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The constitutive equation for a dilute emulsion

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A constitutive equation for dilute emulsions is developed by considering the deformations, assumed infinitesimal, of a small droplet freely suspended in a time-dependent shearing flow. This equation is non-linear in the kinematic variables and gives rise to 'fluid memory' effects attributable to the droplet surface dynamics. Furthermore, it has the same form as the corresponding expression for a dilute suspension of Hookean elastic spheres (Goddard & Miller 1967), and reduces to a relation previously proposed by Schowalter, Chaffey & Brenner (1968) when time-dependent effects become small.

Numerical solutions are also presented for the case of a small bubble in a steady extensional flow for the purpose of estimating the range of validity of the small deformation analysis. It is shown that, unlike the drag of a bubble which, in creeping motion, is known to be relatively insensitive to its exact shape, the macroscopic stress field in an emulsion is not well described by the present analysis unless the shapes of the deformed bubbles agree closely with those given by the first-order theory. Thus, the present rheological equation should prove of value in a qualitative rather than a quantitative sense.

1. Introduction

During the past twenty years a great deal has been learned about the proper formulation of rheological equations of state. Of particular importance have been the contributions of Oldroyd (1950), Noll (1955), and of Truesdell & Toupin (1960), which have been discussed in *Handbuch der Physik*. As a consequence of this effort, a number of quite general and properly invariant constitutive equations have been developed such as those of Noll (1958) and of Ericksen (1959, 1960).

There are, however, several important disadvantages which arise in connexion with the application of existing non-linear continuum theories to actual flow problems. In the first place, the resulting constitutive equations contain numerous coefficients which, in general, cannot be measured with current experimental techniques. In addition, these coefficients, having been generated from a formal phenomenological approach, are usually devoid of any physical significance, and hence their dependence on the physical properties of the material is unknown. And finally, a dilemma is at once encountered when an attempt is made to accurately describe observations by retaining as much generality as possible in

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the existing theories, in that increased generality usually renders the problem unsolvable whereas too much simplification inevitably results in a poor description of the observed phenomena.

It would seem, therefore, that the purely mathematical approach to the formulation of constitutive equations should be supplemented by techniques which would result in simple, appropriate models for particular classes of materials. The object of this article is then to explore this possibility for one such class, consisting of a dilute suspension of droplets of an incompressible Newtonian liquid in another such liquid of different viscosity. The rheology of this system has previously been studied by Oldroyd (1953) and, more recently, by Schowalter, Chaffey & Brenner (1968), but neither of these investigations has treated with sufficient generality the time-varying shearing flows with which we shall be concerned here. The related problem of the rheology of a dilute suspension of solid-like, viscoelastic spheres has recently been the subject of articles by Goddard & Miller (1967), and by Roscoe (1967), following the earlier work of Cerf (1951) and of Fröhlich & Sack (1946).

The aim of the present analysis is to determine how the deformation of small spherical fluid droplets (or bubbles) affects the macroscopic stress field in a time, varying shearing flow. We begin by considering the motion of a single droplet in such a flow.

2. The motion of a single drop

As first noted by Einstein (1906), the hydrodynamic interactions among suspended particles can be neglected for sufficiently dilute suspensions since these lead to terms in the resulting constitutive equation of second order in the volume fraction ϕ. It suffices for our purposes, therefore, to consider the creeping motion of a freely suspended droplet in a uniform, time-dependent shearing flow field.

Let G be the magnitude of the shear flow, a the equivalent radius of the drop, μ^* its viscosity, μ_0 the viscosity of the external fluid and σ the interfacial tension. Then, non-dimensionalizing all velocities by Ga, all stresses within the drop by $G\mu^*$ and those in the external fluid by $G\mu_0$, all distances by a and the time by G^{-1}, we obtain, in the limit of negligible inertia effects, the following equations and boundary conditions relative to a set of axes that move with the centre of the drop:

equation of the surface: $r = 1+\epsilon f\left(\frac{x_1}{r}, \frac{x_2}{r}, \frac{x_3}{r}\right)$ where f is order unity, (2.1)

$$\frac{\partial^2 u_i}{\partial x_k^2} = \frac{\partial p}{\partial x_i}, \quad \frac{\partial u_k}{\partial x_k} = 0 \quad \text{for} \quad r > 1+\epsilon f, \tag{2.2}$$

$$\frac{\partial^2 u_i^*}{\partial x_k^2} = \frac{\partial p^*}{\partial x_i}, \quad \frac{\partial u_k^*}{\partial x_k} = 0 \quad \text{for} \quad 0 \leqslant r < 1+\epsilon f, \tag{2.3}$$

$$u_i \to e_{ij}x_j + \tfrac{1}{2}\epsilon_{ijk}\omega_j x_k \quad \text{as} \quad r \equiv (x_k^2)^{\frac{1}{2}} \to \infty, \tag{2.4}$$

$$u_i - u_i^* = 0, \quad u_j n_j = K\epsilon\, \partial f/\partial t \quad \text{at} \quad r = 1+\epsilon f, \tag{2.5}$$

$$(p_{ij}-\lambda p_{ij}^*)\,n_j = n_i k\left(\frac{1}{R_1}+\frac{1}{R_2}\right) \quad \text{at} \quad r = 1+\epsilon f, \tag{2.6}$$

where n_i is the outer unit normal to the surface, R_1 and R_2 are its principal radii of curvature, p_{ij} is the stress tensor, and

$$\lambda \equiv \mu^*/\mu_0, \quad k \equiv \sigma/\mu_0 Ga, \quad K^{-1} \equiv |\nabla(r-\epsilon f)|.$$

Also, the starred symbols refer to quantities within the drop and ω_i and e_{ij} denote, respectively, the vorticity and the rate of strain tensor of the undisturbed flow field. We shall suppose that ω_i and e_{ij} are functions of time, and that $e_{kk} = 0$ in view of the assumed incompressibility of the fluid.

The problem stated above is, of course, not new having been considered already for small drop deformation by Chaffey, Brenner & Mason (1965), by Chaffey & Brenner (1967) and by Cox (1969), among others. Here, we shall extend the results of these studies by taking into account more fully the time-dependent effects of the flow at infinity and by carrying out the expansion to a higher-order deformation of the drop. As shown by Frankel (1968), the same solution can also be arrived at by first considering a special form for e_{ij} and ω_i and then generalizing the resulting expressions using the techniques of tensor analysis. However, in our presentation we shall adopt, with certain important modifications, the method of Cox (1969) which has the advantage of being more straightforward and somewhat easier to follow than that chosen by Frankel (1968).

