

The elastic and viscous properties of emulsions and suspensions

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A calculation is made of the elastic properties of a dilute emulsion of one incompressible viscous liquid in another, arising from the interfacial tension between the two phases. A linear relation between the stress tensor, the rate-of-strain tensor and their first time derivatives defines the behaviour at small rates of strain; the three constants involved are expressed as functions of the viscosities of the two components, the drop size (assumed small and uniform), the interfacial tension and the concentration. The relaxation time and retardation time for the system vary directly as the drop diameter and inversely as the interfacial tension.

The effect of slip at the interfaces, which might be associated with the presence of a film of a third component introduced as a stabilizer, is also calculated. The values of the rheological constants are appreciably altered if the frictional coefficient specifying the degree of slipping is sufficiently small, but the type of elastic behaviour is unchanged. In the case of a suspension of elastic solid particles in a viscous liquid, slip at the solid-liquid interfaces can cause a change in the type of elastic behaviour.

1. INTRODUCTION

The viscosity of a suspension of small drops of one viscous liquid in another has been calculated by Taylor (1932), making assumptions similar to those of Einstein (1906, 1911) in his investigation of the viscosity of a suspension of rigid spheres in a liquid. The resulting formula, relating the viscosity η^* of the emulsion with the viscosities η , η' of the continuous and disperse phases, is

$$\eta^*/\eta = 1 + (\eta + \frac{5}{2}\eta')c/(\eta + \eta') + O(c^2), \quad (1)$$

where c is the (small) fraction of the whole volume occupied by the disperse phase; this becomes Einstein's formula when η'/η tends to infinity. The deformation of a suspended liquid drop, caused by movement of the outer liquid, has also been discussed by Taylor (1934). The interfacial tension provides a force tending to restore the drop to its equilibrium (spherical) form, so giving the drop elasticity of shape. It is the purpose of the present paper to determine the kind of macroscopic elastic properties to be expected of an emulsion, as a consequence of the interfacial tension.

Following Einstein and Taylor, the individual drops and the concentration of the disperse phase are assumed to be very small, so that inertia effects and hydrodynamic interactions between drops can be ignored in calculating the behaviour of a typical macroscopic element of the emulsion. The interfacial tension is assumed to have a sufficiently large constant value to keep the suspended drops approximately spherical, although small departures from the spherical shape are taken into account. The boundary conditions of no slip and continuity of tangential stress at

an interface are used in the first instance, but in §5 an attempt is made to allow for a non-zero slip, governed by a constant frictional coefficient. The theoretical possibility of slippage at the interfaces appears to be worthy of investigation in view of the frequent practice of introducing, as a stabilizer into an emulsion, a third component which forms a thin film everywhere between the two principal phases.

The rheological properties of a suspension of elastic particles in a viscous liquid have been discussed by Fröhlich & Sack (1946), on the assumption that the suspended particles are solid spheres obeying Hooke's law. Their result was a set of equations of state, relating the stress tensor p_{ik} and the rate-of-strain tensor $e_{ik}^{(1)}$ in sufficiently slow motion, which are essentially of the form†

$$p_{ik} = p'_{ik} - pg_{ik}, \quad (2)$$

where g_{ik} is the metric tensor, the scalar p is independent of the rate of strain when compressibility is neglected, and

$$(1 + \lambda_1 d/dt) p'_{ik} = 2\eta_0(1 + \lambda_2 d/dt) e_{ik}^{(1)}. \quad (3)$$

The relaxation time λ_1 , the retardation time λ_2 , and the coefficient of viscosity η_0 are constants, determined as functions of the elastic and viscous constants of the components and the volume concentration of the disperse phase; d/dt is used here to denote an appropriate total time derivative, to ensure that the equations have the right invariance properties for general validity (cf. Oldroyd 1950). Following Fröhlich & Sack, a perturbation method is used in the present paper to derive the rheological properties of an idealized emulsion. The results are qualitatively similar to those for a suspension of elastic solid spheres.

2. METHOD

A homogeneous liquid L^* is envisaged, with the same macroscopic rheological properties as an emulsion consisting of drops of one Newtonian liquid L' (viscosity η') suspended in another Newtonian liquid L (viscosity η). To fix ideas, we suppose that the drop size is uniform, each drop of L' having radius a , and that L and L' are incompressible. The properties of L^* can be determined by the requirement that if a small part of L^* were replaced by the actual components of the emulsion, no difference in rheological behaviour could be detected by macroscopic observations. A first approximation to the rheological properties—valid for very small values of c —can be obtained by using the simplest possible perturbation, similar to that of Fröhlich & Sack (1946) for a suspension, in which the possibility of two drops being close together is ignored.

