ANISOTROPIES AND INTERACTIONS IN SHEAR FLOW OF MACROMOLECULAR SUSPENSIONS

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George S. Argyropoulos

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ABSTRACT

The problem of determining the orientation distribution function for rigid particles of arbitrary shape is formulated in a general stochastic approach to consider the influence of any acting orientation mechanism, stochastic or deterministic. The effect of the various orientation mechanisms on the partial differential equation of the problem, an equation of the Fokker-Planck type, is analyzed. The question of linearity or non-linearity of the superposition of the effects due to different orientation mechanisms is examined.

The orientation of rigid ellipsoidal particles in uniform shear flow is studied in detail, for different cases of acting orientation mechanisms. When only the viscous stresses act on the particles, the problem for the orientation distribution function becomes a deterministic first-order initial value problem, and its solution displays periodic behavior. In the case of macromolecules, when the Brownian influence is predominant, we examine the effect of a third orientation mechanism acting on the macromolecules in addition to the viscous stresses and the Brownian impulses. In Couette flow between concentric cylinders, the third orientation mechanism is considered to be a deterministic force field in the radial direction x, varying linearly with x. The steady state orientation distribution function is then determined to the third order, and the theory of streaming birefringence of a dilute suspension of rigid ellipsoidal macromolecules in Couette flow is

generalized to include the effect of the additional influence. The direction of the isocline and the amount of birefringence are calculated to the second order.

When spherical macromolecules are added to the suspension in increasing concentration, the effect of hydrodynamic interactions between the two species on the orientation of the ellipsoidal particles is examined in Couette flow. It is shown that an effect of the presence of the spheres is to decrease the drift velocity of the ellipsoids--and thus decrease the amount of birefringence--and that the effect can be described as a decrease in the effective velocity gradient. The theoretical result for this decrease is in good agreement with experimental results for sphere concentrations comparable to the concentration of ellipsoids. On the other hand, as the concentration of spheres increases, the effect of their presence on the rotational diffusion constant of the asymmetrical particles can be large enough to reverse the trend and lead to a positive variation of the amount of birefringence with sphere concentration.

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I. INTRODUCTION

When a viscous fluid undergoes laminar flow with nonvanishing velocity gradient, its optical properties often become anisotropic, i.e., it behaves as a birefringent medium to the transmission of light through it, and double refraction can be observed.

This general phenomenon is known as Streaming Birefringence (SBR). It was first observed by J. C. Maxwell in 1866 and reported in 1873[1] in a paper which described a concentric cylinder apparatus by which SBR could be easily produced. To this day, SBR is usually studied in simple shear flow between two concentric cylinders (Couette apparatus), with a beam of polarized light transmitted in the axial (z) direction, and is often referred to as "the Maxwell effect."

In the case of a suspension, in which both the dispersed particles and the suspending medium are optically isotropic but of different refractive index, birefringence will be observed if the particles are geometrically anisotropic and their orientation distribution is nonuniform. We then say that the suspension presents form birefringence, and its optical properties can be defined in terms of the orientation distribution of the suspended particles. The existence of a velocity gradient in the suspension induces a nonuniform orientation distribution of the suspended asymmetrical particles and thus gives rise to anisotropies and Streaming Birefringence.

When the suspended particles are sufficiently small, as in

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[1] J. C. Maxwell, "On Double Refraction in a Viscous Fluid in Motion," Proc. Roy. Soc. (London), A 22, 46 (1873).

macromolecular suspensions, their orientation distribution is affected by a second mechanism, in addition to the viscous stresses on the surface of the particle due to the velocity gradient. This second mechanism consists of the Brownian impulses acting on the particle due to the thermal motions of the molecules of the surrounding fluid. Further orientation mechanisms may also be acting by the application of external force fields, as, for example, an electric field (Kerr effect) or a magnetic field (Cotton-Mouton effect).

Streaming birefringence of macromolecular suspensions has enjoyed wide application

(a) For the study of macromolecular properties

(b) As a hydrodynamic research tool

since it was placed on a sound theoretical basis[2] by the orientation theory of Peterlin and Stuart[3, 4]. This theory relates the observable optical properties of the suspension, with the size, shape, mass, and dispersity of the macromolecules[5]. Particularly significant is the limiting case of zero shear rate, since it can give the value

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[2] A complete review and discussion of the theoretical work on SBR up to 1959 has been given by H. G. Jerrard, Chem. Reviews, 59, 345 (1959).

[3] A. Peterlin and H. A. Stuart, Z. Physik 112, 1, 129 (1939).

[4] A. Peterlin and H. A. Stuart, Hand-und Jahrbuch der Chemischen Physik, (Becker u. Erler, Leipsig, 1943), Bd VIII, Abt. 1B.

[5] Very clear on this subject is the earlier review on SBR by R. Cerf and H. A. Scheraga, Chem. Reviews, 51, 185 (1952).

of the rotary diffusion coefficient D, as well as an indication of any structurization in the suspension. As a hydrodynamic research tool, on the other hand, SBR is useful for flow visualization[6] since its theory relates the observable direction of the optical axis to the streamline direction at each point.

The orientation theory of Peterlin and Stuart considers the Couette flow of a dilute suspension of rigid ellipsoidal macromolecules and formulates the problem of determining the distribution function for the orientation of the major axis of the rotational ellipsoids (spheroids), taking into account <u>two</u> orientation mechanisms acting on the particles

(a) The viscous stresses

(b) The Brownian impulses.

Then, the steady state distribution function $F(\theta, \varphi)$ is determined in series form and is used to calculate the mean values (see Part VI, 1) in terms of which are expressed the optical properties of the suspension as a refracting medium, namely the extinction angle χ, defining the direction of the isocline, and the amount of birefringence Δn. The following are noteworthy in this theory: the consideration of dilute suspensions justified the neglect of interactions as an orienting mechanism; the consideration of Couette flow allowed the authors to use the expressions obtained earlier by Jeffery[7] for the rotary

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[6] Harold Wayland, J. Polymer Science, Part C, No. 5, 11 (1963).

[7] G. B. Jeffery, Proc. Roy. Soc. (London), <u>A102,</u> 161 (1922).

motion of ellipsoidal particles due to the viscous stresses; finally, the effect of the isotropic Brownian impulses appears as a diffusion term in the partial differentiation equation of the problem, as was shown in the pioneering work of Einstein[8], who had also given the expression for the diffusion coefficient.

An important generalization of this theory was carried out by Wayland[9], avoiding the restriction to Couette flow. In this way, Wayland presented a theory of SBR for general two-dimensional converging or diverging laminar flow and greatly extended its usefulness as a hydrodynamic research tool for flow visualization.

As a consequence of these applications of SBR, it has been the aim of experimenters to refine the measuring techniques, so that even the very small effects characteristic of small concentrations and small shear rates could be analyzed and interpreted. The need for an instrument of sensitivity greater than anything previously used had become apparent for measuring these small effects, and Wayland proposed[10] *sinusoidal modulation of the light beam* so as to achieve an amplitude varying linearly with the observed angle ϵ (between the position of the analyzer and the null position) rather than quadratically. An apparatus based on this principle was designed and built by Intaglietta[11] at the C. I. T. SBR Laboratory

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[8] A. Einstein, Annal. d. Phys., 17, 549 (1905) and 19, 371 (1906).

[9] H. Wayland, J. Chem. Phys., 33, No. 3, 769 (1960).

[10] H. Wayland, Comptes Rendus, 249, 1228 (1959).

[11] Marcos Intaglietta, Ph. D. Thesis, C. I. T., 1963.

and very careful measurements were obtained with it by Intaglietta and Leray.

In the successive refinements of the measuring techniques, some departures from the Peterlin and Stuart theory have been observed, particularly in the range of small shears and concentrations[(12)], which as already mentioned, is precisely the interesting range for the purpose of determining macromolecule properties. In addition, an interesting effect was observed[(13)] in the case where spherical macromolecules, suspended together with the ellipsoidal ones, caused hydrodynamic interactions, an influence which has not been considered at all in the Peterlin and Stuart theory.

In order to provide a theoretical basis for an explanation of these phenomena, it was apparent to the author that the influence of additional orientation mechanisms, of either deterministic or stochastic nature, should be allowed for in the theoretical formulation. In addition, it was felt that the appropriate approach for the theoretical formulation of the whole problem of SBR in macromolecular suspensions, should be one based on the theory of stochastic processes, in view of the presence of stochastic orientation mechanisms, which make the orientation of each particle a random variable of time.

The present study represents an effort to generalize the orientation theory of SBR in this direction. First, to formulate,

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[12] J. Leray, J. de Chimie Physique, 316 (1961).

[13] H. Wayland and M. Intaglietta, Proc. 4th Intern. Congr. on Rheol., Part IV, 317 (1965).

from a stochastic approach, the problem of determining the distribution function for the orientation of a rigid particle of arbitrary shape. Second, to analyze the way in which the various distinct orientation mechanisms, stochastic or deterministic, will appear in the partial differential equation of the problem. And third, to examine the question of linearity or non-linearity of the superposition of the effects due to the different orientation mechanisms.

This generalization is then applied to formulate a theory of SBR in Couette flow taking into consideration a particular orientation mechanism which is likely to be realized in addition to the viscous and Brownian effects in Couette flow, namely a force field in the radial direction x, varying linearly with x. It is shown that an example of this general influence is the effect of a uniform electric field in the radial direction x on polarizable macromolecules, which has been studied at the C. I. T. SBR Laboratory by Demetriades[14]. It also seems possible that the effect of thermal forces due to the energy dissipation and the conduction of heat to the thermostated walls--an effect that was first suggested by Leray[15] to explain the observed discrepancies from the previous theory--may also be expressible in terms of such a force field.

Finally, we examine, in terms of a model, and give a theoretical explanation to the interesting effect which was observed when spheres are added to the suspension, in concentration and

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[14] S. T. Demetriades, J. Chem. Phys., 29, No. 5, 1054 (1958).

[15] Personal communication, November 1963.

dimensions comparable to those of the ellipsoids, namely the fact that the amount of birefringence was observed to initially decrease with sphere concentration, whereas the opposite had been expected. It is shown that the addition of spheres has the effect of decreasing the effective velocity gradient, and the theoretical results give good agreement with the experiment. On the other hand, as the concentration of spheres increases, the effect of their presence on the rotational diffusion constant of the asymmetrical particles can be large enough to reverse the trend and lead to a positive variation of the amount of birefringence with sphere concentration. This effect is studied in terms of various models, and the possibility of the reversal of the trend is shown.

II. THE ORIENTATION OF RIGID PARTICLES AS A STOCHASTIC PROCESS

1. The Orientation Distribution Function

Let us consider a population of identical rigid particles of arbitrary shape, suspended in a continuous medium. The orientation of each particle can be defined by a set of convenient variables, most commonly by the Euler angles θ, φ and ψ, with respect to a defined reference frame. The ranges of these variables form a space R, each point of which uniquely corresponds to an orientation of the particle.

If one or more of the orienting forces, or mechanisms, that act on a particle in a particular physical situation, are of random nature (which means that their properties are only statistically defined), then the orientation of the particle will be a <u>stochastic</u> process; more precisely, the point P which represents the orientation of the particle in the space R will be a random function of time, expressed analytically as $\bar{r} = \bar{r}(t)$. It is clear that $\bar{r}(t)$ will be a continuous random function, although its derivative $\dot{\bar{r}}(t)$ can be discontinuous, depending on the nature of the orienting mechanisms.

For a stochastic process of this nature, we seek a description in terms of the orientation distribution function $f(\bar{r}, t)$, which we define, in the space R, as a <u>probability density</u>: the probability that a particle, any particle, will be so oriented, at time t, that the representative point P lies within a certain domain V of the space R, is given by the relation

$$\Pr\left\{P \in V, t\right\} = \int_V f(\bar{r}, t)\, dV \qquad (1)$$

It is clear that, if we wish to refer to the whole population instead of a single particle, Eq. (1) will be interpreted as giving the fraction of the total number N of particles which are found, at time t, to have orientations whose representative points lie in V. The two methods of interpretation are fully equivalent, although the term "distribution function" seems to derive from the second one.

For every stochastic process, the central problem is the determination of the corresponding probability density. The formulation of this problem is based on the continuity of probability, as it is most generally expressed by the integral relation of Smoluchowski

$$f(\bar{r}, t+\tau) = \int_R f(\bar{r}', t)\, p(\bar{r}', t/\bar{r}, t+\tau)\, dV' \qquad (2)$$

This relation uses the concept of the transition probability: $p(\bar{r}', t/\bar{r}, t+\tau)$ is the probability that the particle will have the orientation given by $\bar{r}$ at the time $t + \tau$, if it is known that, at time t, it had the orientation given by $\bar{r}'$. The physical meaning of the Smoluchowski relation is simple; it fundamentally asserts that the particle had some orientation at time t, from which it underwent a transition so as to have, at time $t + \tau$, the orientation given by $\bar{r}$. We may parenthetically remark that, in expecting the transition probability to have a unique meaning, we are actually supposing that the behavior of $\bar{r}(t)$ after a certain instant t_0 depends only on the instantaneous value $\bar{r}(t_0)$ and is entirely independent of its whole previous history. A stochastic process which has this characteristic, namely, that what happens after a given instant of time t depends only on the state of the system at t, is said to be a Markov process. That we should be able to consider the orientation of a rigid particle, under the stochastic influence of Brownian impulses, as a Markov process appears very reasonable.

2. The Fokker-Planck Equation.

The integral relation of Smoluchowski can be reduced to a partial differential equation for $f(\overline{r}, t)$, if we can give an expression to the transition probability $p(\overline{r}', t/\overline{r}, t+\tau)$, valid for small τ. When $\overline{r}(t)$ is a continuous random function, it is possible to arrive at such an expression in the following way:

Since

$$\int_R p(\overline{r}', t/\overline{r}, t+\tau)\, dV = 1 \tag{3}$$

(expressing the fact that the particle must have some orientation at time $t+\tau$), it is clear that for small τ the transition probability $p(\overline{r}', t/\overline{r}, t+\tau)$ will be sharply centered around the point $\overline{r}'$ in the space R, and will in fact tend to the delta function $\delta(\overline{r} - \overline{r}')$ as $\tau \to 0$. We can thus assume, for small τ, the double expansion

$$p(\overline{r}', t/\overline{r}, t+\tau) = \delta(\overline{r} - \overline{r}') + \tau \Big\{ -\vec{C}(\overline{r}', t) \cdot \nabla\delta(\overline{r} - \overline{r}') + D(\overline{r}', t) : \nabla\nabla\delta(\overline{r} - \overline{r}') \Big\} + O(\tau^2) \tag{4}$$

or, using a cartesian coordinate system defined in the space R,

$$p(\overline{r}', t/\overline{r}, t+\tau) = \delta(\overline{r}-\overline{r}') + \tau \left\{ -C_i(\overline{r}', t)\frac{\partial}{\partial x_i}\delta(\overline{r}-\overline{r}') + D_{ij}(\overline{r}', t)\frac{\partial}{\partial x_i}\frac{\partial}{\partial x_j}\delta(\overline{r}-\overline{r}')\right\} + O(\tau^2) \qquad (4')$$

Using this expression in the Smoluchowski integral relation (2), and taking the limit as $\tau \to 0$, we find that $f(\overline{r}, t)$ satisfies the partial differential equation

$$\frac{\partial f}{\partial t} + \mathrm{div}\left\{ f\vec{C} - \mathrm{div}\, f\overline{\overline{D}} \right\} = 0 \qquad (5)$$

or

$$\frac{\partial f}{\partial t} + \frac{\partial}{\partial x_i} C_i f - \frac{\partial}{\partial x_i}\frac{\partial}{\partial x_j} D_{ij} f = 0 \qquad (5')$$

This equation is known as the Smoluchowski equation, or as a Fokker-Planck Equation. The parameters $\vec{C}$ (a vector) and $\overline{\overline{D}}$ (a symmetrical tensor of second rank) have a well defined physical meaning, for each stochastic process, namely, if $\overline{r}(t) = \overline{r}'$,

$$\vec{C}(\overline{r}', t) = \lim_{\tau \to 0} \frac{< \overline{r}(t+\tau) - \overline{r}(t) >}{\tau} \qquad (6)$$

$$D_{ij}(\overline{r}', t) = \lim_{\tau \to 0} \frac{<[x_i(t+\tau) - x_i(t)]\,[x_j(t+\tau) - x_j(t)]>}{2\tau} \qquad (7)$$

This fact is readily shown by actual evaluation of the mean or expected values

$$< \overline{r}(t+\tau) - \overline{r}(t) >_{\overline{r}', t, \tau} = \int_R (\overline{r}-\overline{r}')p(\overline{r}', t/\overline{r}, t+\tau)\, dV \qquad (8)$$

and

$$<[x_i(t+\tau) - x_i(t)]\,[x_j(t+\tau) - x_j(t)]>_{\overline{r}', t, \tau}$$

$$= \int_R (x_i - x_i')(x_j - x_j')p(\overline{r}', t/\overline{r}', t+\tau)\, dV \qquad (9)$$

with the help of Eq. (4), and taking the limit as $\tau \rightarrow 0$. The meaning of the above two expected values is clear: they are the first and second moments, respectively, of the deflections of the point P in time interval τ. Note that if the process is stationary, which implies that the transition probability is independent of t, the parameters $\vec{C}$ and $\bar{\bar{D}}$ do not depend explicitly on t, a fact that significantly simplifies the corresponding Fokker-Planck Equation.

For a continuous random function $\overline{r}(t)$, therefore, the probability density $f(\overline{r}, t)$ can be analytically determined as the solution of a boundary value problem, involving the Fokker-Planck Equation (5), the appropriate boundary conditions, and the initial condition $f(\overline{r}, 0)$. The problem will be defined, of course, only if the analytical expressions for the parameters $\vec{C}$ and $\bar{\bar{D}}$, that correspond to the stochastic process in question, can be determined.

In particular, if the initial condition is taken to be

$$f(\overline{r}, 0) = \delta(\overline{r} - \overline{r}') \qquad (10)$$

then the solution will represent the transition probability $p(\overline{r}', 0/\overline{r}, t)$.

This formulation of the problem for the probability density $f(\overline{r}, t)$, in terms of a boundary value problem, must be completed by the discussion of three questions of physical interest: the existence of a solution, its uniqueness, and its behavior for large t. Let the following be noted about these questions:

(a) The existence of a solution has not been rigorously shown for the general case. This question is mathematically complicated by the following necessary restrictions on $f(\bar{r}, t)$ in order that it be a valid probability density function:

$$f(\bar{r}, t) \geq 0 \quad \text{for all } \bar{r} \text{ in } R \text{ and } t \geq 0$$

$$\int_R f(\bar{r}, t)\, dV = 1 \quad \text{for all } t \geq 0 \tag{11}$$

(b) The uniqueness of the solution can be shown: two probability density functions, which satisfy a Fokker-Planck Equation and have the same boundary and initial conditions, are identical.

(c) In most physical situations, it is intuitively plausible that the effect of initial conditions would tend to disappear as time went on, leading to a steady state probability density

$$f(\bar{r}, t \rightarrow \infty) = F(\bar{r}) \tag{12}$$

Such a tendency can indeed be formally shown, in the following sense: the difference between two solutions of the Fokker-Planck Equation satisfying different initial conditions can be "measured" by a function of time $A(t)$, which can only decrease.

3. The Fundamental Parameters $\vec{C}$ and $\overline{\overline{D}}$.

We turn now to the fundamental problem of determining the analytical expression for the parameters $\vec{C}$ and $\overline{\overline{D}}$ in any particular stochastic process. This will of course be based on the physical interpretation of these parameters:

$\vec{C}$ is the "drift velocity" of the point P in the space R.

$\overline{\overline{D}}$ is the "diffusion tensor," associated with the second central moments of the deflections of the point P in time interval τ.

The statistical properties of the random function $\overline{r}(t)$ depend on the statistical properties of the forces that act on the system and affect the position of the representative point in the space R. This dependence is defined by the mechanics of the physical situation, namely by the ordinary differential equation in t that $\overline{r}(t)$ must satisfy

$$L_t \left\{ \overline{r} \right\} = 0 \tag{13}$$

Such an equation is known as the Langevin Equation when referring to a stochastic process. It contains the forces, of which we only know the statistical properties, and therefore cannot be solved in the ordinary sense to give $\overline{r}(t)$.[16] It supplies, however, the relation between the given statistical properties of the forces and the

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[16] It is this fact that underlines the important distinction between stochastic forces and deterministic or causal forces. The latter are given explicitly as functions of $\overline{r}$ and t, so that the differential equation for $\overline{r}(t)$ can be solved by the methods of Mechanics. In other words, $\overline{r}(t)$ can be "determined" in that case.

statistical properties of $\overline{r}(t)$; and it is in terms of the latter that $\vec{C}$ and $\overline{\overline{D}}$ are defined in Eqs. (6) and (7).

