liquid interface, it follows that all of the macroscopic fields can be found once the configuration function $f^{(N)}$ is known. The particular macroscopic fields of interest here are the macroscopic velocity $\boldsymbol{u}(\boldsymbol{x})$, defined by

$$\boldsymbol{u}(\boldsymbol{x})=(N!)^{-1}\int \cdots \int \boldsymbol{u}_N(\boldsymbol{x};\boldsymbol{x}^N) f^{(N)}(\boldsymbol{x}^N) d\boldsymbol{x}^N \qquad (1)$$

and the macroscopic stress tensor

$$P(x)=(N!)^{-1}\int\cdots\int P_N(x;x^N)f^{(N)}(x^N)dx^N \qquad (2)$$

Here $u_N(x;x^N)$ and $P(x;x^N)$ are the velocity and the stress tensor at x in the fluid-particle system when the particles are at the particular positions x^N. Similarly, if $S_N(x;\ x^N)$ is the shear rate tensor at x for the configuration x^N, the macroscopic shear rate tensor is given by

$$S(x)\equiv\frac{1}{2}(\nabla u+\nabla u^T)$$
$$=(N!)^{-1}\int\cdots\int S_N(x;x^N)f^{(N)}(x^N)dx^N \qquad (3)$$

The configuration-specific fields u_N, P_N and S_N are governed by the momentum and constitutive equations that hold in the separate phases. In the particle phase (denoted by double primes) these are

$$\nabla\cdot P''_N=0 \qquad (4a)$$

$$P_N''=-p_N''U \qquad (4b)$$

The probability function $f^{(N)}$ cannot be determined from the equations of motion of the particle and fluid phases alone, but depends also on the requirement that it be conserved along the N-particle trajectory in the $3N$-dimensional space of x^N. This requirement follows from the fact that, although the positions of the particles at some instant are not deterministic quantities, their trajectories subsequent (or prior) to some specified configuration are. This conservation property is expressed by the Liouville equation

$$\sum_{i=1}^{N} c_i\cdot\frac{\partial f^{(N)}}{\partial x_i}=0 \qquad (10)$$

Before discussing the determination of the distribution function from (10) we pause to describe an important consequence of the neglect of inertial forces in the fluid and particle phases, namely that the suspension must be newtonian. Since the equation of motion (6) contains no inertial terms it follows from (6)-(8) that u_N', and therefore P_N', must be linear functions of the shear rate κ and the particle velocities c_i. The particle velocities, which are obtained from

$$F_i=\int_{S_i}P_N'\cdot dS_i=0$$

must therefore be linear homogeneous functions of κ, i. e. $c_i=\alpha_i\ \kappa$ where α_i is independent of κ. Eqn. (10) becomes

$$\sum_{i=1}^{N}\alpha_i\cdot\frac{\partial f^{(N)}}{\partial x_i}=0$$

so that $f^{(N)}$ is independent of κ. This means that both P and S are inear functions of κ, hence the suspension is newtonian. We note that if inertial forces are not negligible in both phases, the particle and liquid, this argument no longer holds and the conclusion of a newtonian suspension may not be valid. This conclusion also depends, of course, on the assumption that the particles are rigid and spherical for if they are deformable or orientable the specification of the distribution of particle states must involve internal coordinates (as well as the positions x^N), which in general introduces a dependence of $f^{(N)}$ on κ even when inertial forces are negligible.

The form of $f^{(N)}$ obtained from (10) depends greatly on the particle concentrations in the suspensions. For example, for very dilute suspensions, in which the particles are so far apart that they move independently, the statistical information about the particle configuration is contained entirely in $f^{(1)}(x_1)$, the singlet distribution. For this case (10) becomes

$$c_1\cdot\frac{\partial f^{(1)}}{\partial x_1}=0$$

so $f^{(1)}$ is a constant corresponding to a uniform particle density. At somewhat higher concentrations, where interactions between pairs of particles are significant, the relevant distribution function is the pair density $f^{(2)}\ (x_1, x_2)$. For this situation (10) gives

$$c_1\cdot\frac{\partial f^{(2)}}{\partial x_1}+c_2\cdot\frac{\partial f^{(2)}}{\partial x_2}=0$$

which has as its solution

$$f^{(2)}(\boldsymbol{x}_1, \boldsymbol{x}_2)=f^{(2)}(\boldsymbol{x}_{10}, \boldsymbol{x}_{20})$$

