Int. J. Multiphase Flow Vol. 7, No. 5, pp. 493–505, 1981
Printed in Great Britain.

0301-9322/81/050493-13$02.00/0
Pergamon/Elsevier

THE CONSTITUTIVE EQUATION OF A DILUTE SUSPENSION OF SPHERICAL MICROCAPSULES

D. BARTHES-BIESEL and V. CHHIM

Université de Technologie de Compiègne, BP 233, 60206 Compiègne, France

(*Received* 10 *July* 1980; *in revised form* 26 *November* 1980)

Abstract—This paper studies the rheological behavior of a dilute suspension of spherical microcapsules, i.e. spherical thin elastic membranes filled with an incompressible liquid. Previous results obtained for the motion of such capsules freely suspended in a simple shear flow are first extended to general linear shear flows. Then the stresslet term in the external flow is computed to order ϵ^2, where ϵ, assumed to be small with respect to unity, is the ratio of viscous to elastic forces acting on the particle. The resulting constitutive equation is of the viscoelastic type and is similar to the one obtained for liquid droplets. It predicts that the microcapsule suspension exhibits a shear dependent viscosity and normal stress effects. The exact dependency of these phenomena on the microscopic parameters of the suspension is explicitly provided by the model.

1. INTRODUCTION

The rheological behaviour of dilute suspensions of deformable particles has been extensively studied, in particular when the corpuscles are elastic solids, liquid droplets or flexible threads. There is however a class of particles which have seldom been considered: capsules. In our terminology a capsule (or a microcapsule if it is very small) consists of a thin elastic membrane enclosing a viscous liquid. Such particles are encountered in nature or in industrial processes. For example, depending on their properties, they can represent red blood cells, emulsion droplets stabilized by interfacial polymerization, artificial capsules such as those presently studied for energy storage or for retarded diffusion. Because of their particular structure, capsules suspended in the flow of a viscous fluid will deform, but their motion is very specific. Indeed, their internal medium behaves like that of a liquid droplet, whereas their elastic interface deforms as a solid. Consequently, the rheology of a suspension of microcapsules cannot be directly inferred from presently existing models of other types of suspensions (emulsions, elastic spheres, etc.).

This has been recognized by Brennen (1975) who computed the apparent shear viscosity of a suspension of spherical microcapsules as a function of concentration and for rheologically different interfaces: solid, liquid, viscous or plastic membranes. The most interesting result of this study, is the prediction of an increased viscosity with concentration which depends strongly on the properties of the capsules. However, recent experimental results obtained by Bredimas (1980) on dilute interfacially polymerized emulsions, show clearly that the suspension definitely exhibits a shear thinning viscosity which also depends strongly on the deformability of the capsules. Obviously such a phenomenon cannot be predicted by Brennen's model which is limited to spherical particles undergoing negligible shape alterations. Consequently, it is of interest to conceive a model which will link the bulk properties of a suspension of microcapsules to their microrheological parameters, and which will take into consideration their deformation due to viscous forces. In order to simplify the problem, only dilute suspensions will be considered, thus eliminating interaction effects between particles.

Following Batchelor's (1970) theory of suspensions, the first step consists in determining the motion of a capsule suspended in a viscous shear flow. In general such a problem is quite difficult to solve. Firstly, the position of the interface is unknown, thus making the problem very non-linear. Secondly, the deformations of the membrane are large in general and the corresponding non-linear theory must be introduced. Finally, a double formulation must be used: Eulerian for the fluid particles, Lagrangian for the solid material points. However, as shown by Barthes-Biesel (1980) the problem is amenable to solution in the particular case when

the capsule is initially spherical, the membrane purely elastic, both the internal liquid and the suspending fluid are Newtonian and incompressible, and when the deformations of the particles are moderate. Then a regular perturbation solution can be found where the small parameter, ϵ, is the ratio of viscous to elastic forces. Barthes-Biesel determined the deformation of the capsule up to $0(\epsilon^2)$, when the externally imposed flow is a linear simple shear. In the present paper, we consider a dilute suspension of such microcapsules and we show how the above results can be generalized to any linear shear flow. Then, the stresslet term contributing to the bulk stress of the suspension is computed to $0(\epsilon^2)$ included. The resulting constitutive equation predicts a non-Newtonian viscosity and normal stress effects.

