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On the rheology of a suspension of viscoelastic spheres in a viscous liquid

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The stress in a suspension of incompressible deformable particles exceeds that which would exist in the pure incompressible liquid undergoing the same flow by the product of the volume concentration of the particles and the tensor $\overline{p}_{ik} - 2\eta_0 \overline{e}_{ik}^{(1)}$ where η_0 is the viscosity of the pure liquid, $\overline{p}_{ik}$ is the average stress and $\overline{e}_{ik}^{(1)}$ the average rate of strain in particles in the flowing suspension. For a dilute suspension of viscoelastic spheres these tensors can be determined by using an adaptation of Jeffery's solution of the problem of an isolated rigid ellipsoid. In steady laminar flow, the material of each sphere is continuously deformed and rotates within an ellipsoidal boundary of fixed dimensions and orientation. Approximate expressions are obtained for the steady-rate viscosity and normal stress differences in terms of the dynamic viscosity and dynamic rigidity functions of the suspension. These are valid either when the rate of shear is sufficiently small or when the ratio of the dynamic viscosity of the spheres to η_0 is sufficiently large. The three normal stress components are all unequal. In slow steady elongation of the suspension, the spheres suffer static deformation into prolate spheroids so the elongational viscosity depends only on their static elastic properties. It appears from the investigation of special cases, however, that this static deformation is not possible for rates of elongation above a critical value.

1. Introduction

A phenomenological approach to the study of isotropic elastoviscous liquids is provided by the theory of 'simple fluids with fading memory' of Coleman and Noll, but this theory only gives limited information on account of its extreme generality. In order to obtain further results, it is necessary to construct theories which take some account of the structure of these liquids. Several such theories have been developed for liquid polymers and polymer solutions which take explicit account of the chain structure of the molecules. Difficulties arise, however, and these have only been resolved by making mechanical or hydrodynamic assumptions which are difficult to verify. When such theories fail to agree with observation, it is never clear whether the fault arises from the physical model or from these assumptions.

A more satisfactory approach can be made by choosing a simplified physical model for which the mathematical calculations can be carried out exactly. The multi-lattice theory for strong polymer solutions developed by Lodge (1964) falls into this category, and its failure in points of detail can be ascribed with certainty to shortcomings of the model. Various simple models for dilute polymer solutions have been used by Fröhlich & Sack (1946), Cerf (1951, 1952) and Giesekus (1962). In Cerf's treatment, the model consists of a suspension of viscoelastic spheres in a viscous liquid: a reasonable representation for a polymer solution which is so dilute that the coiled chains are effectively isolated. He assumed rather special viscoelastic properties for the spheres and investigated the behaviour of the suspension under oscillatory motion of small amplitude. The same model is used in the present work, but with general properties for the spheres, and the treatment is not restricted to small rates of strain.

In § 2 a basic relationship, equation (9), is derived for a suspension of particles of any shape and viscoelastic properties. The only assumptions made are that there is no slip at liquid-particle surfaces, that liquid and particles are incompressible and that they possess negligible inertia. The last two assumptions do not usually restrict the validity of the results, although there are cases (such as compressional wave motion and other types of wave motion at high frequency) which require fuller treatment. In the application of this relationship, however, it is assumed that the concentration of the particles is small.

Rectangular Cartesian co-ordinates are used throughout and tensors (stress, rate of strain, etc.) are denoted by small letters (p_{ik}, $e_{ik}^{(1)}$) when they refer to the material of the particles, and by small primed letters (p'_{ik}, $e'^{(1)}_{ik}$) when they refer to the liquid part of the suspension. The symbols p, p' are used to denote arbitrary hydrostatic pressures. Capital letters are used for tensors referring to the whole suspension. Material constants and functions (rigidity, viscosity, etc.) are denoted by Greek symbols (μ, η) without suffix when they refer to the whole suspension, with suffix 1 when they refer to the material of the particles and with suffix zero when they refer to the liquid. In accordance with convention, μ and η are primed when they refer to the dynamic functions. For example, when the material of the particles is subjected to small oscillatory strain of the type

$$e_{ik} = e_{ik}(0)\cos\omega t, \tag{1}$$

the formal expression for the stress is written

$$p_{ik}+p\delta_{ik} = 2\mu_1'(\omega)\,e_{ik}(0)\cos\omega t-2\eta_1'(\omega)\omega\,e_{ik}(0)\sin\omega t. \tag{2}$$

2. The stress in a suspension of deformable particles

It is first necessary to consider the relation between the macroscopic and microscopic motions of a flowing suspension of deformable particles of any shape. At a given instant of time, the difference in velocity between two adjacent points in a particle in the suspension can be written as

$$dv_i = e_{ij}^{(1)}\,dx_j-\zeta_{ij}\,dx_j, \tag{3}$$

where $e_{ik}^{(1)}$ and ζ_{ik} are respectively the local rate of strain and vorticity in the particle. Similarly for two adjacent points in the liquid part of the suspension

$$dv_i = e'^{(1)}_{ij}\,dx_j-\zeta'_{ij}\,dx_j. \tag{4}$$

Thus if there is no slip between liquid and particles and if the origin is taken at an arbitrary point in the suspension, the difference V_i between the velocity at the point x_i and the velocity at the origin is given by

$$V_i = E_{ij}^{(1)} x_j - Z_{ij} x_j, \tag{5}$$

where $E_{ij}^{(1)}$ is the average of the rate of strain of both solid and liquid parts along the line joining x_i to the origin at the instant of time under consideration, and Z_{ik} is the corresponding average for the vorticity. The symbol P_{ik} will be used for the corresponding average of the stress.

It will be assumed, in the first instance, that these three line averages attain sensibly constant values as the point x_i moves in any direction away from the origin to distances of the order of a certain length l; and the symbols $E_{ik}^{(1)}$, Z_{ik}, P_{ik} will now be reserved for these constant values. Equation (5) shows that the motion may now be regarded as homogeneous in a local region round the origin of dimensions of order l, and also that $E_{ik}^{(1)}$ and Z_{ik} can be identified as the local macroscopic rate of strain and vorticity. Furthermore, since the line averages over lengths of order l, $E_{ik}^{(1)}$, Z_{ik}, P_{ik} are constants, it follows that they are equal to the averages of the corresponding tensors over areas or volumes of dimensions of order l situated within distances of order l from the origin. Thus the local macroscopic rate of strain may be written as

$$E_{ik}^{(1)} = (1-c)\,\bar{e}_{ik}^{\prime(1)} + c\,\bar{e}_{ik}^{(1)}, \tag{6}$$

where the bars denote volume averages and c represents the volume concentration of the particles.

The component of force in the k-direction exerted by the suspension on one side of a plane area normal to the i-direction is the area integral of the corresponding stress component (p_{ik} in the particles and p'_{ik} in the liquid) or the product of the area and the area average of the stress component. The latter is equal to P_{ik} and also equal to the volume average, provided the dimensions of the area are of order l. Thus there is a local macroscopic stress equal to P_{ik}, and

$$P_{ik} = (1-c)\bar{p}'_{ik} + c\bar{p}_{ik}. \tag{7}$$

But at any point in the liquid part of the suspension

$$p'_{ik} + p'\delta_{ik} = 2\eta_0 e_{ik}^{\prime(1)}, \tag{8}$$

where η_0 is the viscosity of the liquid. Equations (6), (7) and (8) together give

$$P_{ik} + P\delta_{ik} = 2\eta_0 E_{ik}^{(1)} + c(\bar{p}_{ik} - 2\eta_0 \bar{e}_{ik}^{(1)}), \tag{9}$$

where P has been written for the product of $1-c$ and $\bar{p}'$. Since the materials are incompressible, both p_{ik} and p'_{ik} are indeterminate to the extent of an arbitrary constant hydrostatic pressure, so the magnitudes of $\bar{p}'$ and P are arbitrary. It may be noted that the last term in (9) effectively represents the addition to the stress produced by the presence of the particles.