We therefore consider two systems: in the first, a single spherical drop of L' ($r < a$ referred to spherical polar co-ordinates r, θ, ϕ) is surrounded by L filling the space $a < r < b$, the remaining space $r > b$ being filled with L^* ; in the second, the whole of space is filled with L^* . The radius b is chosen to give the correct volume concentration c of the disperse phase in the emulsion, i.e. $b^3 = a^3/c$. The two systems are required to be indistinguishable to a given degree of accuracy, provided that

† The tensor notation is the same as in Oldroyd (1950); in particular, $e_{ik}^{(1)} = \frac{1}{2}(v_{k,i} + v_{i,k})$ defines the rate-of-strain tensor in terms of the velocity vector v^i .

observations are made at a distance $r = R$ sufficiently large compared with b . The composite or homogeneous sphere $r \leq R$ is to be regarded as a single macroscopic element. This element will be considered in an arbitrary state of flow, during a time in which the boundaries between the different liquids remain approximately spherical, subject to the restriction that the velocity gradients are so small that their squares and products can be neglected. Under these conditions it is not necessary to distinguish total and partial time derivatives in an Eulerian system of reference in which the element is at rest.

The equations of state of an incompressible Newtonian liquid of viscosity η can be written in the form (2), where

$$p'_{ik} = 2\eta e^{(1)}_{ik}, \tag{4}$$

$$e^{(1)i}_i = 0, \tag{5}$$

and p is independent of the rate of strain. In the case of an emulsion with incompressible components, (4) must in general be replaced by a more complicated relationship; so long as attention is confined to small rates of strain, this may be assumed to involve p'_{ik} , $e^{(1)}_{ik}$ and their time derivatives linearly. In the case of L^* we can therefore write

$$p'_{ik} = 2\eta^* e^{(1)}_{ik}, \tag{6}$$

where η^* is an operator of the form

$$\eta^* = \eta_0 \frac{1 + \lambda_2 \Delta + \nu_2 \Delta^2 + \xi_2 \Delta^3 + \dots}{1 + \lambda_1 \Delta + \nu_1 \Delta^2 + \xi_1 \Delta^3 + \dots} \quad (\Delta \equiv d/dt), \tag{7}$$

and $\eta_0, \lambda_1, \lambda_2, \nu_1, \nu_2$, etc., are constants to be determined in terms of the properties of L and L' . The notation can be used without confusion, if (6) is understood to mean precisely

$$(1 + \lambda_1 \Delta + \nu_1 \Delta^2 + \xi_1 \Delta^3 + \dots) p'_{ik} = 2\eta_0 (1 + \lambda_2 \Delta + \nu_2 \Delta^2 + \xi_2 \Delta^3 + \dots) e^{(1)}_{ik}$$

and every equation in which η^* occurs is similarly interpreted. It has the advantage that (6) is formally the same as (4), giving rise to equations of motion expressed in terms of the velocity components which are formally the same as those for a Newtonian liquid.

Displacements and rates of strain will be unaffected by any superposed isotropic pressure, and we need only consider an element of the emulsion subjected to an arbitrary deviatoric stress tensor p_{ik} (satisfying $p^i_i = 0$) varying with the time. The principal directions of stress will in general change with time, and there is in general no specially privileged set of directions of reference fixed in space. Referred to arbitrary orthogonal co-ordinate directions fixed in space, the stress tensor can be written as the sum of six tensors (represented here by Cartesian components) in the following way:

$$p_{ik} = \begin{pmatrix} -\frac{2}{3}S & 0 & 0 \\ 0 & \frac{1}{3}S & S \\ 0 & S & \frac{1}{3}S \end{pmatrix} + \begin{pmatrix} \frac{1}{3}S' & 0 & S' \\ 0 & -\frac{2}{3}S' & 0 \\ S' & 0 & \frac{1}{3}S' \end{pmatrix} + \begin{pmatrix} \frac{1}{3}S'' & S'' & 0 \\ S'' & \frac{1}{3}S'' & 0 \\ 0 & 0 & -\frac{2}{3}S'' \end{pmatrix} \\ + \begin{pmatrix} 2T & 0 & 0 \\ 0 & -T & 0 \\ 0 & 0 & -T \end{pmatrix} + \begin{pmatrix} -T' & 0 & 0 \\ 0 & 2T' & 0 \\ 0 & 0 & -T' \end{pmatrix} + \begin{pmatrix} -T'' & 0 & 0 \\ 0 & -T'' & 0 \\ 0 & 0 & 2T'' \end{pmatrix},$$

where S, S', S'', T, T', T'' are functions of the time. The states of stress represented by all the six tensors individually are essentially of the same form since, for example, a rotation of the second and third directions of reference through 45° about the first direction transforms

$$p_{ik} = \begin{pmatrix} -\frac{2}{3}S & 0 & 0 \\ 0 & \frac{1}{3}S & S \\ 0 & S & \frac{1}{3}S \end{pmatrix} \quad \text{into} \quad p_{ik} = \begin{pmatrix} -\frac{2}{3}S & 0 & 0 \\ 0 & -\frac{2}{3}S & 0 \\ 0 & 0 & \frac{4}{3}S \end{pmatrix}$$