Another theoretical method, which can be used for the evaluation of the second moments, and hence of the diffusion tensor $\overline{\overline{D}}$, is the kinetic approach presented by Einstein in his investigations on the theory of the Brownian motion. In this study we shall use Einstein's results to describe the effect of the Brownian impulses, with only a slight generalization to consider particles of arbitrary shape.

Finally, the statistical properties of the random function $\overline{r}(t)$ can be determined experimentally. Experimental determination of statistical properties has been often used successfully, as in the celebrated experiment of Perrin which allowed calculation of the Avogadro number. In any case, we shall rely on the experiment for the ultimate justification of any analytical expression for $\vec{C}$ and $\overline{\overline{D}}$.

4. The Simultaneous Action of Various Orientation Mechanisms and the Question of Superposition.

In the stochastic process that concerns SBR, namely the orientation of a rigid particle suspended in a flowing medium, various orientation mechanisms of distinct physical nature may be simultaneously acting on the particle. A stochastic mechanism of orientation consists of the Brownian impulses due to thermal motion, when the particle is small enough to be affected by them. A deterministic orientation mechanism would be any force field acting on the particle and resulting in a given torque, i. e., given as a function of $\overline{r}$ and t.

In such cases, there arise two questions of physical interest, concerning the determination of the coefficients $\vec{C}$ and $\bar{\bar{D}}$ of the Fokker-Planck Equation:

(a) How are $\vec{C}$ and $\bar{\bar{D}}$ affected by each of the acting forces, stochastic or deterministic?

(b) If the values $\vec{C}_{(i)}$ and $\bar{\bar{D}}_{(i)}$, that correspond to the i-th force acting alone on the particle, are known for each force, can we superpose them to find the values of $\vec{C}$ and $\bar{\bar{D}}$ that correspond to the simultaneous action of all the forces?

We shall discuss these questions, in the light of the stochastic approach that we have followed, concentrating our attention to those stochastic processes, which, like the one we are concerned with, have a linear Langevin Equation.

First, it is clear that the diffusion tensor $\bar{\bar{D}}$ is solely dependent on the stochastic forces. If a deterministic force were acting alone, the resulting deterministic "course" $\vec{r}_d(t)$ of the point P in the space R would have a finite velocity $\dot{\vec{r}}_d(t)$, so that the second moments of the deflection would then be of order τ^2, and the limit which gives $\bar{\bar{D}}_i$ in Eq. (7) would vanish. If both a deterministic and a stochastic force are acting, then, for a linear Langevin Equation, it would be

$$\vec{r}(t) = \vec{r}_d(t) + \vec{r}_s(t) \tag{14}$$

where the stochastic variable $\vec{r}_s(t)$ is of positive order in t; consequently, the contribution of $\vec{r}_d(t)$ to the second moments of the deflection in time τ will again vanish in the limit which is taken in Eq. (7) to give $\overline{\overline{D}}$.

On the other hand, the drift velocity $\vec{C}$ will be affected by both the stochastic forces (as long as the first moment of the deflection in time τ does not vanish) and the deterministic forces. In fact, the drift velocity $\vec{C}_{(i)}$ caused by a deterministic force acting alone, is to be identified with the deterministic velocity $\dot{\vec{r}}_d(t)$ which can be found by the methods of Mechanics.

As to the second question, we can conclusively assert, that the influence of the various forces on $\vec{C}$ is additive: based on the definition of $\vec{C}$ in Eq. (6), it is clear that, when the corresponding Langevin Equation is linear, the drift velocities $\vec{C}_{(i)}$ are vectorially additive to give the resultant

$$\vec{C} = \sum_i \vec{C}_{(i)} \tag{15}$$

On the other hand, we see from Eq. (7) that the diffusion tensor $\overline{\overline{D}}$ is given by a nonlinear expression in $\vec{r}(t)$. We conclude, therefore, that the effects of more than one stochastic force cannot in general be linearly superposed to give a resultant $\overline{\overline{D}}$. A case when they are linearly superposed is if both of the corresponding $\vec{r}_{(i)}(t)$ have a Gaussian transition probability density.

Specifically, if isotropic Brownian impulses provide the only stochastic mechanism of orientation acting on a rigid particle, then the tensor $\overline{\overline{D}}$ has the following form, when expressed in the system of the principal inertial axes of the particle:

$$D_{ij} = kTB_i\delta_{ij} \qquad \text{(no sum)} \tag{16}$$

In this expression, which is a slightly generalized form of Einstein's result, k is Boltzmann's constant, T the absolute temperature, δ_{ij} the Kronecker symbol and B_i the rotational mobility of the particle around its i-th principal inertial axis, when it is suspended in a medium of viscosity μ_o.

In conclusion, let us summarize the analytical problem of determining the orientation distribution function for a rigid particle suspended in a flowing medium, as it is formulated by this stochastic approach:

The orientation distribution function $f(\bar{r}, t)$ is the solution of a boundary value problem, involving the Fokker-Planck Equation (5), with the values of $\vec{C}$ and $\bar{\bar{D}}$ that correspond to the shape of the particle and the acting orientation mechanisms. The drift velocity $\vec{C}(\bar{r}, t)$ is the linear superposition of

(a) The first moment of the deflection velocity caused by the stochastic mechanisms, and

(b) the "deterministic" velocities of the representative point P caused by the deterministic mechanisms.

The diffusion tensor $\bar{\bar{D}}$ is associated with the second moments of the deflections of the representative point P, and it is solely, and non-linearly, dependent on the stochastic mechanisms of orientation acting on the particle.

III. ANISOTROPIES IN SHEAR FLOW OF MACROMOLECULAR SUSPENSIONS

1. The Orientation of Spheroids in Couette Flow.

Macromolecules can often be considered[17] as rigid prolate ellipsoids of revolution (spheroids), with half-axes $a_1 \neq a_2 = a_3$, and characterized by the axial ratio $p = \frac{a_1}{a_2} > 1$. For this model, since we are interested in the orientation and not in the actual rotational position, the value of the Euler angle ψ is not of importance, and the orientation distribution function becomes $f(\theta, \varphi, t)$, namely a function of only two spacial variables, the polar angle θ and the azimuthal angle φ, which define the position of the major axis of the ellipsoid. As a consequence, we can use, as space R, a spherical surface of unit radius. The representative point P lies on this two-dimensional space, and the Fokker-Planck Equation can be expressed in spherical coordinates with no r-dependence.

We shall examine the case where isotropic Brownian impulses are the only stochastic mechanism of orientation. The diffusion tensor is then given, in the triad of the spherical unit vectors $\vec{e}_r$, $\vec{e}_\theta$, and $\vec{e}_\varphi$ which are always principal inertial axes of the ellipsoid, by Eq. (16) with

$$B_2 = B_3 = \frac{1}{4\mu_o V} \frac{p^2}{p^4-1}\left[-1 + \frac{2p^2-1}{p\sqrt{p^2-1}} \ln\left(p + \sqrt{p^2-1}\right)\right] \quad \text{for} \quad p \geq 1 \qquad (17)$$

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[17] W. Kuhn, H. Kuhn and P. Buckner, Erg. exact. Naturw., 25, 1 (1957).

as can be calculated from hydrodynamics[18]. Note that $\bar{\bar{D}}$ does not depend on the variables in our problem; μ_o is the viscosity of the solvent and V the volume of each particle.

In the cases where the divergence of the tensor $\bar{\bar{D}}$ vanishes, the Fokker-Planck Equation takes the form

$$\frac{\partial f}{\partial t} + \text{div} \left\{ f\vec{C} - \bar{\bar{D}} \cdot \nabla f \right\} = 0 \tag{5''}$$

In our two-dimensional case R, in addition to div $\bar{\bar{D}} = 0$, $B_2 = B_3$ for rotational ellipsoids; as a consequence the diagonal tensor $\bar{\bar{D}}$ acts as a scalar when contracted with the two-dimensional vector ∇f, and the Fokker-Planck Equation of our problem takes the following simple form

$$\frac{\partial f}{\partial t} + \text{div } f\vec{C} - D\nabla^2 f = 0 \tag{18}$$

where

$$D = kTB_2 = kTB_3 \tag{19}$$

If the Brownian impulses are isotropic, the first moment of their effect will vanish and, therefore, there is no Brownian contribution to the drift velocity $\vec{C}$. This parameter will be then determined by the deterministic orientation mechanisms acting on the particle.

One such mechanism is the viscous stress field in laminar Couette flow. The suspended macromolecules have dimensions which are large compared to the molecules of the solvent and can thus be

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[18] F. Perrin, J. Phys., 5, 497 (1934) and 7, 1 (1936). Also see Appendix A.

treated as rigid particles finding themselves in a flowing continuum. Due to the existence of a velocity gradient G in the flow, the viscous stresses acting on the surface of the suspended particles result in a torque, thus causing a rotational motion. The corresponding velocity of the representative point P on the spherical surface R was calculated by Jeffery[19], by means of the Stokes approximation, to be

$$\vec{C}_{viscous} = \frac{G}{2}\sin\theta\left[b\cos\theta\sin 2\varphi\,\vec{e}_\theta + (1+b\cos 2\varphi)\,\vec{e}_\varphi\right] \qquad (20)$$

In this expression,

G = the velocity gradient in the undisturbed field, i. e. before the particles are immersed, and

$b = \frac{a_1^2 - a_2^2}{a_1^2 + a_2^2} = \frac{p^2 - 1}{p^2 + 1}$ a geometrical parameter characteristic of the ellipsoidal particles.

The flow geometry and the selection of axes correspond to the following definition of the undisturbed laminar flow field:

$$\vec{u}_o = Gx\,\vec{e}_y \qquad (G > 0) \qquad (21)$$

The viscous stress field is the only deterministic orientation mechanism which was taken into consideration in the theory of Peterlin and Stuart.

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[19] Loc. cit. If the gap between the two cylinders of the Couette apparatus is much smaller than their radii, then G can be considered to be a constant.

2. Orientation Under the Predominant Action of the Viscous Stresses.

A limiting case of considerable practical interest[20] arises when the dimensions of the particles are large or the velocity gradient is very high. Then the viscous stresses constitute the predominant orientation mechanism and the Brownian effect can be neglected, so that the motion of the particle in the solvent and its orientation at every instant can be "determined" from hydrodynamics alone.

Then the Fokker-Planck Equation becomes.

$$\frac{\partial f}{\partial t} + \operatorname{div} f\vec{C} = 0 \tag{22}$$

i.e., it is no more an equation of the diffusion type. The problem becomes a first order initial value one: to find $f(\theta, \varphi, t)$ given the initial condition $f(\theta, \varphi, t_o) = f_o(\theta_o, \varphi_o)$ and the fact that

$$\vec{C} = \frac{d\bar{r}}{dt} = \frac{d}{dt}\,\bar{r}(\theta, \varphi) = \dot{\theta}\,\frac{\partial \bar{r}}{\partial \theta} + \dot{\varphi}\,\frac{\partial \bar{r}}{\partial \varphi}$$

$$= \dot{\theta}\,\vec{e}_\theta + \dot{\varphi}\,\sin\theta\,\vec{e}_\varphi \tag{23}$$

The equation of the problem becomes, in our spherical coordinates

$$\frac{\partial f}{\partial t} + \frac{1}{\sin\theta}\left\{\frac{\partial}{\partial \theta}(f\dot{\theta}\,\sin\theta) + \frac{\partial}{\partial \varphi}(f\dot{\varphi}\,\sin\theta)\right\} = 0$$

or

$$\frac{\partial f}{\partial t} + \dot{\theta}\,\frac{\partial f}{\partial \theta} + \dot{\varphi}\,\frac{\partial f}{\partial \varphi} + \frac{f}{\sin\theta}\,\frac{\partial}{\partial \theta}(\dot{\theta}\,\sin\theta) + f\,\frac{\partial \dot{\varphi}}{\partial \varphi} = 0$$

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[20] See, for example, S. G. Mason and R. St. J. Manlay, Proc. Roy. Soc. (London), A 238, 117 (1956) and H. L. Goldsmith and S. G. Mason, Ibid., A 282, 569 (1964).

and finally

$$\frac{df}{dt} + f\left\{\frac{1}{\sin\theta}\;\frac{\partial}{\partial\theta}\,\dot{\theta}\;\sin\theta + \frac{\partial\dot{\varphi}}{\partial\varphi}\right\} = 0 \qquad (24)$$

The operator

$$\frac{d}{dt} = \frac{\partial}{\partial t} + \dot{\theta}\;\frac{\partial}{\partial\theta} + \dot{\varphi}\;\frac{\partial}{\partial\varphi} \qquad (25)$$

expresses the rate of change of f on the path that a particle would follow if placed at that position, say θ_o, φ_o. But this path is known. It can be determined from the relations (20), namely

$$\dot{\theta} = \frac{Gb}{4}\sin 2\theta\;\sin 2\varphi$$

$$\dot{\varphi} = \frac{G}{2}\,(1 + b\cos 2\varphi)$$

Hence

$$\frac{\partial}{\partial\theta}\,\dot{\theta}\;\sin\theta = \frac{Gb}{4}\sin 2\varphi\left[2\cos 2\theta\;\sin\theta + \sin 2\theta\;\cos\theta\right] \quad (26)$$

and

$$\frac{\partial\dot{\varphi}}{\partial\varphi} = \frac{G}{2}\,b(-2)\;\sin 2\varphi = -\;Gb\;\sin 2\varphi \qquad (27)$$

The differential equation thus becomes

$$\frac{df}{dt} + f\,\frac{Gb}{2}\sin 2\varphi\left[\cos 2\theta + \cos^2\theta - 2\right] = 0$$

or

$$\begin{aligned}\frac{1}{f}\;\frac{df}{dt} &= \frac{3}{2}\;Gb\;\sin 2\varphi\;\sin^2\theta \\ &= \frac{3}{2}\;\sin^2\theta\;\frac{4\;\dot{\theta}}{\sin 2\theta} \\ &= 3\;tg\;\theta\;\frac{d\theta}{dt} \end{aligned} \qquad (28)$$

Hence on the path of the particle (the characteristic)

$$\frac{1}{f}\,df = -\,3\,\frac{d(\cos\theta)}{\cos\theta}$$

$$\therefore\quad f = f_o\left(\frac{\cos\theta_o}{\cos\theta}\right)^3 \tag{29}$$

This is the value of the distribution function on the path of a particle. The above equation solves the problem; because given the position of the particle at t, we only have to find where it was at t_o (which is possible from the equations of motion) and then f_o is the given initial condition $f_o(\theta_o, \varphi_o)$. In other words

$$f(\theta, \varphi, t) = f_o(\theta_o, \varphi_o)\left[\frac{\cos\theta_o}{\cos\theta}\right]^3 \tag{29'}$$

To complete the solution, therefore, we need to express the initial position of the particle, namely θ_o and φ_o, in terms of its position at time t, namely θ and φ.

$$\frac{d\theta}{\sin\theta\cos\theta} = \frac{Gb}{2}\sin 2\varphi\, dt = \frac{Gb}{2}\sin 2\varphi\,\frac{d\varphi}{\varphi}$$

$$\therefore\quad \frac{d\theta}{tg\theta\,\cos^2\theta} = \frac{b\sin 2\varphi}{1 + b\cos 2\varphi}\,d\varphi$$

or

$$\frac{d(tg\theta)}{tg\theta} = -\,\frac{1}{2}\,\frac{d(1 + b\cos 2\varphi)}{1 + b\cos 2\varphi}$$

and, upon integration

$$\frac{tg\theta}{tg\theta_o} = \left(\frac{1 + b\cos 2\varphi}{1 + b\cos 2\varphi_o}\right)^{-1/2}$$

or

$$tg^2\theta_o = tg^2\theta \; \frac{1 + b\cos 2\varphi}{1 + b\cos 2\varphi_o} \tag{30}$$

This is a first integral of the motion of the ellipsoid and gives the curve that a particle placed at θ_o, φ_o will follow. It is a closed curve on the sphere of radius a_1.

To find the time dependence and the period of this motion in the above closed curve, we integrate the equation

$$\frac{d\varphi}{1 + b\cos 2\varphi} = \frac{G}{2}\,dt$$

It is

$$1 + b\cos 2\varphi = 1 + \frac{p^2-1}{p^2+1}\,\frac{1-tg^2\varphi}{1+tg^2\varphi} = \frac{2(p^2+tg^2\varphi)}{(p^2+1)(1+tg^2\varphi)} = \frac{2\cos^2\varphi}{p^2+1}(p^2+tg^2\varphi) \tag{31}$$

Thus

$$\frac{d\varphi}{\cos^2\varphi(p^2+tg^2\varphi)} = \frac{G}{p^2+1}\,dt$$

Now put $tg\varphi = p\xi$ whence $\dfrac{d\varphi}{\cos^2\varphi} = p\,d\xi$

$$\therefore \frac{p\,d\xi}{p^2(1+\xi^2)} = \frac{G}{p^2+1}\,dt$$

$$\text{arc tg}\xi - \text{arc tg}\xi_o = \frac{pG}{p^2+1}(t - t_o)$$

$$\text{arc tg}\,\frac{\text{tg}\,\varphi_o}{p} = \text{arc tg}\,\frac{\text{tg}\,\varphi}{p} - \frac{pG}{p^2+1}(t-t_o)$$

$$\therefore \quad \text{tg}\,\varphi_o = p\,\frac{\text{tg}\,\varphi - p\,\text{tg}\,\frac{pG}{p^2+1}(t-t_o)}{p + \text{tg}\,\varphi\ \text{tg}\,\frac{pG}{p^2+1}(t-t_o)} \tag{32}$$

From this equation we see that indeed the motion is periodic with frequency

$$\omega = \frac{pG}{p^2+1}$$

or period (33)

$$T = 2\pi\,\frac{p^2+1}{pG}$$

Now to find θ_o as a function of θ, φ and t we eliminate φ_o from equations (30) and (32). Using Eq. (31) we find

$$\text{tg}^2\theta_o = \text{tg}^2\theta\,\frac{(p^2+\text{tg}^2\varphi)\cos^2\varphi}{(p^2+\text{tg}^2\varphi_o)\cos^2\varphi_o}$$

$$= \text{tg}^2\theta\,\frac{(p^2+\text{tg}^2\varphi)\cos^2\varphi}{p^2\cos^2\varphi_o}\,\frac{[p + \text{tg}\,\varphi\ \text{tg}\ \omega(t-t_o)]^2}{p^2+\text{tg}^2\varphi\,\text{tg}^2\omega(t-t_o)+\text{tg}^2\varphi+p^2\text{tg}^2\omega(t-t_o)}$$

$$= \text{tg}^2\theta\,\frac{\cos^2\varphi}{p^2\cos^2\varphi_o}\,[p+\text{tg}\,\varphi\,\text{tg}\,\omega(t-t_o)]^2\cos^2\omega(t-t_o)$$

$$= \text{tg}^2\theta\,\frac{\cos^2\varphi}{p^2}\,[p+\text{tg}\,\varphi\,\text{tg}\,\omega(t-t_o)]^2\cos^2\omega(t-t_o)$$

$$\times \left\{1 + p^2\left[\frac{\text{tg}\,\varphi - p\,\text{tg}\,\omega(t-t_o)}{p+\text{tg}\,\varphi\,\text{tg}\,\omega(t-t_o)}\right]^2\right\}$$

$$= \text{tg}^2\theta\,\frac{\cos^2\varphi}{p^2}\cos^2\omega(t-t_o)\left\{(p+\text{tg}\,\varphi\,\text{tg}\,\omega(t-t_o))^2+p^2(\text{tg}\,\varphi-p\,\text{tg}\,\omega(t-t_o))^2\right\}$$

$$\operatorname{tg}\theta_o = \operatorname{tg}\theta\cos\varphi\cos\omega(t-t_o)\left\{\left(1+\frac{\operatorname{tg}\varphi\operatorname{tg}\omega t}{p}\right)^2 + (\operatorname{tg}\varphi - p\operatorname{tg}\omega(t-t_o))^2\right\}^{1/2} \quad (34)$$