We suppose that ϵ, the parameter appearing in (2.1), the equation of the surface, is a small number. As shown by Cox (1969), ϵ is $O(k^{-1})$ if $k \gg 1$ and λ is $O(1)$, or $O(\lambda^{-1})$ if $k = O(1)$ and $\lambda \gg 1$. Then by expanding all the unknown functions, such as u_i, n_i, f, R_1, R_2, etc., in a power series in ϵ, we can construct, in the usual fashion, a regular perturbation solution to this problem.

We begin by considering the case $\epsilon \equiv k^{-1}$. The first term of the expansion, termed here the zeroth solution, can be obtained simply by assuming the drop to be spherical, solving (2.2)–(2.4) subject to the boundary conditions (2.5) and the tangential part of (2.6) evalued at $r = 1$, and then determining the deformation to first order in ϵ from the normal stress balance, i.e. the component of (2.6) along n_i. As shown by Frankel (1968) and by Cox (1969), this solution involves only the spherical harmonics of order *two*, $p_{-3}^{(0)}$, $\phi_{-3}^{(0)}$, $p_2^{(0)}$ and $\phi_2^{(0)}$. Here we let

$$\left.\begin{aligned} p_{-3}^{(0)} &= T_{lm}^{(0)}\frac{\partial^2 r^{-1}}{\partial x_l \partial x_m}, \quad \phi_{-3}^{(0)} = S_{lm}^{(0)}\frac{\partial^2 r^{-1}}{\partial x_l \partial x_m},\\ p_2^{(0)} &= T_{lm}^{(0)*}\, r^5\frac{\partial^2 r^{-1}}{\partial x_l \partial x_m}, \quad \phi_2^{(0)} = S_{lm}^{(0)*}\, r^5\frac{\partial^2 r^{-1}}{\partial x_l \partial x_m},\end{aligned}\right\} \tag{2.7}$$

where, following Cox (1969), we require that $T_{lm}^{(0)}$ be symmetric, and that $T_{ll}^{(0)} = 0$ since r^{-1} satisfies Laplace's equation. The remaining coefficients $S_{lm}^{(0)}$, $T_{lm}^{(0)*}$, and $S_{lm}^{(0)*}$ have similar properties. Further, to first order in ϵ, f is a surface spherical harmonic of order two, hence

$$f = F_{lm}^{(0)}\left(\frac{\partial^2 r^{-1}}{\partial x_l \partial x_m}\right)_{r=1}. \tag{2.8}$$

As shown by Frankel (1968),

$$T^{(0)}_{lm} = -\frac{10(\lambda-1)}{3(2\lambda+3)}e_{lm} - \frac{8}{2\lambda+3}F^{(0)}_{lm}, \quad T^{(0)*}_{lm} = \frac{84}{19\lambda+16}F^{(0)}_{lm} \tag{2.9a}$$

$$S^{(0)}_{lm} = -\frac{\lambda-1}{3(2\lambda+3)}e_{lm} - \frac{4(3\lambda+2)}{(2\lambda+3)(19\lambda+16)}F^{(0)}_{lm} \tag{2.9b}$$

$$S^{(0)*}_{lm} = \frac{5}{6(2\lambda+3)}e_{lm} - \frac{2(16\lambda+19)}{(2\lambda+3)(19\lambda+16)}F^{(0)}_{lm}, \tag{2.9c}$$

$$\epsilon\frac{\partial F^{(0)}_{lm}}{\partial t} = \frac{10(\lambda+1)}{(2\lambda+3)(19\lambda+16)}\left\{\frac{(19\lambda+16)}{6(\lambda+1)}e_{lm} - 4F^{(0)}_{lm}\right\}. \tag{2.9d}$$

These expressions are somewhat more general than those obtained by Cox (1969) in that they require only that $\epsilon F^{(0)}_{lm}$ be $O(\epsilon)$, whereas Cox imposed the additional restriction that $\epsilon\,\partial F^{(0)}_{lm}/\partial t$ also be $O(\epsilon)$. As a result, the coefficient of the bracketed term in his equation (5.25) agrees with that shown above in (2.9*d*) only when $\lambda \to \infty$. Also, it is worth noting that, by retaining the term $\partial f/\partial t$ of (2.5) in the zeroth-order solution, i.e. by treating $\epsilon\,\partial F^{(0)}_{lm}/\partial t$ as $O(1)$, it was found possible to arrive at (2.9) in a single step, in contrast to Cox's development in which two terms of the expansion were required, the second only partially, before his equation (5.25) could be obtained.

We now proceed to the first-order solution which involves only spherical harmonics of order *two* and *four* (Frankel 1968). The procedure is the same as that outlined above except that care has to be exercised in applying the boundary conditions at $r = 1+\epsilon f$. As shown by Cox (1969),

$$[u_i]_{r=1+\epsilon f} = \left[u^{(0)}_i + \epsilon f x_j \frac{\partial u^{(0)}_i}{\partial x_j} + \epsilon u^{(1)}_i\right]_{r=1} + O(\epsilon^2),$$

with similar expressions for the other variables. Also,

$$n_i = \frac{x_i}{r} - \epsilon\frac{\partial f^{(0)}}{\partial x_i} + O(\epsilon^2), \quad K = 1 + O(\epsilon^2),$$

while (Frankel 1968)

$$f = F^{(0)}_{lm}\left(\frac{\partial^2 r^{-1}}{\partial x_l \partial x_m}\right)_{r=1} + \epsilon\left\{-\tfrac{6}{5}F^{(0)}_{lm}F^{(0)}_{lm} + F^{(1)}_{lm}\frac{\partial^2 r^{-1}}{\partial x_l \partial x_m} + F^{(1)}_{lmpq}\frac{\partial^4 r^{-1}}{\partial x_l \partial x_m \partial x_p \partial x_q}\right\}_{r=1} + O(\epsilon^2), \tag{2.10}$$

where the constant term $-(6\epsilon/5)F^{(0)}_{lm}F^{(0)}_{lm}$ has been added to (2.10) because of the requirement that the volume of the drop be independent of ϵ. Consequently (Frankel 1968)

$$\frac{1}{R_1} + \frac{1}{R_2} = 2 + 4\epsilon F^{(0)}_{lm}\left(\frac{\partial^2 r^{-1}}{\partial x_l \partial x_m}\right)_{r=1} + \epsilon^2\left\{\tfrac{12}{5}F^{(0)}_{lm}F^{(0)}_{lm} + 4F^{(1)}_{lm}\frac{\partial^2 r^{-1}}{\partial x_l \partial x_m} + 18F^{(1)}_{lmpq}\frac{\partial^4 r^{-1}}{\partial x_l \partial x_m \partial x_p \partial x_q} - 10F^{(0)}_{lm}F^{(0)}_{pq}\left(\frac{\partial^2 r^{-1}}{\partial x_l \partial x_m}\right)\left(\frac{\partial^2 r^{-1}}{\partial x_p \partial x_q}\right)\right\}_{r=1} + O(\epsilon^3). \tag{2.11}$$