2. FORMULATION OF THE PROBLEM

The complete formulation of the problem has been given by Barthes-Biesel (1980) (Ref. A thereafter). In this section we shall only recall the essential equations and the solution technique. The details can be found in Ref. A.

The suspending medium is an incompressible Newtonian fluid of viscosity μ. It is subjected to a bulk linear shear flow given by

$$\underline{v}^{\infty} = \underline{e} \cdot \underline{x} + \underline{\Omega} \cdot \underline{x}.$$

$\underline{e}$ and $\underline{\Omega}$ are respectively the strain rate and vorticity dyads. They are constant and have a characteristic magnitude G.

The suspended capsule is a sphere of radius r_0 in its undeformed state. It is filled with an incompressible Newtonian liquid of viscosity $\lambda\mu$. The membrane is thin of thickness h ($h/r_0 \ll 1$), its bending resistance is negligible, but the material has otherwise arbitrary elastic properties, defined by the strain energy function $W(I_1, I_2, I_3)$, and by a general elastic modulus E. All quantities are non dimensionalized, distances by r_0, time by G^{-1}, stresses in the fluids by μG, tensions in the membrane by Eh. Consequently the problem depends on three dimensionless parameters:

$$\lambda, \quad \epsilon = \frac{\mu G r_0}{Eh}, \quad \mathrm{Re} = \frac{\rho G r_0^2}{\mu}.$$

Assuming that the particle Reynolds number Re is very small, all inertia effects are neglected so that the fluid motions are described by the Stokes equations with respect to an Eulerian frame of reference ($\mathscr{E}$) moving with the center of mass of the particle (see figure 1).

$$\nabla^2 \underline{v} = \nabla p \qquad \underline{x} \in D,$$

$$\lambda \nabla^2 \underline{v}^* = \nabla p^* \qquad \underline{x} \in D^*,$$

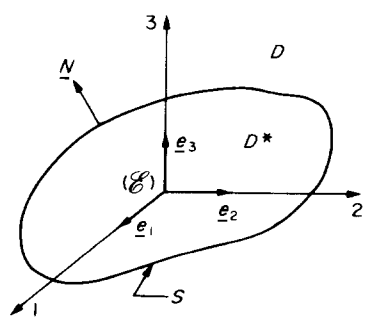

Figure. 1. Definition of the Eulerian frame ($\mathscr{E}$)

where D^*, D, S denote respectively the interior, the exterior and the boundary of the particle. The thickness of the membrane is neglected. The associated boundary conditions for the velocity are

$$\underline{v} \to (\underline{e} + \underline{\Omega}) \cdot \underline{x} \quad \text{as} \quad (\underline{x} \cdot \underline{x})^{1/2} \to \infty, \tag{2.1}$$

$$\underline{v} = \underline{v}^* = \underline{v}^m \quad \text{as} \quad \underline{x} \in S, \tag{2.2}$$

where $\underline{v}^m$ is the velocity of the membrane.

Finally, the membrane must be in dynamic equilibrium under the viscous load $\underline{q}$ due to fluid stresses.

$$\underline{q} = (\underline{\sigma} - \underline{\sigma}^*).\underline{N},$$

where $\underline{\sigma}$ and $\underline{\sigma}^*$ are the viscous stress dyads in the external and in the internal liquids, $\underline{N}$ is the unit outer normal vector to the deformed membrane.