We have then

$$f(\theta,\varphi,t) = f_o\left[\theta_o(\theta,\varphi,t),\varphi_o(\theta,\varphi,t)\right]\cos^{-3}\theta\,(1+\operatorname{tg}^2\theta_o)^{-3/2} \quad (35)$$

In the case when the original distribution is uniform

$$f_o = \frac{1}{4\pi}$$

we get

$$f(\theta,\varphi,t) = \frac{(1+\operatorname{tg}^2\theta_o)^{-3/2}}{4\pi\cos^3\theta} = \frac{1}{4\pi}\left(\frac{\cos\theta_o}{\cos\theta}\right)^3$$

Note: For very long rods, for which $b \to 1$ and $p \to \infty$, we have the following simplifications:

Equation (30) becomes $\frac{\operatorname{tg}\theta_o}{\operatorname{tg}\theta} = \frac{\cos\varphi}{\cos\varphi_o}$

i.e. $\operatorname{tg}\theta\cos\varphi = \text{const.}$

Equation (31) becomes $\operatorname{tg}\varphi_o = \operatorname{tg}\varphi - G(t-t_o)$

Equation (34) becomes $\operatorname{tg}\theta_o = \operatorname{tg}\theta\cos\varphi\{1 + (\operatorname{tg}\varphi - G(t-t_o))^2\}^{1/2}$

3. The Drift Velocity Caused by a Linearly Varying Force Field in The Radial Direction.

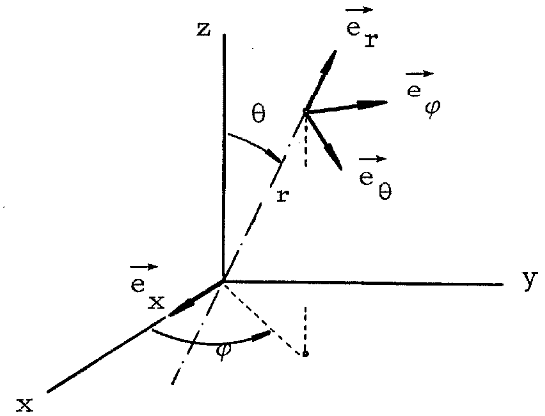

Fig. 1

Consider two symmetrical points on the major axis of the particle. Since the force field varies linearly in the x direction, there is a force differential

$$d\vec{F} = C(x - x') \, dr \, \vec{e}_x \qquad (36)$$

where dr is the element of length on the major axis. Since the points are symmetrical, $x - x' = 2x = 2r \sin\theta \cos\varphi$. Therefore, the torque with respect to the center of the particle is

$$d\vec{M}_o = \vec{r} \times d\vec{F} = 2Cr^2 \sin\theta \cos\varphi \, dr \, \vec{e}_r \times \vec{e}_x \qquad (37)$$

and integrating over the major axis $(r = 0 \ldots a_1)$, we find

$$\vec{M}_o = \frac{2}{3} Ca_1^3 \sin\theta \cos\varphi \, \vec{e}_r \times \vec{e}_x \qquad (38)$$

The resulting rotational velocity of the particle is

$$\vec{\omega} = B_2 \vec{M}_o = \frac{2}{3} Ca_1^3 B_2 \sin\theta \cos\varphi \, \vec{e}_r \times \vec{e}_x \qquad (39)$$

and the corresponding drift velocity of the point P on the spherical surface of unit radius will be

$$\vec{C}_f = \vec{\omega} \times \vec{e}_r \qquad (40)$$

Now note that $\vec{e}_x = \sin\theta \cos\varphi \, \vec{e}_r + \cos\theta \cos\varphi \, \vec{e}_\theta - \sin\varphi \, \vec{e}_\varphi$.

Hence $(\vec{e}_r \times \vec{e}_x) \times \vec{e}_r = \cos\theta \cos\varphi \, \vec{e}_\theta - \sin\varphi \, \vec{e}_\varphi$ and

$$\vec{C}_f = K \sin\theta \cos\varphi \left[\cos\theta \cos\varphi \, \vec{e}_\theta - \sin\varphi \, \vec{e}_\varphi \right] \tag{41}$$

where

$$K = \frac{2C}{3} a_1^3 B_2 \tag{42}$$

The parameter K defines the magnitude and the sign of the effect. One can see, by comparing the expressions given by Demetriades, that the drift velocity caused by a uniform electric field in the radial direction, if the ellipsoidal particles are polarizable, is of this nature, specifically with

$$K = -2BE^2B_2 \tag{43}$$

in our notation[21].

4. Orientation Under the Predominant Action of the Brownian Impulses, and the Influence of the Viscous Stresses Plus a Third Orientation Mechanism.

For macromolecular suspensions, when the suspended particles have high rotational mobility, the Brownian impulses are usually the predominant factor affecting the orientation of the particles. We shall now examine in detail this case.

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[21] The magnitude factor B is defined in Appendix A of Demetriades' article, in which the quantity BE^2B_2 is called M. E is the electric field.

4.1. The Fokker-Planck Equation.

We shall first give explicit form to the Fokker-Planck Equation that will be satisfied by the orientation distribution function of ellipsoidal macromolecules in laminar Couette flow, when the following three orientation mechanisms are acting, namely

(a) Stochastic: Isotropic Brownian Impulses

(b) Deterministic: (1) Viscous stresses resulting in a torque because of the velocity gradient G.

(2) A force field in the radial direction x, varying linearly with x.

Substituting

$$\vec{C} = \vec{C}_v + \vec{C}_f \tag{44}$$

namely

$$c_\theta = \frac{Gb}{4} \sin 2\theta \sin 2\varphi + \frac{K}{2} \sin 2\theta \cos^2\varphi$$

$$c_\varphi = \frac{G}{2} \sin\theta (1 + b \cos 2\varphi) - \frac{K}{2} \sin\theta \sin 2\varphi$$

in the Fokker-Planck Equation (18) we obtain

$$\frac{\partial f}{\partial t} + \frac{1}{\sin\theta} \left\{ \frac{\partial}{\partial\theta} \sin\theta\, f c_\theta + \frac{\partial}{\partial\varphi} f c_\varphi \right\} - D\nabla^2 f = 0 \tag{45}$$

where

$$\nabla^2 = \frac{1}{\sin\theta} \left\{ \frac{\partial}{\partial\theta} \sin\theta \frac{\partial}{\partial\theta} + \frac{\partial}{\partial\varphi} \frac{1}{\sin\varphi} \frac{\partial}{\partial\varphi} \right\} \tag{46}$$

Simplifying we obtain

$$\frac{\partial f}{\partial t} + c_\theta \frac{\partial f}{\partial \theta} + \frac{c_\varphi}{\sin\theta}\frac{\partial f}{\partial \varphi} + \frac{1}{\sin\theta}\left\{\frac{\partial}{\partial\theta} c_\theta \sin\theta + \frac{\partial}{\partial\varphi} c_\varphi\right\} f = D\nabla^2 f$$

Now $c_\theta \sin\theta = \sin\theta \sin 2\theta \left\{\frac{Gb}{4}\sin 2\varphi + \frac{K}{2}\cos^2\varphi\right\}$

$$\therefore \quad \frac{\partial}{\partial\theta} c_\theta \sin\theta = (\cos\theta\sin 2\theta + 2\sin\theta\cos 2\theta)\left\{\frac{Gb}{4}\sin 2\varphi + \frac{K}{2}\cos^2\varphi\right\}$$

$$= 2\sin\theta(3\cos^2\theta - 1)\left\{\frac{Gb}{4}\sin 2\varphi + \frac{K}{2}\cos^2\varphi\right\}$$

and $\frac{\partial}{\partial\varphi} c_\varphi = \sin\theta \left\{- Gb \sin 2\varphi - K\cos 2\varphi\right\}$

Therefore

$$\frac{1}{\sin\theta}\left\{\frac{\partial}{\partial\theta} c_\theta \sin\theta + \frac{\partial}{\partial\varphi} c_\varphi\right\} = (2 - 3\sin^2\theta)\left\{\frac{Gb}{2}\sin 2\varphi + \frac{K}{2}(\cos 2\varphi + 1)\right\}$$

$$- Gb\sin 2\varphi - K\cos 2\varphi$$

$$= K(1 - \frac{3}{2}\sin^2\theta) - \frac{3}{2}\sin^2\theta(K\cos 2\varphi + Gb\sin 2\varphi)$$

$$= \frac{1}{2}\left\{K(2 - 3\sin^2\theta) - 3\sin^2\theta(K\cos 2\varphi + Gb\sin 2\varphi)\right\} \quad (47)$$

So we finally obtain the equation

$$\frac{\partial f}{\partial t} + \frac{\sin 2\theta}{4}\left\{K(1 + \cos 2\varphi) + Gb\sin 2\varphi\right\}\frac{\partial f}{\partial\theta} + \frac{1}{2}\left\{G(1 + b\cos 2\varphi) - K\sin 2\varphi\right\}\frac{\partial f}{\partial\varphi}$$

$$+ \frac{1}{2}\left\{K(2 - 3\sin^2\theta) - 3\sin^2\theta(K\cos 2\varphi + Gb\sin 2\varphi)\right\}$$

$$= \frac{D}{\sin\theta}\left\{\frac{\partial}{\partial\theta}\sin\theta\frac{\partial f}{\partial\theta} + \frac{\partial}{\partial\varphi}\frac{1}{\sin\theta}\frac{\partial f}{\partial\varphi}\right\} \quad (48)$$

The form of the coefficients of this linear partial differential equation is consistent with the boundary conditions that the distribution function is expected to satisfy on grounds of physical symmetry, namely

$$\begin{aligned} f(\theta, \varphi) &= f(\pi-\theta, \varphi+\pi) \\ f(\theta, \varphi) &= f(\pi-\theta, \varphi) \end{aligned} \tag{49}$$

4.2. The Steady State Solution.

The theory of SBR is principally concerned with the optical properties of the suspension under steady state conditions. Therefore, only the steady state solution $F(\theta,\varphi)$ of the Fokker-Planck Equation (48), under the boundary conditions (49), is needed for our purposes.

In addition, the Brownian influence is usually predominant for macromolecules, a fact which is displayed by the value of D being of considerably higher order than the values of either G or K. We are concentrating our attention to this case, which we shall define mathematically by the relations

$$K = \lambda G = \lambda\sigma D \tag{50}$$

and

$$\begin{aligned} \sigma &= \frac{G}{D} \ll 1 \\ |\lambda|\sigma &= \frac{|K|}{D} \ll 1 \end{aligned} \tag{51}$$

The coefficient $|\lambda|$ defines the relative order of magnitude between the two deterministic orientation mechanisms.

The equation for the steady state orientation distribution function can then be solved by a perturbation approach, which will give $F(\theta, \varphi)$ in a series of ascending orders of σ:

$$F(\theta, \varphi) = \sum_{n=0}^{\infty} \sigma^n F^{(n)}(\theta, \varphi) \tag{52}$$

Since $\sigma \ll 1$, this series can be expected to converge rapidly, so that the calculation of the first few orders will be sufficient. This same approach was used by Demetriades, and the calculation carried to the second order. However, a transformation of variables, that he, like Tolstoi[22], has chosen to introduce in order to combine the magnitudes of the viscous and the electrical effects, tends to obscure the results and does not allow a direct calculation of the two parameters of SBR, namely the extinction angle χ and the amount of birefringence Δn. In our study, it is the calculation of these parameters that has dictated the appropriate form of the distribution function. Our solution will of course coincide with that of Demetriades up to the second order, but it will be in a form that will allow us to proceed to the calculation of χ and Δn. Also, it will be carried to the third order.

The equation for the steady state orientation distribution function $F(\theta, \varphi)$ can be written in the form

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[22] N. A. Tolstoi, Doklady, 59, 1563 (1948).

$$\sigma L\left\{F\right\} = \nabla^2 F \tag{53}$$

where L is the differential operator

$$L = \frac{\sin 2\theta}{4}\left\{\lambda(1+\cos 2\varphi)+b\sin 2\varphi\right\}\frac{\partial}{\partial\theta} + \frac{1}{2}\left\{1+b\cos 2\varphi - \lambda\sin 2\varphi\right\}\frac{\partial}{\partial\varphi}$$
$$+\frac{1}{2}\left\{\lambda(2-3\sin^2\theta) - 3\sin^2\theta(\lambda\cos 2\varphi + b\sin 2\varphi)\right\} \tag{54}$$

Substituting the series form (52) in Eq. (53) and equating like orders of σ, we find that the following relations must be satisfied

$$\begin{aligned} &\nabla^2 F^{(0)} = 0 \\ &L\left\{F^{(n-1)}\right\} = \nabla^2\left\{F^{(n)}\right\} \quad \text{for} \quad n = 1, 2, \ldots \end{aligned} \tag{55}$$

These constitute a system of differential recursion relations, from which the various orders $F^{(n)}(\theta,\varphi)$ can be determined. This is best achieved if we consider them expanded in the complete system of the eigenfunctions of the Laplacian operator which satisfy the boundary conditions (49) of the problem:

$$F^{(n)}(\theta,\varphi) = \sum_{\ell=0}^{\infty}\sum_{m=0}^{\ell}\left\{a_{\ell m}^{(n)}\cos 2m\varphi + b_{\ell m}^{(n)}\sin 2m\varphi\right\} P_{2\ell}^{2m}(\cos\theta) \tag{56}$$

Because then, the recursion relation reduces to an algebraic expression for the coefficients of the n-th order, in view of the eigenvalue property

$$\nabla^2\left\{F^{(n)}(\theta,\varphi)\right\} = \sum_{\ell=0}^{\infty} -2\ell(2\ell+1)\sum_{m=0}^{\ell}\left\{a_{\ell m}^{(n)}\cos 2m\varphi + b_{\ell m}^{(n)}\sin 2m\varphi\right\} P_{2\ell}^{2m}(\cos\theta) \tag{57}$$

Let us note, in connection with this calculation, that because of the form of the coefficients of the operator L, the expansion (56) of $F^{(n)}(\theta, \varphi)$ is a finite one, the summation with respect to ℓ stopping at $\ell = n$.

Using the above method, we have determined $F^{(0)}$, $F^{(1)}$, $F^{(2)}$ and $F^{(3)}$, namely we have calculated the steady state distribution function to the third order

$$F(\theta, \varphi) = F^{(0)} + \sigma F^{(1)} + \sigma^2 F^{(2)} + \sigma^3 F^{(3)} \tag{58}$$

The zeroeth order term corresponds to $\ell = 0$

$$F^{(o)}(\theta, \varphi) = a_{oo}^{(o)} \tag{59}$$

and we readily determine that $a_{oo}^{(o)} = \frac{1}{4\pi}$ by using the normalizing condition

$$\int F^{(o)} \, d\Omega = 1$$

$$\therefore \qquad F^{(o)}(\theta, \varphi) = \frac{1}{4\pi} \tag{59'}$$

The first order term will have the form ($\ell = 0, 1$)

$$F^{(1)}(\theta, \varphi) = a_{oo}^{(1)} + a_{10}^{(1)} P_2(\cos\theta) + \left\{ a_{11}^{(1)} \cos 2\varphi + b_{11}^{(1)} \sin 2\varphi \right\} P_2^2(\cos\varphi) \tag{60}$$

Substituting in the recursion relation

$$L\left\{ F^{(o)} \right\} = \nabla^2 F^{(1)}$$

we find

$$\frac{1}{4\pi}\ \frac{1}{2}\left\{\lambda(2-3\sin^2\theta) - 3\sin^2\theta(\lambda\cos 2\varphi + b\sin 2\varphi)\right\}$$

$$= -6a_{10}^{(1)}P_2(\cos\theta) - 6\left\{a_{11}^{(1)}\cos 2\varphi + b_{11}^{(1)}\sin 2\varphi\right\}P_2^2(\cos\theta) \tag{61}$$

Finally, by comparing the coefficients of the orthogonal functions[23] we find

$$a_{10}^{(1)} = -\ \frac{1}{4\pi}\ \frac{\lambda}{6}$$

$$a_{11}^{(1)} = \frac{1}{4\pi}\ \frac{\lambda}{12} \tag{62}$$

$$b_{11}^{(1)} = \frac{1}{4\pi}\ \frac{b}{12}$$

It is obvious that we shall have to take

$$a_{oo}^{(i)} = 0 \quad \text{for every } \ i \geq 1 \tag{63}$$

in view of our choice for $a_{oo}^{(o)}$.

So, the first order term is

$$F^{(1)}(\theta,\varphi) = \frac{1}{4\pi}\ \frac{1}{12}\left[-2\lambda\ P_2(\cos\theta) + \left\{\lambda\cos 2\varphi + b\sin 2\varphi\right\}P_2^2(\cos\theta)\right]$$

$$= -\frac{1}{4\pi}\ \frac{1}{12}\left[\lambda(2-3\sin^2\theta) - 3\sin^2\theta\left\{\lambda\cos 2\varphi + b\sin 2\varphi\right\}\right] \tag{60'}$$

<u>The second order term</u> will have the form

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[23] The Legendre Polynomials $P_{2\ell}$ and the Associated Legendre Polynomials $P_{2\ell}^{2m}$ are tabulated in Appendix B.

$$F^{(2)}(\theta,\varphi) = a_{10}^{(2)}P_2(\cos\theta) + \left\{a_{11}^{(2)}\cos 2\varphi + b_{11}^{(2)}\sin 2\varphi\right\} P_2^2(\cos\theta)$$

$$+ a_{20}^{(2)}P_4(\cos\theta) + \left\{a_{21}^{(2)}\cos 2\varphi + b_{21}^{(2)}\sin 2\varphi\right\} P_4^2(\cos\theta)$$

$$+ \left\{a_{22}^{(2)}\cos 4\varphi + b_{22}^{(2)}\sin 4\varphi\right\} P_4^4(\cos\theta) \tag{64}$$

Substituting in the recursion relation

$$L\left\{F^{(1)}\right\} = \nabla^2 F^{(2)} \tag{65}$$

we have

$$-\frac{1}{4\pi}\frac{1}{12}\frac{1}{2}\Big[\sin\theta\cos^2\theta\left\{\lambda + \lambda\cos 2\varphi + b\sin 2\varphi\right\}$$

$$\times\left\{-6\lambda\sin\theta - 6\sin\theta(\lambda\cos 2\varphi + b\sin 2\varphi)\right\}$$

$$+ (1 + b\cos 2\varphi - \lambda\sin 2\varphi)(-3\sin^2\theta)2(-\lambda\sin 2\varphi + b\cos 2\varphi)$$

$$+ \left\{\lambda(2 - 3\sin^2\theta) - 3\sin^2\theta(\lambda\cos 2\varphi + b\sin 2\varphi)\right\}^2\Big]$$

$$= -6a_{10}^{(2)}P_2(\cos\theta) - 6\left\{a_{11}^{(2)}\cos 2\varphi + b_{11}^{(2)}\sin 2\varphi\right\} 3\sin^2\theta$$

$$- 20\,a_{20}^{(2)}P_4(\cos\theta) - 20\left\{a_{21}^{(2)}\cos 2\varphi + b_{21}^{(2)}\sin 2\varphi\right\} P_4^2(\cos\theta)$$

$$- 20\left\{a_{22}^{(2)}\cos 4\varphi + b_{22}^{(2)}\sin 4\varphi\right\} P_4^4(\cos\theta) \tag{66}$$

By comparing the coefficients of the orthogonal functions we find

$$
\begin{aligned}
a_{10}^{(2)} &= -\frac{1}{16\pi} \; \frac{2\lambda^2 + 3b^2}{7\cdot 9} \\
a_{11}^{(2)} &= \frac{1}{16\pi} \; \frac{2\lambda^2 - 7b^2}{2\cdot 7\cdot 9} \\
b_{11}^{(2)} &= \frac{1}{16\pi} \; \frac{\lambda(2b + 7)}{2\cdot 7\cdot 9} \\
a_{20}^{(2)} &= \frac{1}{16\pi} \; \frac{3\lambda^2 + b^2}{2\cdot 5\cdot 7} \\
a_{21}^{(2)} &= -\frac{1}{16\pi} \; \frac{\lambda^2}{2\cdot 3\cdot 5\cdot 7} \\
b_{21}^{(2)} &= -\frac{1}{16\pi} \; \frac{\lambda b}{2\cdot 3\cdot 5\cdot 7} \\
a_{22}^{(2)} &= \frac{1}{16\pi} \; \frac{\lambda^2 - b^2}{2^4\cdot 3\cdot 5\cdot 7} \\
b_{22}^{(2)} &= \frac{1}{16\pi} \; \frac{\lambda b}{2^3\cdot 3\cdot 5\cdot 7}
\end{aligned}
\qquad (67)
$$