Using Lamb's general solution to the creeping-flow equations as given, for example, by Cox (1969), and applying the boundary conditions leads then to a set of algebraic equations for the coefficients of the harmonics. For example, the requirement that $u_i = u_i^*$ on the surface becomes:

$$3F^{(0)}_{lm}x_l x_m\{e_{ip}x_p + [60S^{(0)}_{pq} - 3T^{(0)}_{pq} + \tfrac{6}{7}T^{(0)*}_{pq}]\,x_p x_q x_i - [24S^{(0)}_{pi} + 6S^{(0)*}_{pi} + \tfrac{15}{7}T^{(0)*}_{pi}]\,x_p\}$$
$$+[-15S^{(1)}_{pq} + \tfrac{3}{2}T^{(1)}_{pq} + \tfrac{2}{7}T^{(1)*}_{pq}]\,x_p x_q x_i + [6S^{(1)}_{pi} - 6S^{(1)*}_{pi} - \tfrac{5}{7}T^{(1)*}_{pi}]\,x_p = 0, \quad (2.12)$$

aside from some terms arising from the fourth-order harmonics that appear in the expressions for $u_i^{(1)}$ and $u_i^{(1)*}$. Multiplying through by $x_j d\Omega$, where Ω is a solid angle, and integrating over the surface of a unit sphere then results in

$$T^{(1)}_{ij} - 10S^{(1)*}_{ij} - T^{(1)*}_{ij} = -\frac{60(\lambda-1)}{7(2\lambda+3)}\mathscr{S}d[F^{(0)}_{ip}e_{pj}] - \frac{720(\lambda-1)}{7(2\lambda+3)(19\lambda+16)}\mathscr{S}d[F^{(0)}_{ip}F^{(0)}_{pj}], \quad (2.13)$$

with use of the well-known orthogonality relations

$$\int x_i x_j d\Omega = \frac{4\pi}{3}\delta_{ij}, \quad \int x_i x_j x_p x_q d\Omega = \frac{4\pi}{15}(\delta_{ij}\delta_{pq} + \delta_{ip}\delta_{jq} + \delta_{iq}\delta_{jp}),$$
$$\int x_i x_j x_p x_q x_l x_m d\Omega = \frac{4\pi}{105}(\delta_{ij}\delta_{pq}\delta_{lm} + 14 \text{ other terms})$$

and the definition $\qquad \mathscr{S}d[b_{ij}] \equiv \tfrac{1}{2}[b_{ij} + b_{ji} - \tfrac{2}{3}\delta_{ij}b_{ll}].$

Likewise, multiplying through by $x_i x_s x_t d\Omega$ and integrating gives

$$T^{(1)}_{ij} - 6S^{(1)}_{ij} - 4S^{(1)*}_{ij} - \tfrac{2}{7}T^{(1)*}_{ij} = 0. \quad (2.14)$$

In a similar fashion, we obtain from the kinematic condition in (2.5),

$$\epsilon\frac{\partial F^{(1)}_{ij}}{\partial t} = -3S^{(1)}_{ij} + \tfrac{1}{2}T^{(1)}_{ij} - \frac{10}{7(2\lambda+3)}\mathscr{S}d[F^{(0)}_{ip}e_{pj}]$$
$$+\frac{48(11\lambda+14)}{7(2\lambda+3)(19\lambda+16)}\mathscr{S}d[F^{(0)}_{ip}F^{(0)}_{pj}] + \frac{\omega_s}{2}\{\epsilon_{pjs}F^{(0)}_{ip} + \epsilon_{pis}F^{(0)}_{jp}\}, \quad (2.15)$$

whereas, from the stress balance (2.6),

$$T^{(1)}_{ij} - 16S^{(1)}_{ij} - 4\lambda S^{(1)*}_{ij} - \tfrac{16}{21}\lambda T^{(1)*}_{ij}$$
$$= \frac{40(\lambda-1)}{7(2\lambda+3)}\mathscr{S}d[F^{(0)}_{ip}e_{pj}] + \frac{48(74\lambda^2+117\lambda-16)}{7(2\lambda+3)(19\lambda+16)}\mathscr{S}d[F^{(0)}_{ip}F^{(0)}_{pj}] \quad (2.16)$$

and

$$T^{(1)}_{ij} - 8S^{(1)}_{ij} + \tfrac{4}{3}\lambda S^{(1)*}_{ij} - \frac{\lambda}{21}T^{(1)*}_{ij}$$
$$= \frac{40(\lambda-1)}{7(2\lambda+3)}\mathscr{S}d[F^{(0)}_{ip}e_{pj}] + \frac{8(214\lambda^2+517\lambda+144)}{7(2\lambda+3)(19\lambda+16)}\mathscr{S}d[F^{(0)}_{ip}F^{(0)}_{pj}] - \tfrac{4}{3}F^{(1)}_{ij}. \quad (2.17)$$

On solving these algebraic equations we finally arrive at

$$\epsilon\frac{\partial F^{(1)}_{ij}}{\partial t} = -\frac{\omega_s}{2}\{\epsilon_{psi}F^{(0)}_{pj} + \epsilon_{psj}F^{(0)}_{pi}\} - \frac{40(\lambda+1)}{(2\lambda+3)(19\lambda+16)}F^{(1)}_{ij} + \frac{10(4\lambda-9)}{7(2\lambda+3)^2}\mathscr{S}d[F^{(0)}_{ip}e_{pj}]$$
$$+\frac{288(137\lambda^3+624\lambda^2+741\lambda+248)}{7(2\lambda+3)^2(19\lambda+16)^2}\mathscr{S}d[F^{(0)}_{ip}F^{(0)}_{pj}], \quad (2.18)$$

and

$$T^{(1)}_{ij} = -\frac{120(\lambda-1)^2}{7(2\lambda+3)^2}\mathscr{S}d[F^{(0)}_{ip}e_{pj}] - \frac{8}{2\lambda+3}F^{(1)}_{ij} + \frac{96(6-\lambda)}{7(2\lambda+3)^2}\mathscr{S}d[F^{(0)}_{ip}F^{(0)}_{pj}]. \quad (2.19)$$

Since, as will be seen below, the expression for the stress of a dilute suspension only involves T_{ij}, the corresponding formulae for the coefficients of the remaining spherical harmonics need not concern us here.