The average stress $\bar{p}_{ik}$ in a particle is related to the distribution of force over its surface. If T_i represents the force per unit area at a given point on the surface and n_i is the unit vector along the outwards drawn normal,

$$T_i = p_{ij} n_j. \tag{10}$$

Any variation of p_{ik} within the particle is subject to the condition that $p_{ij,j}$ shall be zero, so

$$p_{ik} = \partial(p_{ij}x_k)/\partial x_j. \tag{11}$$

With these two equations, the average stress can be obtained by application of Green's theorem as

$$\bar{p}_{ik} = \frac{1}{V}\int_S T_i x_k dS, \tag{12}$$

where V is the particle volume and dS an element of surface area. Furthermore, since

$$e_{ik}^{(1)} = \frac{1}{2}\left(\frac{\partial v_k}{\partial x_i} + \frac{\partial v_i}{\partial x_k}\right), \tag{13}$$

the average rate of strain is given by Green's theorem as

$$\bar{e}_{ik}^{(1)} = \frac{1}{2V}\int_S (v_i n_k + v_k n_i)\, dS. \tag{14}$$

Equation (9) has previously been given as equation (11) of a paper by Peterson & Fixman (1963) concerned with the special case of spherical particles, and equation (12) above is equivalent to their equation (14). It seems, however, that their argument is unnecessarily involved, and they advance only intuitive reasons for taking the macroscopic tensors equal to the corresponding volume averages. In the case of rigid particles the internal distribution of p_{ik} is indeterminate, but its average value is given by (12) so that (9) can still be employed. Here $\bar{e}_{ik}^{(1)}$ is zero and the expression for P_{ik} becomes equivalent to that given in equations (41) and (42) of a paper by Giesekus (1962).

For very dilute suspensions of identical particles, $\bar{p}_{ik}$ and $\bar{e}_{ik}^{(1)}$ can be replaced by the corresponding tensors for a single particle in pure liquid undergoing the macroscopic motion of the suspension (5). In solving the single-particle problem it is assumed that the slow-motion condition $p'_{ij,j} = 0$ holds in the liquid, and together with equation (8) this gives the linear Stokes equations. Similarly it is assumed that $p_{ij,j} = 0$ holds in the particle, and this relation has to be used together with the constitutive equation of its material. A velocity field has then to be found which (*a*) approaches the undisturbed field at great distances from the particle, (*b*) is continuous across the particle–liquid boundary and (*c*) is such that the distribution of force exerted by the liquid on the particle surface balances the stress distribution within it. For a rigid particle it is only necessary to solve the Stokes equations subject to conditions (*a*) and (*b*), and such solutions have been given for ellipsoidal particles by Jeffery (1922) together with expressions for the surface force T_i.

More complicated methods of determining the macroscopic stress in dilute suspensions have been used by Einstein (1906, 1911), Jeffery (1922), Burgers (1938) and Landau & Lifshitz (1959). Objection may be raised, however, to all these methods in that P_{ik} is obtained from the long-range disturbance produced by a single particle as calculated using the linear Stokes equations. Now in the derivation of those equations inertia effects have been neglected ($p'_{ij,j}$ being set equal to zero), and it has been pointed out by Saito (1952) that this approximation leads to solutions which are always incorrect at great distances from the particle however slow the motion may be. Exact solutions, obtained from the full Navier–Stokes equations, are not at present available. On the other hand, the linear

Stokes equations give solutions which are correct in the neighbourhood of the particle when the motion is slow, and the local flow is only needed for the determination of $\overline{p}_{ik}$ and $\overline{e}_{ik}^{(1)}$ for use in (9). In fact all the results obtained for special cases by the authors cited are identical with those obtained by use of (9) although, as indicated by Peterson & Fixman (1963), application of their methods must in general lead to anomalous results.

At present it is only possible to apply equation (9) in this limiting case of extreme dilution, and since $\overline{p}_{ik}$ and $\overline{e}_{ik}^{(1)}$ are then independent of the concentration c, the increase in P_{ik} produced by the presence of the particles is simply proportional to c.

The use of (9) is not restricted to problems in which the flow of the suspension as a whole is homogeneous: solutions of other problems can be obtained by applying the equation to sufficiently small elements of the suspension. It must be remembered, however, that an assumption was made in the derivation of (9): that the line averages of the rate of strain, vorticity and stress tensors are sensibly constant over distances of the order of a certain length l. This assumption, which implies that there is some scale on which the flow of the suspension may be regarded as homogeneous, is justifiable if the calculated variations of $E_{ik}^{(1)}$, Z_{ik}, P_{ik} are found to be altogether negligible over distances of order a/c, where a is a certain average dimension of the particles. For in this case it is always possible to construct a line of length l much greater than a/c (the condition that it shall intersect a large number of particles) and yet so short that the general flow conditions (characterized by the macroscopic tensors $E_{ik}^{(1)}$, Z_{ik}, P_{ik}) remain sensibly constant along its length. This corrects the condition arbitrarily laid down by Peterson & Fixman (1963) that the variations must be negligible over distances of order $10a$. Even in problems where the flow of the suspension as calculated using (9) is homogeneous throughout, the validity of the results is evidently restricted by the condition that the smallest dimension of the whole body of the suspension shall be much greater than a/c.

3. Ellipsoids with moving boundaries

The problem of a rigid ellipsoid in a sea of liquid undergoing homogeneous deformation has been solved by Jeffery (1922). His equation (34) gives an expression for the force per unit area exerted by the liquid on the surface of the ellipsoid, and this may be written in any co-ordinate system as

$$T_i = -p'' n_i + \eta_0 A_{ij} n_j, \tag{15}$$

where p'' is a constant of arbitrary magnitude and A_{ik} is a certain deviatoric tensor. The components of this tensor in a fixed co-ordinate system with axes instantaneously coinciding with the ellipsoid axes are related to the quantities A, B, C, etc., appearing in Jeffery's equations (25) and (26) by the scheme

$$A_{ik} = \tfrac{1}{8} a_0^3 \begin{pmatrix} A & H & G' \\ H' & B & F \\ G & F' & C \end{pmatrix}, \tag{16}$$

where a_0 is the radius of a sphere which has the same volume as the ellipsoid. Thus for this co-ordinate system his equation (25) gives

$$A_{11} = \frac{4}{3}\frac{2g_1''e_{11}' - g_2''e_{22}' - g_3''e_{33}'}{g_2''g_3'' + g_3''g_1'' + g_1''g_2''}, \tag{17}$$

with similar expressions for A_{22} and A_{33} obtained by cyclic change of indices. Here e_{ik}' is used to denote the rate of strain in the undisturbed liquid, and g_1'', g_2'', g_3'' are defined as integrals of the type

$$g_1'' = \int_0^\infty \frac{\lambda\, d\lambda}{(\alpha_2^2+\lambda)(\alpha_3^2+\lambda)\Delta'}, \tag{18}$$

where $$\Delta' = \{(\alpha_1^2+\lambda)(\alpha_2^2+\lambda)(\alpha_3^2+\lambda)\}^{\frac{1}{2}}$$

and α_1, α_2, α_3 are the ratios of the ellipsoid semi-axes to a_0. Expressions for the remaining tensor components can be obtained from Jeffery's equation (26) after that has been corrected for some errors in transcription. For the case in which the ellipsoid is not rotating these take forms of the type

$$A_{12} = \frac{g_1 e_{12}' - \alpha_2^2 g_3' \zeta_{12}'}{2g_3'(\alpha_1^2 g_1 + \alpha_2^2 g_2)}, \tag{19}$$

where ζ_{ik}' is the vorticity of the undisturbed liquid, g_1, g_2, g_3 are integrals of the type

$$g_1 = \int_0^\infty \frac{d\lambda}{(\alpha_1^2+\lambda)\Delta'} \tag{20}$$

and g_1', g_2', g_3' are integrals of the type

$$g_1' = \int_0^\infty \frac{d\lambda}{(\alpha_2^2+\lambda)(\alpha_3^2+\lambda)\Delta'}. \tag{21}$$

Here the case to be considered is of a non-rigid particle with a changing ellipsoidal surface enclosing a fixed volume $\frac{4}{3}\pi a_0^3$ with fixed centre at the origin, surrounded by liquid which has the undisturbed flow

$$v_i' = e_{ij}'^{(1)} x_j - \zeta_{ij}' x_j. \tag{22}$$

Any such motion of the particle surface could be produced by a suitable homogeneous deformation of the material within it. The internal and surface velocity could then be written as

$$v_i = \bar{e}_{ij}^{(1)} x_j - \bar{\zeta}_{ij} x_j \tag{23}$$

since the rate of strain and vorticity at every point are here equal to their average values. But equation (14) shows that the average rate of strain of a particle is always fixed by the velocity distribution over its surface, and the same applies to the average vorticity which is given by a similar expression to (14) but with the positive sign replaced by a negative one. Thus (23) always applies to the surface velocity so long as the changing surface remains ellipsoidal, irrespectively of the internal velocity distribution.