So the second order term is

$$F^{(2)}(\theta,\varphi) = \frac{1}{16\pi}\ \frac{1}{7}\Bigg\{ -\frac{2\lambda^2+3b^2}{9}\ P_2(\cos\theta) + \frac{3\lambda^2+b^2}{10} P_4(\cos\theta)$$

$$+\left[\frac{2\lambda^2-7b^2}{18}\cos 2\varphi + \frac{\lambda(2b+7)}{18}\cos 2\varphi\right] P_2^2(\cos\theta)$$

$$-\left[\frac{\lambda^2}{30}\cos 2\varphi + \frac{\lambda b}{30}\sin 2\varphi\right] P_4^2(\cos\theta)$$

$$+\left[\frac{\lambda^2-b^2}{240}\cos 4\varphi + \frac{\lambda b}{120}\sin 4\varphi\right] P_4^4(\cos\theta)\Bigg\}$$

$$= \frac{1}{16\pi}\Bigg\{\frac{3\lambda^2+b^2}{16}\sin^4\theta - \frac{\lambda^2}{6}\sin^2\theta + \frac{\lambda^2-3b^2}{90}$$

$$+\left[\frac{\lambda^2}{4}\sin^4\theta - \frac{\lambda^2+b}{6}\sin^2 0\right]\cos 2\varphi$$

$$+\left[\frac{b\lambda}{4}\sin^4\theta + \frac{\lambda(1-b)}{6}\sin^2\theta\right]\sin 2\varphi$$

$$+\frac{\lambda^2-b^2}{16}\sin^4\theta\cos 4\varphi + \frac{\lambda b}{8}\sin^4\theta\sin 4\varphi\Bigg\} \qquad (64')$$

The third order term will have the form

$$F^{(3)}(\theta,\varphi) = a_{10}^{(3)}P_2(\cos\theta) + \left[a_{11}^{(3)}\cos 2\varphi + b_{11}^{(3)}\sin 2\varphi\right]P_2^2(\cos\theta)$$

$$+ a_{20}^{(3)}P_4(\cos\theta) + \left[a_{21}^{(3)}\cos 2\varphi + b_{21}^{(3)}\sin 2\varphi\right]P_4^2(\cos\theta)$$

$$+\left[a_{22}^{(3)}\cos 4\varphi + b_{22}^{(3)}\sin 4\varphi\right]P_4^4(\cos\theta) + a_{30}^{(3)}P_6(\cos\theta)$$

$$+\left[a_{31}^{(3)}\cos 2\varphi + b_{31}^{(3)}\sin 2\varphi\right]P_6^2(\cos\theta)$$

$$+\left[a_{32}^{(3)}\cos 4\varphi + b_{32}^{(3)}\sin 4\varphi\right]P_6^4(\cos\theta)$$

$$+\left[a_{33}^{(3)}\cos 6\varphi + b_{33}^{(3)}\sin 6\varphi\right]P_6^6(\cos\theta) \qquad (68)$$

Substituting in the recursion relation

$$L\left\{F^{(2)}\right\} = \nabla^2 F^{(2)} \tag{69}$$

we have

$$\frac{\sin^2\theta\cos^2\theta}{32\pi}\left\{\lambda+\lambda\cos 2\varphi+b\sin 2\varphi\right\}\left\{\frac{3\lambda^2+b^2}{4}\sin^2\theta-\frac{\lambda^2}{3}\right.$$

$$+\left[\lambda^2\sin^2\theta-\frac{\lambda^2+b}{3}\right]\cos 2\varphi+\left[\lambda b\sin^2\theta+\frac{\lambda(1-b)}{3}\right]\sin 2\varphi$$

$$\left.+\frac{\lambda^2-b^2}{4}\sin^2\theta\cos 4\varphi+\frac{\lambda b}{2}\sin^2\theta\sin 4\varphi\right\}$$

$$+\frac{1}{32\pi}\left\{1+b\cos 2\varphi-\lambda\sin 2\varphi\right\}\left\{\left[-\frac{\lambda^2}{2}\sin^4\theta+\frac{\lambda^2+b}{3}\sin^2\theta\right]\sin 2\varphi\right.$$

$$+\left[\frac{b\lambda}{2}\sin^4\theta+\frac{\lambda(1-b)}{3}\sin^2\theta\right]\cos 2\varphi-\frac{\lambda^2-b^2}{4}\sin^4\theta\sin 4\varphi$$

$$\left.+\frac{\lambda b}{2}\sin^4\theta\cos 2\varphi\right\}+\frac{1}{32\pi}\left\{\lambda(2-3\sin^2\theta)-3\sin^2\theta(\lambda\cos 2\varphi+b\sin 2\varphi)\right\}$$

$$\times\left\{\frac{3\lambda^2+b^2}{16}\sin^4\theta-\frac{\lambda^2}{6}\sin^2\theta+\frac{\lambda^2-b^2}{90}+\left[\frac{\lambda^2}{4}\sin^4\theta-\frac{\lambda^2+b}{6}\sin^2\theta\right]\cos 2\varphi\right.$$

$$+\left[\frac{b\lambda}{4}\sin^4\theta+\frac{\lambda(1-b)}{6}\sin^2\theta\right]\sin 2\varphi+\frac{\lambda^2-b^2}{16}\sin^4\theta\cos 4\varphi$$

$$\left.+\frac{\lambda b}{8}\sin^4\theta\sin 4\varphi\right\}$$

$$= -6a_{10}^{(3)}P_2(\cos\theta)-6\left[a_{11}^{(3)}\cos 2\varphi+b_{11}^{(3)}\sin 2\varphi\right]P_2^2(\cos\theta)-20a_{20}^{(3)}P_4(\cos\theta)$$

$$-20\left[a_{21}^{(3)}\cos 2\varphi+b_{21}^{(3)}\sin 2\varphi\right]P_4^2(\cos\theta)$$

$$-20\left[a_{22}^{(3)}\cos 4\varphi+b_{22}^{(3)}\sin 4\varphi\right]P_4^4(\cos\theta)-42a_{30}^{(3)}P_6(\cos\theta)-$$

$$- 42 \left[a_{31}^{(3)} \cos 2\varphi + b_{31}^{(3)} \sin 2\varphi\right] P_6^2(\cos\theta)$$

$$- 42 \left[a_{32}^{(3)} \cos 4\varphi + b_{32}^{(3)} \sin 4\varphi\right] P_6^4(\cos\theta)$$

$$- 42 \left[a_{33}^{(3)} \cos 6\varphi + b_{33}^{(3)} \sin 6\varphi\right] P_6^6(\cos\theta) \qquad (70)$$

By using the relations

$$\cos 2\varphi \cos 4\varphi = \frac{1}{2}\cos 6\varphi + \frac{1}{2}\cos 2\varphi \qquad \sin 4\varphi \cos 2\varphi = \frac{1}{2}\sin 6\varphi + \frac{1}{2}\sin 2\varphi$$

$$(71)$$

$$\sin 2\varphi \sin 4\varphi = \frac{1}{2}\cos 2\varphi - \frac{1}{2}\cos 6\varphi \qquad \sin 2\varphi \cos 4\varphi = \frac{1}{2}\sin 6\varphi - \frac{1}{2}\sin 2\varphi$$

and comparing coefficients of the orthogonal functions, we find the coefficients of $\cos 2\varphi$ and $\sin 2\varphi$ in $F^{(3)}(\theta, \varphi)$:

$$a_{11}^{(3)} = -\frac{1}{16\pi}\frac{\lambda}{2^2 \cdot 3^3 \cdot 5 \cdot 7}(35 + 15b + 3b^2 + 4\lambda^2)$$

$$b_{11}^{(3)} = \frac{1}{16\pi}\frac{15\lambda^2 - 4\lambda^2 b - 3b^3 - 35b}{2^2 \cdot 3^3 \cdot 5 \cdot 7}$$

$$a_{21}^{(3)} = \frac{1}{16\pi}\frac{\lambda(44b - 20\lambda^2 - 15b^2)}{2^2 \cdot 3^2 \cdot 5^2 \cdot 7 \cdot 11}$$

$$b_{21}^{(3)} = -\frac{1}{16\pi}\frac{44\lambda^2 + 20\lambda^2 b + 15b^3}{2^2 \cdot 3^2 \cdot 5^2 \cdot 7 \cdot 11} \qquad (72)$$

$$a_{31}^{(3)} = \frac{1}{16\pi}\frac{\lambda(5\lambda^2 + b^2)}{2^4 \cdot 3^2 \cdot 5 \cdot 7 \cdot 11}$$

$$b_{31}^{(3)} = \frac{1}{16\pi}\frac{5\lambda^2 b + b^3}{2^4 \cdot 3^2 \cdot 5 \cdot 7 \cdot 11}$$

IV. STREAMING BIREFRINGENCE OF MACROMOLECULAR SUSPENSIONS UNDER THE INFLUENCE OF A THIRD ORIENTATION MECHANISM

1. The Optical Properties of Suspensions and the Parameters of Streaming Birefringence.

Consider a suspension of prolate ellipsoidal macromolecules which consist of optically isotropic matter. Each macromolecule will then have principal axes of optical polarizability along the major axis (the axis of revolution) and along any equatorial axis, with corresponding values of optical polarizability Vg_1 and Vg_2, where V is the volume of the macromolecule.

If n is the number density of macromolecules in suspension, and n_o is the isotropic refractive index of the solvent, then the square of the refractive index of the solution is the matrix

$$\hat{n}^2 = \begin{pmatrix} n_{xx}^2 & n_{xy}^2 & n_{xz}^2 \\ n_{yx}^2 & n_{yy}^2 & n_{yz}^2 \\ n_{zx}^2 & n_{zy}^2 & n_{zz}^2 \end{pmatrix} \tag{73}$$

where

$$\begin{aligned}
n_{xx}^2 &= n_o^2 + 4\pi n V\left[g_2 + (g_1 - g_2) < \sin^2\theta \cos^2\varphi >\right] \\
n_{yy}^2 &= n_o^2 + 4\pi n V\left[g_2 + (g_1 - g_2) < \sin^2\theta \sin^2\varphi >\right] \\
n_{zz}^2 &= n_o^2 + 4\pi n V\left[g_2 + (g_1 - g_2) < \cos^2\theta >\right] \\
n_{xy}^2 &= n_{yx}^2 = 4\pi n V(g_1 - g_2) < \sin^2\theta \cos\varphi \sin\varphi > \\
n_{xz} &= n_{zx} = 4\pi n V(g_1 - g_2) < \sin\theta \cos\theta \cos\varphi > = 0 \\
n_{yz} &= n_{zy} = 4\pi n V(g_1 - g_2) < \sin\theta \cos\theta \sin\varphi > = 0
\end{aligned} \tag{74}$$

The last two must vanish since the orientation distribution is symmetric with respect to the xy plane.

Now the direction and the magnitude of the principal optical axes of the anisotropic solution will be obtained by the transformation of the matrix $\hat{n}^2$ into diagonal form within the xy plane, i.e., by diagonalizing the submatrix

$$\begin{pmatrix} n_{xx}^2 & n_{xy}^2 \\ n_{xy}^2 & n_{yy}^2 \end{pmatrix} \tag{75}$$

This matrix is Hermitian, hence the eigenvalues will be real and its eigenvectors will be orthogonal. We first find the eigenvalues λ_1 and λ_2 from the equation

$$\begin{vmatrix} n_{xx}^2 - \lambda & n_{xy}^2 \\ n_{xy}^2 & n_{yy}^2 - \lambda \end{vmatrix} = 0 \tag{76}$$

or

$$\lambda^2 - (n_{xx}^2 + n_{yy}^2)\lambda + n_{xx}^2 n_{yy}^2 - n_{xy}^4 = 0$$

$$\therefore \quad \lambda_{1,2} = \frac{1}{2}\left\{ n_{xx}^2 + n_{yy}^2 \pm \sqrt{(n_{xx}^2 + n_{yy}^2)^2 - 4(n_{xx}^2 n_{yy}^2 - n_{xy}^4)} \right\}$$

$$= \frac{1}{2}\left\{ n_{xx}^2 + n_{yy}^2 \pm \sqrt{(n_{xx}^2 - n_{yy}^2)^2 + 4n_{xy}^4} \right\} \tag{77}$$

$$= \frac{1}{2}\left\{ n_{xx}^2 + n_{yy}^2 \pm |n_{xx}^2 - n_{yy}^2| \sqrt{1 + \left(\frac{2n_{xy}^2}{n_{xx}^2 - n_{yy}^2}\right)^2} \right\}$$

The eigenvectors $\vec{V}_1$ and $\vec{V}_2$ are now defined by the relation between their components V_x and V_y:

$$\left[n_{xx}^2 - \frac{1}{2}\left\{ n_{xx}^2 + n_{yy}^2 \pm |n_{xx}^2 - n_{yy}^2| \sqrt{1 + \left(\frac{2n_{xy}^2}{n_{xx}^2 - n_{yy}^2}\right)} \right\} \right] V_x + n_{xy}^2 V_y = 0$$

$$\frac{1}{2}\left\{ n_{xx}^2 - n_{yy}^2 \mp |n_{xx}^2 - n_{yy}^2| \sqrt{1 + \left(\frac{2n_{xy}^2}{n_{xx}^2 - n_{yy}^2}\right)^2} \right\} V_x + n_{xy}^2 V_y = 0$$

$$\therefore \quad \frac{V_y}{V_x} = \frac{-1 \pm \operatorname{sign}(n_{xx}^2 - n_{yy}^2)\sqrt{1 + \left(\frac{2n_{xy}^2}{n_{xx}^2 - n_{yy}^2}\right)^2}}{\frac{2n_{xy}^2}{n_{xx}^2 - n_{yy}^2}} \tag{78}$$

Call $\frac{2n_{xy}^2}{n_{xx}^2 - n_{yy}^2} = \operatorname{tg} 2\psi \quad (-\frac{\pi}{2} < 2\psi < \frac{\pi}{2})$. Then

$$\operatorname{sign}(n_{xx}^2 - n_{yy}^2) = \operatorname{sign} \psi \tag{79}$$

and

$$\frac{V_y}{V_x} = \frac{-1 \pm \operatorname{sign}\psi \frac{1}{\cos 2\psi}}{\operatorname{tg} 2\psi} = \frac{-\cos 2\psi \pm \operatorname{sign}\psi}{\sin 2\psi} \tag{80}$$

Now in Couette flow with the flow field defined by

$$\vec{u}_o = G x \vec{e}_y$$

it is physically obvious that, for prolate ellipsoids of revolution, the viscous effect will tend to orient the major axis near the streamline, so that it will be

$$n_{yy}^2 > n_{xx}^2$$

Thus sign $\psi = -1$ and we get

$$\frac{V_y}{V_x} = - \frac{\cos 2\psi \pm 1}{\sin 2\psi} \tag{81}$$

It is also obvious that we shall get the direction X of the eigenvector which forms the <u>smaller</u> (in absolute value) angle with the x axis, if we choose the negative sign in the numerator (remember that $\cos 2\psi \geq 0$)

$$\frac{V_y}{V_x} = - \frac{\cos 2\psi - 1}{\sin 2\psi} = \frac{2 \sin^2\psi}{2 \sin \psi \cos \psi} = \text{tg } \psi \tag{82}$$

or

$$\frac{V_y}{V_x} = - \text{tg } |\psi| \tag{83}$$

which is indeed the smaller of the two angles of the cross of the eigenvectors with the x axis, since $|\psi| < \frac{\pi}{4}$, and it is <u>negative</u>. Hence the position of the eigenvectors is always as pictured in Fig. 2.[24]

Now to find this direction X, we have used the lower sign in Eq. (81) which means that this direction is the direction 2 with refractive index $\lambda_2 < \lambda_1$. We have called this direction (in the 4th quadrant) X

---

[24] In view of this analysis, it is clear that the directions of the optical axes are not correctly shown in Figs. 1 of the articles by R. Cerf and H. A. Scheraga, <u>loc. cit.</u> and by H. A. Scheraga, J. T. Edsall and J. O. Gadd Jr., <u>J. Chem.</u> Phys. <u>19</u>, 1101 (1951).

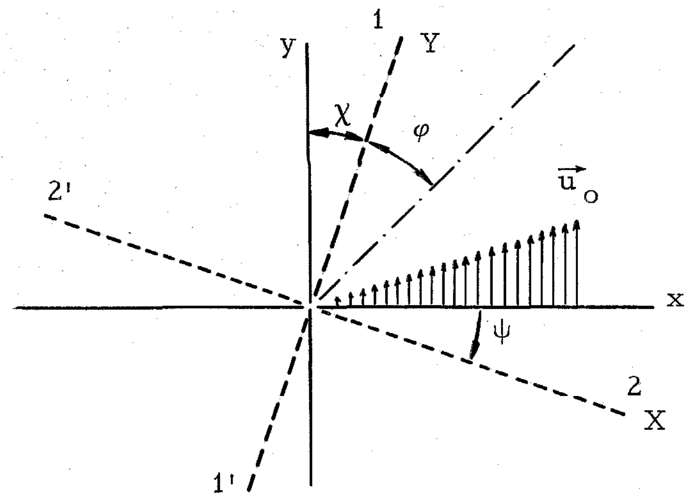

Fig. 2

and we take the other orthogonal direction (in the first quadrant) as Y.

Now in the orthogonal system, X, Y, z, the matrix $\hat{n}^2$ takes the diagonal form

$$\hat{n}^2 = \begin{pmatrix} n^2_{XX} & 0 & 0 \\ 0 & n^2_{YY} & 0 \\ 0 & 0 & n^2_{zz} \end{pmatrix} \tag{84}$$

where

$$n^2_{XX} = \lambda_2 = \frac{1}{2}\left\{n^2_{xx} + n^2_{yy} - \sqrt{(n^2_{xx} - n^2_{yy})^2 + 4n^4_{xy}}\right\}$$

$$n^2_{YY} = \lambda_1 = \frac{1}{2}\left\{n^2_{xx} + n^2_{yy} + \sqrt{(n^2_{xx} - n^2_{yy})^2 + 4n^4_{xy}}\right\}$$

We can now express the parameters of Streaming Birefringence:

The extinction angle χ is defined as the smaller of the two angles between the cross of the eigenvectors and the direction of the streamline at each point. We see, from the definition, and the geometry we have used, that

$$\chi \equiv |(y, Y)| \tag{85}$$

Note that $(y, Y) = (x, X) = -\psi$

$$\chi = |\psi| = \frac{1}{2} tg^{-1} \frac{2n_{xy}^2}{|n_{xx}^2 - n_{yy}^2|} \tag{86}$$

$$= \frac{1}{2} tg^{-1} \frac{2n_{xy}^2}{n_{yy}^2 - n_{xx}^2} \qquad \text{in our case}$$

Note, in addition, that this is the angle between the streamline and the optical axis with the higher refractive index.