where $\boldsymbol{x}_i$ and $\boldsymbol{x}_{io}$ are the positions of particle i at time t and t_o, respectively, and hence are related by

$$\boldsymbol{x}_i=\boldsymbol{x}_{io}+\int_{to}^{t}\boldsymbol{c}_i(s)ds$$

These trajectories can be calculated because the velocities $\boldsymbol{c}_i$ are known at each instant from the force-free condition $\boldsymbol{F}_i=0$. Similarly, the higher-order configuration functions, which are significant at greater concentrations, can be determined from analyses of the appropriate multi-particle trajectories. When this sequential ordering of the interactions according to the number of particles involved is applied to the calculation of the viscosity, there results [5]

$$\mu/\mu_o=1+k_1\phi+k_2\phi^2+k_3\phi^3+\cdots$$

where the coefficient k_M is an integral moment of the M-particle configuation function $f^{(M)}(\boldsymbol{x}_1, \cdots \boldsymbol{x}_M)$. Such an expansion, for μ, while useful for small concentrations, is completely impractical for calculations when a significant fraction of the interactions involve more than two particles (i. e., for $\phi \gtrsim .15$) because of the difficulty of calculating both the M-particle trajectories and $P'_M(x;\ x^M)$ for $M\geq 3$. However, it may be possible to obtain accurate values of viscosities of concentrated suspensions from (2), (3) and (4) by using approximate models to represent particle configurations at high densities. The remainder of this paper is devoted to an examination of one such model.

III. Calculations for Model System of Simple Cubic Configuration

The more concentrated a suspension is, the more complex are the coupled motions of the interacting particles. Hence it is necessary to make some idealizations in order to do a hydrodynamic analysis of the flow field around a group of closely spaced spheres such as occurs in concentrated suspensions. As a convenient choice of the multiparticle configuration we take a simple cubic lattice arrangement.

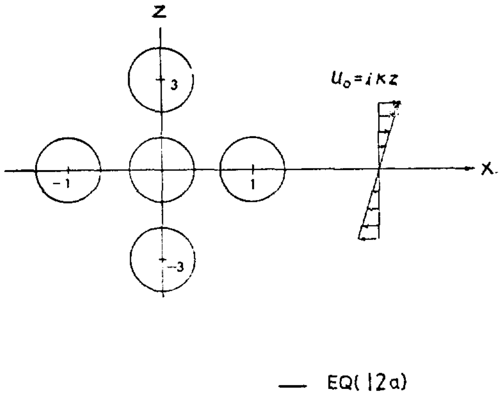

Fig. 1. Coordinate geometry.

Thus, a representative sphere has six nearest-neighbor spheres aligned along the coordinate axes as depicted in Fig. 1. The distance of separation between the spheres, which is assumed to be the same for each sphere, is a variable. This alignment implies that all the possible orientations of the neighbor spheres, if assumed equally probable, are averaged spatially. The number of nearest neighbors of this arrangement is reasonably close to the measured coordination number for randomly packed spheres of about seven [6], although the maximum attainable concentration of the simple cubic configuration, 52.4%, is much smaller than the 62% measured for the randomly packed configuration [7, 8].

The first problem to be considered is the determination of the instantaneous velocity field when the spheres are arranged in simple cubic configuration and move with the free-motion translational and rotational velocities in a simple shear field. The flow field near the central sphere, which is used for the viscosity calculations, is of particular interest in the analysis. The local velocity and pressure fields are denoted by $\boldsymbol{u}'_N$ and p'_N, and the corresponding fields without spheres by $\boldsymbol{u}_0$ and p_0, where the undisturbed fields are presumed known. The relative velocity and pressure fields, $\boldsymbol{v}=\boldsymbol{u}'_N-\boldsymbol{u}_0$ and $q=p'_N-p_0$, are then the solutions of

$$\mu_0\nabla^2\boldsymbol{v}=\nabla q \qquad (11a)$$

and $\nabla \cdot v = o$ (11b)

which satisfy the boundary conditions on the central sphere and its six neighbor spheres

$$v(r_i)=c_i+\omega_i\times r_i-u_0(r_i) \quad \text{at } r_i=a,\ i=1 \text{ to } 7$$

where $r_i=x-x_i$ and a is the radius of the spheres. Under free-motion conditions the particle velocities c_i and ω_i are equal to $u_0(x_i)=i\kappa z_i$ and $\frac{1}{2}\nabla\times u_0=j\kappa/2$, respectively. This can be seen as follows. Since the instantaneous forces on the spheres are zero, the average translational velocity of the spheres with centers in the plane $z=z_i$ must equal the average velocity of the suspension as a whole at that plane, that is, $u_0(z_i)$. By the symmetry of the presumed cubic arrangement of the spheres, all the spheres located in that plane must have the same velocity; hence each one has velocity $u_0(z_i)$. Similarly, since the torques on the particles vanish, the rotational velocity of the particle phase (and, therefore, of each particle) must equal the vorticity of the suspension.

