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Constitutive equations in suspension mechanics. Part 1. General formulation

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Neither the phenomenological nor the structural approach to the determination of constitutive equations has yet shown itself to be capable of producing useful and predictive descriptions of the majority of technologically important complex fluids. In the present paper we explore the suggestion that significant progress *can* be made when these two complementary approaches to rheology are combined. For this initial study we restrict our attention to materials which can be modelled as a suspension of particles in a Newtonian fluid, thereby including most polymer solutions while excluding polymer melts. By applying phenomenological techniques to the basic formulation of suspension mechanics we are able to deduce a common simplified constitutive model for all suspension-like materials and to reveal its physical origin. The present analysis demonstrates that the constitutive model of Hand (1962), involving a single second-order tensor, is not sufficiently general for a rigorous description of the majority of suspension-like materials. Consideration of the constitutive forms for the limiting cases of near-equilibrium and strongly non-equilibrium microstructure suggests, however, that Hand's model may provide a reasonable approximation to the exact constitutive behaviour which is useful over the whole range of flow strengths.

1. Introduction

The phenomenological approach to continuum mechanics has been reasonably successful except in the case of genuinely nonlinear fluids, for which it has not yet been able to provide a quantitative or even a fair qualitative description when extrapolating from one flow to another. Rather than such immediate rheological aims, strict phenomenology is more concerned with expressing explicitly the restrictions which result from a small number of plausible assumptions about invariance and causality. The trouble is that the restricted functionals which result are still excessively flexible, so that they cannot, at present, be quantified for a particular fluid by any reasonable experimental programme nor successfully applied in the theoretical solution of any but the simplest dynamical flow. The question thus arises as to whether or not it is possible to

impose further, new types of restrictions which will make the experimental and theoretical programmes practical while still allowing a tolerable approximate description of technologically interesting fluids. Such further restrictions cannot come from rational mechanics itself, but must derive from experience with the real world.

An alternative method for calculating constitutive equations is the structural approach, which is based upon a detailed analysis of the microstructure of a given material. In contrast to the phenomenology of rational mechanics, this structural approach is purely deductive and capable of giving useful insight into the relationships between the microstructure and measurable macroscopic properties of real materials. Unfortunately, however, the simplifying assumptions necessary to produce a tractable mathematical description of the microstructure all too often idealize the material beyond the range of technological interest. Thus the structural studies are but model studies and again usually fail to provide quantitative predictions for technologically important materials.

Although the phenomenological and structural approaches thus fail individually, we believe that significant progress can be made when these two complementary approaches to rheology are combined. Phenomenology can generalize the idealized structural calculations such that they may be useful outside the limits initially imposed for mathematical tractability. On the other hand, both the general form of and subsequent restrictions on the phenomenological functions can be usefully guided by the qualitatively correct, but idealized constitutive models of the structural approach. In particular, the structural models can hint at preferred forms of the constitutive equations, suggest which structural features have important macroscopic consequences, and provide a physical realization or mechanical analogue of the mathematical constitutive equations.

One example of a material whose rheological properties can be calculated using the deductive structural approach is a suspension of particles in a Newtonian fluid. We restrict our attention in this paper to such materials, thereby including most polymer solutions while excluding polymer melts. At the turn of the century Einstein calculated the increase in effective viscosity for a dilute suspension of rigid spheres. Various other simple suspensions have been analysed over the intervening years, including a dilute suspension of rigid spheroids with rotary Brownian motion (Hinch & Leal 1972), a dilute emulsion of nearly spherical drops (Frankel & Acrivos 1970), a dilute suspension of elastic and simple viscoelastic spheres (Roscoe 1967; Goddard & Miller 1967), a suspension of rigid spheres with significant hydrodynamic interactions (Batchelor & Green 1972). There are also extensive studies of dumb-bell, bead–rod and bead–spring models of macromolecules (see Bird, Warner & Evans 1971). Sufficient results for such simple suspensions are now available for a general pattern to begin to emerge. A first attempt to recognize this pattern was made by Barthès-Biesel & Acrivos (1973*a*), who recast many of the existing constitutive equations for suspensions into the form suggested by Hand (1962) involving an anisotropy described by a single second-order tensor. In the present paper, we take an approach fundamentally different (though comple-

mentary) from that of Barthès-Biesel & Acrivos in which we combine the standard phenomenological techniques with the basic formulation of suspension mechanics. By this means we are able to deduce a common constitutive form for all simple suspensions and to reveal its physical origin in detail. The present analysis demonstrates that the constitutive model of Hand (1962) is not sufficiently general for a rigorous description of the majority of simple suspensions. Analysis of the constitutive forms for the limiting cases of near equilibrium and strongly non-equilibrium microstructures suggests, however, that Hand's model *may* provide a reasonable approximation to the exact constitutive behaviour which is useful over the whole range of flow strengths. We do not intend the present paper to be a review of suspension or macromolecular-solution dynamics in any sense. Thus, though we have been influenced by many studies in addition to those cited above, the need to maintain reasonable brevity has simply not allowed us to cite systematically all possible examples of a particular behaviour in the text.