The disturbance of the liquid flow produced by the particle will be denoted by $\Delta v_i'$. Then as there is no slip between particle and liquid, at the surface

$$\Delta v_i' = (\bar{e}_{ij}^{(1)} - e_{ij}'^{(1)})\, x_j - (\bar{\zeta}_{ij} - \zeta_{ij}')\, x_j. \tag{24}$$

Now $\Delta v_i'$ is completely determined by this surface condition and the condition that it shall vanish at great distances away from the particle. In the case of a rigid non-rotating ellipsoid $\bar{e}_{ij}^{(1)}$ and $\bar{\zeta}_{ij}$ would both vanish. Thus if the surface of the particle actually moves with the velocity (23), it follows from (22) and (24) that the disturbance is the same as would be produced by a rigid, non-rotating ellipsoid in a liquid undergoing the undisturbed flow

$$v_i'' = (e_{ij}'^{(1)} - \bar{e}_{ij}^{(1)})\,x_j - (\zeta_{ij}' - \bar{\zeta}_{ij})\,x_j \tag{25}$$

although the actual undisturbed part of the flow is given by (22).

Jeffery's results for rigid ellipsoids can thus be adapted to apply to particles with moving boundaries. It must be noted, however, that the surface force on a rigid ellipsoid given by (15) can be divided into two parts: one due to the undisturbed flow (22) and one due to the disturbance $\Delta v_i'$. Apart from arbitrary hydrostatic pressures, these are

$$2\eta_0 e_{ij}'^{(1)} n_j \quad \text{and} \quad \eta_0(A_{ij} - 2e_{ij}'^{(1)})\,n_j.$$

In the case of an ellipsoid with moving boundary, the surface force can again be divided into parts due to the undisturbed flow and the disturbance $\Delta v_i'$. The former is unaltered, but the latter is calculated as for a rigid, non-rotating ellipsoid after substituting $e_{ik}'^{(1)} - \bar{e}_{ik}^{(1)}$ for $e_{ik}'^{(1)}$ and $\zeta_{ik}' - \bar{\zeta}_{ik}$ for ζ_{ik}' in accordance with (25). On combining the parts, the surface force is found to be

$$T_i = -p'' n_i + \eta_0(A_{ij}' + 2\bar{e}_{ij}^{(1)})\,n_j, \tag{26}$$

where A_{ik}' represents the tensor A_{ik} as calculated for an undisturbed flow (25) instead of the actual undisturbed flow (22). A similar adaptation of Jeffery's results to ellipsoids with moving boundaries has been made by Cerf (1951) for the particular case of laminar flow and nearly spherical boundaries, but he has missed the explicit appearance of $\bar{e}_{ik}^{(1)}$ in (26). It may have been noticed that the symbols $\bar{e}_{ik}^{(1)}$, $\bar{\zeta}_{ik}$ have here been used for averages in a single particle, while in the previous section they were used for averages over all particles in a suspension. No confusion will arise in the following work, however, since only suspensions of identical particles will be considered.

4. Viscoelastic spheres, steady laminar flow

The results of the last section may be used to find the solution of the problem of a single viscoelastic sphere in a sea of liquid which has the undisturbed motion

$$v_1' = \kappa x_2, \quad v_2' = 0, \quad v_3' = 0. \tag{27}$$

The problem is approached by investigating the possibility of a steady-state solution in which the material of the sphere is at every instant under homogeneous deformation and undergoing continuous rate of strain and rotation within a constant ellipsoidal boundary having one axis along the x_3-direction and the other axes making an angle θ with the x_1- and x_2-directions respectively. The lengths of the corresponding semi-axes will be written as $\alpha_3 a_0$, $\alpha_1 a_0$, $\alpha_2 a_0$ where a_0 is the radius of the undeformed sphere, and since the material is considered to be incompressible

$$\alpha_1\alpha_2\alpha_3 = 1. \tag{28}$$

The type of motion here envisaged for the material of the deformed sphere may be illustrated as follows. Suppose that the sphere (with centre at the origin) is first subjected to a homogeneous deformation such that each material point which originally occupied the position x_1', x_2', x_3' now occupies the position $\alpha_1 x_1'$, $\alpha_2 x_2'$, $\alpha_3 x_3'$. Then from time $t = 0$ onwards let it undergo a continuous deformation such that the co-ordinates x_1, x_2, x_3 of the material point at any time t are given by

$$\begin{aligned} x_1 &= \alpha_1(x_1' \cos \nu t - x_2' \sin \nu t), \\ x_2 &= \alpha_2(x_1' \sin \nu t + x_2' \cos \nu t), \\ x_3 &= \alpha_3 x_3', \end{aligned} \tag{29a}$$

where ν is a constant. This deformation is at every instant homogeneous and the material point which originally occupied the position x_1', x_2', x_3' lies at all times on the ellipse

$$(x_1^2/\alpha_1^2) + (x_2^2/\alpha_2^2) = x_1'^2 + x_2'^2, \quad x_3 = \alpha_3 x_3'.$$

Thus material points which were originally at the surface of the sphere now lie at all times on the surface of the ellipsoid with semi-axes $\alpha_1 a_0$, $\alpha_2 a_0$, $\alpha_3 a_0$ along the x_1-, x_2-, x_3-axes respectively, so the material as a whole is continuously moving within this boundary. From (29a) the velocity field is obtained as

$$v_1 = -\alpha_1 \nu x_2/\alpha_2, \quad v_2 = \alpha_2 \nu x_1/\alpha_1, \quad v_3 = 0. \tag{29b}$$

The only non-zero components of the rate of strain and vorticity are therefore

$$e_{12}^{(1)} = e_{21}^{(1)} = -[(\alpha_1^2 - \alpha_2^2)\nu]/2\alpha_1\alpha_2, \tag{30}$$

$$\zeta_{12} = -\zeta_{21} = [(\alpha_1^2 + \alpha_2^2)\nu]/2\alpha_1\alpha_2. \tag{31}$$

Since both the strain and rate of strain are at all times homogeneous, the stress within the deformed sphere is uniform so that the condition $p_{ij,j} = 0$ is satisfied.

Equations (29a)–(31) refer to motion within an ellipsoidal boundary having axes along the co-ordinate axes, and from these it would be possible to obtain corresponding equations for the case in which the α_1- and α_2-axes are inclined at an angle θ to the x_1- and x_2-axes respectively. At this stage, however, it is simpler to keep to a co-ordinate system with axes along the ellipsoid axes, and in this system the undisturbed motion (27) for the liquid becomes

$$\begin{aligned} v_1' &= \kappa(x_1 \sin\theta \cos\theta + x_2 \cos^2\theta), \\ v_2' &= -\kappa(x_1 \sin^2\theta + x_2 \sin\theta\cos\theta), \\ v_3' &= 0. \end{aligned} \tag{32}$$

The disturbance of this flow by an ellipsoid with boundary velocity (29b) is the same as that produced by a rigid, non-rotating ellipsoid in an undisturbed flow of the form (25) with $\bar{e}_{ik}^{(1)}$ and $\bar{\zeta}_{ik}$ given by (30) and (31), and $e_{ik}'^{(1)}$ and ζ_{ik}' derived from (32). The only non-zero components of the rate of strain and vorticity for this flow are

$$e_{11}'^{(1)} = -e_{22}'^{(1)} = \tfrac{1}{2}\kappa \sin 2\theta, \tag{33}$$

$$e_{12}'^{(1)} = e_{21}'^{(1)} = \tfrac{1}{2}\kappa \cos 2\theta + [(\alpha_1^2 - \alpha_2^2)\nu]/2\alpha_1\alpha_2, \tag{34}$$

$$\zeta_{12}' = -\zeta_{21}' = -\tfrac{1}{2}\kappa - [(\alpha_1^2 + \alpha_2^2)\nu]/2\alpha_1\alpha_2, \tag{35}$$

and these can be used in (17) and (19) to obtain the components of A'_{ik}. All of these vanish except A'_{11}, A'_{22}, A'_{33}, A'_{12}, A'_{21}.