Since the equations of state, the equations of slow motion and the conditions at boundaries and interfaces all involve stresses, displacements and rates of strain linearly, it suffices to consider the axially symmetric stress represented by

$$p_{ik} = \begin{pmatrix} 2T & 0 & 0 \\ 0 & -T & 0 \\ 0 & 0 & -T \end{pmatrix} \quad (8)$$

applied to a spherical element of radius R , T being an arbitrary function of the time. The velocity distribution associated with any other state of stress is then obtainable by superposition.

From symmetry, the physical components of the velocity vector referred to spherical polar co-ordinates, anywhere within the macroscopic element, can be taken as $u, v, 0$, and the non-vanishing physical components of the stress tensor in L^* are related to these by the equations

$$\left. \begin{aligned} \widehat{rr} &= -p + 2\eta^* \frac{\partial u}{\partial r}, & \widehat{\theta\theta} &= -p + 2\eta^* \left(\frac{u}{r} + \frac{1}{r} \frac{\partial v}{\partial \theta} \right), \\ \widehat{\phi\phi} &= -p + 2\eta^* \left(\frac{u}{r} + \frac{v}{r} \cot \theta \right), & \widehat{r\theta} &= \eta^* \left(\frac{1}{r} \frac{\partial u}{\partial \theta} + r \frac{\partial}{\partial r} \left(\frac{v}{r} \right) \right). \end{aligned} \right\} \quad (9)$$

All the variables are assumed to be independent of ϕ . The incompressibility condition (5) and the equations of slow motion can be written as

$$\frac{1}{r^2} \frac{\partial(r^2 u)}{\partial r} + \frac{1}{r \sin \theta} \frac{\partial(v \sin \theta)}{\partial \theta} = 0, \quad (10)$$

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial u}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left\{ \sin \theta \left(\frac{\partial u}{\partial \theta} - 2v \right) \right\} - \frac{2u}{r^2} = \frac{1}{\eta^*} \frac{\partial p}{\partial r}, \quad (11)$$

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial v}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial v}{\partial \theta} \right) + \frac{2}{r^2} \frac{\partial u}{\partial \theta} - \frac{v}{r^2 \sin^2 \theta} = \frac{1}{\eta^*} \frac{1}{r} \frac{\partial p}{\partial \theta}. \quad (12)$$

Formally identical equations, with the operator η^* replaced by the constant η (η'), apply in L (L').

The various boundary conditions to be satisfied in the homogeneous and composite spheres of radius R are now considered separately.

(a) Homogeneous element

The applied stress (8) gives rise to the boundary conditions

$$\left. \begin{aligned} \widehat{rr} &= T(3 \cos^2 \theta - 1), & \widehat{\theta\theta} &= T(2 - 3 \cos^2 \theta), & \widehat{\phi\phi} &= -T, \\ \widehat{\theta\phi} &= 0, & \widehat{\phi r} &= 0, & \widehat{r\theta} &= -3T \cos \theta \sin \theta \end{aligned} \right\} \quad (13)$$

on $r = R$. It is easily verified that the values of u, v and p which are finite at the origin, satisfy (10) to (12) everywhere, and correspond to stresses (9) satisfying (13) on $r = R$, are

$$u = \frac{1}{2}Tr(3 \cos^2 \theta - 1)/\eta^*, \quad v = -\frac{3}{2}Tr \cos \theta \sin \theta/\eta^*, \quad p = 0. \tag{14}$$

(b) Composite element

In this case we seek a velocity distribution with the same symmetry as (14), i.e. given by

$$u = f(r, t) (3 \cos^2 \theta - 1), \quad v = g(r, t) \cos \theta \sin \theta, \tag{15}$$

which satisfies (13) and (14) on $r = R$ with the smallest possible error when R is large, and the appropriate continuity conditions at $r = a$ and $r = b$. In order to satisfy equations (10) to (12) in L ($a < r < b$), we must have (cf. Fröhlich & Sack 1946)

$$u = (\frac{1}{7}Ar^3 + \frac{1}{2}Br^{-2} + 2Cr - 3Dr^{-4}) (\frac{3}{2} \cos^2 \theta - \frac{1}{2}), \tag{16}$$

$$v = -(\frac{5}{14}Ar^3 + 3Cr + 3Dr^{-4}) \cos \theta \sin \theta, \tag{17}$$

$$p = \eta(Ar^2 + Br^{-3}) (\frac{3}{2} \cos^2 \theta - \frac{1}{2}) + p_0, \tag{18}$$