Our contention that significant progress towards tractable constitutive models of technologically significant materials can be made from the interplay between structural and phenomenological rheology is supported by the rather surprising fact that the idealized suspension models do exhibit *qualitatively* essentially all of the rheological phenomena which have been observed in laboratory investigations of complex fluids such as emulsions and especially macromolecular solutions. An example of the extent of the qualitative correctness of these models is provided by our recent study (Leal & Hinch 1972) of the response in a variety of common rheological flows of a dilute suspension of rigid nearly spherical particles affected by Brownian rotations.

2. Material structure

A characteristic of suspensions as well as many other non-Newtonian fluids is their heterogeneity on some small scale. Two (separate descriptions of the material may thus be distinguished: the macroscopic view, in which the fluid is considered as a complex but homogeneous continuum, and the microscopic view, in which the individual particles rotate, deform and interact with one another. The usefulness of this decomposition depends on the disparity in magnitude between the (large) length scale of variations in the homogeneous continuum and the (small) length scale of the particles. The large bulk-material length scale characterizes variations of the intrinsic properties due to spatial gradients in the constituents, as well as variations in the bulk flow. The microscopic length scale characterizes the size and shape of the particles as well as the particle spacing when interactions are considered. When there is a large difference between the two appropriate length scales, many particles are in a similar situation, so that one becomes representative of many. This simplifies the statistical averaging which connects the homogeneous continuum to the microscopic view. Volume averaging may be used, with an averaging volume chosen to be sufficiently large to contain many particles in a similar situation but sufficiently small that bulk variables are constant throughout it.

The first problem in the study of any particular complex suspension is to decide on the important features for a simplified model and to identify the relevant microscopic variables. This first step necessarily introduces variables of state quantifying the structure, which we shall denote by S. These variables do not describe all the details of the suspension at the microscopic particle level, only those relevant to the simplified model. Thus, for example, we do not retain the mass of information detailing the precise position of every particle. These ignored details are lost or smeared over by the statistical averaging used in the transition from the complex microscopic picture to the simple macroscopic picture.

The simplest structure needs as a state variable only a simple scalar, e.g. the volume of identical spherical gas bubbles in a dilute suspension. This may be extended to a mixture of several species with a finite number of volume variables. In the natural limit there can be a continuous spectrum of species, for which the structural state variable would be a function of a continuously varying parameter. This first class of materials is very special in that the structure has no directional dependence.

The simplest structure with a directional dependence is one where each state is described by a function of a single direction. This is adequate, for example, to specify the distortion of the surface of identical droplets in an emulsion or the orientation statistics of similar axisymmetric rigid particles. Generalization to a function of two (albeit orthogonal) directions is required for the orientation statistics of non-axisymmetric particles. A function of a continuum of directions is necessary to describe the variable relative position of the two beads in the elastic dumb-bell model of polymer solutions, and to describe the hydrodynamic interaction between a pair of rigid spheres, which is responsible for the first correction to Einstein's result due to non-diluteness.

The action of a bulk flow is to change the structure from its rest state. This flow-induced change is the origin of any non-Newtonian behaviour. Since the rest state in a realistic suspension represents a thermodynamic equilibrium of the whole material, the rest state is isotropic and a move away from it is always resisted by a restoring mechanism. Associated with each restoring mechanism will be a relaxation rate, which we denote by λ. The dimensions of λ involve only time because we concern ourselves only with fluids, which are rate materials. Specific examples are surface tension, tending to return a droplet to its equilibrium spherical shape, elasticity playing a similar role for deformable solid particles, and rotational and translational Brownian motions producing a uniform distribution of orientation and spatial position for rigid particles. Brownian motions are especially important because they are always present and will on their own ensure a return to an isotropic rest state. The deterministic nature of the flow-induced changes in the microstructure, coupled with the tendency to return to the rest state, gives the material a fading memory with a characteristic time scale λ^{-1}. The restoring force also enables the material to be nonlinear by providing an intrinsic measure, λ, with which to gauge the strength of the bulk flow and thus the degree of departure of the microstructure from its isotropic rest state.

Having identified appropriate variables S for description of the microstructure, it is next necessary to derive relationships between these and the relevant macroscopic variables. There are two groups of relations, corresponding to the microscopic and macroscopic views of the material. At the microscopic level, evolution equations which relate the development of the structure to the bulk flow and the restoring force are required. The most general form which is relevant for a Newtonian suspending fluid is

$$\dot{S} = \dot{S}\{S, \nabla\mathbf{U}; \lambda\}. \tag{1}$$

At the macroscopic level the volume averaging described earlier is used to obtain a relationship between the macroscopic observables such as the bulk stress, bulk flow and the material structure:

$$\boldsymbol{\sigma} = \boldsymbol{\sigma}\{S, \nabla\mathbf{U}; \lambda\}. \tag{2}$$

The two sets of functional relationships (1) and (2) together comprise the constitutive equations for a general suspension, and include both present values and the past history of S and $\nabla\mathbf{U}$. The rate-like nature of fluid suspensions allows us to write down an equation for the rate of change of the structure, and allows this and the bulk stress to depend on the rate of bulk deformation rather than the deformation itself. The case of several distinct restoring mechanisms does not need any notational extension: the structure S would then be a collection of labelled substructures with λ a label tensor.