In order that the steady state may exist, the surface force given by (26) must balance the uniform stress p_{ik} in the material undergoing the motion (29*b*). This gives the conditions

$$\left.\begin{aligned} p_{11} &= -p+\eta_0 A'_{11}, \quad p_{22} = -p+\eta_0 A'_{22}, \quad p_{33} = -p+\eta_0 A'_{33}, \\ p_{12} &= \eta_0 A'_{12}-\eta_0[(\alpha_1^2-\alpha_2^2)\nu]/\alpha_1\alpha_2, \quad p_{21} = \eta_0 A'_{21}-\eta_0[(\alpha_1^2-\alpha_2^2)\nu]/\alpha_1\alpha_2, \end{aligned}\right\} \tag{36}$$

with all other stress components zero. Elimination of the arbitrary quantity p between the first three equations and use of (17) gives

$$p_{11}-p_{22} = 5\eta_0 I\kappa \sin 2\theta, \tag{37}$$

$$p_{11}+p_{22}-2p_{33} = 5\eta_0 J\kappa \sin 2\theta, \tag{38}$$

where

$$I = \frac{2}{5}\,\frac{g''_1+g''_2}{g''_2 g''_3+g''_3 g''_1+g''_1 g''_2}, \tag{39}$$

$$J = \frac{2}{5}\,\frac{g''_1-g''_2}{g''_2 g''_3+g''_3 g''_1+g''_1 g''_2}. \tag{40}$$

But p_{12} must be equal to p_{21}, so it follows from the last two equations in (36) that A'_{12} must be equal to A'_{21}. With (19) this gives the condition

$$\nu = -\frac{\alpha_1^2+\alpha_2^2}{2\alpha_1\alpha_2}\left\{1-\frac{\alpha_1^2-\alpha_2^2}{\alpha_1^2+\alpha_2^2}\cos 2\theta\right\}\frac{\kappa}{2}, \tag{41}$$

and the shear stress components are then given by (36) as

$$p_{12} = p_{21} = \tfrac{5}{2}\eta_0 K\left\{\cos 2\theta-\frac{\alpha_1^2-\alpha_2^2}{\alpha_1^2+\alpha_2^2}\right\}\kappa-\eta_0\frac{\alpha_1^2-\alpha_2^2}{\alpha_1\alpha_2}\nu, \tag{42}$$

where

$$K = \frac{1}{5g'_3}\,\frac{\alpha_1^2+\alpha_2^2}{\alpha_1^2\alpha_2^2}. \tag{43}$$

Now the normal stress differences appearing in (37) and (38) and the shear stress components in (42) are all determined by the constitutive equation of the material of the particle as functions of the parameters α_1, α_2, ν of the deformation (29*a*), and that deformation gives rise to no other stress components. There are thus four equations, (37), (38), (41), (42), which involve the four parameters θ, α_1, α_2, ν. If real solutions can be obtained for all these parameters, the steady state can exist. In that case the uniform stress in the deformed sphere given (apart from an arbitrary hydrostatic pressure) by (37), (38) and (42) may be used as $\overline{p}_{ik}$ in (9) to obtain the stress in a dilute suspension of viscoelastic spheres undergoing the flow (32). On transforming back to the original co-ordinate system so that the flow of the suspension is now in the x_1-direction and given by (27), the following expressions are obtained for the stress components:

$$\frac{P_{11}-P_{22}}{5\eta_0 c\kappa} = (I-K)\sin 2\theta\cos 2\theta+K\frac{\alpha_1^2-\alpha_2^2}{\alpha_1^2+\alpha_2^2}\sin 2\theta, \tag{44}$$

$$\frac{P_{11}+P_{22}-2P_{33}}{5\eta_0 c\kappa} = J\sin 2\theta, \tag{45}$$

$$\frac{\Delta P_{12}}{2\cdot 5\eta_0 c\kappa} = I\sin^2 2\theta+K\left\{\cos 2\theta-\frac{\alpha_1^2-\alpha_2^2}{\alpha_1^2+\alpha_2^2}\right\}\cos 2\theta, \tag{46}$$

where ΔP_{12} represents the excess of the components P_{12}, P_{21} over the value $\eta_0\kappa$ which they would have in the pure liquid undergoing the same rate of shear κ. The remaining stress components are zero.

5. Special properties for the spheres, small deformations

When the suspension is undergoing laminar flow, there are certain conditions under which the deformation of the spheres is small. The solution of (37), (38), (41), (42) is then much simplified because the theory of first-order (linear) visco-elasticity can be applied to the material of the spheres, and because the functions I, J, K can be expressed in series form. It is convenient to write

$$e_1 = \alpha_1 - 1, \quad e_2 = \alpha_2 - 1, \quad e_3 = \alpha_3 - 1 \tag{47}$$

and it then follows from (28) that

$$e_1 + e_2 + e_3 + e_1 e_2 + e_2 e_3 + e_3 e_1 + e_1 e_2 e_3 = 0. \tag{48}$$

Since e_1, e_2, e_3 are here small, g_1'', g_2'', g_3'', g_3' can be expanded in series, and these can be inserted in (39), (40), (43) to give

$$I = 1 + \tfrac{3}{7}(e_1 + e_2) - \tfrac{3}{14}(e_1^2 + e_2^2) + \tfrac{33}{49}e_3^2 + O(e^3), \tag{49}$$

$$J = \tfrac{3}{7}(e_1 - e_2) + \tfrac{3}{14}(e_1^2 - e_2^2) + O(e^3), \tag{50}$$

$$K = 1 + \tfrac{3}{7}(e_1 + e_2) + \tfrac{53}{42}(e_1^2 + e_2^2) - \tfrac{50}{147}e_3^2 + O(e^3), \tag{51}$$

where e denotes the numerically largest of the three quantities e_1, e_2, e_3.

In this section, special viscoelastic properties are assumed for the spheres: the stress is taken to be that which would exist in a purely elastic material under the same strain with an addition proportional to the rate of strain. Now when a sphere is deformed into an ellipsoid, the axes of the latter are the principal axes of strain, and for small deformations e_1, e_2, e_3 are the principal components of strain. Thus with the co-ordinate system used in (29a) with axes along the ellipsoid axes, the elastic part of the stress has no shear components and the normal stress differences are

$$p_{11} - p_{22} = 2\mu_1\{(e_1 - e_2) + o(e)\}, \tag{52}$$

$$p_{11} + p_{22} - 2p_{33} = 2\mu_1\{3(e_1 + e_2) + o(e)\}, \tag{53}$$

where μ_1 is the rigidity.

Now the only components of the rate of strain are $e_{12}^{(1)}$, $e_{21}^{(1)}$ as given by (30), so the viscous part of the stress which is proportional to the rate of strain has only the components

$$p_{12} = p_{21} = -\eta_1[(\alpha_1^2 - \alpha_2^2)\nu]/\alpha_1\alpha_2, \tag{54}$$

where η_1 is a constant: the 'viscosity' of the material. Thus equations (52), (53), (54) together apply to the material of the spheres undergoing the deformation (29a), so equations (37), (38), (42) can be written

$$2\mu_1\{(e_1 - e_2) + o(e)\} = 5\eta_0 I\kappa \sin 2\theta, \tag{55}$$

$$2\mu_1\{3(e_1 + e_2) + o(e)\} = 5\eta_0 J\kappa \sin 2\theta, \tag{56}$$

$$-\eta_1 \frac{\alpha_1^2 - \alpha_2^2}{\alpha_1\alpha_2}\nu = \tfrac{5}{2}\eta_0 K\left\{\cos 2\theta - \frac{\alpha_1^2 - \alpha_2^2}{\alpha_1^2 + \alpha_2^2}\right\}\kappa - \eta_0 \frac{\alpha_1^2 - \alpha_2^2}{\alpha_1\alpha_2}\nu. \tag{57}$$

Also, since the deformation is small, equation (41) may be written

$$\nu = -\tfrac{1}{2}\{1+O(e)\}\kappa, \tag{58}$$

and the following results can then be obtained from (55) and (57) after substituting the expressions for I and K given by (49) and (51):

$$\sin 2\theta = \{e_1 - e_2 + o(e)\}/\sigma\kappa, \tag{59}$$

$$\cos 2\theta = \tau\{e_1 - e_2 + o(e)\}/\sigma, \tag{60}$$

$$e_1 - e_2 = \sigma\kappa/(1+\tau^2\kappa^2)^{\frac{1}{2}} + o(e), \tag{61}$$

where
$$\sigma = 5\eta_0/2\mu_1, \quad \tau = (3\eta_0 + 2\eta_1)/2\mu_1. \tag{62}$$

Furthermore, it follows from (55) and (56) with substitution of the expressions for I and J given by (49) and (50) and use of (48), that

$$e_1 + e_2 = o(e), \quad e_3 = o(e). \tag{63}$$

It appears from this equation together with (61) that the quantity e appearing in the order terms may be written as

$$e = \tfrac{1}{2}\sigma\kappa/(1+\tau^2\kappa^2)^{\frac{1}{2}}. \tag{64}$$

This completes the first-order solution for θ, α_1, α_2, ν.