So far, we have restricted our attention to the case $\epsilon \equiv k^{-1}$. However, when k is $O(1)$ but $\lambda \gg 1$, a slightly different approach is indicated because, here, the drop remains almost spherical not by virtue of the large surface tension forces but rather on account of the large viscosity of the interior phase. Letting then $\epsilon \equiv \lambda^{-1}$, we proceed as before except that now we require that the zeroth solution satisfy, at $r = 1$, both the tangential and normal components of (2.6) and that the first-order deformation be determined from the kinematic condition of (2.5). This is so because, when $\lambda \to \infty$, the drop behaves essentially as a rotating solid sphere, so that, to a first approximation, the quantity $u_j n_j$ evaluated on its surface becomes $O(\lambda^{-1})$ which then balances the term $\epsilon \partial f/\partial t$. This procedure, which can be justified rigorously, yields the following results:

$$T^{(0)}_{ij} = -\tfrac{5}{3}e_{ij}, \quad \frac{\partial F^{(0)}_{ij}}{\partial t} + \frac{\omega_s}{2}(\epsilon_{psi}F^{(0)}_{pj} + \epsilon_{psj}F^{(0)}_{pi}) = \tfrac{5}{6}e_{ij}, \quad (2.20)$$

$$T^{(1)}_{ij} = -\tfrac{30}{7}\mathscr{S}d[F^{(0)}_{ip}e_{pj}] - 4kF^{(0)}_{ij}, \quad (2.21)$$

$$\frac{\partial F^{(1)}_{ij}}{\partial t} + \frac{\omega_s}{2}(\epsilon_{psi}F^{(1)}_{pj} + \epsilon_{psj}F^{(1)}_{pi}) = \tfrac{10}{7}\mathscr{S}d[F^{(0)}_{ip}e_{pj}] - \tfrac{20}{19}kF^{(0)}_{ij}. \quad (2.22)$$

Evidently, the above are very similar to the corresponding expressions for the case $\epsilon = k^{-1}$, but considerably simpler. Also, these simplify still further when $k \ll 1$. Note from (2.20) that, as already discussed by Cox (1969), no steady state solution exists to the small deformation analysis for the case $\lambda \gg 1$, $k \sim O(1)$, if the shear flow far from the drop is irrotational and $e_{ij} \neq 0$.

3. The constitutive equation

The development of the previous section will now be utilized to formulate a continuum theory for the rheology of dilute emulsions. Wall effects and interactions among droplets will be neglected.

We consider a volume V_1 large enough to contain many drops, yet small enough so that its linear dimension $V_1^{\frac{1}{3}}$ is small compared with the distance over which the bulk properties of the emulsion, such as the stress and the rate of strain, change appreciably. As discussed by Hashin (1964), Roscoe (1967), Goddard & Miller (1967) and, in considerable detail, by Batchelor (1970), the appropriate definition for these bulk properties involves then a volume average of the corresponding local quantities within the space V_1. For example, the bulk velocity gradient tensor $\langle \partial u_i/\partial x_j \rangle$ becomes

$$\left\langle \frac{\partial u_i}{\partial x_j} \right\rangle \equiv \frac{1}{V_1}\int \frac{\partial u_i}{\partial x_j}\,dV. \quad (3.1)$$

A similar definition applies for the bulk rate of strain tensor $\langle e_{ij}\rangle$ and for the bulk stress $\langle p_{ij}\rangle$. Then, as already shown by, for example, Batchelor (1970), if the fluid external to the drops is Newtonian and inertia effects are neglected,

$$\mathscr{S}d[\langle p_{ij}\rangle - 2\mu_0\langle e_{ij}\rangle] = \frac{1}{V_1}\Sigma\int_{A_0} \mathscr{S}d[p_{ik}x_j n_k - 2\mu_0 u_i n_j]\,dA$$

$$= \frac{1}{V_1}\Sigma\int_{A_1} \mathscr{S}d[p_{ik}x_j n_k - 2\mu_0 u_i n_j]\,dA, \tag{3.2}$$

where A_0 is the surface of a drop, A_1 is an arbitrary surface enclosing a single drop, and the summation is over all the drops within V_1.

It is evident that the right-hand side of (3.2) represents the extra deviatoric stress resulting from the presence of the individual drops. For the case of non-interacting drops, it can be evaluated simply by choosing A_1 to be a sphere of large radius r, using the results of the previous section for a single drop, and then adding the contributions from all the drops contained within V_1. In this way, introducing the usual isotropic term $-p\delta_{ij}$ and reverting back to dimensional quantities, we arrive at

$$\langle p_{ij}\rangle = -p\delta_{ij} + 2\mu_0\{\langle e_{ij}\rangle - \tfrac{3}{2}\phi T_{ij}\}, \tag{3.3}$$

where ϕ denotes the volume fraction occupied by the drops in the emulsion.

Finally, to obtain T_{ij}, and thereby complete the derivation of the constitutive equation for the dilute emulsion, we refer to the dimensional form of (2.9*a*), (2.9*d*), (2.18) and (2.19) for the case $\epsilon = k^{-1}$, or of (2.20), (2.21) and (2.22) for the case $\epsilon = \lambda^{-1}$. Noting that the bulk rate of strain tensor, and e_{ij}, the tensor appearing in these expressions differ at most by $O(\phi)$, we easily deduce the following results, after replacing all time derivatives $\partial/\partial t$ by the substantial derivative $\partial/\partial t + u_k\partial/\partial x_k$ since we now revert to fixed co-ordinate axes.