The amount of birefringence Δn is defined as the difference in refractive index between the two principal directions, namely $\Delta n \equiv n_{YY} - n_{XX}$ $(\Delta n > 0)$

$$\Delta n = \frac{n_{YY}^2 - n_{XX}^2}{n_{YY}^2 + n_{XX}^2} = \frac{\sqrt{(n_{yy}^2 - n_{xx}^2)^2 + 4n_{xy}^4}}{2\bar{n}} \tag{87}$$

Finally note that, using the volume ratio

$$\phi = nV \tag{88}$$

we find from Eqs. (74)

$$n_{xx}^2 - n_{yy}^2 = 4\pi\phi(g_1 - g_2) < \sin^2\theta \cos 2\varphi >$$

and (89)

$$2n_{xy}^2 = 4\pi\phi(g_1 - g_2) < \sin^2\theta \sin 2\varphi >$$

Defining then

$< \sin^2\theta \cos 2\varphi > = A$ (it must be negative)

$< \sin^2\theta \sin 2\varphi > = B$ (it must be positive) we can express

$$\chi = \frac{1}{2} \, tg^{-1} \left(- \frac{B}{A}\right) \tag{90}$$

and

$$\Delta n = \frac{4\pi\phi(g_1 - g_2)}{2\bar{n}} \sqrt{A^2 + B^2}$$

$$= \frac{2\pi\phi(g_1 - g_2)}{\bar{n}} \sqrt{A^2 + B^2} \tag{91}$$

2. The Direction of the Isocline and the Amount of Birefringence Calculated to the Second Order.

We can now use the obtained distribution function to calculate the mean values $A = \langle \sin^2\theta \cos 2\varphi \rangle$ and $B = \langle \sin^2\theta \sin 2\varphi \rangle$ in terms of which the parameters χ and Δn of SBR are defined in Eqs. (90) and (91). In connection with this calculation, it is noted that, since

$$\sin^2\theta = \frac{1}{3} P_2^2(\cos\theta)$$

the quantities $\sin^2\theta \cos 2\varphi$ and $\sin^2\theta \sin 2\varphi$ are among the eigenfunctions of the Laplacian operator which were used to express $F^{(n)}(\theta, \varphi)C_n$ and therefore only the coefficients $a_{11}^{(n)}$ and $b_{11}^{(n)}$ will appear in view of the orthogonality relations. Specifically, since the norms

$$||P_2^2(\cos\theta)||^2 = \frac{2}{2 \cdot 2+1} \, \frac{(2+2)!}{(2-2)!} = \frac{48}{5}$$

and

$$||\cos 2\varphi||^2 = ||\sin 2\varphi||^2 = \pi$$

we find

$$A = \frac{16\pi}{5} \sum_n a_{11}^{(n)} \sigma^n \tag{92}$$

and

$$B = \frac{16\pi}{5} \sum_n b_{11}^{(n)} \sigma^n \tag{93}$$

The values of the coefficients $a_{11}^{(n)}$ and $b_{11}^{(n)}$, to the third order, are

$$\begin{aligned}
a_{11}^{(0)} &= 0 \\
a_{11}^{(1)} &= \frac{1}{16\pi} \frac{\lambda}{3} \\
a_{11}^{(2)} &= \frac{1}{16\pi} \frac{2\lambda^2 - 7b}{2 \cdot 3^2 \cdot 7} \\
a_{11}^{(3)} &= \frac{1}{16\pi} \frac{-\lambda(35 + 15b + 4\lambda^2 + 3b^2)}{2^2 \cdot 3^3 \cdot 5 \cdot 7} \\
b_{11}^{(0)} &= 0 \\
b_{11}^{(1)} &= \frac{1}{16\pi} \frac{b}{3} \\
b_{11}^{(2)} &= \frac{1}{16\pi} \frac{\lambda(2b + 7)}{2 \cdot 3^2 \cdot 7} \\
b_{11}^{(3)} &= \frac{1}{16\pi} \frac{15\lambda^2 - 4\lambda^2 b - 35b - 3b^3}{2^2 \cdot 3^3 \cdot 5 \cdot 7}
\end{aligned} \tag{94}$$

Thus, to the third order,

$$A = \frac{\lambda}{3 \cdot 5} \sigma + \frac{2\lambda^2 - 7b}{2 \cdot 3^2 \cdot 5 \cdot 7} \sigma^2 - \frac{\lambda(35 + 15b + 4\lambda^2 + 3b^2)}{2^2 \cdot 3^3 \cdot 5^2 \cdot 7} \sigma^3 \quad (95)$$

$$B = \frac{b}{15} \sigma + \frac{\lambda(2b + 7)}{2 \cdot 3^2 \cdot 5 \cdot 7} \sigma^2 + \frac{15\lambda^2 - 4\lambda^2 b - 35b - 3b^3}{2^2 \cdot 3^3 \cdot 5^2 \cdot 7} \sigma^3 \quad (96)$$

and using these we find χ and Δn from Eqs. (90) and (91).

Note that

$$\varphi = \frac{\pi}{4} - \chi \quad (97)$$

is the angle formed between the isocline and the principal strain axis in Couette flow. It appears in the theory of SBR in a more fundamental way that χ, as was shown by Wayland when he considered the more general case of any two-dimensional laminar flow[(25)]. We shall therefore use φ to define the direction of the isocline, rather than χ. It is

$$2\varphi = \frac{\pi}{2} - 2\chi = \text{arc tg} \left(-\frac{A}{B}\right) \quad (98)$$

Using the obtained expressions for A and B, we find

$$\text{tg } 2\varphi = -\frac{A}{B} = -\gamma + \frac{\gamma^2 + 1}{6} \sigma + \frac{\gamma(\gamma^2 + 1)(b - 7)}{252} \sigma^2 \quad (99)$$

where we have put

$$\gamma = \frac{\lambda}{b} = \frac{K}{Gb} \quad (100)$$

---

[25] Loc. cit. In fact, Wayland has assigned the symbol χ to what we have defined as φ, and not to the extinction angle, as it is conventionally defined and used in this study, namely as the smaller of the two angles between the direction of the isocline and the streamlines.

Then, using the Taylor series expansion

$$\text{arc tg } z = z - \frac{1}{3} z^3 + \frac{1}{5} z^5 \ldots \tag{101}$$

we find

$$\varphi = -\frac{\gamma}{2}\left(1 - \frac{\gamma^2}{3} + \frac{\gamma^4}{5}\right) + \frac{\gamma^6 + 1}{12}\sigma + \frac{\gamma}{504}\left\{(b-21)\gamma^6 - 21\gamma^4 + b\right\}\sigma^2 \tag{102}$$

Similarly, we find

$$\Delta n = 2\pi\phi \frac{g_1 - g_2}{\bar{n}} \frac{\sqrt{\gamma^2+1}}{15} b\left\{\sigma + \frac{b\gamma}{21}\sigma^2\right\} \tag{103}$$

The above two relations give the parameters of SBR for our case.

3. Discussion.

It is interesting to note how the presence of the third orientation mechanism influences the two parameters of SBR.

First, in both the expression for φ and Δn, both even and odd powers appear, whereas in the absence of the third orientation mechanism ($\gamma = 0$) the even powers disappear, and Eqs. (102) and (103) reduce, of course, to the expressions given by Peterlin and Stuart.

Secondly, if we let $\sigma \to 0$ but keep the ratio $\frac{K}{G}$ (and hence also γ) constant[26], we see that $\Delta n \to 0$, but that the angle φ no longer vanishes. Its limiting value for $\sigma \to 0$ is in fact associated with γ

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[26] The three variables are the magnitudes of G, K and D, characterizing the strength of each of the three acting mechanisms.

$$\lim_{\substack{\sigma \to 0 \\ \gamma = \text{const}}} \varphi = -\frac{1}{2}\gamma\left\{1 - \frac{\gamma^2}{3} + \frac{\gamma^4}{5}\right\} \qquad (104)$$

so that its experimental determination allows calculation of K, i.e., the magnitude of the third orientation mechanism through equation (100).

Thirdly, if we let $G \to 0$ but keep K and D constant, then $\sigma \to 0$ but $|\gamma| \to \infty$, hence we obtain from Eq. (99) that $\varphi = 45^o$ or $\chi = 0$, which means that the cross of the optical axes coincides with the x and y axes. On the other hand, since the quantity $\sigma\gamma = \frac{K}{bD}$ remains constant in this case, we obtain from Eq. (103) that

$$\lim_{\substack{\sigma \to 0 \\ \gamma \to \infty}} \Delta n \quad 2\pi\phi \frac{g_1 - g_2}{\bar{n}} \frac{K}{15D} \qquad (105)$$

i.e., Δn is proportional to the magnitude of the third orientation mechanism, as has been observed in the case of the Kerr effect.

Finally, if we keep K and D constant, and start increasing G, then χ will also increase up to a point; for large values of G, χ will again tend to zero as in ordinary streaming birefringence.

V. HYDRODYNAMIC INTERACTIONS IN A SUSPENSION OF ELLIPSOIDS AND SPHERES IN SHEAR FLOW

1. The Experimental Evidence

One of the most interesting experiments performed at the C. I. T. SBR Laboratory was the one[27] involving a suspension of both ellipsoidal macromolecules (in this case the rod-like Tobacco Mosaic Virus - TMV) and spherical ones (Southern Bean Mosaic Virus - SBMV). It was observed, for example, that at equal weight concentrations of the two species at 3 Kg per m^3 of the suspension, the amount of birefringence Δn was lower than what it would have been in the absence of the spheres. This was considered opposite to what could be expected, since the addition of the spheres tends to increase the macroscopic viscosity of the medium in which the asymmetrical particles find themselves; it should therefore also, if anything, tend to increase the observed Δn, which depends linearly on the viscosity of the suspending medium. The discrepancy had to be attributed to hydrodynamic interactions between the spheres and the rods.

That hydrodynamic interactions can indeed influence the macroscopic properties of suspensions has been suggested by the results of numerous experiments. Specifically at C. I. T., where a systematic investigation of this subject has been carried out under the direction of Professor Wayland, the importance of hydrodynamic

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27 H. Wayland and M. Intaglietta, loc. cit.

interactions has also been demonstrated by Collins and Wayland[28] in measurements of the viscosity of a dilute suspension of TMV rods and Polystyrene Latex (PSL) spheres in Poiseuillian flow, as a function of the concentration of the two species.

In what follows, we shall try to examine theoretically the phenomena occurring in a uniform shear flow of a suspension of both ellipsoidal and spherical macromolecules due to hydrodynamic interactions between the two species. Our aim will be to investigate the processes by which these phenomena affect the macroscopic properties of the suspension, and particularly the observed amount of birefringence.

2. Birefringence and Viscosity. The Various Aspects of the Phenomenon.

The amount of birefringence in a suspension of ellipsoidal macromolecules undergoing shear flow is given by the following expression for low shear rates $(\sigma \equiv \frac{G}{D} << 1)$, as can be seen from Eq. (103) at the absence of a third orientation mechanism:

$$\Delta n = 2\pi\phi \, \frac{g_1 - g_2}{\bar{n}} \, \frac{b}{15} \, \frac{G}{D} \tag{106}$$

It is clear from this simple expression that the velocity gradient G represents the mechanism that orients the particles, namely the anisotropic action of the viscous stresses, whereas the

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[28] D. J. Collins and H. Wayland, Trans. Soc. Rheol., VII, 275 (1963).

diffusion constant D represents the "disorienting" mechanism, namely the isotropic Brownian impulses which "fight" towards a random distribution of orientations.

We have already seen (Eqs. 16 and 19) that the diffusion constant is a linear function of the rotational mobility of the particle when subjected to a torque. We may therefore deduce from Eq. (106) the following statement: the amount of birefringence increases with increasing velocity gradient G, since G measures the orienting mechanism; and it decreases with increasing rotational mobility of the particle in the suspension, since this mobility measures the effectiveness of the "disorienting" Brownian mechanism.

If we use the expression given in Eq. (17) for the appropriate rotational mobility of a spheroid suspended in a medium of viscosity μ_o, we have

$$D = kTB_2 = \frac{kT}{4\mu_o V} \frac{p^2}{p^4-1} \left[-1 + \frac{2p^2-1}{p(p^2-1)^{1/2}} \ln \left(p + (p^2-1)^{1/2}\right) \right]$$

$$= \frac{D_\mu}{\mu_o} \tag{107}$$

where D_μ depends only on the particle and the temperature, and not on the suspending medium. We can then express

$$\Delta n = 2\pi\phi \frac{g_1 - g_2}{\bar{n}} \frac{b}{15\, D_\mu} G\mu_o \tag{108}$$

which explicitly displays the linear dependence of the amount of birefringence on the viscosity of the suspending medium μ_o, i.e. the local viscosity felt by the suspended particle.

It is important to differentiate μ_o from the macroscopically observable bulk viscosity of the suspension. Consider for example the following two statements:

(a) A suspension is made more viscous by dissolving glycerol in it.

(b) A suspension is made more viscous by adding rigid particles to it, like the spheres of our case of interest.

It is clear that the first concerns the local viscosity, whereas the second concerns the macroscopic or bulk viscosity. It is clear also that the local viscosity is the one that is naturally involved in the rotational mobility of a single particle.

On the other hand, the presence of other particles in the suspension may influence the rotational mobility of the single particle, specifically it may reduce it. The effect of particle concentration on the rotational mobility of a single particle is especially pronounced in the case of chain molecules, where it has received extensive theoretical and experimental attention[29]. It was found that the quantity $\frac{\Delta n}{G\phi}$ is linear in ϕ, for small values of G and ϕ, and both theoretical and empirical expansions have been given. As it is well known, a similar behavior is displayed by the bulk viscosity of the suspensions for low values of ϕ. It was therefore natural to associate the birefringence behavior with the bulk viscosity behavior with

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[29] See, for example, the reviews by Cerf and Scheraga and by Jerrard, loc. cit.

concentration.[30] Indeed, the possibility that a relationship may be set up between viscosity and streaming birefringence hinges on the act that both are conditioned by the rotational mobility of the particle. ecifically, it has been suggested[31] that the concentration depend e of Δn could be taken into consideration by replacing μ_o with an ctive viscosity μ^*, depending on the bulk viscosity μ and the s ent viscosity μ_o, in the relation giving the rotational mobility, and hei also in the relation giving Δn.

The effect of the presence of the spheres, however, cannot properly be described by this macroscopic argument of the increased bulk viscosity of the suspension.[30] Such an argument would refer this effect entirely to the stochastic side of the orientation mechanisms acting on the ellipsoidal particle, by having it affect the Brownian influence alone. This does not seem justified at all, especially in view of the fact that, as expressed by Broersma[32], "in dilute suspensions a first-order perturbation in the velocity pattern produces only a second order change in the value of the effective viscosity." And the velocity pattern represents the orienting mechanism !

The effect of the presence of the spheres should then also be connected to the deterministic as well as the stochastic side of the orientation mechanisms. To the deterministic side, by considering the perturbation of the flow field and the energy dissipation due

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[30] Ch. Sadron, Ch. IV, § 1.2 in "Flow Properties of Disperse Systems" edited by J. J. Hermans, North-Holland Publ. Co. (1953).

[31] A. Peterlin, Proc. 2nd Inter. Congr. Rheol., 343 (1954).

[32] S. Broersma, J. Chem. Phys., 30, 707 (1959).

to the presence of the spheres, and then determining the drift velocity of the ellipsoids in this perturbed flow field. And to the stochastic side, by considering the change in the rotational mobility of the ellipsoids and the probability of collisions and associations between the spheres and between spheres and ellipsoids.

The deterministic side of the phenomenon, which has not received attention, will be studied in what follows. We shall show that the presence of the spheres has the effect of retarding the rotational motion of the ellipsoids and that this effect can be described as a change in the velocity gradient experienced by the ellipsoids from the value G in the undisturbed flow to a new value, G_{eff}, smaller than G. On the stochastic side, we shall describe the change in the rotational mobility of the ellipsoids due to the presence of the spheres by using for the diffusion constant the value D_{eff}, smaller than D. We shall then have, for the amount of birefringence

$$\Delta n = 2\pi\phi \frac{g_1 - g_2}{\bar{n}} \frac{b}{15} \frac{G_{eff}}{D_{eff}} \tag{109}$$

and denoting by $(\Delta n)_o$ the amount of birefringence <u>in the absence of the spheres,</u> which is given by Eq. (106), we have

$$\frac{\Delta n}{(\Delta n)_o} = \frac{G_{eff}}{G} \frac{D}{D_{eff}} \tag{110}$$

The behavior of the amount of birefringence, when spheres are added to the suspension in increasing concentration, will be studied in terms of this relation.

3. The Effect of the Spheres on the Drift Velocity of the Ellipsoids.

We shall attempt to analyze this interaction effect by using the concept of the energy dissipation. The approach will be based on the flow properties of very viscous fluids.

3.1. Introduction

Consider the Stokes flow of a homogeneous viscous fluid in a region V_o bounded by the well-defined closed surface S_o. Let the fluid velocity and pressure be $\vec{u}^{(0)}$ and $p^{(0)}$ respectively, and consistently refer all velocities to a stationary coordinate system.

Given the velocities on the surface S_o, the flow field everywhere in V_o can be found as the solution of a boundary value problem involving the linear equations

$$\nabla \cdot \vec{u}^{(0)} = 0 \tag{111}$$

$$-\nabla p^{(0)} + \mu_o \nabla^2 \vec{u}^{(0)} = 0 \tag{112}$$

where μ_o is the viscosity of the fluid. These equations of motion describe the flow of incompressible fluids, in the absence of non-conservative external body forces, when the effects of fluid inertia are either absent (uniform flow) or negligible (creeping flow). In the latter case these equations correspond to what is termed "Stokes approximation."

Note that "time" does not appear in these equations. Therefore the solution of the boundary value problem is independent of time, in the sense that it describes the instantaneous flow field under the instantaneous boundary conditions given. This does not mean that the flow field is necessarily time independent: if the boundary conditions vary with time, so will the flow field. However, at any instant t, the flow field is given, within the Stokes approximation, by the solution of the boundary value problem involving the boundary conditions corresponding to this t, independently of the time history of the boundary conditions. This, of course, is a direct consequence of the fact that the contribution of inertia is negligible, which was what allowed us to neglect the corresponding terms from the Navier-Stokes equation and thus transform it to the linear form (112). The flow field will be strictly steady only if the velocities prescribed on S_o are constant in time; for example, if S_o is the surface of the well-defined boundaries of a viscometry apparatus.

Consider now that a small volume V of the fluid (much smaller than V_o) has been replaced by a rigid particle of arbitrary shape, bounded by the surface S, while the boundary condition on S_o is constant in time. There arise two problems of interest:

(1) The motion of the particle as a rigid body. This can be defined by giving, at every instant t, the two vectors $\vec{V}$ and $\vec{\omega}$, where $\vec{V}$ is the velocity of a point of the body (say its geometrical center O) and $\vec{\omega}$ the rotational velocity around that point. Then, the velocity of any point $\vec{r}$ of the rigid body at this time t, is given by the expression

$$\vec{u}_b(\vec{r}, t) = \vec{V}(t) + \vec{\omega}(t) \times (\vec{r} - \vec{r}_o) \tag{113}$$

(2) The fluid flow field $\vec{u}(r)$ in the region between S_o and the particle surface S, at every instant t. It is clear that, in general, this flow field will vary with time, since both the part of the geometrical boundary represented by S and the boundary conditions on it vary with time. At any given instant t, however, the flow field will be uniquely determined by the instantaneous conditions on its boundary, which is now the surface $S_o + S$; the boundary condition on S is given by Eq. (113).

It is thus clear that the two problems are coupled: the solution to the first problem is needed in order to know the complete boundary condition for the second, and the solution to the second is needed in order to calculate the hydrodynamic force and torque on the particle, the motion of which is determined by the condition that, within the framework of creeping flow, there can exist no net force or torque on it.

The solution to both problems can be obtained simultaneously by the approach used by Jeffery in the case of ellipsoids: Begin by solving the second problem, the problem of the flow field, by using arbitrary values for $\vec{V}$ and $\vec{\omega}$. Then, using the obtained solution, calculate the hydrodynamic force and torque on the particle as functions of $\vec{V}$ and $\vec{\omega}$. Finally, equate the net force and torque on the particle to zero, and thus obtain the actual values of $\vec{V}$ and $\vec{\omega}$, namely the solution to problem (1).

It is interesting to examine what the vectors $\vec{V}$ and $\vec{\omega}$, determined as above, will depend on. They, together with the position of the particle with respect to S_o at the instant in question, determine the geometrical region <u>and</u> the complete boundary conditions for the problem (2). Therefore, the solution to this problem, namely the flow field at t--and consequently also the hydrodynamic force and torque on S, the energy dissipation and any other quantity defined in the flow field--depend exclusively on the position and the motion of the rigid particle with respect to S_o, on the viscosity of the fluid and on the boundary conditions on S_o. In addition, if all points of the surface S_o are very far away from the particle, then the actual position of the particle stops being of importance, while the boundary conditions on S_o are important only in the sense that they define uniquely the undisturbed flow field $\vec{u}^{(0)}$ that would exist at the region V if the particle were absent. We conclude that the perturbed flow field due to the presence of the particle

$$\vec{u}(\bar{r}) = \vec{u}^{(0)} + \vec{u}'(\bar{r}) \tag{114}$$

depends only on (a) the unperturbed flow field $\vec{u}^{(0)}$ in the region around V, (b) the viscosity of the fluid μ_o and (c) the shape, and motion (defined by $\vec{V}$ and $\vec{\omega}$), of the body. As a direct consequence of the above, we conclude that the hydrodynamic force $\vec{F}_H$ and torque $\vec{T}_H$ on the particle will also exclusively depend on (a), (b) and (c). But it is $\vec{F}_H$ and $\vec{T}_H$ that determine the motion of the particle, in conjunction with any external force and torque on it. Therefore: The motion of a particle which is immersed in a fluid flow field $\vec{u}^{(0)}(\bar{r})$ depends only on the undisturbed field $\vec{u}^{(0)}$ and the shape of the particle.