The evolution functional (1) can be formally inverted to give the structure as a functional over time of the deformation rate and the initial structure state. In any real suspension possessing a fading memory with a characteristic span λ^{-1}, the dependence upon the initial state can be suppressed by taking the initial moment sufficiently far back in time (i.e. $t - t_{\text{initial}} \gg \lambda^{-1}$) and setting the initial state to be the rest state. If the structure functional were then formally substituted into the relation (2) for the bulk stress, the result would be a grand functional relationship between the stress and the bulk deformation rate alone. A material whose constitutive relation can be expressed in this form is a simple fluid provided that the rest state is isotropic. Hence our argument demonstrates that *real* suspensions, and more generally real structured fluids, are simple fluids. This conclusion was also effectively reached by Barthès-Biesel & Acrivos (1973*a*).

The general policy of eliminating the structure from the constitutive relations by the inversion of (1) may, however, have disastrous consequences as we now explain, and is not recommended unless the algebra is trivial. Typically the functionals involved are too complex for anything more than the formal notion of an elimination, and one must still seek a simple approximation to the final functional if the constitutive relation is either to be quantified by experiments or to be used in the solution of useful boundary-value problems. With the structure suppressed in blind mathematics, one's understanding of it is wasted and the way is open to ill-behaved approximations when constructing these simpler forms. Direct approximation to the physically based functionals (1)

and (2) will generally be more economical and contain fewer undesirable features. A specific example illustrating the difficulties in eliminating the microstructure will be considered in the next section after (1) and (2) have been reduced to a more specific form for simple suspensions and solutions.

3. Linearity and instantaneity

Little useful progress has been made by diagnosing the form of the constitutive equations as (1) and (2). These are in fact more complicated than those of a simple fluid for they contain no explicit restriction to fading memories with isotropic rest states as would be the case for realistic suspensions. We now apply the major restrictions employed in most model calculations and appropriate to technological situations, which will significantly reduce the complexity of the general form.

Typically the suspended particles are small (especially true for macromolecules), the Newtonian solvent is viscous and the microscale flow is slow in the sense that the Reynolds number based on the microscopic scale is very small. The vorticity in the flow around each particle therefore diffuses very efficiently, much faster than on the time scale for either the bulk deformation or relaxation of the microstructure. Under such conditions the particle dynamics and its disturbance flow are inertialess.† A restriction to inertialess microstructure dynamics does not imply that the homogeneous bulk continuum is also inertialess; the appropriate Reynolds number for the latter is an order of magnitude larger through the difference between the microscopic and macroscopic length scales.

The flow of a typical suspension at the microscopic level is thus governed by the Stokes equations. Given the configuration of the particles (i.e. the present structural state) the boundary-value problem for the microscale velocity field is thus linear in the applied forces, i.e. in the bulk flow and the restoring force. As a consequence of this linearity of the microscale flow, any quantities linearly derived from the flow will also be linear. In particular the bulk stress and the rate of change of the structure as represented in (1) and (2) will be linear in the bulk flow and the restoring mechanism. As well as being linear, the Stokes equations are also quasi-time independent. They carry no explicit knowledge of past events; only the present, instantaneous configuration of the particles is relevant to the instantaneous flow. The major restrictions of linearity and instantaneity which derive from the neglect of micro-inertia reduce the general constitutive equations (1) and (2) to the much simpler form

$$\dot{S} = \hat{\boldsymbol{\alpha}}(S) : \nabla \mathbf{U} - \beta(S)\lambda, \quad \boldsymbol{\sigma} = \mathbf{a}(S) : \mathbf{E} + \mathbf{b}(S)\lambda, \qquad (3a), (4)$$

† When micro-inertia must be taken into account, the mathematical problems become severe. There have been two model suspension calculations which have included inertia to some extent. Lin, Peery & Schowalter (1970) investigated the first effects of inertia on a steady shear flow of a dilute suspension of rigid spheres, by using an asymptotic expansion in a low Reynolds number. Hinch (1972*b*) looked at the simpler case of the effects of inertia on the high frequency response to weak flow of arbitrary type, using the linear time-dependent Stokes equations.