Lamb's general solution [9, 10] of (11) provides the velocity field $v(r)$ around the spheres, where $r=(r,\theta,\phi)$ is the position vector in a spherical coordinate system having its origin at the center of the central sphere

$$v=\sum_{k=-(K+1)}^{K}\left\{\nabla\times(r\chi_k)+\nabla\Phi_k+\frac{(k+3)\,r^2}{2(k+1)(2k+3)\mu_0}\nabla p_k-\frac{k}{(k+1)(2k+3)\mu_0}\,r p_k\right\}$$

and $$q=\sum_{k=-(K+1)}^{K}p_k$$

where χ_k, Φ_k, and p_k are solid spherical harmonics and $K\to\infty$. The solution of the boundary value problem is effected when the unspecified coefficients in these harmonic functions are determined. Although the solution that satisfies exactly the given boundary conditions on all of the spheres could, in principle, be determined, no such solution is feasible because of the difficulty of expressing the complex geometry of the liquid region in terms of the coordinates, r, θ and ϕ. Hence an approximate solution must be obtained. The procedure that we have used to obtain a solution is a version of the boundary collocation method [11, 12] in which the boundary conditions are satisfied everywhere on the surface of the central sphere, but only at a small number of selected points on the surfaces of the six neighbor spheres. Since only a finite number of coefficients in the spherical harmonic expansion for $v(r)$ can be obtained in this way, we choose as a first trial solution v^*, the truncated form of the Lamb solution obtained by taking K=2:

$$v^*=\nabla\times r\chi_1+\nabla\times r\chi_{-2}+\nabla\Phi_2+\nabla\Phi_{-3}+\frac{5\,r^2}{42\mu_0}\nabla p_2-\frac{2}{21\mu_0}r p_2+\frac{1}{2\mu_0}r p_{-3}$$

The spherical harmonics have the general form

$$\Phi_n=r^n[A_n^m\cos m\phi+B_n^m\sin m\phi]P_n^m(\cos\theta)$$

and

$$\Phi_{-(n+1)}=r^{-(n+1)}[A_n^m\cos m\phi+B_n^m\sin m\phi]P_n^m(\cos\theta)$$

for $0\le m\le n$, where $P_n^m(\cos\theta)$ is the associated Legendre polynomial of the first kind of order n and rank m. However, the symmetry of the flow field, including point symmetry with respect to the origin and plane symmetries with respect to the $x-z$ and the $y-z$ planes, require that

$$\chi_1=A_1^1\, r\sin\phi\, P_1^1(\cos\theta),\quad \chi_{-2}=A_{-2}^1 r^{-2}\sin\phi\, P_1^1(\cos\theta)$$

$$\Phi_2=B_2^1 r^2\cos\phi\, P_2^1(\cos\theta),\quad \Phi_{-3}=B_{-3}^1 r^{-3}\cos\phi\, P_2^1(\cos\theta)$$

$$p_2=C_2^1\mu_0 r^2\cos\phi P_2^1(\cos\theta) \text{ and } p_{-3}=C_{-3}^1\mu_0 r^{-3}\cos\phi P_2^1(\cos\theta)$$

Thus the first trial solution contains six unknown constants to be determined by satisfying the boundary conditions at the collocation points. The location of these points on the neighbor sphere surfaces is completely arbitrary, but it seems reasonable to use points closest to the central sphere since the evaluation of the stress tenosr P_N' requires a solution only on the surface of the central sphere. The location of the ten points used to evaluate the six constants are indicated in Table 1.