This general statement is consistent with the expression given by Giesekus[32] and by Bretherton[33] to the rotation $\vec{\omega}$ of a rigid particle of arbitrary shape which is immersed in any viscous flow $\vec{u}^{(0)}$, in the absence of external force or torque. If we denote by $\vec{\zeta} = \frac{1}{2}(\nabla \times \vec{u}^{(0)})_o$ the rotation and by $\bar{\bar{\epsilon}} = (\nabla \vec{u}^{(0)})_o^{\text{symmetric}}$ the rate of strain in the undisturbed flow in the neighborhood of the point where the body is immersed, then

$$\vec{\omega} = \vec{\zeta} + \frac{1}{2}\bar{\bar{\bar{B}}} : \bar{\bar{\epsilon}} \tag{115}$$

or in tensor notation

$$\omega_i = \zeta_i + \frac{1}{2} B_{i\alpha\beta}\epsilon_{\alpha\beta} \tag{115'}$$

where $\bar{\bar{\bar{B}}}$ is a third rank tensor, characteristic of the particle shape, and symmetric in the last two indices.

Finally, the following expression can be shown for the hydrodynamic torque acting on a rigid particle of arbitrary shape immersed in an arbitrary flow provided there is no coupling between the translational and rotational motions of the particle[34] (i.e. that the particle is of such shape that a forced translation through a fluid at rest at infinity does not induce rotation of the particle)

$$\vec{T}_H = \bar{\bar{R}} \cdot \left[\vec{\zeta} - \vec{\omega} + \frac{1}{2}\bar{\bar{\bar{B}}} : \bar{\bar{\epsilon}}\right] \tag{116}$$

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[32] H. Giesekus, Rheol. Acta, 2, 101 (1962).

[33] F. P. Bretherton, J. Fluid Mech., 14, 284 (1962).

[34] H. Brenner, Chem. Eng. Science, 19, 631, (1964).

where $\overline{\overline{R}} \; (= \overline{\overline{B}}^{-1})$ is the rotational resistance tensor of the particle, calculated from the completely different problem of the particle having a steady forced rotation in a fluid at rest at infinity.

Equation (116) of course proves the theorem of Giesekus and Bretherton in the absence of external torque, since then it must be $\vec{T}_H = 0$. In addition, it establishes in the general case that $\overline{\overline{R}} = \overline{\overline{B}}^{-1}$, which can be noticed to be true in the results of Jeffery for the hydrodynamic torque in ellipsoids, for which the six non-zero components of $B_{i\alpha\beta}$ are

$$B_{123} = B_{132} = \frac{a_2^2 - a_3^2}{a_2^2 + a_3^2}$$
$$B_{231} = B_{213} = \frac{a_3^2 - a_1^2}{a_3^2 + a_1^2} \qquad (117)$$
$$B_{312} = B_{321} = \frac{a_1^2 - a_2^2}{a_1^2 + a_2^2}$$

3.2. Energy Dissipation

According to the heuristic argument presented in the previous paragraph, the energy dissipation in the perturbed flow field due to the presence of the particle, depends only on (a) the unperturbed flow field $\vec{u}^{(0)}$ in the neighborhood of V, (b) the viscosity of the fluid and (c) the shape of the particle. We shall show that consistent results are produced in the case of spheres and ellipsoids immersed in Couette flow by the statement that the energy dissipation due to the perturbation field $\vec{u}'(\bar{r})$ in the region between S_o and S is given by the expression

$$E' = \vec{\omega} \cdot \bar{\bar{B}}^{-1} \cdot \vec{\omega} \tag{118}$$

where $\bar{\bar{B}}$ is the rotational mobility tensor as given in Appendix A. If n is the number density of dilutely suspended particles in the flow, then the energy dissipation increment is, per unit volume

$$e = n\vec{\omega} \cdot \bar{\bar{B}}^{-1} \cdot \vec{\omega} \tag{119}$$

The fact that Eq. (119) properly describes the energy dissipation increment in the above two cases suggests the possibility of proving its validity in more generality, subject to certain restrictions as to the form of the undisturbed flow field. This task will not be attempted here.

3.3. The Energy Dissipation in Couette Flow of Suspensions of Ellipsoids or Spheres

When the suspended particles are of asymmetrical shape, the rotational velocity $\vec{\omega}$ and the energy dissipation e will depend on the momentary orientation of the particle with respect to the shear flow field

$$e = e(\theta, \varphi, \psi) \tag{120}$$

However, if the distribution function $f(\theta, \varphi, \psi)$ is steady in time, one can consider the time independent mean value

$$\langle e \rangle = \int fe \, dV = (f, e) \tag{121}$$

and thus define the increase in the viscosity of the suspension over that of the solvent in terms of the relation

$$< e > = (\mu - \mu_o)G^{*2} \tag{122}$$

where μ_o is the viscosity of the solvent and G^* is the velocity gradient in the suspension.

For prolate ellipsoids of revolution, the mobility tensor has, in the system of the principal inertial axes, the diagonal form

$$\overline{\overline{B}} = \begin{pmatrix} B_1 & 0 & 0 \\ 0 & B_2 & 0 \\ 0 & 0 & B_2 \end{pmatrix} \tag{123}$$

as it has been already mentioned. The constants B_1 and B_2 are given in Appendix A.

Substituting in Eq. (119) we obtain

$$e = n\left[\frac{\omega_1^2}{B_1} + \frac{\omega_2^2 + \omega_3^2}{B_2}\right] = n\,\frac{16\,\pi\mu_o}{3}\left[\frac{\omega_1^2}{\beta_o} + \frac{(a_1^2 + a_2^2)(\omega_2^2 + \omega_3^2)}{a_2^2\beta_o + a_1^2\alpha_o}\right] \tag{124}$$

But

$$\omega_2^2 + \omega_3^2 = \dot{\theta}^2 + (\dot{\varphi}\sin\theta)^2 = \left(\frac{Gb}{2}\sin\theta\cos\theta\sin 2\varphi\right)^2 + \left[\frac{G}{2}\sin\theta(1 + b\cos 2\varphi)\right]^2$$

and

$$\omega_1^2 = (\dot{\varphi}\cos\theta + \dot{\psi})^2 = \left(\frac{G}{2}\cos\theta\right)^2$$

We thus have

$$e = n\,\frac{4}{3}\,\pi\mu_o G^2\left[\frac{\cos^2\theta}{\beta_o} + \frac{a_1^2+a_2^2}{a_2^2\beta_o + a_1^2\alpha_o}\sin^2\theta(1+2b\cos 2\varphi + b^2 - b^2\sin^2\theta\sin^2 2\varphi)\right] \tag{125}$$

This corresponds to Jeffery's result.

The energy dissipation in the case of suspended spheres, namely Einstein's result, is found immediately by this approach. We know that spheres rotate in simple shear flow with rotation axis perpendicular to the plane of flow and rotational velocity $\omega = \frac{G}{2}$. Therefore

$$e = n\,\frac{\omega^2}{B} = \frac{n}{B}\,\frac{G^2}{4}$$

For a sphere we know that $B = \frac{1}{6\mu_o V_s}$ where V_s is the volume of the sphere, hence

$$e = n\,6\mu_o V_s\,\frac{G^2}{4} = \frac{3}{2}\,n\,V_s\,\mu_o G^2$$

But $nV_s \equiv \phi$ (the volume ratio), and we conclude that the energy dissipation due to the rotation of the sphere is

$$e = \frac{3}{2}\phi\mu_o G^2 \tag{126}$$

Now the total energy dissipation per unit volume, namely the dissipation due to both the solvent occupying $1 - \phi$ of the volume and the sphere, is

$$\frac{dW}{dt} = (1-\phi)\mu_o G^2 + \frac{3}{2}\phi\mu_o G^2$$
$$= (1 + \frac{1}{2}\phi)\mu_o G^2 \tag{127}$$

This is Einstein's result.

Note: Einstein then proceeds to find the viscosity of the suspension by proving that $G^* = G(1-\phi)$, hence $G^{*2} = G^2(1-2\phi)$ and defining $\frac{dW}{dt} \equiv \mu G^{*2}$ he found $\mu = \frac{1}{G^{*2}}\frac{dW}{dt} = (1+\frac{1}{2}\phi)\mu_o \frac{G^2}{G^{*2}} = \mu_o \frac{1+\frac{1}{2}\phi}{1-2\phi}$ or $\mu = \mu_o(1+\frac{5}{2}\phi)$ to the first order.

3.4. Energy dissipation under hydrodynamic interactions.

Consider now that the particles interact hydrodynamically, in the sense that the perturbation of the flow field around particle 1, caused by its presence, is felt by particle 2 as a significant change of the local field that it (i.e. particle 2) experiences, and vice versa.

The situation can be analyzed as follows:

(a) The presence of particle 1 at position $\vec{r}_1$ will perturb the flow field by the perturbation $\vec{u}_1'(\vec{r}-\vec{r}_1)$, so that now

$$\vec{u}(\vec{r}) = \vec{u}^{(0)}(\vec{r}) + \vec{u}_1'(\vec{r}-\vec{r}_1) \tag{128}$$

where $\vec{u}^{(0)}$ is the undisturbed flow field.

(b) If there are many particles of type 1 influencing the field, we can write

$$\bar{u}(\bar{r}) = \vec{u}^{(0)}(\bar{r}) + \sum_{\nu} \vec{u}_1'(\bar{r}-\vec{r}_\nu) \tag{129}$$

(c) If a particle of type 2 is now placed at $\vec{r}_2$, it will follow the flow field (129), rotating in the way prescribed for it by the velocity gradient tensor of this flow field, namely in the way described by Eq. (115). This corresponds to our case of interest, where a TMV finds itself surrounded by many spherical particles.

(d) In addition, however, the presence of the particle 2 at $\vec{r}_2$ will perturb the flow field by the amount $\vec{u}'_2(\bar{r} - \vec{r}_2)$. This field will depend on the rotational velocity $\vec{\omega}$ of the particle 2, and will affect the motion of the spheres. Due to the presence of the spheres in this field there is an energy dissipation increment, which, as calculated by Einstein[35], is, per sphere

$$e_{12} = 5\mu_o(A^2 + B^2 + C^2)V_s \tag{130}$$

where A, B, C are the three principal rates of strain in the field $\vec{u}'_2(\bar{r})$ and V_s is the volume of each sphere.

(e) This energy is directly due to the interaction between the spheres and the rod, since it is calculated not in the actual flow field existing in the suspension and felt by the outside world, but as a result of the presence of the spheres in the flow $\vec{u}'_2$, which, as has been mentioned, represents the perturbation due to the presence of a rod <u>alone</u> in the original flow field. If we accept, therefore, that the external world does not provide <u>any</u> part of this energy, then the energy dissipation due to the presence of the rod in the original flow must be smaller by the same amount, so that the rod will now rotate slower, and we shall obtain in this way a valid estimate of the maximum change that can be expected in the rotational velocity of the rod due to the presence of the spheres. In other words: If this interaction were not present, the rod would rotate with angular velocity $\vec{\omega}$ which was the object of the discussion given in the previous paragraph. Due to

[35] A. Einstein, Annalen d. Physik, <u>19</u>, 289 (1906).

interaction of the field $\vec{u}_2'$ with the spheres, however, the rod will rotate with a smaller angular velocity $\vec{\omega}'$, so that

$$\vec{\omega} \cdot \bar{\bar{B}}^{-1} \vec{\omega} - \vec{\omega}' \cdot \bar{\bar{B}}^{-1} \cdot \vec{\omega}' = e_{12} \tag{131}$$

By comparing Equations (130) and (131) we obtain the relation

$$\vec{\omega} \cdot \bar{\bar{B}}^{-1} \cdot \vec{\omega} - \vec{\omega}' \cdot \bar{\bar{B}}^{-1} \vec{\omega}' = 5\mu_o \sum_{\text{spheres}} (A^2 + B^2 + C^2) V_s \tag{132}$$

This is the relation that we shall use for the study of the deterministic effect of hydrodynamic interactions. The perturbation velocity $\vec{u}_2'$ is known as a function of $\vec{\omega}'$ from the solution of the hydrodynamic problem. Its magnitude is proportional to the magnitude of $\vec{\omega}'$. The rotation $\vec{\omega}$ is also known from the hydrodynamic problem. It is well to note, at this point, that $\vec{\omega}$ depends on G but not on μ_o; this is physically expected, since the torque acting on the particle is due to the viscous stresses and is thus proportional to μ_o, but also the resistance to rotation is proportional to μ_o, so μ_o does not appear in $\vec{\omega}$. One can, therefore, calculate $\vec{\omega}'$ from Eq. (132), and thus one can find the change in the angular velocity of the rod, in the presence of the spheres due to $\vec{u}_2'$.

Of course, in order to find the total change in the angular velocity of the particle 1, one also has to consider the change due to the field $\vec{u}_1'$, namely the perturbation field produced at the position of the rod by the spheres, using Eq. (115). We shall calculate that contribution also, although it can be expected to be small for our case of interest.

4. Application

We shall now proceed to apply the above approach in the specific case of the experiments of Intaglietta, namely when:

Particles 1 are particles of SBMV: spheres of diameter

$$2a = 2.52 \times 10^{-8} \text{ m}$$

Particle 2 is a particle of TMV: a long cylindrical rod of dimensions

$$2a_1 = 30 \times 10^{-8} \text{ m}$$

$$2a_1 = 1.8 \times 10^{-8} \text{ m}$$

$$(p = 16.7)$$

We are interested in any change in the rotational velocity of the rods due to the presence of the spheres. The spheres do not affect the observed parameters of SBR, except if they were to form doublets. This possibility will be examined later. Also, their presence will tend to raise $\overline{n}$, if their refractive indix is higher than that of the solvent, but this effect has been shown by Wayland and Intaglietta to be insignificant for the concentrations involved.

4.1. Definitions of concentrations, number densities and volume ratios.

We shall note by c the concentration of a certain substance in a suspension in

$$\frac{\text{Kg of the substance}}{1 \text{ m}^3 \text{ of the suspension}}$$

(1) We can immediately relate c to the number density of the molecules of this substance: If M is the molecular weight of the substance,

there are $\frac{c}{M}$ Kg-moles of the substance per m^3, hence, using the Avogadro number

$$N_A = 6.025 \times 10^{26} \text{ (Kg-mole)}^{-1}$$

we obtain, in m^{-3}

$$n = \frac{c}{M} N_A \tag{133}$$

Particularly, for TMV which has a molecular weight of 39×10^6, we obtain

$$n_{TMV} = 1.544 \times 10^{19}\ c_{TMV}$$

and for SBMV, which has a molecular weight of 6.63×10^6,

$$n_{SBMV} = 9.1 \times 10^{19}\ c_{SBMV}$$

(2) We note that

$$\xi \equiv \frac{n_{SBMV}}{n_{TMV}} = 5.88\ \frac{c_{SBMV}}{c_{TMV}} = \frac{5.88}{k}$$

We have defined $k = \dfrac{c_{TMV}}{c_{SBMV}}$.

(3) The volumes of each particle of the two species are

$$V_{TMV} = \pi a_2^2 \cdot 2a_1 = \pi (0.9)^2 30 \times 10^{-24}\ m^3$$

$$= 7.63 \times 10^{-23}\ m^3$$

$$V_{SBMV} = \frac{4}{3}\pi a^3 = \frac{4}{3}\pi(1.26)^3 \times 10^{-24}$$

$$= 8.38 \times 10^{-24}\ m^3$$

(4) $\phi_{TMV} = 1.18 \times 10^{-3}\ c_{TMV}$; $\phi_{SBMV} = 7.63 \times 10^{-4}\ c_{SBMV}$

TABLE 1

	Pure TMV	k = 2.9	k = 1	k = 0.31	
c_{TMV}	3	3	3	3	Kg m^{-3}
n_{TMV}	4.63×10^{19}	4.63×10^{19}	4.63×10^{19}	4.63×10^{19}	m^{-3}
ϕ_{TMV}	3.54×10^{-3}	3.54×10^{-3}	3.54×10^{-3}	3.54×10^{-3}	
c_{SBMV}	-	1.03	3	9.7	Kg m^{-3}
n_{SBMV}	-	9.4×10^{19}	2.73×10^{20}	8.8×10^{20}	m^{-3}
ϕ_{SBMV}	-	7.87×10^{-4}	2.28×10^{-3}	7.37×10^{-3}	
ξ	-	2.03	5.88	18.95	

4.2. The effect of the field $\vec{u}_1'$.

The field $\vec{u}_1'(\bar{r} - \bar{r}_1)$ has been defined as the perturbation field due to the presence of a sphere at $\vec{r}_1$. This field has been calculated by Einstein, who has found that, assuming spheres are uniformly distributed around, its effect is to decrease the principal shear rates at position 1 by the factor $1 - \phi_s$, where ϕ_s is the volume ratio of the spheres. This result indicates, in our case of interest, that the TMV particles find themselves in pure shear flow of velocity gradient

$$G^* = G(1 - \phi_{SBMV}) \tag{134}$$

It is clear however (see Table 1) that this effect is too small to account for the results of the Intaglietta experiment, where the changes in Δn were of the order of 10% whereas ϕ_{SBMV} is much smaller.

4.3. The effect of the field $\vec{u}_2'$.

The effect of this field will be studied in terms of the energy dissipation approach described in paragraph 3.4.

The perturbation velocity field around a long cylindrical rod immersed in a simple shear flow of velocity gradient G has been given by Burgers[37]. If we take as origin the center of the rod, and if the axis of the rod has an orientation θ, φ with respect to the flow (see Part III of this thesis), we can then express, in vector notation, the perturbation field at every point $\vec{r}$ as follows:

$$\vec{u}_2'(\vec{r}) = \frac{G_{eff} a_1^3}{6[\ln 2p - 1.8]} \sin^2\theta \cos\varphi \sin\varphi \left[1 - 3(\vec{e}_r \cdot \vec{e})^2\right] \frac{\vec{r}}{r^3} \quad (135)$$

where the vector $\vec{e}$ gives the direction of the axis of the rod, i.e. it has coordinates $(\sin\theta \cos\varphi, \sin\theta \sin\varphi, \cos\theta)$, so that

$$\vec{e}_r \cdot \vec{e} = \frac{x}{r} \sin\theta \cos\varphi + \frac{y}{r} \sin\theta \sin\varphi + \frac{z}{r} \cos\theta \quad (136)$$

For a body of revolution, like our long cylindrical rod, we have

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[37] J. M. Burgers, Second Report on Viscosity and Plasticity, Ch. II, North-Holland Publishing Co., Amsterdam, 1938.

$$\vec{\omega} \cdot \overline{\overline{B}}^{-1} \cdot \vec{\omega} = \frac{\omega_1^2}{B_1} + \frac{\omega_2^2 + \omega_3^2}{B_2} \qquad (137)$$

and since, in our case, $B_1 >> B_2$, we can put equation (132) in the form

$$\frac{(\omega_2^2 + \omega_3^2) - (\omega_2'^2 + \omega_3'^2)}{B_2} = 5\mu_o V_{SBMV} \sum_{\text{spheres}} (A^2+B^2+C^2) \qquad (138)$$

In our case of interest there are ξ $(= n_{SBMV}/n_{TMV})$ spheres per TMV particle, which we shall assume uniformly distributed around the TMV particle, so that the probability density of finding a sphere at $\vec{r}$ is constant. Then, the result of the presence of the ξ spheres around the rod, will be given by the average

$$\frac{\omega_2^2 + \omega_3^2 - (\omega_2'^2 + \omega_3'^2)}{B_2} = 5\mu_o V_{SBMV} \frac{\xi}{V} \int_V (A^2+B^2+C^2)\, dV$$

$$= 5\mu_o \phi_{SBMV} \int_V (A^2+B^2+C^2)\, dV \qquad (139)$$

The domain of integration V will be a spherical shell, around the center of the rod, starting at $r = a + a_2$ and corresponding to each rod.

Calling R the outer radius of this domain, we have

$$n_{TMV} \cdot \frac{4}{3}\pi R^3 = 1$$

or

$$R = \left(\frac{4}{3}\pi n_{TMV}\right)^{-1/3}$$

In our case, where $n_{TMV} = 4.63 \times 10^{19}\ m^{-3}$ we find

$$R = 1.73 \times 10^{-7}\ m$$

$$= 1.15\ a_1 \tag{140}$$

Note that the volume $\frac{4}{3}\pi R^3 = 1/n_{TMV} = 2.16 \times 10^{-20}\ m^3$ is much larger than the volumes of the SBMV or the TMV particle.