where A, B, C, D and p_0 are functions of the time only. The non-vanishing components of stress are

$$\widehat{rr} = \eta(-\frac{1}{7}Ar^2 - 3Br^{-3} + 4C + 24Dr^{-5}) (\frac{3}{2} \cos^2 \theta - \frac{1}{2}) - p_0, \tag{19}$$

$$\widehat{\theta\theta} = \eta[(\frac{5}{14}Ar^2 + 3Dr^{-5}) (3 - 7 \cos^2 \theta) + C(4 - 6 \cos^2 \theta)] - p_0, \tag{20}$$

$$\widehat{\phi\phi} = \eta[(\frac{5}{14}Ar^2 + 3Dr^{-5}) (1 - 5 \cos^2 \theta) - 2C] - p_0, \tag{21}$$

$$\widehat{r\theta} = -\eta(\frac{8}{7}Ar^2 + \frac{3}{2}Br^{-3} + 6C - 24Dr^{-5}) \cos \theta \sin \theta. \tag{22}$$

Exactly similar expressions, in which the symbols A, B, C, D, p_0 and η are distinguished by primes and asterisks, are valid in L' ($r < a$) and L^* ($r > b$). The fifteen functions of time $A, A', A^*, B, B', B^*, C, C', C^*, D, D', D^*, p_0, p'_0, p_0^*$ and the operator η^* are unknowns, to be determined from boundary and continuity conditions.

The conditions for a finite velocity at the origin are

$$B' = 0, \quad D' = 0. \tag{23}$$

For sufficiently large values of the interfacial tension γ between L and L' , the components of displacement at any point in L' from a standard configuration can be assumed to be small and to have the same form as the velocity components with A'', C'' written for A', C' . Hence the shape of the interface between L and L' is given parametrically by

$$r = a + (\frac{1}{7}a^3A'' + 2aC'') (\frac{3}{2} \cos^2 \alpha - \frac{1}{2}), \quad \theta = \alpha - (\frac{5}{14}a^2A'' + 3C'') \cos \alpha \sin \alpha,$$

where $\Delta A'' = A', \quad \Delta C'' = C'.$

A simple calculation shows that the sum of the two principal curvatures at the point (r, α, ϕ) of this surface is

$$2a^{-1} + (\frac{2}{7}aA'' + 4a^{-1}C'') (3 \cos^2 \alpha - 1),$$

with an error of the second order in displacements, and the discontinuity in $\widehat{r\bar{r}}$ across $r = a$ is therefore approximately

$$2a^{-1}\gamma[1 + (\frac{1}{7}a^2A'' + 2C'')(3\cos^2\theta - 1)].$$

The following equations express this condition and the continuity of $\widehat{r\bar{r}}$, u and v at $r = a$:

$$p_0 = p'_0 - 2\gamma/a, \quad (24)$$

$$\eta\Delta(-\frac{1}{7}a^2A - 3a^{-3}B + 4C + 24a^{-5}D) = \frac{1}{7}(4a\gamma - a^2\eta'\Delta)A' + 4(2a^{-1}\gamma + \eta'\Delta)C', \quad (25)$$

$$\eta(\frac{8}{7}a^2A + \frac{3}{2}a^{-3}B + 6C - 24a^{-5}D) = \eta'(\frac{8}{7}a^2A' + 6C'), \quad (26)$$

$$\frac{1}{7}a^2A + \frac{1}{2}a^{-3}B + 2C - 3a^{-5}D = \frac{1}{7}a^2A' + 2C', \quad (27)$$

$$\frac{5}{14}a^2A + 3C + 3a^{-5}D = \frac{5}{14}a^2A' + 3C'. \quad (28)$$

The equations (23) to (28) are seven conditions on the sixteen unknowns, five similar equations express the continuity of $\widehat{r\bar{r}}$, $\widehat{r\bar{\theta}}$, u and v at $r = b$, and we may therefore impose four further conditions at $r = R$. We can, in fact, make all the components of stress and velocity at $r = R$ the same as those at the boundary of the homogeneous element (as given by (13) and (14)) with a proportional error of order $D^*/(C^*R^5)$, by putting

$$A^* = 0, \quad B^* = 0, \quad p_0^* = 0 \quad (29)$$

and

$$2\eta^*C^* = T. \quad (30)$$

Making use of (29), we can write the continuity conditions at $r = b$ as

$$p_0 = p_0^*, \quad (31)$$

$$\eta(-\frac{1}{7}b^2A - 3b^{-3}B + 4C + 24b^{-5}D) = \eta^*(4C^* + 24b^{-5}D^*), \quad (32)$$

$$\eta(\frac{8}{7}b^2A + \frac{3}{2}b^{-3}B + 6C - 24b^{-5}D) = \eta^*(6C^* - 24b^{-5}D^*), \quad (33)$$