The next order of approximation can be obtained by the same procedure. Here the trial solution is chosen by taking the summation in the Lamb's solution from $k=-5$ to $k=4$, i.e. $K=4$. (The results for the trial function with $K=3$ are found to be equivalent to those obtained with $K=2$). For $K=4$ the additional spherical harmonics that are needed have the forms

$$\chi_3=r^3[A_3^1\sin\phi P_3^1(\cos\theta)+A_3^3\sin3\phi P_3^3(\cos\theta)]$$

$$\chi_{-4}=r^{-4}[A_{-4}^1\sin\phi P_3^1(\cos\theta)+A_{-4}^3\sin3\phi P_3^3(\cos\theta)]$$

$$\Phi_4=r^4[B_4^1\cos\phi P_4^1(\cos\theta)+B_4^3\cos3\phi P_4^3(\cos\theta)]$$

$$\Phi_{-5}=r^{-5}[B_{-5}^1\cos\phi P_4^1(\cos\theta)+B_{-5}^3\cos3\phi P_4^3(\cos\theta)]$$

$$p_4=r^4[C_4^1\mu_0\cos\phi P_4^1(\cos\theta)+C_4^3\mu_0\cos3\phi P_4^3(\cos\theta)]$$

and

$$p_{-5}=r^{-5}[C_{-5}^1\mu_0\cos\phi P_4^1(\cos\theta)+C_{-5}^3\mu_0\cos3\phi P_4^3(\cos\theta)]$$

The second approximate solution also satisfies exactly the field equations (11), the boundary conditions on the surface of the central sphere and the boundary conditions at selected points on the neighbor spheres. The location of the collocation points that are needed to determine values for the 18 constants of the trial solution are given in Table 1. We expect this solution to be a better approximation since it contains more terms and satisfies the boundary conditions at more points. However, there is no assurance that the results will be more accurate or that inclusion of more and more terms will result in a solution that converges to the exact solution. A comparison of the viscosities obtained from the two solutions are compared with measured values below.

The configurational description of particles in suspension is given by the full set of distribution functions $f^{(M)}$. Their determination from the Liouville equation is exceedingly difficult, in general, because of the complexity of many-body interactions, and at the present time only the radial distribution function $g^{(2)}(r)$ has been calculated and that only for the case when no more than two spheres at a time ever

Table 1. Selected Collocation Points

First Solution (K=2):

Sphere 3	$P_0^z, P_{\pm x}^z$	Sphere−3	$P^{-z}_0, P^{-z}_{\pm x}$
Sphere 1	P_0^x	Sphere−1	P^{-x}_0
Sphere 2	P_0^Y	Sphere−2	P^{-y}_0

Second Solution ($K=4$):

Sphere 3	$P_0^z, P_{\pm x}^z, P_{\pm y}^z$	Sphere−3	$P^{-z}_0, P^{-z}_{\pm x}, P^{-z}_{\pm y}$
Sphere 1	$P_0^x, P_{\pm z}^x, P_{\pm y}^x$	Sphere−1	$P^{-x}_0, P^{-x}_{\pm z}, P^{-x}_{\pm y}$
Sphere 2	$P_0^y, P_{\pm x}^y$	Sphere−2	$P^{-y}_0, P^{-y}_{\pm x}$

Here, for example, P_0^z refers to the nearest point at z-axis on sphere 3, and $P_{\pm x}^z$ refers to the points rotated by $\pm45°$ from P_0^z in zx-plane on sphere 3. The numbering of the spheres is as follows: spheres ±1 are those on the $\pm x$-axes, spheres ±2 are those on the $\pm y$-axes, and spheres ±3 are those on the $\pm z$-axes. The conditions on the negatively numbered spheres are eqnal to those on the corresponding positively numbered spheres by symmetry.

interact as they move in the shear field [5]. The reduced distribution function appropriate to the symmetric six-neighbor model is the six-particle radial distribution function $g^{(6)}(r)$, which is defined by the statement: $g^{(6)}(r)dr$ is the probability that there is a neighbor sphere at a distance between r and $r+dr$. A good approximate expression can be obtained as follows. Let $w^{(1)}(r)dr$ denote the probability that there is a sphere in $(r, r+dr)$ with no sphere in (D, r) where D is the diameter of the spheres; similarly let $w^{(m)}(r)dr$ be the probability that there is a sphere in $(r, r+dr)$ with $(m-1)$ spheres in (D, r). Then [13]

$$W^{(1)}=h\left[1-\int_D^r W^{(1)}dr\right]$$

and

$$W^{(m+1)}=h\left[1-\int_D^r W^{(m+1)}dr \Big/ \int_D^r W^{(m)}dr\right]\cdot\int_D^r W^{(m)}dr$$