From Eq. (135) we see that $\vec{u}_2'$ has only a component in the radial direction in spherical coordinates, namely that

$$\vec{u}_2'(\bar{r}) = v\vec{e}_r$$

We calculate therefore the gradient of this vector field in spherical coordinates. We find

$$(\nabla\vec{u}_2')_{rr} = \epsilon_{rr} = \frac{\partial v}{\partial r}$$

$$(\nabla\vec{u}_2')_{\theta\theta} = \epsilon_{\theta\theta} = \frac{v}{r}$$

$$(\nabla\vec{u}_2')_{\varphi\varphi} = \epsilon_{\varphi\varphi} = \frac{v}{r}$$

$$\therefore\quad \epsilon_{rr}^2 + \epsilon_{\theta\theta}^2 + \epsilon_{\varphi\varphi}^2 = \left(\frac{\partial v}{\partial r}\right)^2 + 2\,\frac{v^2}{r^2}$$

Now

$$\frac{\partial v}{\partial r} = -\frac{G_{eff}a_1^3}{3[\ln 2p - 1.8]}\sin^2\theta\cos\varphi\sin\varphi\,[1 - 3(\vec{e}_r\cdot\vec{e})^2]\,r^{-3}$$

$$\frac{v}{r} = \frac{G_{eff}\,a_1^3}{6[\ln 2p - 1.8]}\sin^2\theta\cos\varphi\sin\varphi\,[1 - 3(\vec{e}_r\cdot\vec{e})^2]\,r^{-3}$$

Hence

$$\epsilon_{rr}^2 + \epsilon_{\theta\theta}^2 + \epsilon_{\varphi\varphi}^2 = \frac{G_{eff}^2 a_1^6}{6[\ln 2p - 1.8]^2} \sin^4\theta \cos^2\varphi \sin\varphi \, [1 - 3(\vec{e}_r \cdot \vec{e})^2]^2 r^{-6}$$

In order now to integrate this expression in the domain V (see Eq. 139) we use a spherical coordinate system with the polar axis in the direction of the rod $\vec{e}$. Calling then λ the polar angle in this system (in order to avoid confusion with θ which has been already used) we have

$$\vec{e}_r \cdot \vec{e} = \cos\lambda$$

and the integration of the quantity $[1 - 3(\vec{e}_r \cdot \vec{e})^2]^2 r^{-6}$ in the domain V becomes

$$\int_V [1 - 3(\vec{e}_r \cdot \vec{e})] \, r^{-6} dV = 2\pi \int_0^{\pi} \int_{a+a_2}^{R} (1 - 6\cos^2\lambda + 9\cos^4\lambda) r^{-4} \sin\lambda \, d\lambda \, dr$$

$$= 2\pi \int_{-1}^{+1} (1 - 6x^2 + 9x^4) \, dx \int_{a+a_2}^{R} r^{-4} \, dr$$

$$= 4\pi(1 - 2 + \frac{9}{5}) \frac{1}{3} \left[\left(\frac{1}{a+a_2}\right)^3 - \left(\frac{1}{R}\right)^3 \right]$$

$$= \frac{16\pi}{15} \left[\left(\frac{1}{a+a_2}\right)^3 - \left(\frac{1}{R}\right)^3 \right]$$

Therefore we find

$$\int_V (A^2 + B^2 + C^2) dV = \frac{8\pi}{45} \frac{a_1^3}{[\ln 2p - 1.8]^2} (\omega_2'^2 + \omega_3'^2) \left[\left(\frac{a_1}{a+a_2}\right)^3 - \left(\frac{a_1}{R}\right)^3 \right] \tag{142}$$

Substituting now in Eq. (139), and using the fact that

$$\frac{\omega_2^2 + \omega_3^2}{\omega_2'^2 + \omega_3'^2} = \frac{G^2}{G_{eff}^2} \tag{143}$$

we obtain

$$\frac{G^2}{G_{eff}^2} - 1 - B_2 \frac{8\pi}{9} \mu_o \phi_{SBMV} \frac{a_1^3}{[\ln 2p - 1.8]^2} \left[\left(\frac{a_1}{a+a_2} \right)^3 - \left(\frac{a_1}{R} \right)^3 \right]$$

$$= \frac{8\pi}{9} B_2 \mu_o \phi_{SBMV} \frac{a_1^3}{[\ln 2p - 1.8]^2} \left[\left(\frac{a_1}{a+a_2} \right)^3 - \left(\frac{a_1}{R} \right)^3 \right]$$

Finally remembering that for a long rod $B_2 \mu_{\bar{o}} \frac{\ln 2p - 0.8}{\frac{8}{3} \pi a_1^3}$ (see Appendix A), we have

$$G_{eff} = \frac{G}{(1 + K)^{1/2}} \tag{144}$$

where

$$K = \frac{1}{3} \phi_{SBMV} \frac{\ln 2p - 0.8}{[\ln 2p - 1.8]^2} \left[\left(\frac{a_1}{a+a_2} \right)^3 - \left(\frac{a_1}{R} \right)^3 \right] \tag{145}$$

4.3.1. The numerical calculation.

In equation (145) we can put

$$\phi_{SBMV} = 7.63 \times 10^{-4} \frac{c_{TMV}}{k}$$

in which case we obtain

$$K = 7.63 \times 10^{-4} \frac{1}{k} \frac{3.51-0.8}{[3.51-1.8]^2} \left[\left(\frac{30}{4.32}\right)^3 - \left(\frac{1}{1.15}\right)^3 \right]$$

$$K = \frac{0.238}{k} \tag{146}$$

(1) For $k = 2.9$ we find $K = 0.082$ and from Eq. (144)

$$\frac{G_{eff}}{G} = 0.96$$

(2) For $k = 1$ we have $K = 0.238$ and

$$\frac{G_{eff}}{G} = 0.90$$

(3) For $k = 0.31$ we have $K = 0.768$ and

$$\frac{G_{eff}}{G} = 0.752$$

Let us also find two intermediate points:

(4) For $k = 2$, i.e. $c_{SBMV} = 1.5$ Kg m^{-3}, we have $K = 0.119$ and

$$\frac{G_{eff}}{G} = 0.945$$

(5) For $k = 0.5$, i.e. $c_{SBMV} = 6$ Kg m^{-3}, we have $K = 0.476$ and

$$\frac{G_{eff}}{G} = 0.824$$

4.4. Comparison with experiment. Discussion.

Using the above results, the curve

$$\frac{\Delta n}{G} = \frac{(\Delta n)_o}{G} \frac{G_{eff}}{G} \tag{147}$$

which describes the deterministic effect alone, has been plotted in Fig. 3 against the concentration of spheres, by using the result of Intaglietta that

$$\frac{(\Delta n)_o}{G} = 1.82 \ \frac{\text{Å sec}}{\text{cm}}$$

We notice fairly good agreement with the experimental results for k = 2.9 and k = 1. However, for k = 0.31 our curve continues to decrease, whereas the experimental results show a reversed trend.

It should be pointed out, in addition, that the results obtained in the previous paragraph described the maximum effect that can be expected from the interaction of the spheres and the rod, in view of the argument that was used in writing down Eq. (132), and that the calculation is very sensitive to the lower limit of the domain of integration in the averaging process (Eq. 139) since the largest contribution comes from the spheres which are nearer to the rod. On the other hand, the obtained results are seen to describe very adequately the observed effect of the addition of spheres to the suspension up to sphere concentration equal to that of the rods (k = 1).

As it has already been mentioned, the behavior of the birefringence curve with sphere concentration depends also on the stochastic side of the phenomenon, namely the decrease of D_{eff} as we add spheres, so that

$$\frac{\Delta n}{G} = \frac{(\Delta n)_o}{G} \frac{G_{eff}}{G} \frac{D}{D_{eff}} \tag{148}$$

This decrease of D_{eff} with the addition of spheres will tend to reverse the trend. We shall now examine this side of the phenomenon.

5. The Effect of the Spheres on the Diffusion Constant of the Ellipsoids. Other Related Stochastic Phenomena.

It has already been pointed out that, unlike the effect on the drift velocity, the variation of the diffusion constant D due to various stochastic interaction effects has received attention by several authors. We shall review here the various approaches as they can be applied to the stochastic side of the phenomenon of our interest.

5.1. The viscosity approach.

We have already referred to this method of describing the effect of increased concentrations by using the "effective" viscosity in the expressions which are valid for very dilute suspensions. This approach can be readily applied to our case when spheres are added to the suspension. Then it will be (subscript s for spheres)

$$\frac{D}{D_{eff}} = \frac{\mu(k)}{\mu_o} = \frac{\mu(\phi_s)}{\mu_o} \tag{149}$$

If we now use the Einstein relation, we would find

$$\frac{D}{D_{eff}} = 1 + \frac{5}{2}\phi_s \tag{150}$$

On the other hand, if we use the Burger's relation[37] we would have

$$\frac{D}{D_{eff}} = \frac{1}{1 - \frac{5}{2}\phi_s} \tag{151}$$

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[37] Loc. cit.

Intaglietta has measured the viscosity of the suspension he was using for the experiment and had found that

$$\frac{\mu(k)}{\mu_o} \doteq 1 + 3.8 \times 10^{-3} c_s \tag{152}$$

It is obvious from the above three expressions, that at the interval of our interest in sphere concentration, such a description would give a small effect, which could not account for the reversal of the trend in the birefringence curve. For example, at the largest concentration of spheres that was used in the experiment, namely $\phi_s = 7.37 \times 10^{-3}$ or $c_s = 9.7$ Kg m^{-3}, we would get a factor

$$\frac{D}{D_{eff}} = 1.02 \ldots 1.04 \tag{153}$$

namely an increase in Δn of $2 \ldots 4\%$ only.

5.2. The Formation of Doublets by the Spheres.

It has been experimentally observed[38] that when spheres come in contact while suspended in shear flow, they form a doublet of which the subsequent motion, up to the point of separation, can be described by Jeffery's equations for spheroids with $p = 2$. There is also a steady number density n_2 of doublets in the solution. Calling n_1 the number density of singlets and n_s the total number density of spherical particles, it is clear that

$$n_1 + 2n_2 = n_s \tag{154}$$

[38] S. G. Mason *et al.*, *loc. cit.*

If the number density of doublets is significant, then there are two effects that may influence the streaming birefringence of the suspension:

(a) The drift velocity of the ellipsoids will be affected, since the energy dissipation due to a doublet in $\vec{u}_2'$ is different from the energy dissipation due to two spheres.

(b) Since the doublets are geometrically anisotropic, their formation will lead to a second birefringence, and the suspension must then be studied as a polydisperse system.

We shall examine these possibilities for our case of interest.

The volume ratio of doublets is connected to the volume ratio of spheres in terms of the theoretical relation[39]

$$\phi_2 = \frac{20}{3} \phi_s^2 \tag{155}$$

Experimentally, however, it has been determined[39] that ϕ_2 was approximately twice as large; the discrepancy has been attributed to the formation of permanent (non-separating) doublets. We shall take into consideration this experimental result in our numerical calculations and we shall double the theoretical results when estimating the number of doublets.

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[39] H. L. Goldsmith and S. G. Mason, loc. cit.

Noting that, of course, $\phi_1 + \phi_2 = \phi_s$, we have from Eq. (155),

$$\frac{\phi_1}{\phi_s} = 1 - \frac{20}{3}\phi_s$$

$$\frac{\phi_2}{\phi_s} = \frac{20}{3}\phi_s \tag{156}$$

We also note that

$$\frac{n_1}{n_s} = \frac{\phi_1}{\phi_s}$$

$$\frac{2n_2}{n_s} = \frac{\phi_2}{\phi_s} \tag{157}$$

To calculate, now, the magnitude of this effect in our case of interest, we consider the largest concentration of spheres that was used, and obtain

$$\phi_2(k = 0.31) = \frac{20}{3}\phi_s^2 = \frac{20}{3}(7.37 \times 10^{-3})^2$$

$$= 3.62 \times 10^{-4}$$

In view of the experimental evidence, we can take $\phi_2\,(k = 0.31) \doteq 7 \times 10^{-4}$ which is approximately 20% of ϕ_{TMV}. On the other hand we find

$$\frac{n_2}{n_s} = \frac{10}{3}\phi_s = 2.46\%$$

From this last result we see that, for the concentration of the experiment, the number of doublets is too small to influence the drift velocity of the ellipsoids. Even if we adjust, in view of the experimental evidence, n_2 to the value $n_2/n_s = 5\%$, the effect on Eq. (136) is negligible.

It remains to calculate the amount of birefringence Δn_2 due to the doublets and compare it to the amount of birefringence due to the rods, at the same G. Using Eq. (106) we obtain

$$\frac{\Delta n_2}{\Delta n_{TMV}} = \frac{\phi_2}{\phi_{TMV}} \frac{(g_1 - g_2)_2}{(g_1 - g_2)_{TMV}} \frac{b_2}{b_{TMV}} \frac{D_{TMV}}{D_2} \tag{158}$$

As can be seen from the above expression, Δn_2 will be much smaller than Δn_{TMV} since the mobility of the SBMV doublet is much higher than the mobility of the TMV rod. Let us calculate, using Appendix A:

$$(B_2)_2 = \frac{1}{4\mu_o V_2} \frac{p^2}{p^4 - 1} \left\{ -1 + \frac{2p^2 - 1}{p(p^2-1)^{1/2}} \ln\left(p + (p^2-1)^{1/2}\right) \right\}$$

$$= \frac{1}{4\times10^{-3}\times2\times8.38\times10^{-24}} \frac{4}{15} \left\{ -1 + \frac{7}{2(3)^{1/2}} \ln\left(2+(3)^{1/2}\right) \right\}$$

$$= \frac{10^{26}}{3\times8.38} \times 1.66 = 6.6\times10^{24}\ \mathrm{Kg^{-1}m^{-2}sec}$$

and

$$D_2 = kT(B_2)_2 = 1.38\times10^{-23}\times293\times6.6\times10^{24}\ \mathrm{sec^{-1}}$$

$$= 2.67\times10^{4}\ \mathrm{sec^{-1}}$$

On the other hand it is

$$(B_2)_{TMV} = \frac{3}{4\mu_o V} \frac{\ln 2p - 0.8}{p^2}$$

$$= \frac{3}{4 \times 10^{-3} \times 7.63 \times 10^{-23}} \frac{2.71}{16.7^2} \text{ Kg}^{-1}\text{m}^{-2}\text{sec}$$

$$= 9.55 \times 10^{22} \text{ Kg}^{-1}\text{m}^{-2}\text{sec}$$

and

$$D_{TMV} = kT(B_2)_{TMV} = 3.88 \times 10^2 \text{ sec}^{-1}$$

We therefore see that

$$\frac{D_{TMV}}{D_2} = 1.45 \times 10^{-2}$$

and since the other three fractions which appear on the right hand side of Eq. (158) all have absolute values smaller than unity, we conclude that the birefringence due to the doublets is very much smaller than the one due to the rods. In fact, if we neglect the difference between the optical factors we get, at the highest concentration of spheres, from Eq. (158)

$$\frac{\Delta n_2}{\Delta n_{TMV}} \leq 2 \times 10^{-1} \frac{3}{5} 1.45 \times 10^{-2} = 1.74 \times 10^{-3}$$

5.3. The Possibility of Association Between Spheres and Rods

In the flowing suspension, the spheres will collide with the rods as well as with themselves. It is clear that if the phenomenon occurs strongly enough so that spheres associate with the rods in the way that they have been observed to do between themselves, then the mobility of the rods will be significantly affected. The mobility, and the diffusion constant, of the composite particle will be lower and hence the amount of birefringence due to it will be higher than that due to the single rod, all other things being equal.

This effect can be large enough, at sufficient sphere concentrations, to reverse the effect of the smaller effective velocity gradient and to lead, in fact, to positive variation of Δn with sphere concentration. We shall examine this possibility by treating the suspension as a polydisperse medium, in which the suspended particles are single rods (of volume $V_1 = V$ and axial ratio $p_1 = p$), rods associated with one sphere in line (the composite particle having volume V_2 and axial ratio p_2) and also rods associated with two and three spheres in line (the composite particles having volume V_3 resp. V_4 and axial ratio p_3 resp. p_4).

The parameters of SBR in a polydisperse medium are given [40] by the following expressions:

$$\mathrm{tg}\ 2\varphi = \frac{\sum_i \Delta n_i \sin 2\varphi_i}{\sum_i \Delta n_i \cos 2\varphi_i} \tag{159}$$

[40] Ch. Sadron, J. Phys. Rad., (7), 9, 381 (1938).

$$\Delta n = \left[\left(\sum_i \Delta n_i \sin 2\varphi_i \right)^2 + \left(\sum_i \Delta n_i \cos 2\varphi_i \right)^2 \right]^{1/2} \tag{160}$$

where φ_i and Δn_i are the parameters that would have been observed if the ith species existed alone in the suspension at the same concentration.

We are interested in the amount of birefringence in a polydisperse medium of elongated particles for low σ_i ($\equiv \frac{G}{D_i}$). Indeed, in the experiments of Intaglietta σ_i never exceeded the value 10^{-1}. In this case φ_i is nearly zero for all the species. More precisely, it is

$$\sin 2\varphi_i = \frac{\sigma_i}{6} + O(\sigma_i^2)$$
$$\cos 2\varphi_i = 1 + O(\sigma_i^2) \tag{161}$$

which shows that the second term on the right-hand side of Eq. (160) is dominant, so that this equation takes the simple form

$$\Delta n = \sum_i \Delta n_i \tag{162}$$

The above equation can be given another useful form. If we consider Δn as due to a certain monodisperse system of suspended particles with diffusion constant D_{eff} and concentration $\phi = \sum \phi_i$, we obtain from Eq. (162), using the expression (106) for the amount of birefringence of elongated particles of the same optical factor, the following expression for D_{eff}

$$\frac{1}{D_{eff}} = \sum_i \frac{x_i}{D_i} \tag{162'}$$

where we have defined as x_i the volume proportion

$$x_i = \frac{\phi_i}{\sum_i \phi_i} \tag{163}$$

[Note: If we wish to characterize also the angle φ, which is observed in a polydisperse medium, as due to a certain monodisperse system of suspended particles, we must use as diffusion constant $D^* \equiv (D_{eff})_\varphi \neq (D_{eff})_{\Delta n}$. This is immediately seen from Eqs. (159), (106) and (161) and the fact that

$$\text{tg } 2\varphi^* = \frac{\sigma^*}{6} + O(\sigma^{*3}) \tag{164}$$

which lead to the expression

$$\frac{1}{D^*} = \frac{\sum_i \frac{x_i}{D_i^2}}{\sum_i \frac{x_i}{D_i}} \tag{165}$$

This relation has been reported by Donnet[41].]

Using Eq. (162') in our case we have

$$\frac{1}{D_{eff}} = \frac{x_1}{D_1} + \frac{x_2}{D_2} + \frac{x_3}{D_3} + \frac{x_4}{D_4} \tag{166}$$

where, of course

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41 J. B. Donnet, Comptes rendus, 229, 189 (1949).

$$x_1 + x_2 + x_3 + x_4 = 1 \tag{167}$$

The factor $\frac{D}{D_{eff}}$ which appears in Eq. (148), and which describes the magnitude of the effect, is then $(D = D_1)$

$$\frac{D}{D_{eff}} = x_1 + x_2 \frac{D}{D_2} + x_3 \frac{D}{D_3} + x_4 \frac{D}{D_4} \tag{168}$$

We shall calculate this factor for various distributions of the four kinds of particles, namely (1) single rods, (2) rods plus one sphere, (3) rods plus two spheres, and (4) rods plus three spheres. We know[42] that the concentration of particles of type (2) is proportional to the concentration of the spheres, whereas the concentration of particles of type (3) and (4) is proportional to the square and cube respectively of the concentration of the spheres. Thus, if the distribution of the three kinds of particles is known at a certain concentration of spheres, then it is known for any other: x_2 varies linearly, x_3 quadratically and x_4 with the cube of sphere concentrations. In addition, at any given concentration of spheres, it will be $x_3 = x_2^2$ and $x_4 = x_2^3$.

The ratios $\frac{D}{D_i}$ which appear in Eq. (168) can readily be expressed by using Eq. (A-12):

$$\frac{D}{D_i} = \frac{V_i}{V} \frac{\ln 2p - 0.8}{\ln 2p_i - 0.8} \left(\frac{p_i}{p}\right)^2 \tag{169}$$

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[42] Goldsmith and Mason, loc. cit.