where $\mathbf{E}$ is the strain rate (the symmetric part of $\nabla\mathbf{U}$). The vorticity (the antisymmetric part of $\nabla\mathbf{U}$) has been eliminated from the right-hand side of (4) by appealing to material-frame objectivity. The minus sign in (3 *a*) is used to denote the restoring nature of that term. Only first-order time derivatives have been included in the microstructure evolution equation. This is sufficient for almost all suspensions with a low microscale Reynolds number, including the specific examples of rigid particles with Brownian motion (Leal & Hinch 1972), rigid spheres with particle–particle interactions (Batchelor & Green 1972), elastic particles (Roscoe 1967), fluid droplets with small but finite deformation (Frankel & Acrivos 1970) and polymer-solution models of the bead–spring or bead–rod type (Bird *et al.* 1971). The only case which may not be included (that we can think of) is a particle with arbitrary viscoelastic properties, which might require inclusion of higher-order time derivatives. We specifically exclude such particles for this reason, as well as the more persuasive reason that the introduction of a *phenomenological* viscoelastic description of the particles would totally defeat the philosophical foundations of the present work; the deduction of constitutive laws for a simple suspension from the proven laws of physics. Finally it may be noted that, in the absence of microinertia, appropriate characteristic scales for the translational and angular velocities of the particles are provided by the local velocity and vorticity of the bulk flow. Thus the natural time derivative for (3*a*) is the spin or generalized Jaumann derivative. Whether the particles actually translate or rotate with the bulk velocity or vorticity of course depends on the individual situation. For example buoyant particles will sediment out relative to the bulk flow. Similarly an irrotational component of the bulk motion (as exists in simple shear flow) acting on non-spherical particles, or a magnetic couple externally applied to the particles (cf. Hall & Busenberg 1969; Leal 1971), will cause rotation relative to the vorticity. In all cases, however, these departures from translation and rotation with the bulk flow can be retained in the first term on the right-hand side of (3*a*), so that $\dot{S}$ can be replaced without further approximation or assumptions by the natural spin derivative $\mathscr{D}/\mathscr{D}t$, taken to be advected with the bulk flow $\mathbf{U}$ and rotating with the vorticity $\boldsymbol{\Omega}$, i.e.

$$\mathscr{D}S/\mathscr{D}t = \boldsymbol{\alpha}(S)\colon \mathbf{E} - \beta(S)\,\lambda. \tag{3b}$$

The constitutive form (3*b*) and (4) is common to all simple suspensions and solutions.

There are strong restrictions on the general forms of the four material tensors $\boldsymbol{\alpha}$, β, $\mathbf{a}$, and $\mathbf{b}$ which result from the use of the Stokes equations for the microscale flow. These restrictions can be found by application of Lorentz's reciprocal theorem, which is associated with the Stokes equation. One example (Hinch 1972*a*) is that the fourth-order tensor $\mathbf{a}$ must be symmetric under interchange of its first pair of indices with its last pair.

While the constitutive equations (3) and (4) are both instantaneous and linear, the bulk stress itself will have a nonlinear and history-dependent relation to the bulk deformation rate. The elimination of S between (3*b*) and (4) to produce a single functional relationship between $\boldsymbol{\sigma}$ and $\nabla\mathbf{U}$, as discussed

in the preceding section, thus introduces unnecessary complexity into the form of the constitutive equations. Furthermore, by suppressing the structure, the ability to use one's physical understanding of the structure in constructing simpler limiting forms is lost, and the possibility of ill-behaved approximations is increased. The disadvantages of eliminating the structure variables S can be illustrated by a simple example. Consider the pair of constitutive equations involving a second-order tensor $\mathbf{A}$

$$\mathscr{D}\mathbf{A}/\mathscr{D}T + \lambda\mathbf{A} = \mathbf{E}, \quad \boldsymbol{\sigma} = \mu\lambda\mathbf{A}. \tag{5}$$

These occur naturally as physically motivated approximations to (3b) and (4) in some model suspensions (e.g. Leal & Hinch 1972). The single eliminated form has a retarded-motion expansion (a mathematical approximation for slow weak flows)

$$\boldsymbol{\sigma} = \mu \sum_{n=0}^{\infty} \left(-\frac{1}{\lambda}\frac{\mathscr{D}}{\mathscr{D}t}\right)^n \mathbf{E},$$

which gives a shear-rate-dependent viscosity for steady simple shear flow of the form

$$\mu(\gamma) = \mu[1 - \gamma^2/\lambda^2 + \gamma^4/\lambda^4 - \ldots]. \tag{6}$$

Clearly the 'blind' mathematical approximation of the eliminated form, equation (6), has a finite radius of convergence at $|\gamma| = \lambda$, which does not restrict either the original pair of equations (3b) and (4) or the physically based simplified approximate form, equations (5). The extra power of the structure approximation can be compared to the power of rational fractions over polynomials, the former being able to analytically continue the latter beyond non-physical boundaries in the representation. In the above example we can see that the structure equation takes the place of the simple denominator in the expression

$$\boldsymbol{\sigma} = \mu\lambda\mathbf{A} = \mu[1 + \lambda^{-1}\mathscr{D}/\mathscr{D}t]^{-1}\mathbf{E}.$$

Even if microscale variables are explicitly included, similar complexity in (3b) and (4) may result if the structural variables are inadvertently chosen as functionals of the natural or primitive underlying variables. The appropriate primitive variables depend strongly on the particular microphysics and it is difficult to give any general guidance to aid in their recognition.