$$\frac{1}{7}b^2A + \frac{1}{2}b^{-3}B + 2C - 3b^{-5}D = 2C^* - 3b^{-5}D^*, \quad (34)$$

$$\frac{5}{14}b^2A + 3C + 3b^{-5}D = 3C^* + 3b^{-5}D^*. \quad (35)$$

The equations (23) to (35) determine the operator η^* , and velocity and stress distributions in the composite element which do not depend on R explicitly. The conditions at $r = R$ in the homogeneous and composite elements can be made to differ by as small an amount as we please by choosing R sufficiently large. Hence the operator η^* defined by these equations can be identified with the generalized viscosity operator for the emulsion.

3. SOLUTION OF THE EQUATIONS FOR η^*

The form of the operator η^* can be deduced from the equations (25) to (28), (30) and (32) to (35). If all the symbols in these equations represented algebraic quantities, A, B, C, D, A', C', C^* and D^* would be determined as simple multiples of T , provided the determinant of the coefficients—a quadratic expression in η^* —vanished. Of the two possible values of η^* , one could be rejected on the grounds that η^* must tend to η as c tends to zero. Taylor's equation (1) can in fact be obtained in this way if (25) is first replaced by

$$\frac{1}{7}a^2A' + 2C' = 0,$$

the condition that $u = 0$ on $r = a$. When Δ occurs in the equations and η^* denotes an operator, the argument is not quite so straightforward.

In the general case, equations (27) and (28) give

$$a^{-3}B = 10(C' - C) + a^2(A' - A),$$

$$a^{-5}D = C' - C + \frac{5}{42}a^2(A' - A).$$

Substituting these expressions in (25) and (26) we have

$$[\frac{2}{7}a\gamma + \frac{1}{14}a^2(\eta - \eta')\Delta]A' + [4a^{-1}\gamma + (3\eta + 2\eta')\Delta]C' = 5\eta\Delta C,$$

$$\frac{1}{14}a^2(19\eta + 16\eta')A' + 3(3\eta + 2\eta')C' = \frac{5}{2}a^2\eta A + 15\eta C,$$

$$\text{and hence} \quad a^2\Gamma A' = 840\eta\gamma C + 35a^2\eta[4\gamma + a(3\eta + 2\eta')\Delta]A, \quad (36)$$

$$\Gamma C' = 5\eta[-12\gamma + a(16\eta + 19\eta')\Delta]C - \frac{5}{2}a^2\eta[4\gamma + a(\eta - \eta')\Delta]A, \quad (37)$$

$$a^{-3}\Gamma B = 20[-4(2\eta + 5\eta')\gamma + a(\eta - \eta')(16\eta + 19\eta')\Delta]C \\ + 2a^2[-20\eta'\gamma + a(\eta - \eta')(16\eta + 19\eta')\Delta]A, \quad (38)$$

$$a^{-5}\Gamma D = 2[-20\eta'\gamma + a(\eta - \eta')(16\eta + 19\eta')\Delta]C \\ + \frac{5}{21}a^2[4(2\eta - 5\eta')\gamma + a(\eta - \eta')(18\eta + 19\eta')\Delta]A, \quad (39)$$

$$\text{where} \quad \Gamma \equiv 40(\eta + \eta')\gamma + a(3\eta + 2\eta')(16\eta + 19\eta')\Delta.$$

Explicit expressions for C^* , D^* , η^*C^* and η^*D^* are given by simple linear combinations of equations (34) and (35), and of (32) and (33). Eliminating C^* and D^* we have

$$\eta^*(10C + b^{-3}B + b^2A) = \eta(10C - \frac{3}{2}b^{-3}B + b^2A) \quad (40)$$

$$\text{and} \quad \eta^*(b^{-3}B - 10b^{-5}D - \frac{4}{21}b^2A) = \eta(b^{-3}B - 10b^{-5}D + \frac{19}{84}b^2A). \quad (41)$$

If both sides of (40) and (41) are now operated upon† by Γ , and the expressions (38) and (39) are substituted for ΓB and ΓD , we have two differential equations relating A and C as functions of t . The form of η^* must be such as to make these equations equivalent.