We have

$$p = 16.7 \qquad V = 7.63 \times 10^{-23}\ m^3$$

$$p_2 = 18.1 \qquad V_2 = 8.47 \times 10^{-23}\ m^3$$

$$p_3 = 19.5 \qquad V_3 = 9.31 \times 10^{-23}\ m^3$$

$$p_4 = 20.9 \qquad V_4 = 10.15 \times 10^{-23}\ m^3$$

therefore, we find

$$\frac{D}{D_2} = 1.27$$

$$\frac{D}{D_3} = 1.58$$

$$\frac{D}{D_4} = 1.93$$

In order to calculate the magnitude of this effect, we shall examine two cases of different distribution of the four species. It has been already mentioned that it is sufficient to know <u>any one</u> of the four x_i, at a certain sphere concentration c_s, in order to know all four functions $x_i = x_i(c_s)$. The two cases that we shall examine are defined by the value of x_2, at the maximum concentration of spheres reported in the experimental results, namely $c_s = 9.7\ Kg\ m^{-3}$:

<u>Case I</u> $\quad x_2 = 30\,\%$ at $c_s = 9.7\ Kg\ m^{-3}$

<u>Case II</u> $\quad x_2 = 40\,\%$ at $c_s = 9.7\ Kg\ m^{-3}$

For each case we shall calculate the variation of $\frac{D}{D_{eff}}$ as a function of c_s. For purposes of comparison, we shall find the points on these curves that correspond to the reported experimental points. The numerical calculation follows.

5.3.1. Case I

At $c_s = 9.7$ Kg m^{-3}, if $x_2 = 30\%$, the distribution of the four species will be

$$x_1 = 58.3\% \quad x_2 = 30\% \quad x_3 = 9\% \quad x_4 = 2.7\%$$

Therefore

$$\frac{D}{D_{eff}} = 0.583 + 1.27 \times 0.30 + 1.58 \times 0.09 + 1.93 \times 0.027$$

$$= 1 + 0.27 \times 0.30 + 0.58 \times 0.09 \div 0.93 \times 0.027$$

$$= 1.158$$

At $c_s = 6$ Kg m^{-3}, it is $x_2 = 0.03 \frac{6}{9.7} = 18.56\%$ and the distribution is

$$x_1 = 77.35\% \quad x_2 = 18.56\% \quad x_3 = 3.45\% \quad x_4 = 0.64\%$$

Therefore

$$\frac{D}{D_{eff}} = 1 + 0.27 \times 0.1856 + 0.58 \times 0.0345 + 0.93 \times 0.0064$$

$$= 1.076$$

At $c_s = 3$ Kg m^{-3}, it is $x_2 = 0.30 \frac{3}{9.7} = 9.28\%$ and the distribution is

$$x_1 = 89.78\% \quad x_2 = 9.28\% \quad x_3 = 0.86\% \quad x_4 = 0.08\%$$

Therefore

$$\frac{D}{D_{eff}} = 1 + 0.27 \times 0.0928 + 0.58 \times 0.0086 + 0.93 \times 0.0008$$

$$= 1.030$$

<u>At $c_s = 1.03$ Kg m^{-3}</u>, $x_2 = 0.30 \times \frac{1.03}{9.7} = 3.18\%$ and the distribution is

$$x_1 = 96.72\% \quad x_2 = 3.18\% \quad x_3 = 0.10\% \quad x_4 \text{ negligible}$$

Therefore

$$\frac{D}{D_{eff}} = 1 + 0.27 \times 0.0318 + 0.58 \times 0.0010$$

$$= 1.009$$

5.3.2. Case II

<u>At $c_s = 9.7$ Kg m^{-3}</u>, if $x_2 = 40\%$, the distribution of the four species will be

$$x_1 = 38.4\% \quad x_2 = 40\% \quad x_3 = 16\% \quad x_4 = 5.6\%$$

Therefore

$$\frac{D}{D_{eff}} = 1 + 0.27 \times 0.40 + 0.58 \times 0.16 + 0.93 \times 0.056$$

$$= 1.253$$

At $c_s = 6$ Kg m^{-3}, $x_2 = 0.40 \times \frac{6}{9.7} = 24.75\%$ and the distribution is

$$x_1 = 67.65\% \quad x_2 = 24.75\% \quad x_3 = 6.10\% \quad x_4 = 1.50\%$$

Therefore

$$\frac{D}{D_{eff}} = 1 + 0.27 \times 0.2475 + 0.58 \times 0.061 + 0.93 \times 0.015$$

$$= 1.116$$

At $c_s = 3$ Kg m^{-3}, $x_2 = 0.40 \times \frac{3}{9.7} = 12.37\%$ and the distribution is

$$x_1 = 85.91\% \quad x_2 = 12.37\% \quad x_3 = 1.53\% \quad x_4 = 0.19\%$$

Therefore

$$\frac{D}{D_{eff}} = 1 + 0.27 \times 0.1237 + 0.58 \times 0.0153 + 0.93 \times 0.0019$$

$$= 1.044$$

At $c_s = 1.03$ Kg m^{-3}, $x_2 = 0.40 \times \frac{1.03}{9.7} = 4.25\%$ and the distribution is

$$x_1 = 95.56\% \quad x_2 = 4.25\% \quad x_3 = 0.18\% \quad x_4 = 0.01\%$$

Therefore

$$\frac{D}{D_{eff}} = 1 + 0.27 \times 0.0425 + 0.58 \times 0.0018 + 0.93 \times 0.0001$$

$$= 1.012$$

The results of these calculations can now be summarized in the following table, using Eqs. (147) and (148) and the experimental result that

$$\frac{(\Delta n)_o}{G} = 1.82$$

TABLE 2

VALUES OF THE SPECIFIC RETARDATION $\frac{\Delta n}{G}$ IN $\frac{\mathring{A}\ \mathrm{sec}}{\mathrm{cm}}$ FOR INCREASING CONCENTRATION OF SPHERES AT CONSTANT ROD CONCENTRATION

Method					
	c_{TMV} = 3	3	3	3	3
	c_{SBMV} = 0	1.03	3	6	9.7
	k = ∞	2.9	1	0.5	0.31
Experimental	1.82	1.72	1.61	-	1.67
Velocity Gradient Effect Alone	1.82	1.75	1.64	1.50	1.37
Velocity Gradient plus Association (Case I) Effect	1.82	1.76	1.69	1.61	1.59
Velocity Gradient plus Association (Case II) Effect	1.82	1.77	1.71	1.67	1.72

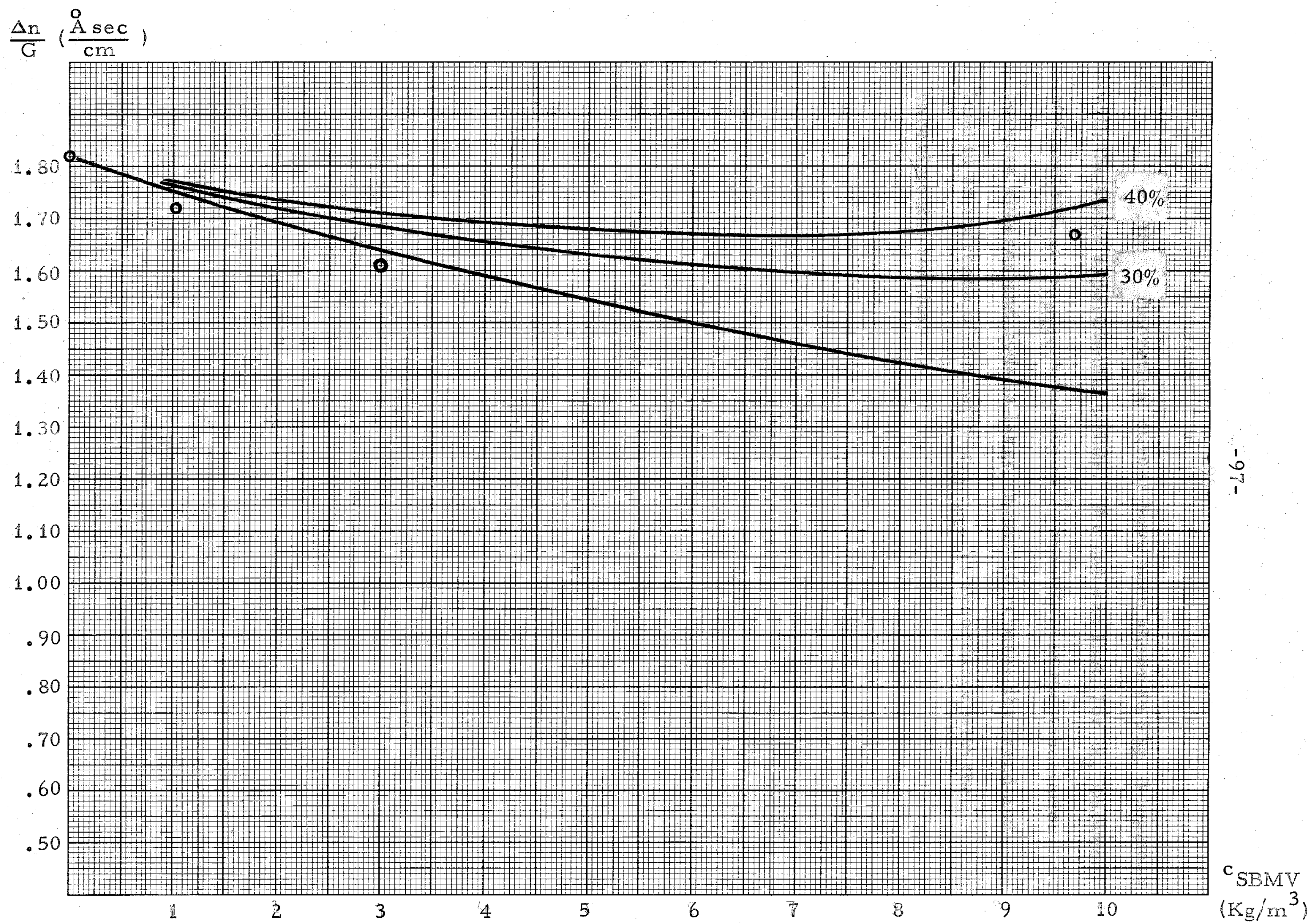
Δn/G (Å sec/cm)
1.80
1.70
1.60
1.50
1.40
1.30
1.20
1.10
1.00
.90
.80
.70
.60
.50
40%
30%
1
2
3
4
5
6
7
8
9
10
c SBMV (Kg/m3)

Fig. 3

The three theoretical curves have been shown in Fig. 3 together with the three experimental points. We can see that, for x_2 between 30% and 40% at $c_{SBMV} = 9.7$ Kg m^{-3}, the effect of the association between spheres and rods is large enough to reverse the trend and lead to an increase of Δn with c_{SBMV}, in accordance with the experimental results.

APPENDIX A

THE ROTATIONAL MOBILITY TENSOR FOR PROLATE SPHEROIDS AND ELONGATED RODS

In the system of the principal inertial axes, the rotational mobility tensor for such particles of revolution has the form

$$\overline{\overline{B}} = \begin{pmatrix} B_1 & 0 & 0 \\ 0 & B_2 & 0 \\ 0 & 0 & B_2 \end{pmatrix} \qquad \text{(A-1)}$$

where the constants B_1 and B_2 depend on the volume and the elongation of the particles in terms of the relations given in this Appendix. Note that the volumes are

$$V_{spheroid} = \frac{4}{3}\pi a_2^2 a_1 = \frac{4}{3}\pi \frac{a_1^3}{p^2}$$

$$V_{rod} = 2\pi a_2^2 a_1 = 2\pi \frac{a_1^3}{p^2}$$

1. For spheroidal particles it is, in the notation used by Jeffery,

$$B_1 = \frac{1}{2a_2^2 A_1} = \frac{3\beta_o}{2a_2^2}\,\frac{2a_2^2}{16\pi\mu_o} = \frac{3\beta_o}{16\pi\mu_o} \qquad \text{(A-2)}$$

$$B_2 = B_3 = \frac{1}{(a_1^2+a_2^2)A_2} = \frac{3(a_2^2\beta_o + a_1^2\alpha_o)}{(a_1^2+a_2^2)16\pi\mu_o} \qquad \text{(A-3)}$$

Now, for prolate spheroids ($p > 1$)

$$\alpha_o = \frac{2 \ln (p + \sqrt{p^2 - 1})}{(a_1^2 - a_2^2)^{3/2}} - \frac{2}{a_1(a_1^2 - a_2^2)} \tag{A-4}$$

$$\beta_o = - \frac{\ln(p + \sqrt{p^2 - 1})}{(a_1^2 - a_2^2)^{3/2}} + \frac{p^2}{a_1(a_1^2 - a_2^2)} \tag{A-5}$$

Hence

$$B_1 = \frac{3}{16\pi\mu_o a_2^2 a_1} \frac{p^2}{p^2-1} \left\{ 1 - \frac{\ln(p + \sqrt{p^2 - 1})}{p\sqrt{p^2 - 1}} \right\}$$

$$= \frac{1}{4\mu_o V} \frac{p^2}{p^2 - 1} \left\{ 1 - \frac{\ln(p + \sqrt{p^2 - 1})}{p\sqrt{p^2 - 1}} \right\} \tag{A-6}$$

and

$$B_2 = B_3 = \frac{3}{16\pi\mu_o a_2^2 a_1} \frac{p^2}{p^4 - 1} \left\{ -1 + \frac{2p^2 - 1}{p\sqrt{p^2 - 1}} \ln (p + \sqrt{p^2 - 1}) \right\}$$

$$= \frac{1}{4\mu_o V} \frac{p^2}{p^4 - 1} \left\{ -1 + \frac{2p^2 - 1}{p\sqrt{p^2 - 1}} \ln (p + \sqrt{p^2 - 1}) \right\} \tag{A-7}$$

For large values of the axial ratio $(p \geq 10)$, it is, to a very good approximation,

$$B_1 = \frac{1}{4\mu_o V} \tag{A-8}$$

and

$$B_2 = B_3 = \frac{1}{4\mu_o V} \frac{2 \ln 2p - 1}{p^2}$$

$$= \frac{3(\ln 2p - 0.5)}{8\pi\mu_o a_1^3} \tag{A-9}$$

The mobility constant B for a sphere of radius a can be obtained from Eqs. (A-2) or (A-3) by noting that for a sphere

$$\alpha_o = \beta_o = \int_o^\infty \frac{d\lambda}{(a^2+\lambda)^{5/2}} = \left.\frac{(a^2+\lambda)^{-3/2}}{-3/2}\right|_o^\infty = \frac{2}{3}a^{-3} \quad \text{(A-10)}$$

Hence

$$B = \frac{3}{16\pi\mu_o}\,\frac{2}{3}a^{-3} = \frac{1}{8\pi\mu_o a^3} = \frac{1}{6\mu_o V} \quad \text{(A-11)}$$

2. For an elongated cylindrical rod of length $2a_1$ and diameter $2a_2$ (we again define $p = a_1/a_2$), Burgers[43] gives

$$B_2 = B_3 = \frac{3(\ln 2p - 0.8)}{8\pi\mu_o a_1^3}$$

$$= \frac{3}{4\mu_o V}\,\frac{\ln 2p - 0.8}{p^2} \quad \text{(A-12)}$$

[43] Loc. cit.

APPENDIX B

ASSOCIATED LEGENDRE POLYNOMIALS

The associated Legendre polynomials that have been used in Part II, namely $P_{2\ell}^{2m}$ (cos θ) for $\ell, m = 0, 1, 2$ and 3 $(\ell \geq m)$ are given by the following expressions, where we have put

$$x = \cos\theta$$

$$y = \sin\theta$$

$$P_o(x) = 1$$

$$P_2(x) = \frac{1}{2}(3x^2 - 1) = \frac{1}{2}(2 - 3y^2)$$

$$P_2^2(x) = (1 - x^2)3 = 3y^2$$

$$P_4(x) = \frac{1}{8}(35x^4 - 30x^2 + 3) = \frac{1}{8}(35y^4 - 40y^2 + 8)$$

$$P_4^2(x) = (1 - x^2)\frac{15}{2}(7x^2 - 1) = \frac{15}{2}y^2(-7y^2 + 6)$$

$$P_4^4(x) = (1 - x^2)^2 105 = 105\ y^4$$

$$P_6(x) = \frac{1}{16}(231x^6 - 315x^4 + 105x^2 - 5) = \frac{1}{16}(-231y^6 + 378y^4 - 168y^2 + 16)$$

$$P_6^2(x) = (1-x^2)\frac{105}{8}(33x^4 - 18x^2 + 1) = \frac{105}{8}y^2(33y^4 - 48y^2 + 16)$$

$$P_6^4(x) = (1-x^2)^2\frac{9 \times 105}{2}(11x^2 - 1) = \frac{9 \times 105}{2}y^4(-11y^2 + 10)$$

$$P_6^6(x) = (1-x^2)^3 9 \times 11 \times 105 = 9 \times 11 \times 15\ y^6$$

APPENDIX C

EXPERIMENTAL RESULTS

The experimental measurements reported by Intaglietta concerning the amount of birefringence for a suspension of both TMV and SBMV are as follows:[44]

	Concentrations ($Kg\ m^{-3}$)		$\Delta n/G$ (10^{-8} sec)
	TMV	SBMV	
(1)	3.0	-	1.82
(2)	3.0	1.03	1.72
(3)	3.0	3.0	1.61
(4)	3.0	9.7	1.67

[44] Marcos Intaglietta, Ph.D. Thesis, C.I.T., 1963.

REFERENCES

Brenner, H., Chem. Eng. Science, 19, 631 (1964).

Bretherton, F. P., J. Fluid Mech., 14, 284 (1962).

Broersma, S., J. Chem. Phys., 30, 707 (1959).

Burgers, J. M., Second Report on Viscosity and Plasticity, Ch. II, North-Holland Publishing Co., Amsterdam, 1938.

Collins, D. J., and Wayland, H., Trans. Soc. Rheol., VII, 275 (1963).

Cerf, R. and Scheraga, H. A., Chem. Reviews, 51, 185 (1952).

Demetriades, S. T., J. Chem. Phys., 29, No. 5, 1054 (1958).

Donnet, J. B., Comptes rendus, 229, 189 (1949)

Einstein, A., Annal. d. Phys., 17, 549 (1905) and 19, 289, 371 (1906).

Giesekus, H., Rheol. Acta, 2, 101 (1962).

Goldsmith, H. L. and Mason, S. G., Proc. Roy. Soc. (London), A 282, 569 (1964).

Intaglietta, Marcos, Ph.D. Thesis, C.I.T., 1963.

Jeffery, G. B., Proc. Roy. Soc. (London), A 102, 161 (1922).

Jerrard, H. G., Chem. Reviews, 59, 345 (1959).

Kuhn, W., Kuhn, H., and Buckner, P., Erg. exact. Naturw., 25, 1 (1957).

Leray, J., J. de Chimie Physique, 316 (1961).

Mason, S. G. and Manlay, R. St. J., Proc. Roy. Soc. (London), A 238, 117 (1956) .

Maxwell, J. C., Proc. Roy. Soc. (London), A 22, 46 (1873).

Perrin, F., J. Phys., 5, 497 (1934) and 7, 1 (1936).

Peterlin, A. and Stuart, H. A., Z. Physik 112, 1, 129 (1939).

Peterlin, A. and Stuart, H. A., Hand-und Jahrbuch der Chemischen Physik, (Becker u. Erler, Leipsig, 1943), Bd VIII, Abt 1B.

Sadron, Ch., J. Phys. Rad., (7), 9, 381 (1938).

Sadron, Ch., Ch. IV, "Flow Properties of Disperse Systems," edited by J. J. Hermans, North-Holland Publ. Co. (1953).

Scheraga, H. A., Edsall, J. T., and Gadd, J. O. Jr., J. Chem. Phys. 19, 1101 (1951).

Tolstoi, N. A., Doklady, 59, 1563 (1948).

Wayland, H., J. Polymer Science, Part C, No. 5, 11 (1963).

Wayland, H., J. Chem. Phys., 33, No. 3, 769 (1960).

Wayland, H., Comptes Rendus, 249, 1228 (1959).

Wayland, H. and Intaglietta, M., Proc. 4th Intern. Congr. on Rheol., Part IV, 317 (1965).