It may be noted that when κ is small, equations (60), (61), (62) give

$$\theta = \frac{\pi}{4} - \frac{0{\cdot}75\eta_0 + 0{\cdot}5\eta_1}{\mu_1}\kappa + \dots. \tag{65}$$

Now Cerf (1951) has investigated the case of a suspension of spheres (with the same special viscoelastic properties) undergoing a small rate of shear κ. His equation (II 55) for θ differs from the above in that the coefficient of η_0 appears as 1·25 instead of 0·75. This is the result of his omission of one of the terms in the expression (26) for the surface force (which has already been mentioned). It would therefore appear that some correction is necessary to his formulae for the flow-birefringence of the suspension.

Equations (44)–(46) can now be used to obtain expressions for the stress components in a suspension undergoing the motion (27). These may be written

$$\frac{P_{11} - P_{22}}{\mu_1 c} = \frac{2\sigma^2\kappa^2}{1+\tau^2\kappa^2} + o(e^2), \tag{66}$$

$$\frac{P_{11} + P_{22} - 2P_{33}}{\mu_1 c} = \frac{6}{7}\frac{\sigma^2\kappa^2}{1+\tau^2\kappa^2} + o(e^2), \tag{67}$$

$$\frac{\Delta\eta(\kappa)}{2{\cdot}5\eta_0 c} = 1 - \frac{\sigma\tau\kappa^2}{1+\tau^2\kappa^2} + o(e), \tag{68}$$

where $\Delta\eta(\kappa)$ represents the excess of the viscosity $\eta(\kappa)$ of the suspension above the viscosity η_0 of the pure liquid. These equations are of use when the order terms are negligible, that is to say when e is much less than unity. This is the case when κ is very small, and it is also the case for all values of κ when $\eta_1 \gg \eta_0$ as can be seen from (62) and (64). In the latter case the second term on the right-hand side of

(68) is not superfluous: when $\tau\kappa$ is of order unity or greater, that term is of order e and hence of higher order of magnitude than the third term.

It is of interest to compare these results with the expressions for the dynamic rigidity $\mu'(\omega)$ and dynamic viscosity $\eta'(\omega)$ of the suspension under sinusoidal rate of strain of small amplitude and of frequency $\omega/2\pi$. These can be obtained from Cerf's (1952) results for the small oscillatory motion of this type of suspension. They are

$$\frac{\mu'(\omega)}{\mu_1 c} = \frac{\sigma^2\omega^2}{1+\tau^2\omega^2}, \tag{69}$$

$$\frac{\Delta\eta'(\omega)}{2\cdot5\eta_0 c} = 1 - \frac{\sigma\tau\omega^2}{1+\tau^2\omega^2}, \tag{70}$$

where $\Delta\eta'(\omega)$ is the excess of the dynamic viscosity of the suspension above the viscosity η_0 of the liquid. Thus when κ is very small or $\eta_1 \gg \eta_0$, the stress components in steady laminar flow may be expressed approximately in terms of the dynamic functions by the relations

$$P_{11} - P_{22} = 2\mu'(\kappa), \tag{71}$$

$$P_{11} + P_{22} - 2P_{33} = \tfrac{6}{7}\mu'(\kappa), \tag{72}$$

$$\eta(\kappa) = \eta'(\kappa). \tag{73}$$

6. Special properties for the spheres, large deformations

When conditions in laminar flow are such that the deformation of the spheres is large, it is not possible to use the expansions (49)–(51) for I, J, K, nor is it possible to use first-order expressions for the stress components in the material of the spheres. Numerical calculations can be made, however, provided the viscoelastic properties of the spheres are fully specified. There is considerable latitude in such specification, and only two cases will be considered here in order to form some idea of the range of validity of the results already obtained for small deformations. In both cases, the stress in the material of the deformed spheres is supposed to be the sum of the stress which would exist in a purely elastic material under the same strain plus an addition proportional to the rate of strain. The viscoelastic properties are thus specialized in the same way as in the preceding section, but here the strain-energy function W of the purely elastic material must be specified. For the two cases it is supposed that

$$W = \tfrac{1}{2}\mu_1(I_1 - 3) \quad \text{(type A)}, \tag{74}$$

and

$$W = \tfrac{1}{2}\mu_1(I_2 - 3) \quad \text{(type B)}, \tag{75}$$

where I_1 and I_2 are the first and second strain invariants. The first strain–energy function is of the type given by the theory of ideal rubber-elasticity, while the second gives a very different stress–strain relationship under large deformations.

When the material of the spheres undergoes the deformation (29*a*), the normal stress differences depend only on the strain energy function. For type A they are

$$p_{11} - p_{22} = \mu_1(\alpha_1^2 - \alpha_2^2), \tag{76}$$

$$p_{11} + p_{22} - 2p_{33} = \mu_1(\alpha_1^2 + \alpha_2^2 - [2/\alpha_1^2\alpha_2^2]). \tag{77}$$

Two equations are obtained by inserting these expressions in (37) and (38), and these can be combined to give

$$\frac{\alpha_1^2+\alpha_2^2-(2/\alpha_1^2\alpha_2^2)}{\alpha_1^2-\alpha_2^2} = \frac{J}{I}, \tag{78}$$

$$\sigma\kappa \sin 2\theta = (\alpha_1^2+\alpha_2^2)/2I, \tag{79}$$

where σ is defined by (62). The components of shear stress are given as before by (54), and with (42) this gives (57) again. Elimination of ν between (41) and (57) gives

$$\cos 2\theta = \left(\frac{\alpha_1^2-\alpha_2^2}{\alpha_1^2+\alpha_2^2}\right)\left\{1+\frac{\tau-\sigma}{K\sigma}\left(\frac{\alpha_1^2+\alpha_2^2}{2\alpha_1\alpha_2}\right)^2\right\}\Big/\left\{1+\frac{\tau-\sigma}{K\sigma}\left(\frac{\alpha_1^2-\alpha_2^2}{2\alpha_1\alpha_2}\right)^2\right\}, \tag{80}$$

where τ is defined by (62). The solution of the problem involves the determination of θ, α_1, α_2 from these three equations as functions of $\sigma\kappa$ for the given value of the ratio τ/σ.

It is simplest to start with a chosen value of α_1 and solve (78) numerically for α_2, and the corresponding values of $\sigma\kappa$ and θ are then obtainable from (79) and (80). The calculation is repeated for other values of α_1. It is necessary, of course, to have available numerical values of I, J, and K which are functions of both α_1 and α_2. For the present work, it was found to be sufficient to prepare graphs of I, J, K against α_1 for the three cases $\alpha_2 = 0{\cdot}8/\alpha_1$, $1/\alpha_1$, $1{\cdot}3/\alpha_1$, and since the functions are rather insensitive to changes in α_2 linear interpolation and extrapolation could be used. Successive approximations are necessary in the calculation of α_2 by means of (78), but the process is rapid if a start is made by setting $\alpha_2 = 1/\alpha_1$ in the term on the right-hand side of that equation. Once θ, α_2 and $\sigma\kappa$ have been determined for a set of values of α_1, the normal stress differences and viscosity of the suspension can be obtained from (44)–(46) and plotted as functions of $\sigma\kappa$ or $\tau\kappa$ for the given value of the ratio τ/σ.

For type B, equations (76) and (77) have to be replaced by

$$p_{11}-p_{22} = \mu_1(\alpha_2^{-2}-\alpha_1^{-2}), \tag{81}$$

$$p_{11}+p_{22}-2p_{33} = \mu_1(2\alpha_1^2\alpha_2^2-\alpha_1^{-2}-\alpha_2^{-2}). \tag{82}$$

The appropriate alterations are made to (78) and (79) and the calculations are carried out as before.