The manipulation of the equations to this point has not involved any approximation. But the condition for η^* is of the form

$$Q\eta^{*2} + Q'\eta^* + Q'' = 0,$$

where Q , Q' , Q'' are quadratic expressions in Δ , such that it is not possible to obtain a closed expression for η^* . An approximate expression for η^* can be obtained by using the fact that $c (= a^3/b^3)$ is small, solving equations (38) to (41) formally by treating all symbols as if they were algebraic, and verifying the results when Δ has its operational significance. Rejecting an alternative solution in which η^*/η tends to -1.1875 as c tends to zero, we find that

$$\frac{\eta^*}{\eta} = \frac{40(\eta + \eta')\gamma + a(3\eta + 2\eta')(16\eta + 19\eta')\Delta \\ + 3c[4(2\eta + 5\eta')\gamma - a(\eta - \eta')(16\eta + 19\eta')\Delta]}{40(\eta + \eta')\gamma + a(3\eta + 2\eta')(16\eta + 19\eta')\Delta \\ - 2c[4(2\eta + 5\eta')\gamma - a(\eta - \eta')(16\eta + 19\eta')\Delta]}, \quad (42)$$

† I.e. after the symbolic equations have been written out in full, by making use of (7).

with an error of order c^3 . Approximate differential equations relating the variables A, B, C , etc., with T can readily be written down if required, by first noting that the relative magnitudes of the various quantities are given by

$$\left. \begin{aligned} A &= O(a^6 b^{-8} C), & B &= O(a^3 C), & D &= O(a^5 C), & A' &= O(a^{-2} C), \\ C' &= O(C), & C^* &= O(C), & D^* &= O(a^3 b^2 C). \end{aligned} \right\} \quad (43)$$

4. DISCUSSION

The expression (42) for η^* can be written in the form $\eta^* = \eta_0(1 + \lambda_2 \Delta)/(1 + \lambda_1 \Delta)$, i.e. the behaviour of a dilute emulsion at low rates of strain is governed by the equation (3), where

$$\eta_0 = \eta[1 + (\eta + \frac{5}{2}\eta')c/(\eta + \eta') + O(c^2)], \quad (44)$$

$$\lambda_1 = \frac{a(16\eta + 19\eta')}{40(\eta + \eta')\gamma} \left\{ 3\eta + 2\eta' + \frac{\eta(16\eta + 19\eta')c}{5(\eta + \eta')} + O(\eta c^2) \right\}, \quad (45)$$

$$\lambda_2 = \frac{a(16\eta + 19\eta')}{40(\eta + \eta')\gamma} \left\{ 3\eta + 2\eta' - \frac{3\eta(16\eta + 19\eta')c}{10(\eta + \eta')} + O(\eta c^2) \right\}. \quad (46)$$

The viscosity η_0 is seen to be independent of the interfacial tension, and has the value given for η^* by Taylor's formula (1).

It can be shown that no physical significance can be attached to the coefficients of c^2 in the expressions for η_0 , λ_1 and λ_2 derivable from (42), by considering a special case for which the values of the physical constants are already known. When γ is so large that the Δ terms in equation (25) can be omitted, the method gives

$$\eta^* = \eta[1 + (\eta + \frac{5}{2}\eta')c/(\eta + \eta') + \frac{2}{5}(\eta + \frac{5}{2}\eta')^2 c^2/(\eta + \eta')^2 + O(c^3)],$$

$$\text{which reduces to} \quad \eta^* = \eta[1 + \frac{5}{2}c + \frac{5}{2}c^2 + O(c^3)] \quad (47)$$

when η' is infinitely large. This formula differs from the known result for the viscosity of a suspension of rigid spheres, namely

$$\eta^* = \eta[1 + \frac{5}{2}c + 14 \cdot 1 c^2 + O(c^3)] \quad (48)$$

(Guth & Simha 1936; Gold 1937), from which it is concluded that the simplified perturbation method used in the present paper cannot be relied upon to give more than first-order terms in c .

The above method of analysis gives the same result as that of Fröhlich & Sack (1946), when the spheres of radius a are taken to be elastic solid spheres with a constant rigidity modulus μ . In that case, all the equations (25) to (42) are valid with γ replaced by zero, A' by $\Delta A''$, C' by $\Delta C''$ and $\eta'\Delta$ by μ . The argument requires only slight modification in order to avoid redundant factors in the equations,† and the resulting formula for η^* is

$$\eta^* = \frac{\eta[2\mu + 3\eta\Delta + 3c(\mu - \eta\Delta)]}{2\mu + 3\eta\Delta - 2c(\mu - \eta\Delta)} = \frac{\eta_0(1 + \lambda_2 \Delta)}{1 + \lambda_1 \Delta}, \quad (49)$$

† This ready adaptation of the method to a different problem draws attention to its flexibility. The same analysis defines a generalized viscosity operator η^* for a suspension whose continuous and disperse phases each have both viscous and elastic properties combined in a known way; it is only necessary to give η and η' the appropriate operational meanings in terms of Δ .

where

$$\eta_0 = \eta[1 + \frac{5}{2}c + O(c^2)], \quad \lambda_1 = \frac{3}{2}\eta[1 + \frac{5}{3}c + O(c^2)]/\mu, \quad \lambda_2 = \frac{3}{2}\eta[1 - \frac{5}{2}c + O(c^2)]/\mu. \quad (50)$$

These are recognized as Fröhlich & Sack's equations in a slightly different notation.