Finally, in order to provide some concrete examples, we examine the general forms (3b) and (4) for the fluids described in the previous section with the simplest structure. The simplest non-directional structure depends on a single state variable S, e.g. the volume of identical gas bubbles in a dilute suspension. In this case (3) and (4) become

$$\mathscr{D}S/\mathscr{D}t = \alpha(S)\,\mathbf{I}:\mathbf{E} - \beta(S)\lambda,$$

$$\boldsymbol{\sigma} = a_1(S)\,\mathbf{E} + a_2(S)\,\mathbf{I}:\mathbf{E}\mathbf{I} + b(S)\lambda\,\mathbf{I},$$

with five scalar material functions of the single scalar variable S. Other terms must be excluded on grounds of invariance. Because the structure has no directional properties it is not affected by the vorticity or the anisotropic part

of the strain rate. Only the isotropic dilatation rate can move the structure away from its equilibrium. Similarly there are only two isotropic fourth-order tensors with the appropriate symmetry for **a**.

For the simplest directional structure, the state variable is a function of a single direction. We have previously noted suspensions of rigid spheroids as one example of a material to which this case is applicable. Let the direction be specified by a unit vector **p** so that the state variable is $S(\mathbf{p})$ defined over the unit sphere. The concrete forms of (3) and (4) in this case are

$$\mathscr{D}S/\mathscr{D}t \equiv DS/Dt + \mathbf{p}.\boldsymbol{\Omega}.\boldsymbol{\partial}S = \mathbf{I}:\mathbf{E}\alpha_1 + \mathbf{p}.\mathbf{E}.\mathbf{p}\alpha_2 + (\mathbf{p}.\mathbf{E}.\boldsymbol{\partial} + \boldsymbol{\partial}.\mathbf{E}.\mathbf{p})\,\alpha_3 + \mathbf{E}:\boldsymbol{\partial}\boldsymbol{\partial}\alpha_4 - \beta_1\lambda, \quad (7)$$

$$\boldsymbol{\sigma} = \bar{a}_1\mathbf{E} + \bar{a}_2\mathbf{I}:\mathbf{E}\mathbf{I} + \overline{a_3\mathbf{p}\mathbf{p}}.\mathbf{E} + \mathbf{E}.\overline{a_3\mathbf{p}\mathbf{p}} + \overline{a_4\mathbf{p}\mathbf{p}}:\mathbf{E}\mathbf{I} + \overline{a_5\mathbf{p}\mathbf{p}\mathbf{p}\mathbf{p}}:\mathbf{E} + \bar{b}_1\overline{\mathbf{p}\mathbf{p}}\lambda, \quad (8)$$

where $\boldsymbol{\partial}$ is the gradient operator in the directional **p** space and an overbar indicates integration over **p** space. For this fluid eleven scalar material instantaneous functionals are required, each of which yields a scalar function over **p** space for a given $S(\mathbf{p})$. Other terms in (7) and (8) must be excluded on the grounds of invariance.

4. Approximate forms for small departures from the equilibrium microstructure

The full descriptions for suspensions of the single-scalar type and of the single-direction-function type are complex and difficult to comprehend. In the present section we consider approximate forms for small departures from equilibrium, $S = 0$ say. The familiar linear viscoelastic and second-order-fluid approximations fall into this category, but require the additional restrictions of rheologically weak flow and slow weak flow respectively.

We begin with the simplest directional materials described by (7) and (8). The treatment can be immediately taken over to the simpler case of non-directional structures. To reduce the algebra we present only the case of incompressible structures. In this special case we may ignore, and will not display, the isotropic pressure in the stress and also the non-deviatoric parts of the structure.

The desired approximation is obtained from the lowest terms of a Taylor series expansion of the remaining eight functionals about the equilibrium $S(\mathbf{p}) \equiv 0$. When we evaluate the structural deforming terms α_2, α_3 and α_4 in this equilibrium state, we obtain three constant functions. Upon the operation of the derivatives in the **p** space the last two have no effect. Initially the structure function $S(\mathbf{p})$ is distorted by $(\mathbf{p}.\mathbf{E}.\mathbf{p})\alpha_2\{0\}$ into a small quadratic form

$$S(\mathbf{p}) = \mathbf{p}.\mathbf{A}.\mathbf{p} + \text{smaller terms}, \quad (9)$$

for some second-order tensor **A**. The spin and restoring terms do not produce any non-quadratic distortions of comparable magnitude from this initial **A**. Thus the lowest-order distortions of the simplest directional structures are described by a second-order tensor **A**. Many suspension studies (see Leal &

Hinch 1972; Frankel & Acrivos 1970; Goddard & Miller 1967) have led to a similar result. Indeed Barthès-Biesel & Acrivos (1973*a*) have recently emphasized the importance of Hand's (1962) constitutive model, which is based only on a second-order tensor anisotropy. However the number of suspension studies which have produced a second-order tensor description is greatly exaggerated compared with the actual importance of such materials, simply because the physical description in most model studies has been limited to some form of near-equilibrium expansion in order to simplify analysis of the microstructure.