There is, of course, little difference in the viscosity of the suspension calculated using either type of viscoelasticity when τ is large compared with $\sigma\,(\eta_1 \gg \eta_0)$. Even when τ is only twice $\sigma\,(\eta_1 = 3{\cdot}5\eta_0)$ the difference is quite small as can be seen from the curves of $\Delta\eta(\kappa)$ plotted against $\tau\kappa$ in figure 1. Furthermore, both curves are fairly close to the curve for $\Delta\eta'(\kappa)$ calculated from (70), and this shows that (73) is still a reasonable approximation. However, for $\tau = \sigma\,(\eta_1 = \eta_0)$ a considerable separation of all three curves takes place when $\tau\kappa$ is greater than unity. The normal stress differences in the suspension for types A and B also remain close down to $\tau = 2\sigma$, but here they depart considerably from values calculated from (71) and (72). In figure 2, $P_{11}-P_{22}$ and $P_{33}-P_{22}$ are plotted against $\tau\kappa$ for the case of $\tau = 6\sigma\,(\eta_1 = 13{\cdot}5\eta_0)$ and the differences between types A and B cannot be

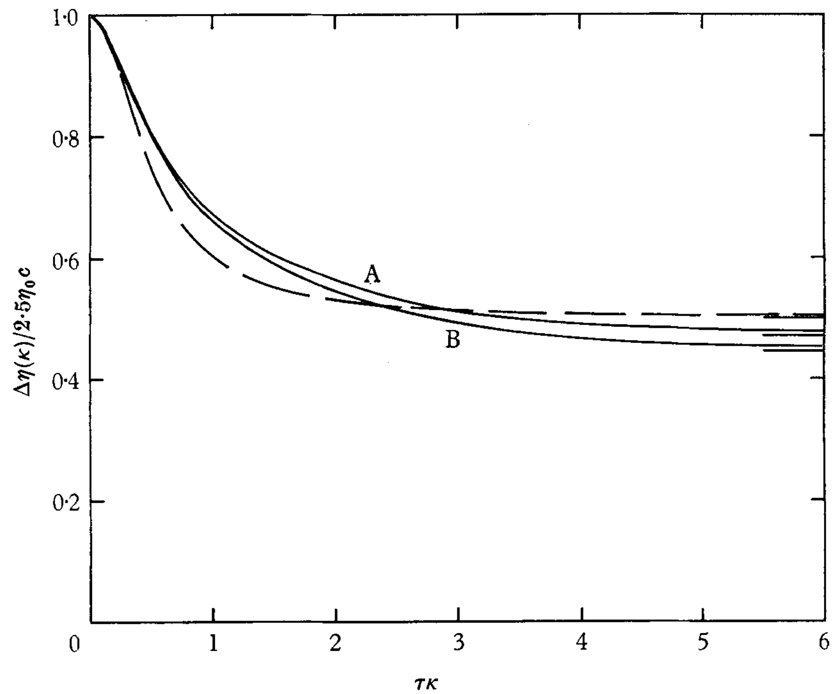

FIGURE 1. Increase of steady-rate viscosity $\Delta\eta(\kappa)$ produced by presence of spheres with types A and B viscoelasticity, shown as functions of $\tau\kappa$. Broken line calculated from dynamic viscosity function using equations (70) and (73). $\tau = 2\sigma(\eta_1 = 3{\cdot}5\eta_0)$ in all cases.

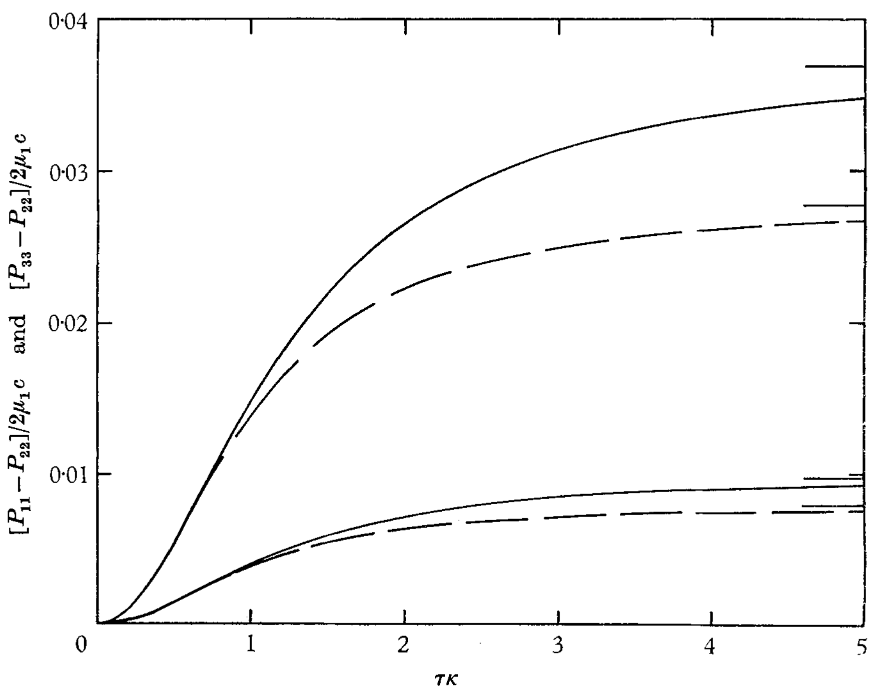

FIGURE 2. Normal stress differences $P_{11}-P_{22}$ (upper full line) and $P_{33}-P_{22}$ (lower full line) produced by presence of spheres with either types A or B viscoelasticity, shown as functions of $\tau\kappa$. Broken lines calculated from dynamic rigidity function using equations (69), (71) and (72). $\tau = 6\sigma(\eta_1 = 13{\cdot}5\eta_0)$ in all cases.

shown as they never amount to as much as 2 %. On the other hand, there is appreciable departure even here from the curves given by (71) and (72), indicating that the range of validity of those equations is more restricted than that of (73).

7. General properties for the spheres, small deformations

The results of the last section illustrate the extent of the departure of the stress components in the suspension from the formulae (71), (72), (73) when the deformation of the spheres is large. In both §§ 5 and 6, however, it has been assumed that the viscoelastic properties of the spheres are such that the stress can be separated into elastic and viscous parts. This section is concerned with the laminar flow of a suspension of spheres which have general viscoelastic properties, but once more under the restriction that the deformation of the spheres is small. Thus equations (49), (50), (51) are still applicable, and the theory of first-order viscoelasticity may be applied to determine the stress in the material of the spheres. That theory is usually formulated using a co-ordinate system chosen so that the displacement of particles of the material is small. Such a system may be obtained from the fixed system used in (29*a*) by rotating the x_1- and x_2-axes with angular velocity ν about the x_3-axis. On transforming to this system, the non-zero components of the strain tensor for infinitesimal deformations are found to be

$$e_{11}(t) = \tfrac{1}{2}(e_1+e_2)+\tfrac{1}{2}(e_1-e_2)\cos 2\nu t, \tag{83}$$

$$e_{22}(t) = \tfrac{1}{2}(e_1+e_2)-\tfrac{1}{2}(e_1-e_2)\cos 2\nu t, \tag{84}$$

$$e_{33}(t) = -e_1-e_2, \tag{85}$$

$$e_{12}(t) = e_{21}(t) = -\tfrac{1}{2}(e_1-e_2)\sin 2\nu t, \tag{86}$$

where t is time measured from an instant at which fixed and rotating axes coincide. The strain may therefore be divided into three deviatoric parts, one varying as $\cos 2\nu t$, one independent of time and one varying as $\sin 2\nu t$; and for first-order viscoelasticity the stress is the sum of the stresses calculated for each separately. Using equations (1) and (2) for the material of the spheres, the following expressions are obtained for the stress components at $t = 0$:

$$p_{11}-p_{22} = 2\mu_1'(2\nu)\{e_1-e_2+o(e)\}, \tag{87}$$

$$p_{11}+p_{22}-2p_{33} = 2\mu_1'(0)\{3(e_1+e_2)+o(e)\}, \tag{88}$$

$$p_{12} = p_{21} = -2\eta_1'(2\nu)\,2\nu\{e_1-e_2+o(e)\}, \tag{89}$$

where $\mu_1'(\omega)$ and $\eta_1'(\omega)$ represent the dynamic rigidity and viscosity of the material of the spheres at a frequency $\omega/2\pi$. These equations have been derived for the rotating co-ordinate system at the instant at which it coincides with the fixed system and, since that instant has been chosen arbitrarily, they apply at all times in the fixed system.