Case 1. $k \gg 1$, $\epsilon = k^{-1}$, λ *arbitrary but not too large*

Let $$T_{ij} = T_{ij}^{(0)} + k^{-1}T_{ij}^{(1)} + \ldots, \quad F_{ij} = G(F_{ij}^{(0)} + k^{-1}F_{ij}^{(1)} + \ldots).$$

Then, dropping the brackets in (3.3) with the understanding that the tensors p_{ij} and e_{ij} will now refer to the corresponding bulk quantities, we find that

$$p_{ij} = -p\delta_{ij} + 2\mu_0 e_{ij} + \mu_0\phi\left\{\frac{10(\lambda-1)}{2\lambda+3}e_{ij} + \frac{24}{2\lambda+3}F_{ij} + \frac{360(\lambda-1)^2}{7(2\lambda+3)^2}\beta\mathscr{S}d[F_{ip}e_{pj}]\right.$$
$$\left. + \frac{288(\lambda-6)}{7(2\lambda+3)^2}\beta\mathscr{S}d[F_{ip}F_{pj}] + O(Gk^{-2})\right\}, \tag{3.4}$$

where F_{ij} satisfies the expression

$$F_{ij} + \frac{(2\lambda+3)(19\lambda+16)}{40(\lambda+1)}\beta\frac{\mathscr{D}F_{ij}}{\mathscr{D}t} = \frac{19\lambda+16}{24(\lambda+1)}e_{ij} + \frac{(4\lambda-9)(19\lambda+16)}{28(2\lambda+3)(\lambda+1)}\beta\mathscr{S}d[F_{ip}e_{pj}]$$
$$+ \frac{36(137\lambda^3+624\lambda^2+741\lambda+248)}{35(2\lambda+3)(19\lambda+16)(\lambda+1)}\beta\mathscr{S}d[F_{ip}F_{pj}] + O(Gk^{-2}), \tag{3.5}$$

and $\beta \equiv a\mu_0/\sigma = (kG)^{-1}$ is a parameter having the units of time. As is expected in such cases (Fredrickson 1964; Goddard & Miller 1967), the governing equation for F_{ij} involves the Jaumann derivative

$$\frac{\mathscr{D}F_{ij}}{\mathscr{D}t} \equiv \frac{\partial F_{ij}}{\partial t} + u_k \frac{\partial F_{ij}}{\partial x_k} + \frac{\omega_s}{2}[\epsilon_{ksi}F_{kj} + \epsilon_{ksj}F_{ki}],$$

which is seen to arise naturally from our development.

Case 2. $\lambda \gg 1$, $\epsilon = \lambda^{-1}$, k arbitrary but not too large

Let $\quad \epsilon = \lambda^{-1}, \quad T_{ij} = T_{ij}^{(0)} + \lambda^{-1}T_{ij}^{(1)} + \ldots, \quad F_{ij} = F_{ij}^{(0)} + \lambda^{-1}F_{ij}^{(1)} + \ldots.$

Then,

$$p_{ij} = -p\delta_{ij} + 2\mu_0 e_{ij} + \mu_0\phi \times \{5e_{ij} + 12(\beta\lambda)^{-1}F_{ij} + \tfrac{90}{7}\lambda^{-1}\mathscr{S}d[F_{ip}e_{pj}] + O(G\lambda^{-2})\}, \tag{3.6}$$

where

$$\tfrac{20}{19}(\beta\lambda)^{-1}F_{ij} + \frac{\mathscr{D}F_{ij}}{\mathscr{D}t} = \tfrac{5}{6}e_{ij} - \tfrac{10}{7}\lambda^{-1}\mathscr{S}d[F_{ip}e_{pj}] + O(G\lambda^{-2}). \tag{3.7}$$

These rheological equations, (3.4)–(3.7), summarize then the principal results of our analysis. They are identical in form to a constitutive equation recently derived by Goddard & Miller (1967) for a dilute suspension of Hookean elastic particles, and are also consistent with the findings of Oldroyd (1958) in that the relaxation time of the suspension, which is proportional to β or to $\beta\lambda$ according to whether case 1 or case 2 is being examined, is seen to increase sharply as the surface tension at the droplet interface approaches zero.

Of course, in their full generality, the constitutive equations presented above are difficult to handle. In some instances, they can be integrated using a calculus for the Jaumann derivative which has been discussed in some detail by Goddard & Miller (1966). However, for the most part, their usefulness appears to be limited to special cases. For example for steady or for weakly time-dependent flows, the term containing the Jaumann derivative in (3.5) is generally $O(Gk^{-1})$,† hence by successive substitutions,

$$F_{ij} = \frac{19\lambda+16}{24(\lambda+1)}\left\{e_{ij} - \frac{(2\lambda+3)(19\lambda+16)}{40(\lambda+1)}\beta\frac{\mathscr{D}e_{ij}}{\mathscr{D}t} + \frac{1202\lambda^3+3589\lambda^2+3191\lambda+768}{140(2\lambda+3)(\lambda+1)^2}\beta\mathscr{S}d[e_{pi}e_{pj}] + O(Gk^{-2})\right\}. \tag{3.8}$$

Therefore, (3.4) simplifies to

$$p_{ij} = -p\delta_{ij} + 2\mu_0\left\{1 + \frac{5\lambda+2}{2(\lambda+1)}\phi\right\}e_{ij} + \beta\mu_0\phi\left\{-\frac{1}{40}\left(\frac{19\lambda+16}{\lambda+1}\right)^2\frac{\mathscr{D}e_{ij}}{\mathscr{D}t} + \frac{3(19\lambda+16)(25\lambda^2+41\lambda+4)}{140(\lambda+1)^3}\mathscr{S}d[e_{ip}e_{pj}] + O(G^2k^{-1})\right\}, \tag{3.9}$$

which is identical to a relation deduced by Schowalter *et al.* (1968) from a steady-state hydrodynamical analysis.

† As emphasized in §2 following equations (2.9), the term $\beta\,\partial F_{ij}/\partial t$ could be $O(1)$ rather than $O(\epsilon)$ if the flow is unsteady.