In the lowest approximation described by (9) the constitutive equations (7) and (8) become

$$\mathscr{D}\mathbf{A}/\mathscr{D}t = \alpha_2 \mathbf{E} - \beta_1' \lambda \mathbf{A}, \quad \boldsymbol{\sigma} = a_1 \mathbf{E} + b_1' \lambda \mathbf{A}, \qquad (10), (11)$$

with the four constants α_2, β_1', a_1 and b_1' easily related to the respective functionals evaluated at the equilibrium state. For the two λ terms we have had to go to the second terms in the Taylor series because the leading terms vanish. The rest state is an equilibrium from which the restoring force produces no movement: $\beta_1\{0\} = 0$. The rest state is isotropic and so cannot support an anisotropic bulk stress: $\overline{b_1\{0\}\,\mathbf{pp}} = 0$.

If the flow is very weak, i.e. $\|\mathbf{E}\|$ is very much smaller than λ, then the solution of the approximate structure equation

$$\mathbf{A} = \int^t \alpha_2 \mathbf{E}(\tau) \exp[-\beta_1' \lambda (t-\tau)]\, \mathscr{D}\tau$$

remains sufficiently small to approximate the exact solution of (7). Thus we have the linear viscoelastic form of the constitutive equation

$$\boldsymbol{\sigma} = a_1 \mathbf{E} + b_1' \lambda \int^t \alpha_2 \mathbf{E}(\tau) \exp[-\beta_1' \lambda (t-\tau)]\, \mathscr{D}\tau.$$

The simplest directional suspension has an exponentially fading memory with only a single time constant $\beta_1'\lambda$. The more general directional structures with state variables which are functions of finitely many or a continuum of directions have respectively a finite number of time constants or a continuous spectrum. When the flow is in addition slowly varying, so that $\mathbf{E}$ is effectively constant during the time interval $1/\beta_1'\lambda$, the linear viscoelastic form reduces to the Newtonian approximation

$$\boldsymbol{\sigma} = [a_1 + b_1' \alpha_2/\beta_1']\, \mathbf{E}.$$

In the last two expressions the first terms come from the unchanged equilibrium state, while the second terms come from the small but non-negligible change from the equilibrium. While $\mathbf{A}$ is small the terms $\beta_1'\lambda\mathbf{A}$ and $b_1'\lambda\mathbf{A}$ are not small because λ is large. In this way even the Newtonian approximation feels some change in structure.

The first nonlinear response of the simplest directional material enters at the next level of the expansion about the equilibrium state, which is obtained by retaining one further term in the Taylor series of each functional. When the functionals α_2, α_3 and α_4 are evaluated using the quadratic approximation to

$S(\mathbf{p})$ they force a new quartic distortion $\mathbf{B}\vdots\mathbf{pppp}$ in the structure function. The combination of quadratic and quartic forms

$$S(\mathbf{p}) = \mathbf{A}:\mathbf{pp} + \mathbf{B}\vdots\mathbf{pppp} + \text{smaller terms} \tag{12}$$

is a consistent second approximation.

When extending Taylor's (1932) calculation of droplet deformation, Frankel & Acrivos (1970) used such a combination. In two special model suspensions the quartic terms are not needed. Cerf (1951) noted that an elastic sphere is deformed only into an ellipsoid whatever the magnitude of the deformation. Introducing another small parameter, the near-sphericity of the rigid particles, Leal & Hinch (1972) found that the orientation distribution was always described by the quadratic form to the first non-trivial approximation in the near-sphericity. Nevertheless a single second-order tensor is not usually adequate to describe fully the microstructure.

Working at the consistent second approximation displayed by (12), the constitutive equations of the linear approximation become amended with small correction terms,

$$\mathscr{D}A/\mathscr{D}t = \alpha_2\,\mathbf{E} - \beta_1'\lambda\mathbf{A} + \{\alpha_3'(\mathbf{A}.\,\mathbf{E} + \mathbf{E}.\,\mathbf{A}) - \tfrac{1}{2}\beta_1''\lambda\mathbf{A}.\,\mathbf{A} - \bar{\beta}_1'\lambda\mathbf{B}:\mathbf{I}\}, \tag{13}$$

$$\boldsymbol{\sigma} = a_1\,\mathbf{E} + b_1'\lambda\mathbf{A} + \{(a_3' + a_5')\,(\mathbf{A}.\,\mathbf{E} + \mathbf{E}.\,\mathbf{A}) + \tfrac{1}{2}b_1''\lambda\mathbf{A}.\,\mathbf{A} + \bar{b}_1'\mathbf{B}:\mathbf{I}\}, \tag{14}$$

and supplemented with an equation for the quartic deformation,

$$\mathscr{D}\mathbf{B}/\mathscr{D}t = (\bar{\alpha}_2' + \bar{\alpha}_3')\,\mathbf{A}\,\mathbf{E} + \text{permutations}) \doteq -\beta_1'\lambda\mathbf{B}. \tag{15}$$

The numerous coefficients are constant scalars derived from the functionals evaluated in the equilibrium state, the overbars being used to denote different appropriate differentials. The permutations are over the indices and are necessary to produce a symmetric $\mathbf{B}$ as its definition in (12).