Insertion of the first and last of the above expressions in (37) and (42) gives equations identical with (55) and (57) except that μ_1 is replaced by $\mu_1'(2\nu)$ and η_1 by $\eta_1'(2\nu)$. Hence (59), (60), (61) still hold if the same replacements are made in the expressions for σ and τ given by (62). Furthermore, (58) still applies and 2ν can be replaced by κ in these expressions without affecting the order terms. Now

(66), (67), (68) follow from (59), (60), (61), so they apply here when μ_1 is replaced by $\mu_1'(\kappa)$ and σ, τ are taken to be the functions

$$\sigma = 5\eta_0/2\mu_1'(\kappa), \quad \tau = (3\eta_0 + 2\eta_1'(\kappa))/2\mu_1'(\kappa). \tag{90}$$

Insertion of (88) in (38) gives an equation identical with (56) except that μ_1 is here replaced by $\mu_1'(0)$. This can be used with the equation obtained by replacing μ_1 by $\mu_1'(\kappa)$ in (55) to obtain a result for $e_1 + e_2$ corresponding to (63). In fact, if $\mu_1'(\kappa)$ is of the same order as $\mu_1'(0)$ that equation still applies. Measurements on

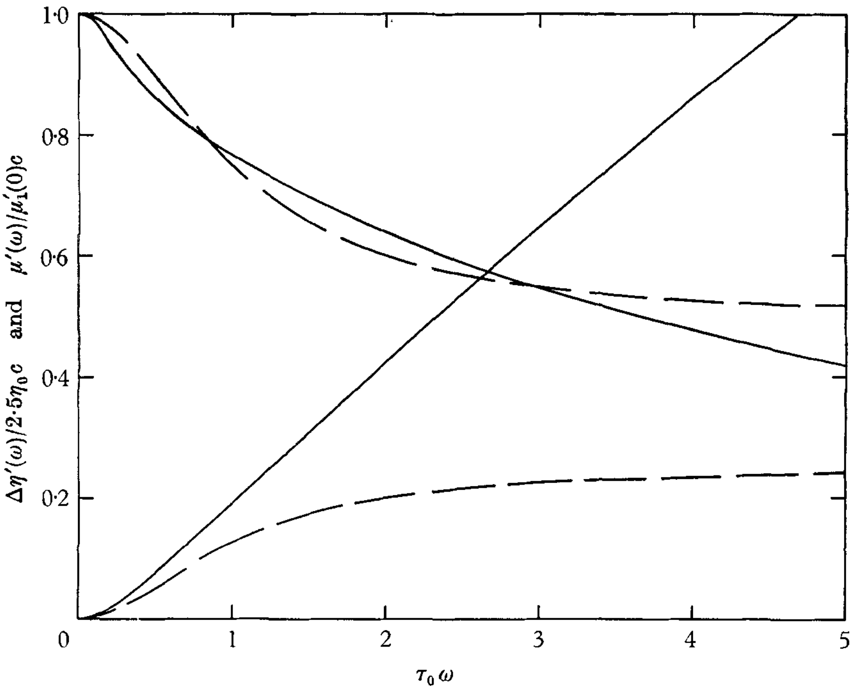

FIGURE 3. Ascending and descending full lines show respectively the dynamic rigidity $\mu'(\omega)$ and increase in dynamic viscosity $\Delta\eta'(\omega)$ produced by presence of spheres having Kirkwood-type viscoelasticity with $\tau_0\mu_1'(0) = 3{\cdot}5\eta_0$. Broken lines are corresponding curves for case when spheres have constant rigidity and viscosity ($\eta_1 = 3{\cdot}5\eta_0$), with $\tau\omega$ as abscissae.

real solids, however, often give values of $\mu_1'(\omega)$ which increase slowly with ω up to values much greater than $\mu_1'(0)$. In order to allow for this effect, the largest term involving the ratio $\mu_1'(\kappa)/\mu_1'(0)$ has to be retained in the expression for $e_1 + e_2$ which becomes

$$e_1 + e_2 = \tfrac{1}{7}\{\mu_1'(\kappa)/\mu_1'(0)\}(e_1 - e_2)^2 + o(e). \tag{91}$$

It then follows from (61) that e_1 is numerically larger than e_2 and e_3, so e may be written

$$e = \tfrac{1}{2}[\sigma\kappa/(1+\tau^2\kappa^2)^{\frac{1}{2}}]\{1 + \tfrac{1}{7}[\mu_1'(\kappa)/\mu_1'(0)]\,[\sigma\kappa/(1+\tau^2\kappa^2)^{\frac{1}{2}}]\}. \tag{92}$$

Thus e is much less than unity if κ is very small and also if τ/σ (or $\eta_1'(\kappa)/\eta_0$) is much greater than unity and at least of order $\mu_1'(\kappa)/\mu_1'(0)$.

Now if the suspension is subjected to sinusoidal shear stress of frequency $\omega/2\pi$ and small amplitude, the surface forces on the spheres vary sinusoidally with the same frequency and the stress–strain relation for their material is given by equations (1) and (2). This relation is determined by the values of $\mu_1'(\omega)$ and $\eta_1'(\omega)$, and for any particular value of ω it is identical with that for a material having constant rigidity μ_1 and viscosity η_1 of corresponding values. Equations (69) and (70) for the dynamic rigidity and viscosity of the suspension therefore hold in the general case provided μ_1 is replaced by $\mu_1'(\omega)$ and σ, τ are taken to be functions of ω of the forms given by (90). Thus equations (71), (72), (73), which give the stress components of the suspension in steady laminar flow in terms of its dynamic rigidity and viscosity functions, hold in the general case provided either κ is very small or $\eta_1'(\kappa)/\eta_0$ is sufficiently large.

It may be noted that the forms of the dynamic rigidity and viscosity functions of the suspension depend markedly upon the type of viscoelasticity possessed by the spheres. For example, figure 3 shows these functions calculated for a case in which the material of the spheres has the simple retardation-time spectrum proposed by Kirkwood (1946) for polymers in bulk. Here the viscosity η_0 of the suspending liquid has been chosen so that $\tau_0\mu_1'(0)$ is equal to $3{\cdot}5\eta_0$ where τ_0 is the constant which characterizes the spread of the Kirkwood spectrum. The curves are compared with those for a suspension of spheres with constant rigidity μ_1 and viscosity η_1, the latter being chosen equal to $3{\cdot}5\eta_0$.

8. A suspension undergoing steady elongation

Here a quite different type of motion will be considered: that in which the suspension is being extended at a constant fractional rate ζ in the x_1-direction, the fractional contractions in the other two directions being equal. Such motion can be produced by the rapid extension of a cylinder of the liquid if it is sufficiently viscous. For the solution of the problem it is necessary first to consider a single sphere in a sea of pure liquid which has the undisturbed motion

$$v_1' = \zeta x_1, \quad v_2' = -\tfrac{1}{2}\zeta x_2, \quad v_3' = -\tfrac{1}{2}\zeta x_3. \tag{93}$$

A steady-state solution is sought in which the sphere is deformed into a spheroid (with its axis of symmetry along the x_1-axis) without rotation of its material. Since there is no motion at its surface, the spheroid is effectively rigid and the surface force is given by (15). Here the only non-zero components of A_{ik} can be seen from (17) and (19) to be

$$A_{11} = \tfrac{4}{3}(\zeta/g_2''), \quad A_{22} = A_{33} = -\tfrac{2}{3}(\zeta/g_2''), \tag{94}$$

where g_2'' is the integral of the type (18) calculated for an ellipsoid having $\alpha_2 = \alpha_3 = \alpha_1^{-\frac{1}{2}}$. Thus the surface force is such as to balance a homogeneous internal stress with non-zero components p_{11}, p_{22}, p_{33} such that

$$p_{11}-p_{22} = p_{11}-p_{33} = 2\eta_0(\zeta/g_2''). \tag{95}$$

If the viscoelasticity of the sphere is of the type A considered in § 6, the stress components are simply obtained from the strain–energy function (74) since there is no viscous contribution when the deformation is static. Thus

$$p_{11}-p_{22} = p_{11}-p_{33} = \mu_1(\alpha_1^2-[1/\alpha_1]). \tag{96}$$

On the other hand, if the sphere has type B viscoelasticity, the strain–energy function (75) gives

$$p_{11}-p_{22} = p_{11}-p_{33} = \mu_1[\alpha_1-(1/\alpha_1^2)]. \tag{97}$$

On combining these results with (95) it is found that for type A

$$\sigma\zeta = \tfrac{5}{4}g_2''[\alpha_1^2-(1/\alpha_1)], \tag{98}$$

while for type B

$$\sigma\zeta = \tfrac{5}{4}g_2''[\alpha_1-(1/\alpha_1^2)]. \tag{99}$$

Values of g_2'' are calculated for a suitable range of α_1 and corresponding values of $\sigma\zeta$ are then obtained from the above equations.