for $m=1, 2, \cdots 5$. Here $h\ dr$ is the unconditional probability that there is a sphere in $(r, r+dr)$. Solving the above equations, we obtain

$$W^{(1)} = h\,e^{-H}$$

$$W^{(m+1)}=\frac{1}{m!}H^m he^{-H}$$

where $H(r)=\int_D^r h(r)dr$ is the probability that there is a sphere in (D, r). In a field of randomly distributed particles the probability that there is a sphere in $(r, r+dr)$ will simply be $4\pi nr^2$ where n denotes the number density of the particles. In the shear field, however, there exist strong repulsive forces between nearly touching spheres so that we assume zero probability of contact, that is, $h(r)$ is assumed to vanish at $r=D$ and $r=P$, where P is the average distance between a sphere and its shell of second nearest neighbors. If H_m denotes the mean interparticle distance, $P=2H_m-D$. We note parenthetically that unless $h(D)=O$ the calculated shear stress is infinite. A simple choice for $h(r)$ for particles in a shear field is $4\pi n(r-D)(P-r)$ for $D\leq r\leq P$. The distribution function $g^{(6)}$ is just the sum of the functions $w^{(m)}(r)$.

$$g^{(6)}(r)=\sum_{m=1}^{6} w^{(m)}$$
$$=he^{-H}\left[1+H+\frac{1}{2!}H^2+\frac{1}{3!}H^3+\frac{1}{4!}H^4+\frac{1}{5!}H^5\right]$$

where, for random distribution

$$h = 4\pi nr^2$$

and
$$H = \frac{4}{3}\pi n(r^3-D^3) \tag{12a}$$

and for constrained distribution

$$h=4\pi n(r-D)(P-r)$$

and
$$H=\frac{4}{3}\pi n(r-D)^3\left[\frac{3}{2}\frac{(P-D)}{(r-D)}-1\right] \tag{12b}$$

The functions $g^{(6)}(r)$ for these two situations are plotted in Figure 2 together with a measured distribution [14] obtained in a stationary suspension having a particle concentration of 35%. The reason that the peak point for the stationary case (12a) is located somewhat to the right of the experimental peak is

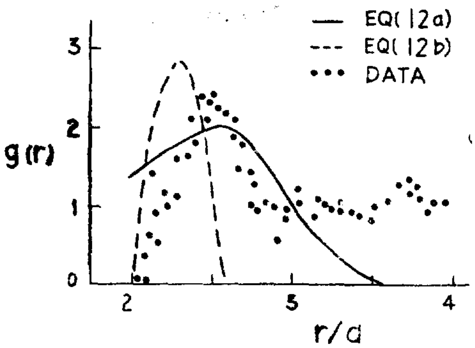

Fig. 2. The distribution functions of the neighbor particles in the random field, Eqn. (12a), and in the shear field, Eqn. (12b), both for ϕ=.35. The experimental data are taken from Figure 2-C of the paper by Morrell & Hildebrand [14].

the effect of the second nearest-neighbor shell on the location of the nearest neighbors is neglected when a random particle distribution is used. Although experimental data for the shear field are not available for comparison, we believe the distribution function obtained from Eqn. (12b) is a good approximation of the particle distribution in a shear suspension.

IV. Results and Discussion

With the approximate expressions for the velocity field u'_N and the radial distribution function $g^{(6)}$ described above it is a simple matter to evaluate macroscopic stress tensor from (2), which becomes

$$\mathrm{P}=-p\mathrm{U}+2\mu_0\mathrm{S}+\mathrm{P}'' \quad \text{and}$$

$$\mathrm{P}''=\frac{3}{4\pi a^3}\iint_{S_i} g^{(6)}(r)r\mathrm{P}'_N\cdot dS_i dr\equiv(\boldsymbol{ki}+\boldsymbol{ik})p_{zx}$$