The truncated structural evolution equations (13) and (15) can be solved iteratively because $\mathbf{A}$ and $\mathbf{B}$ must be small for the expansion to be valid, and the solution substituted into the stress equation (14) in the same manner as the linear approximation. The details are too lengthy to present here. The result, however, is the familiar quadratic nonlinear viscoelastic approximation involving a double Jaumann integral over the product of the strain rate evaluated at different times and a fading-memory function. The quadratic memory function of two past times is simply a sum of products of the linear memory function, both for this simplest directional structure and generally.

The extension of the results (10), (11) and (13)–(15) of this section to suspensions of general structure with a microstate which is dependent on more than a single direction is straightforward with no surprises, although the algebra is excessively tedious.

The mechanical basis of the approximate equations (13)–(15) provided by the investigations into many particular suspensions† allows us to discuss further

† The elastic sphere of Goddard & Miller (1967) and Roscoe (1967) and the deformed droplets of Frankel & Acrivos (1970) provide the simplest mechanical picture, although Brownian motion may also be simply included using the familiar concept of the entropic spring.

some of the constant coefficients. In order that the bulk motion is dissipated when the structure is in the rest state, a_1 must be positive. In a real suspension the changes in structure away from the rest state are resisted by a restoring mechanism. This means that β_1' and $\bar{\bar{\beta}}_1'$ are positive, as we have suggested by the insertion of the minus sign. The signs of β_1'' and $\bar{\bar{\beta}}_1'$ depend on whether the particular restoring force is harder or softer than linear in the nonlinear regime. The signs of **A** and **B** are arbitrary. If we pick the sensible sign, however, in which the distorting **E** produces distortion of similar sign in **A**, then by definition α_2 is positive (and similarly for $\bar{\alpha}_2'+\bar{\alpha}_3'$). This choice makes b_1' and $\bar{b}_1'$ both positive, in order that the structure generates a bulk flow which moves the structure back towards the rest state. If the correct energy-based units are used for **A**, there are in fact two equalities, $\alpha_2 = b_1'$ and $\bar{\alpha}_2'+\bar{\alpha}_3' = \bar{b}_1'$, which come from Lorentz's reciprocal theorem. It is difficult to speculate on the signs of $a_3'+a_5'$ and the pair α_3' and b_1''. Barthès-Biesel & Acrivos (1973*a*) found, however, that $a_3'+a_5'$ was positive for each of the several model suspensions which they examined, while α_3' and b_1'' had both signs.

The positivity of a_1, b_1', α_2 and β_1' implies that, at the start of a flow where the linear viscoelastic approximation is adequate, the value of the viscosity changes from an initial rest value to a higher steady-flow value. Also the primary normal-stress difference $\sigma_{11}-\sigma_{22}$ must be positive in a shear flow $u_1 = \gamma x_2$. The secondary normal-stress difference $\sigma_{22}-\sigma_{33}$ has been found in all model suspension studies to be negative and smaller in magnitude than the primary difference. This result does not appear to follow immediately from any of the general restrictions of mechanical feasibility we have imposed already.

In our discussion of the natural time derivative for (3*a*) we chose the Jaumann generalized spin derivative. The α_3' term in the evolution equation for **A** can be interpreted as a time-derivative term, although we do not do so because α_3' varies between ± 1 for different suspensions. The limits on the magnitude of α_3' seem to be intimately connected with the sign of the second normal-stress difference and the prediction of a shear-thinning viscosity. We note here only that the Rouse–Zimm models of macromolecules which produce a viscosity independent of flow strength (cf. Ferry 1970) have an Oldroyd convective time derivative, corresponding to $\alpha_3' = 1$.

To go further than (11)–(15) in an expansion about the equilibrium state usually produces intolerable complexity. For a suspension of droplets, which is typical, Barthès-Biesel & Acrivos (1973*b*) found it necessary to resort to a computer for the algebraic manipulations in the theoretical analysis at the next level of approximation. At this level there are already too many coefficients to be reasonably determined experimentally for even the simplest directional structure. Instead of an asymptotic expansion about a single point, one must attempt to find a numerically adequate but simple approximation over an extended domain.