The above can also be recast into a different form. For, if

$$\beta|e_{ip}e_{pj}| \ll |e_{ij}|, \tag{3.10}$$

then, operating on (3.9) with $(1+\Lambda \mathscr{D}/\mathscr{D}t)$, where

$$\Lambda = \frac{(2\lambda+3)(19\lambda+16)}{40(\lambda+1)}\beta, \tag{3.11}$$

we obtain, to the present order of approximation,

$$p_{ij}+\Lambda\frac{\mathscr{D}p_{ij}}{\mathscr{D}t} = -p\delta_{ij}+2\mu_0\left\{1+\frac{5\lambda+2}{2(\lambda+1)}\phi\right\}\left\{e_{ij}+\Lambda\frac{\mathscr{D}e_{ij}}{\mathscr{D}t}\right\}$$
$$+\beta\mu_0\phi\left\{-\frac{1}{40}\left(\frac{19\lambda+16}{\lambda+1}\right)^2\frac{\mathscr{D}e_{ij}}{\mathscr{D}t}\right.$$
$$\left.+\frac{3(19\lambda+16)(25\lambda^2+41\lambda+4)}{140(\lambda+1)^3}\mathscr{S}d[e_{ip}e_{pj}]+O(G^2k^{-1})\right\}. \tag{3.12}$$

Equation (3.12) represents also a particular case of a constitutive equation proposed by Oldroyd (1958) who showed that a fluid whose behaviour is precisely described by (3.12) has unequal normal stresses in a steady laminar shearing flow, and a shear dependent viscosity that decreases with increasing rates of shear. In addition, Oldroyd showed that such a fluid exhibits the positive Weissenberg effect (rising of the fluid surface at the inner cylinder) when confined between vertical cylinders with the inner one rotating and of sufficiently small diameter, and that its behaviour in a time-dependent flow is characterized by the relaxation time, Λ, which approaches infinity as the interfacial tension of the droplet interface approaches zero. This last result should not be taken at face value, however, because, evidently, the present analysis ceases to apply when the interfacial tension becomes small.

Another simplification results if the flow is irrotational and homogeneous, for then $\omega_i = 0$, and e_{ij}, and, therefore, F_{ij} is independent of position. Consequently, since the Jaumann derivative $\mathscr{D}/\mathscr{D}t$ reduces here to $\partial/\partial t$, (3.5) and (3.7) are amenable to solution. In particular, if we consider the case in which a sample of the emulsion, at rest when the time t equals zero, is suddenly subjected to a steady bulk straining motion, it is easy to see from (3.4) to (3.7) that the fluid will react to the sudden change in the flow conditions by setting up extra viscous stresses linear in e_{ij} which, however, will diminish with increasing time to be replaced by non-Newtonian stresses, quadratic in e_{ij}. The relaxation times for this process, which incidentally is consistent with observations on polymeric materials and other viscoelastic fluids, are Λ and $\frac{1}{2}\Lambda$, where Λ is given by (3.11).

The bulk elastic property of the emulsion is probably the most important feature of our constitutive equations (3.4)–(3.7). This is further borne out by the remarkable similarity, already briefly referred to earlier, between the present results and a constitutive equation derived by Goddard & Miller (1967) for a suspension of Hookean elastic particles, which has the same form as (3.4) and (3.5), and involves a characteristic time $\tau \equiv 3\mu_0/2K$ where K is the elastic modulus of the particles. In the present case, such elastic behaviour results of course from the presence of a finite interfacial tension σ which always acts so as to oppose any deformation of a drop from the spherical shape.

4. Numerical calculation of the drop shape in a steady pure straining motion

If now $\omega_i = 0$, and e_{ij} is chosen such that $e_{11} = e_{22} = -G$, $e_{33} = 2G$ with its remaining elements set equal to zero, then, in view of (3.9) which, in the present case, is identical with (3.4) and (3.5) to $O(k^{-2})$, the only non-zero elements of the bulk stress tensor p_{ij} become

$$p_{33}-p_{11} = p_{33}-p_{22} = 6G\mu_0\left\{1+\frac{5\lambda+2}{2(\lambda+1)}\phi + \frac{3(19\lambda+16)(25\lambda^2+41\lambda+4)}{280(\lambda+1)^3}\phi k^{-1} + \phi O(k^{-2})\right\}, \quad (4.1)$$

where, as before, $k \equiv \sigma/\mu_0 Ga$. In particular, if $\lambda = 0$ (corresponding to gas bubbles)

$$p_{33}-p_{11} = p_{33}-p_{22} = 6G\mu_0\{1+\phi[1+\tfrac{24}{35}k^{-1}+O(k^{-2})]\}. \quad (4.2)$$

The order k^{-2} term in (4.2) could be computed in principle by extending the perturbation analysis of §2 to $O(k^{-2})$; however, instead of proceeding in this fashion, we shall estimate the magnitude of this correction, and hence the expected region of validity of the constitutive equation (3.4) by solving numerically the boundary-value problem given by (2.1)–(2.6) for a bubble of steady shape, using the expression for e_{ij} given above. The numerical solution, which is not limited to small deformations of the bubble-fluid interface, was computed for successively large values of k^{-1} until, as discussed more fully below, the numerical scheme could no longer be applied. Since the findings of this study are of interest in their own right as well as for comparison with (4.2), the computational outline and results are presented below.

The analysis was performed in terms of the dimensionless variables of §2 and the dimensionless stream function ψ given by, in spherical co-ordinates,

$$u_r = \frac{1}{r^2}\frac{\partial\psi}{\partial\eta}, \quad u_\theta = \frac{1}{r(1-\eta^2)^{\frac{1}{2}}}\frac{\partial\psi}{\partial r}, \quad (4.3)$$

where η denotes $\cos\theta$. Also, use was made of expansions in terms of Legendre polynomials, $P_n(\eta)$, and their integrals, $Q_n(\eta)$, defined by

$$Q_n(\eta) \equiv \int_{-1}^{\eta} P_n(\xi)\,d\xi.$$

The droplet surface was denoted by $r = g(\eta)$, where the function $g(\eta)$ had to be determined numerically.