It is concluded that a dilute emulsion of one viscous liquid in another should possess elasticity of the same kind as a suspension of elastic solid particles in a viscous liquid; this is the type of elastic behaviour which has actually been observed in some dilute solutions of linear polymers (Oldroyd, Strawbridge & Toms 1951). The viscosity of an emulsion η_0 is in theory independent of the size of the drops, depending only on the volume concentration and on the viscosities of the components. The relaxation time λ_1 and the retardation time λ_2 will vary directly as the drop diameter and inversely as the interfacial tension between the two liquids, and also depend on η , η' and c .

A strictly quantitative experimental test of the formulae (44) to (46) may not be easy to achieve with present techniques because of the need for measuring, in an instrument such as that described by Oldroyd *et al.* (1951), a relaxation time and a retardation time so nearly equal that $(\lambda_1 - \lambda_2)/\lambda_1$ is of the order of c , i.e. of the order of 2 or 3 % under the conditions in which the theory might be expected to be accurate. No experimental results are yet available with which to compare the theoretical predictions.

5. THE EFFECT OF INTERFACIAL SLIPPING

In practice a small quantity of a suitable third component may be introduced into an emulsion in order to increase its stability by reducing the effective interfacial tension γ . Such a stabilizer will be present as a very thin film at the interfaces between L and L' , and it may be necessary to modify the continuity conditions in order to allow for an effective velocity of slip across an interface. The consequences of slipping can be estimated by assuming that a discontinuity in tangential velocity occurs, which is proportional to the shear stress across the surface (cf. Burgers 1948). (Such a proportionality would occur, for example, if the apparent slip were due to a thin lubricating layer of constant viscosity and thickness.)

The condition

$$\widehat{r\theta} = \kappa(v_L - v_{L'}) \quad (51)$$

on $r = a$; where κ is a constant frictional coefficient, requires that equation (28) be replaced by

$$\frac{5}{14}a^2A + 3C + 3a^{-5}D = (\frac{5}{14}a^2 + \frac{8}{7}a\eta'/\kappa)A' + [3 + 6\eta'/(a\kappa)]C'. \quad (52)$$

The remainder of equations (23) to (35) remain unchanged, and the arguments of §3 yield the result

$$\eta^* = \eta(\Gamma' + 3c\Gamma'')/(\Gamma' - 2c\Gamma''), \quad (53)$$

where

$$\Gamma' \equiv 40[\eta + \eta' + 5\eta\eta'/(a\kappa)]\gamma + [a(3\eta + 2\eta')(16\eta + 19\eta') + 10\eta\eta'(24\eta + 19\eta')/\kappa]\Delta$$

and

$$\Gamma'' \equiv 4[2\eta + 5\eta' + 10\eta\eta'/(a\kappa)]\gamma - [a(\eta - \eta')(16\eta + 19\eta') + 2\eta\eta'(40\eta - 19\eta')/\kappa]\Delta.$$

η^* is again of the form $\eta_0(1 + \lambda_2\Delta)/(1 + \lambda_1\Delta)$, with

$$\eta_0 = \eta \left\{ 1 + \frac{[\eta + \frac{5}{2}\eta' + 5\eta\eta'/(a\kappa)]c}{\eta + \eta' + 5\eta\eta'/(a\kappa)} + O(c^2) \right\}, \quad (54)$$

$$\lambda_1 = \frac{a(3\eta + 2\eta')(16\eta + 19\eta') + 10\eta\eta'(24\eta + 19\eta')/\kappa}{40[\eta + \eta' + 5\eta\eta'/(a\kappa)]\gamma} + \frac{a\eta[16\eta + 19\eta' + 80\eta\eta'/(a\kappa)]^2c}{200[\eta + \eta' + 5\eta\eta'/(a\kappa)]^2\gamma} + O(a\eta c^2/\gamma), \quad (55)$$

$$\lambda_2 = \frac{a(3\eta + 2\eta')(16\eta + 19\eta') + 10\eta\eta'(24\eta + 19\eta')/\kappa}{40[\eta + \eta' + 5\eta\eta'/(a\kappa)]\gamma} - \frac{3a\eta[16\eta + 19\eta' + 80\eta\eta'/(a\kappa)]^2c}{400[\eta + \eta' + 5\eta\eta'/(a\kappa)]^2\gamma} + O(a\eta c^2/\gamma). \quad (56)$$

It is possible therefore that the introduction of a stabilizer into an emulsion might not only reduce the value of γ , thereby increasing λ_1 and λ_2 in the same proportion, but also affect the values of η_0 , λ_1 and λ_2 independently in a rather complicated way. In principle it would suffice to measure η_0 , which is the limiting viscosity at low rates of shear in a suitably designed steady-state experiment, in order to ascertain whether a finite value of κ was appropriate in any particular case.