An example virtually in the form of (10) and (11) which has been studied extensively for a variety of flows of technological interest is the pair of constitutive equations (5) and (6) of Leal & Hinch (1972) for a dilute suspension of nearly spherical particles subject to Brownian rotations. This study of Leal &

Hinch (1972) shows that a constitutive model of the form (10) and (11) is capable of reproducing most, though not all, of the most commonly observed rheological behaviour for simple suspensions and polymeric solutions. A similar comprehensive study of the extended constitutive model given by (13)–(15) has not yet been carried out so far as we are aware, and it is difficult to anticipate the degree of improvement, in comparison with (10) and (11), which is inherent in the addition of a fourth-order tensor contribution in anisotropy.

5. A proposal for the strong-flow regime

The strong-flow regime far from the equilibrium rest state is more difficult. At present we can only speculate from our own limited experience on what might prove useful as a crude approximation. Clearly, however, the expansions about equilibrium which we have discussed in the preceding section cannot hope to provide a useful representation when the microstructure is far removed from its equilibrium state. We exclude from our present considerations any irreversible changes, such as droplet breakup or macromolecular fracture, which may occur in a suspension at strong enough strain rates. Thus we assume that a well-defined strong-flow regime exists.

Relatively few model suspension calculations have actually been carried out in the strong-flow limit ($\|\mathbf{E}\| \gg \lambda$). One interpretation of those studies which do exist is that the structure eventually becomes characterized by a single direction and a single scalar parameter. For example, deformable particles and macromolecules, which are highly distorted by most strong flows, become long thin objects which can essentially be described by their direction and length. In the case of rigid particles affected by Brownian couples, the particles virtually all align in a single direction under most strong flows. While such a simple-minded description of the strong-flow state by a single director $\mathbf{d}$ may not always be sufficient, our own experience to date indicates it might be appropriate as an approximation. When the structure is describable by a single director, the general constitutive equations (3*b*) and (4) for a suspension become the equations of Ericksen (1960):

$$\mathscr{D}\mathbf{d}/\mathscr{D}t = \alpha_1 \mathbf{E}.\mathbf{d} + \alpha_2 \mathbf{E}:\mathbf{ddd} - \lambda\beta_1\mathbf{d},$$

$$\boldsymbol{\sigma} = a_1 \mathbf{E} + a_2(\mathbf{E}.\mathbf{dd} + \mathbf{dd}.\mathbf{E}) + a_3 \mathbf{E}:\mathbf{dddd} + \lambda b_1 \mathbf{dd},$$

with seven scalar instantaneous functions of $|\mathbf{d}|$. Model suspension calculations provide some further insight into the relative importance of the seven terms. For deforming particles with $\mathbf{d}$ a non-dimensional measure of the extended length, it can be shown using low-Reynolds-number slender-body theory that

$$\alpha_1 = 1 - O(d^{-2}), \quad \alpha_2 = O(d^{-4}), \quad a_1 = O(1), \quad a_2 = O(d^{-2}), \quad a_3 = O(d^{-4}),$$
$$b_1 = O(\beta_1) \quad \text{as} \quad d \to \infty.$$

In a suspension of rigid particles affected by Brownian couples α_1 tends to a constant of modulus less than unity, $\alpha_2 \to -\alpha_1$, and for needle-like particles a_3 and b_1 are of a similar magnitude and dominate the first two stress terms.

Some examples of rheological effects which are inherent in the strong-flow limit, but not included in the near-equilibrium expansion, are the levelling of extensional viscosity in a steady straining motion to a constant value at large strain rates and the attainment of constant viscosity and normal-stress values in simple shear flow at large shear rates.

6. Discussion

We have noted that the weak-flow limit (simplest directional structure) is describable at the lowest level of approximation by a form of Hand's (1962) constitutive model, in which the microstructure is described completely by a single second-order tensor. In addition we have suggested in the previous section that the strong-flow limit may be modelled using the constitutive equations of Ericksen (1960), which are also included in Hand's model. It would thus appear possible that the suggestions for strong and weak flows could be pragmatically combined by using a linear and instantaneous form of Hand's equation to provide an interpolation between the two limits. We noted earlier that a more complex structure than a second-order tensor is generally required for an exact description of a suspension. Nevertheless, as a practical approximation, Hand's equation may be adequate since it is apparently capable of separately describing both the strong- and weak-flow limits. Our study of one case of Hand's equations, which was applicable to one model suspension (Leal & Hinch 1972), showed that all the common rheological phenomena could be simply represented by the model. Thus we have returned to the opinion that a certain version of Hand's constitutive equations should receive more application and more investigation. Though a similar view was also taken by Barthès-Biesel & Acrivos (1973*a*), their investigation was limited to several specific examples of the near-equilibrium state, and thus could neither reveal the physical origin of the common constitutive form suggested, nor provide any guidance for flow regimes corresponding to strongly non-equilibrium states.

In subsequent papers of this series, we shall explore our concluding ideas by demonstrating the feasibility of such simple interpolations between the strong- and weak-flow regimes for model suspensions where exact results are available for comparison.

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