The stress in the suspension is given by (9) with $\bar{p}_{ik}$ set equal to p_{ik} and $\bar{e}_{ik}^{(1)}$ set equal to zero. The non-zero components of the rate of strain of the suspension are obtained from (93) as

$$E_{11}^{(1)} = \zeta, \quad E_{22}^{(1)} = E_{33}^{(1)} = -\tfrac{1}{2}\zeta. \tag{100}$$

Thus with (95) it is found that

$$P_{11}-P_{22} = P_{11}-P_{33} = 3\eta_0\{1+\tfrac{2}{3}(c/g_2'')\}\zeta. \tag{101}$$

This stress difference is equal to the tension necessary to extend a cylinder of the suspension with a free curved surface, and the elongational viscosity η_e is obtained by dividing it by the rate of elongation ζ. The excess $\Delta\eta_e$ of this quantity above the elongational viscosity of the pure liquid $3\eta_0$ is thus given by

$$\Delta\eta_e = 2\eta_0(c/g_2''). \tag{102}$$

From the sets of values of g_2'' with corresponding values of $\sigma\zeta$ already obtained, graphs of $\Delta\eta_e/3\eta_0 c$ against $\sigma\zeta$ have been plotted in figure 4.

There are no real solutions of (98) for α_1 when $\sigma\zeta$ exceeds 0·83. This implies that no steady state in which the deformed spheres keep a fixed spheroidal shape can exist when $\sigma\zeta$ is greater than that value. On the other hand there are two real solutions for α_1 when it lies below 0·83, and the peculiar form of the type A curve in figure 4 results from this. The upper part of the curve, corresponding to the higher of the two values of α_1, is shown as a broken curve as it represents states which are not attained when a steady elongational motion having $\sigma\zeta$ less than 0·83 is imposed on a suspension initially at rest. The same pecularities occur with type B, but the maximum value of $\sigma\zeta$ for a steady state is 0·31.

A steady state exists for sufficiently small values of $\sigma\zeta$ whatever the form of the strain–energy function. Thus equation (96) can be generalized by replacing the bracket term with $3e_1+o(e_1)$ where $e_1 = \alpha_1-1$. For small values of e_1

$$\tfrac{15}{4}g_2'' = 1-\tfrac{3}{7}e_1-\tfrac{3}{7}e_1^2+O(e_1^3). \tag{103}$$

With the same bracket substitution equation (98) then gives the real solution

$$e_1 = \sigma\zeta+o(e_1). \tag{104}$$

The elongational viscosity is obtained from (101) or (102) as

$$\eta_e/3\eta_0 = 1+\tfrac{5}{2}c+\tfrac{15}{14}c\sigma\zeta+co(\sigma\zeta). \tag{105}$$

When $\sigma\zeta$ is small, this gives the straight line shown in figure 4.

The discussion has here been limited to the case of spheres having the special property that the stress can be represented as the sum of separate elastic and viscous parts. The results are nevertheless of general application, because only the static properties are relevant. Thus the calculations made for types A and B viscoelasticity apply to all cases in which the static elasticity has a strain–energy function of the form (74) or (75), and (104) and (105) apply in general if σ is replaced by $\sigma(0)$.

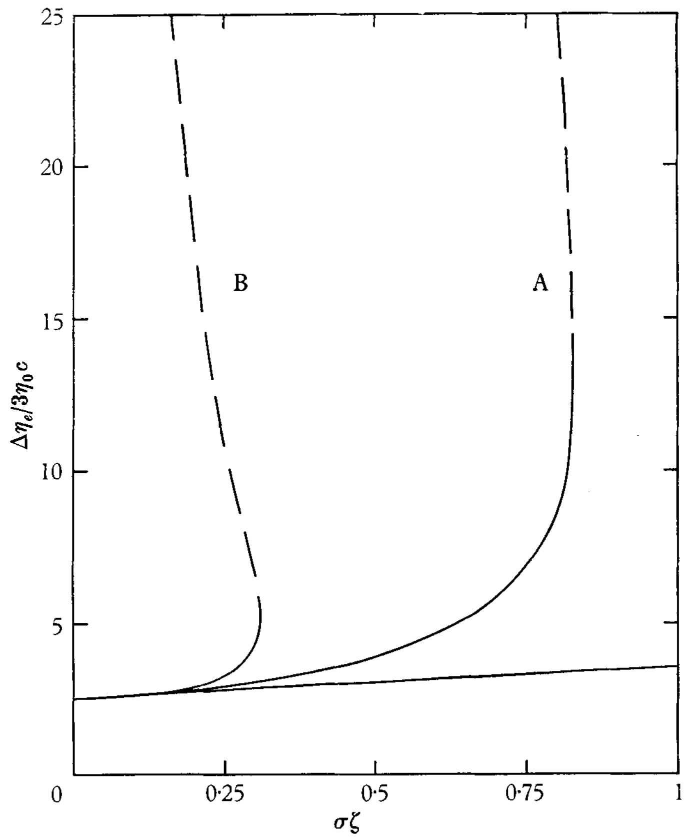

FIGURE 4. Increase in elongational viscosity $\Delta\eta_0$ produced by presence of spheres with types A and B viscoelasticity, shown as functions of $\sigma\zeta$. Straight line is relation given by theory of simple fluids with fading memory for very small rates of elongation ζ.

9. Discussion of the results

The approximate relations (71), (72), (73) express the stress components in steady laminar flow in terms of the dynamic rigidity and viscosity functions of the suspension. These functions are given in general by (69) and (70) with μ_1 replaced by $\mu_1'(\omega)$ and σ, τ taken to be functions of ω of the forms given by (90). The relations become accurate if the rate of shear is sufficiently small or if the ratio of the dynamic viscosity of the spheres to the viscosity of the liquid is sufficiently large. They are of interest in connexion with observations on polymer solutions made by Padden & DeWitt (1954), DeWitt, Markovitz, Padden &

Zapas (1955) and Markovitz & Williamson (1957). These authors have noted the similarity of form between the steady-state and dynamic viscosity functions and between the normal stress difference functions and the dynamic rigidity function.

Equation (71) does not express an entirely new result: it has been shown by Coleman & Markovitz (1964) to hold generally for simple fluids with fading memory when the rate of shear is small. By combining (71) and (72) it is found that

$$P_{33}-P_{22} = \tfrac{2}{7}(P_{11}-P_{22}). \tag{106}$$

This relation is of interest because it has sometimes been maintained that there are physical reasons for supposing that P_{33} should be equal to P_{22} in any elasto-viscous liquid.

It may be noted that if a suspension of spheres is to be used as a model for a polymer solution, it is not sufficient to assume the simple viscoelastic properties for the spheres used in §§5 and 6. Under small deformation, spheres with these properties have a single retardation time, and the dynamic rigidity and viscosity functions of the suspension have simple forms such as those shown by the broken lines in figure 3. The observed forms of these functions for polymer solutions are much more like those calculated using a broad distribution of retardation times for the material of the spheres and shown by the full lines in figure 3.

In the problem of the steady elongation of a suspension, a solution exists in which the spheres suffer a static deformation into spheroids, provided the rate of elongation ζ is sufficiently small. The elongational viscosity is then given by (105): a formula which may alternatively be deduced from a general result for simple fluids with fading memory given by the author (Roscoe 1965) taken together with the present results for the normal stress differences in steady laminar flow. Two special cases have been investigated for finite values of ζ, and in each it was found that no such solution exists when ζ exceeds a critical value. This implies that if the suspension is subjected to a steady elongation in excess of the critical value, the spheres suffer a deformation which increases continuously with time. There is here a contrast with the case of steady laminar flow where the material of each sphere rotates continuously within an ellipsoidal boundary of fixed dimensions and orientation, the ellipticity of the boundary being small for all rates of shear if the ratio of the dynamic viscosity of the spheres to the viscosity of the liquid is sufficiently high. These results suggest that for polymer solutions, rapid elongation should be more effective than rapid shearing in uncoiling (and in some special cases rupturing) the polymer chains.

The method of determining the macroscopic stress in a suspension, based on equations (9) and (26), has only been applied here to steady laminar flow and steady elongation. The results of the former case can be applied to all viscometric flows, subject to the condition given in the last paragraph of §2. Other simple problems can be solved by the same method, as for example the case of small oscillatory deformation. The solution for the latter problem has not been given here since the basic results have already been obtained by Cerf (1952). For the solution of more complicated problems it would be necessary to derive the general constitutive equation for the suspension from (9) and (26). It must be remembered, however, that when the deformation of the spheres is large, the tensor A'_{ik} depends in a complicated way on the axial ratios α_1, α_2, α_3, and a numerical calculation involving successive approximations has to be used even in the case of steady laminar flow. The derivation of an exact constitutive equation would therefore seem to be an intractable problem.

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