The macroscopic shear rate tensor S is equal to $\mathrm{S}_0(1-\phi)=\frac{1}{2}(\nabla\boldsymbol{u}_0+\nabla\boldsymbol{u}_0^T)(1-\phi)$, because the contribution of the disturbance field $\boldsymbol{v}$ can be shown to vanish by symmetry during the integration of $\frac{1}{2}(\nabla\boldsymbol{v}+\nabla\boldsymbol{v}^T)$ over the cube of volume $\frac{4}{3}\pi a^3/\phi$ surrounding each sphere in the cubic configuration. The viscosity is then calculated for different concentrations from

$$\mu/\mu_0=1+\frac{\phi}{1-\phi}(p_{zx}/\mu_0\kappa)$$

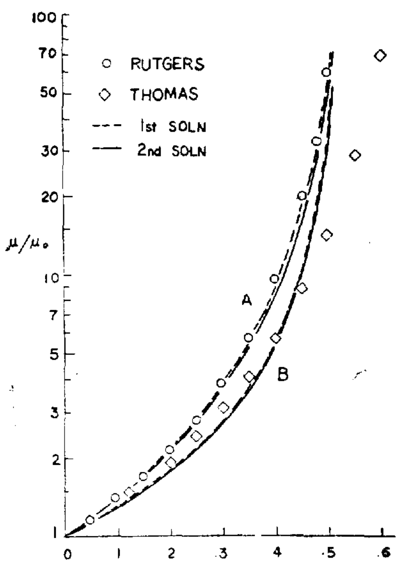

Fig. 3. The viscosity of suspensions of rigid spheres. The theoretical lines of A and B are obtained using the distribution function(12b) and the delta function, respectively.

giving the results shown in Fig. 3 as the two curves labeled A. The solid curve was calculated from the approximate solution for $v(r)$ with $K=4$ and the dashed curve from the solution with $K=2$. Also shown (curves B) for comparison are the results obtained with the same two solutions for $v(r)$, but assuming the interparticle separation is fixed at $r=H_m$, i. e., $g^{(5)}(r)=\delta(r-H_m)$. For both particle distributions the viscosities for the two solutions for $v(r)$ differ by less than 4.5%, which indicates good convergence of the approximate solutions. The importance of the particle distribution is clear, particularly at intermediate concentrations, which have been the most difficult to treat theoretically. For this reason it would be desirable to find a more accurate way of determining the particle distribution in shear suspensions than the one used here.

The statistical mechanics developed in Section. Ⅱ is not restricted to the simple cubic configuration, so the results for several configurations could be compared to determine how sensitive the viscosity is to the choice of the model. Another test of the present model is a comparison with experimental data [15, 16]. This is done in Fig. 4 which shows fairly close

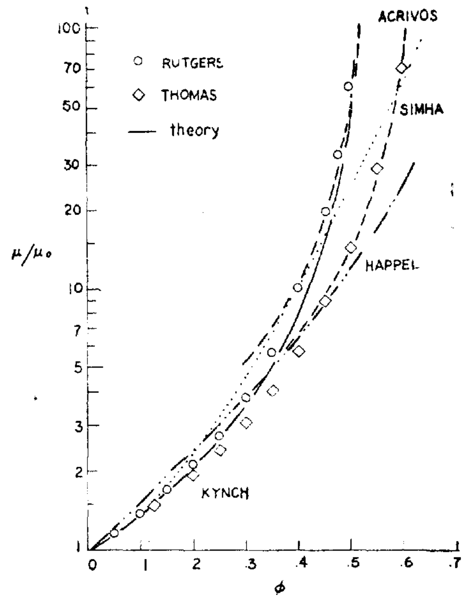

Fig. 4. Comparison of theoretical and experimental viscosities of suspensions of rigid spherical particles. The experimental data points are taken from the averaged data lines drawn by Rutgers [15] and Thomas [16], respectively. Simha's theoretical curve(……) calculated with $b=a\phi^{-1/3}$ is shown, as are Acrivos' asymptotic curves (----) for $\phi_m=0.535$ and $\phi_m=0.625$.

agreement over the entire range of concentrations, especially when compared to the performance of the previous theories of Simha, Happel, Kynch and Acrivos. The increasing deviation of our viscosity curve from Thomas' collected data as the concentration increases can be attributed to the fact that the maximum attainable concentration of 52.4% for the simple cubic model is considerably smaller than both the 62.5% implted by Thomas' data and the 66% packiing density measured in flowing suspensions by Rutgers [8]. In summary, the work described here, although burdened with approximations of uncertain consequence and limited to suspensions of spherical particles, appears to be a significant improvement over previous studies of concentrated suspensions, and is unique in the sense that the statistical aspect of the particle motion are treated explicitly in the calculation of the macroscopict quantities.

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