The general solution of the creeping-flow equation,

$$\left(\frac{\partial^2}{\partial r^2}+\frac{1-\eta^2}{r^2}\frac{\partial^2}{\partial\eta^2}\right)^2\psi = 0, \quad (4.4)$$

taking into account the symmetry of the flow and truncating the expansion after the $2m$-th term, is

$$\psi = 2r^3 Q_2(\eta) + \sum_{n=1}^{m} \{c_n r^{2-2n} + c_{n+m} r^{-2n}\} Q_{2n}(\eta) \tag{4.5}$$

and the corresponding expression for the pressure is

$$p = 2 \sum_{n=1}^{m} \frac{4n-1}{2n-1} c_n r^{-2n-1} P_{2n}(\eta). \tag{4.6}$$

The boundary conditions are as follows: the normal velocity condition is

$$\psi = 0 \quad \text{at} \quad r = g(\eta); \tag{4.7}$$

the continuity of tangential stress, at $r = g(\eta)$, is

$$(1-\eta^2)\frac{g'}{g}\{p_{rr} - p_{\theta\theta}\} + (1-\eta^2)^{\frac{1}{2}} p_{r\theta}\left\{(1-\eta^2)\left(\frac{g'}{g}\right)^2 - 1\right\} = 0; \tag{4.8}$$

and the normal stress balance becomes

$$\frac{2}{\int_0^1 g^3(\eta)\,d\eta} + \frac{g^2 p_{rr} + (1-\eta^2)(g')^2 p_{\theta\theta} + 2(1-\eta^2)^{\frac{1}{2}} g g' p_{r\theta}}{g^2 + (1-\eta^2)(g')^2} = k\left(\frac{1}{R_1} + \frac{1}{R_2}\right), \tag{4.9}$$

where the first term on the left results from the assumption of an ideal gas within the bubble. Furthermore, it can be shown that (Frankel 1968)

$$\frac{1}{R_1} + \frac{1}{R_2} = \frac{-\{[(1-\eta^2)g']' - 2g\}g + \eta(1-\eta)^2((g')^3/g) + 3(1-\eta^2)(g')^2}{\{g^2 + (1-\eta^2)(g')^2\}^{\frac{3}{2}}}. \tag{4.10}$$

The system (4.5) to (4.10) was solved using a method of moments with the Legendre polynomials $P_{2n}(\eta)$ as weight functions, together with an iterative successive substitutions routine for satisfying the normal stress balance. To initiate the iteration, a trial function $g^{(0)}(\eta)$ was chosen. Next, (4.7) and (4.8) with $r = g^{(0)}(\eta)$ were successively multiplied by P_{2k}, $1 \leqq k \leqq m$, and integrated with respect to η from 0 to 1. This resulted in a linear system of $2m$ algebraic equations. The solution vector of this system, the trial values $c_n^{(0)}$, was now substituted into (4.9) to produce a non-linear equation for the function $g^{(1)}(\eta)$, which was solved iteratively using the scheme

$$\{(1-\eta^2) g_{(i+1)}^{(1)\prime}\}' - 4 g_{(i+1)}^{(1)} = R(g_i^{(1)}, c_n^{(0)}), \tag{4.11}$$

where R denotes the right-hand side, a functional of $g_{(i)}^{(1)}$, and

$$g_{(0)}^{(1)} = g^{(0)}. \tag{4.12}$$

Convergence was usually attained in this manner within a few iterations, provided the trial function $g^{(0)}(\eta)$ was sufficiently close to $g^{(1)}(\eta)$. The entire plan was then repeated with $g^{(0)}$ replaced by $g^{(1)}$, and iterations were continued until the desired degree of convergence was obtained.

The results for $g(\eta)$ are shown in figure 1 for several values of k^{-1}. It will be noted that two distinct types of deformations are possible in the present flow field, with negative values of k^{-1} resulting in bubbles that are oblate or flattened at the poles, whereas positive values produce bubbles that are prolate or cigar-shaped. This, of course, is in qualitative accord with the first-order perturbation theory, except that the surfaces in figure 1 are not spheroids since first-order theory was found to hold only if $|k^{-1}| < 0{\cdot}02$.

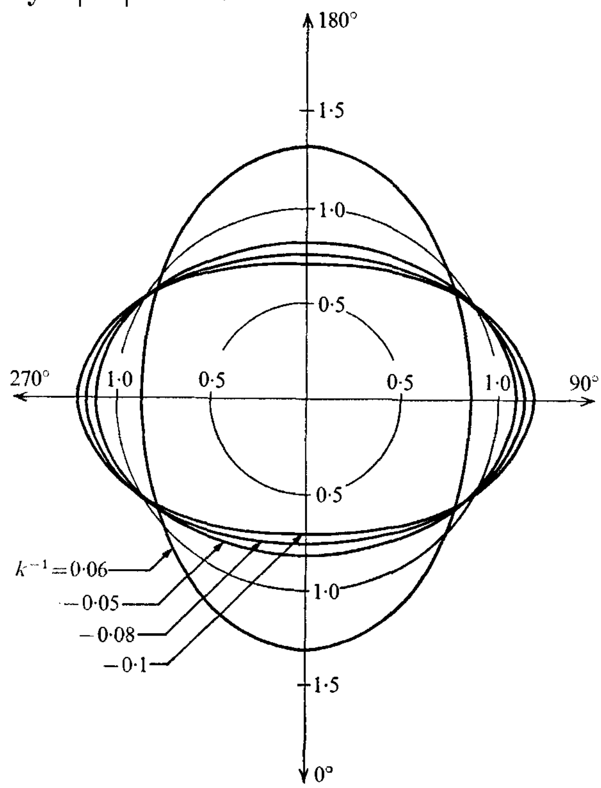

FIGURE 1. The surface of a bubble suspended in an extensional flow for various values of the dimensionless strain rate k^{-1}.

As a rule, the numerical scheme converged readily for moderate values of $|k^{-1}|$, but failed at certain critical values that depended on the sign of k^{-1}. Failure for negative k^{-1} was reached at $-0{\cdot}1$, even though, as shown in figure 1, an apparent equilibrium configuration could still be attained after several iterations. Further iterations, however, revealed that this configuration was not stable since deformation continued and in fact accelerated until the computations had to be terminated. On the other hand, the behaviour noted for positive k^{-1} was somewhat different in that it was found impossible to obtain an accurate representation for the stream function at $k^{-1} = 0{\cdot}08$ even with the largest system of polynomials considered, corresponding to $m = 15$ in (4.5). Thus, although large deformations were achieved for $k^{-1} > 0$, as shown in figure 1, the state of continuous deformation noted at $k^{-1} = -0{\cdot}1$ could not be observed.