In the case of free slipping at the interfaces ($\kappa = 0$), a slightly different procedure is necessary for solving the equations, but the final result for η^* is that obtained by allowing κ to tend to zero in equation (53); hence

$$\left. \begin{aligned} \eta_0 &= \eta[1 + c + O(c^2)], \quad \lambda_1 = \frac{1}{20}a(24\eta + 19\eta')/\gamma + \frac{3}{25}a\eta c/\gamma + O(a\eta c^2/\gamma), \\ \lambda_2 &= \frac{1}{20}a(24\eta + 19\eta')/\gamma - \frac{4}{25}a\eta c/\gamma + O(a\eta c^2/\gamma). \end{aligned} \right\} \quad (57)$$

It is interesting that the value of η' in this case has no effect on η_0 , but is involved in the expressions for λ_1 and λ_2 . If η' is vanishingly small, the physical constants given by (57) agree with those for the case of finite or infinite κ with vanishingly small η' . In all these cases the value of η_0 agrees with the value obtained by Eizenschitz (1933) for the viscosity of a suspension of rigid spherical particles with free slipping at the boundary of each sphere.

An idealized suspension of elastic solid spheres, in which slipping occurs at the solid-liquid boundaries in accordance with (51), is found to have elastic properties of a more complex kind than any so far predicted. Making the same substitutions for γ , A' , C' and $\eta'\Delta$ which led to Fröhlich & Sack's equations (50), but with equation (52) in place of (28), we obtain by the same method

$$\frac{\eta^*}{\eta} = \frac{(2\mu + 3\eta\Delta)(19\mu + 16\eta\Delta) + 10\mu\eta(19\mu + 24\eta\Delta)/(a\kappa) + 3c[(\mu - \eta\Delta)(19\mu + 16\eta\Delta) + 2\mu\eta(19\mu - 40\eta\Delta)/(a\kappa)]}{(2\mu + 3\eta\Delta)(19\mu + 16\eta\Delta) + 10\mu\eta(19\mu + 24\eta\Delta)/(a\kappa) - 2c[(\mu - \eta\Delta)(19\mu + 16\eta\Delta) + 2\mu\eta(19\mu - 40\eta\Delta)/(a\kappa)]}. \quad (58)$$

This result corresponds to rheological behaviour represented by

$$(1 + \lambda_1 d/dt + \nu_1 d^2/dt^2)p'_{ik} = 2\eta_0(1 + \lambda_2 d/dt + \nu_2 d^2/dt^2)e_{ik}^{(1)}, \quad (59)$$

where

$$\eta_0 = \eta \left[1 + \frac{5}{2} (a\kappa + 2\eta) c / (a\kappa + 5\eta) + O(c^2) \right], \quad (60)$$

$$\lambda_1 = \frac{\eta}{38\mu} \left\{ \frac{89a\kappa + 240\eta}{a\kappa + 5\eta} + \frac{(95a^2\kappa^2 + 608a\kappa\eta + 1280\eta^2)c}{(a\kappa + 5\eta)^2} + O(c^2) \right\}, \quad (61)$$

$$\lambda_2 = \frac{\eta}{38\mu} \left\{ \frac{89a\kappa + 240\eta}{a\kappa + 5\eta} - \frac{3(95a^2\kappa^2 + 608a\kappa\eta + 1280\eta^2)c}{2(a\kappa + 5\eta)^2} + O(c^2) \right\}, \quad (62)$$

$$\nu_1 = \frac{24a\kappa\eta^2}{19(a\kappa + 5\eta)\mu^2} \left\{ 1 + \frac{(5a\kappa + 16\eta)c}{3(a\kappa + 5\eta)} + O(c^2) \right\}, \quad (63)$$

$$\nu_2 = \frac{24a\kappa\eta^2}{19(a\kappa + 5\eta)\mu^2} \left\{ 1 - \frac{(5a\kappa + 16\eta)c}{2(a\kappa + 5\eta)} + O(c^2) \right\}. \quad (64)$$

In the case of free slipping, the same formulae apply, ν_1 and ν_2 vanish, and the type of elasticity is the same as for a suspension with no slipping; η_0 , as given by (60), is then the same as the viscosity of a suspension of rigid spheres with free slipping (Einsenschitz 1933).

It is concluded that interfacial slip in a dilute emulsion should not affect the type of elastic behaviour, although it will affect the values of the rheological constants—quite considerably if a state of free slipping is approached. On the other hand, the presence of a thin lubricating layer at the solid-liquid interfaces in a suspension of elastic solid particles in a viscous liquid might be expected to cause an essentially more complicated type of macroscopic elastic behaviour, requiring additional physical constants to specify it.

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