It is noteworthy that the failure of the numerical procedure occurred at values of $|k^{-1}|$ reasonably close to that given by Taylor's (1932) approximate empirical criterion for droplet break-up which, in this case, would predict break-up at $|k^{-1}| = 0{\cdot}125$. Experimentally, bubbles and droplets composed of very low viscosity fluids are known to develop pointed ends in a hyperbolic flow (Taylor 1934) when

$$0{\cdot}26 < \frac{L-B}{L+B} < 0{\cdot}44, \tag{4.13}$$

with L and B representing the length and breadth of the deformed bubble, respectively, and when

$$0{\cdot}07 < |k^{-1}| < 0{\cdot}10. \tag{4.14}$$

The observed values of $(L-B)/(L+B)$ after several iterations at $k^{-1} = -0{\cdot}1$ was 0·26, and the corresponding value for the largest positive convergent k^{-1} ($k^{-1} = 0{\cdot}06$) was 0·21. The numerical findings are thus within the range of observed values.

k^{-1}	Numerical results	$-\frac{48}{35}k^{-1}$ (equation (4.16))
−0·005	0·006	0·007
−0·02	0·022	0·027
−0·05	0·039	0·069
−0·06	0·040	0·082
−0·08	0·037	0·110
+0·02	−0·032	−0·027
+0·06	−0·138	−0·082

TABLE 1. Values of c_1+2

These conclusions are of course tentative, since it is by no means certain that the lack of convergence of our numerical scheme should necessarily be attributed to drop break-up. Rather, the difficulties described above could result from other causes, for example, straightforward numerical instabilities, and/or the use of the series (4.5) and (4.6) which, although adequate for spheroidal shapes, become increasingly less desirable as representations of the solution when the bubble develops pointed ends, unless perhaps a prohibitive large number of terms are retained. This question, though, deserves further study.

The numerical results can finally be used to compute the stresses in a dilute suspension of bubbles in the present flow field, for, as can be shown from the definition of p_{ij}, equations (3.2) and (3.3), the only non-zero elements of the bulk dimensional stress are given by

$$p_{33}-p_{11} = p_{33}-p_{22} = 6G\mu_0[1-\tfrac{1}{2}c_1\phi]. \tag{4.15}$$

Hence, to the extent that the perturbation procedure of § 2 is valid, c_1 is given by, c.f. (4.2) and (4.15),

$$c_1 = -2(1+\tfrac{24}{35}k^{-1})+O(k^{-2}). \tag{4.16}$$

Comparison of c_1, as predicted by (4.16),† with that obtained from the numerical results is made in table 1 where the differences between the corresponding values in the second and the third column give some indication of the magnitude of the k^{-2} term in (4.16). This term appears to have a rather large coefficient. It will be noted that the perturbation procedure is unreliable for $|k^{-1}| > 0{\cdot}02$ where,

† Qualitative similar results are obtained if (3.4) and (3.5) are used in lieu of (3.9) to derive an analytical expression for c_1.

as mentioned earlier, the first-order theory also fails to accurately predict the shape of the deformed droplet.

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REFERENCES

BATCHELOR, G. K. 1970 The stress system in a suspension of force-free particles. *J. Fluid Mech.* **41**, 545–570.

CERF, R. 1951 Recherches théoriques et expérimentales sur l'effet Maxwell des solutions de macromolécules déformables. *J. Chim. Phys.* **48**, 59–84.

CHAFFEY, C. E. & BRENNER, H. 1967 A second-order theory for shear deformation of drops. *J. Colloid Int. Sci.* **24**, 258–269.

CHAFFEY, C. E., BRENNER, H. & MASON, S. G. 1965 Particle motions in sheared suspensions XVIII: Wall migration (theoretical). *Rheol. Acta*, **4**, 64–72; 1967 Corrections. *Rheol. Acta*, **6**, 100.

COX, R. G. 1969 The deformation of a drop in a general time-dependent fluid flow. *J. Fluid Mech.* **37**, 601.

EINSTEIN, A. 1906 Eine neue bestimmung der molekuldimensionen. *Annln. Phys.* **19**, 289–306; 1911 Corrections. *Annln. Phys.* **34**, 591–592.

ERICKSEN, J. L. 1959 Anistropic fluids. *Arch. Rat. Mech. Anal.* **4**, 231–237.

ERICKSEN, J. L. 1960 Transversely isotropic fluids. *Kolloid Z.* **173**, 117–122.

FRANKEL, N. A. 1968 Ph.D. Dissertation, Stanford University.

FREDRICKSON, A. G. 1964 *Principles and Applications of Rheology*. Englewood Cliffs, N.J.: Prentice-Hall.

FRÖHLICH, H. & SACK, R. 1946 Theory of the rheological properties of dispersions. *Proc. Roy. Soc.* A **185**, 415–430.

GODDARD, J. D. & MILLER, C. 1966 An inverse for the Jaumann derivative and some applications to the rheology of viscoeleastic fluids. *Rheol. Acta*, **5**, 177–184.

GODDARD, J. D. & MILLER, C. 1967 Nonlinear effects in the rheology of dilute suspensions. *J. Fluid Mech.* **28**, 657–673.

HASHIN, Z. 1964 Theory of mechanical behaviour of heterogeneous media. *Appl. Mech. Rev.* **17**, 1–9.

NOLL, W. 1955 On the continuity of the solid and fluid states. *J. rat. Mech. Analysis* **4**, 3–81.

NOLL, W. 1958 A mathematical theory of the mechanical behaviour of continuous media. *Arch. Rat. Mech. Anal.* **2**, 198–226.

OLDROYD, J. G. 1950 On the formulation of rheological equations of state. *Proc. Roy. Soc.* A **200**, 523–541.

OLDROYD, J. G. 1953 The elastic and viscous properties of emulsions and suspensions. *Proc. Roy. Soc.* A **218**, 122–132.

OLDROYD, J. G. 1958 Non-Newtonian effects in steady motion of some idealized elastico-viscous liquids. *Proc. Roy. Soc.* A **245**, 278–297.

ROSCOE, R. 1967 On the rheology of a suspension of viscoelastic spheres in a viscous liquid. *J. Fluid Mech.* **28**, 273–293.

SCHOWALTER, W. R., CHAFFEY, C. E. & BRENNER, H. 1968 Rheological behaviour of a dilute emulsion. *J. Colloid Int. Sci.* **26**, 152.

TAYLOR, G. I. 1932 The viscosity of a fluid containing small drops of another fluid. *Proc. Roy. Soc.* A **138**, 41–48.

TAYLOR, G. I. 1934 The formation of emulsions in definable fields of flow. *Proc. Roy. Soc.* A **146**, 501–523.

TRUESDELL, C. A. & TOUPIN, R. A. 1960 *Handbuch der Physik*, vol. 3, part 1, § 293. Berlin: Springer.