This latter equilibrium condition balances the viscous forces with the elastic tensions in the membrane. The tensions are related to the local deformations, which can be expressed in terms of the displacement of material points, from which the deformed profile equation is obtained. The theory of large elastic deformations of membrane shells, as formulated by Green & Adkins (1960), is now summarized. Local curvilinear coordinates θ^1 and θ^2 are first defined and then used to label the different material points. Correspondingly the position of a point of the middle surface of the membrane is $\underline{a}\ (\theta^1, \theta^2)$ before deformation and $\underline{A}\ (\theta^1, \theta^2)$ after deformation. We adopt here the classical notation where Greek indices take the values 1 and 2, where summation on repeated indices is implicit and where $,\alpha$ denotes derivation with respect to θ^α. Then the metric tensors of the surface before and after deformation are given by:

$$a_{\alpha\beta} = \underline{a}_{,\alpha} \cdot \underline{a}_{,\beta}, \quad A_{\alpha\beta} = \underline{A}_{,\alpha} \cdot \underline{A}_{,\beta},$$

with contravariant components defined in the usual fashion.

The strain invariants for an incompressible material are defined by

$$I_1 = a^{\alpha\beta} A_{\alpha\beta} + k^2, \quad I_2 = a_{\alpha\beta} A^{\alpha\beta} + k^{-2}, \quad I_3 = 1,$$

where k is the thickness ratio between the deformed and undeformed states. The constitutive equation of the membrane material relates the tensions $\tau^{\alpha\beta}$ to the deformations. In its most general form this relationship reads as

$$\tau^{\alpha\beta} = k\{\Phi a^{\alpha\beta} + \Psi D^{\alpha\beta} - k^2[\Phi + \Psi(I_1 - k^2)]A^{\alpha\beta}\},$$

with

$$D^{\alpha\beta} = k^2 a^{\alpha\beta} + (a^{\delta\gamma} a^{\alpha\beta} - a^{\alpha\delta} a^{\beta\gamma}) A_{\gamma\delta}.$$

The material coefficients Φ and Ψ are obtained from the strain energy function W:

$$\Phi = 2\frac{\partial W}{\partial I_1}, \quad \Psi = 2\frac{\partial W}{\partial I_2}.$$

Finally the equilibrium of the membrane is written as

$$\tau^{\alpha\beta}{}_{,\alpha} + \Gamma^{\alpha}_{\alpha\gamma} \tau^{\gamma\beta} + \Gamma^{\beta}_{\alpha\gamma} \tau^{\alpha\gamma} + \epsilon \underline{q} \cdot \underline{A}_{,\beta} = 0,$$

$$\tau^{\alpha\beta} B_{\alpha\beta} + \epsilon \underline{q} \cdot \underline{N} = 0,$$

where $\Gamma^{\gamma}_{\alpha\beta}$, the Christoffel symbols of the deformed surface, and $B_{\alpha\beta}$, the second fundamental form, are given by

$$\Gamma^{\alpha}_{\gamma\beta} = \frac{1}{2} A^{\alpha\mu} (A_{\mu\beta,\gamma} + A_{\mu\gamma,\beta} - A_{\beta\gamma,\mu}),$$

$$B_{\alpha\beta} = \underline{N} \cdot \underline{A}_{,\alpha,\beta}.$$

Obviously, as such, these equations are not amenable in general to an analytical solution even when the initial geometry is spherical. However, in the case when ϵ is much smaller than unity, a regular perturbation solution can be found. As shown in Ref. A, the technique consists in expanding all quantities in terms of ϵ, and in solving the linearized equations by successive approximations.

In expanded form, the deformed position of membrane points, the equation of the surface, and the velocities can be written as

$$\underline{A} = \underline{a} + \epsilon \overset{(1)}{\underline{A}} + \epsilon^2 \overset{(2)}{\underline{A}} + 0(\epsilon^3),$$

$$r = 1 + \epsilon \overset{(1)}{f} + \epsilon^2 \overset{(2)}{f} + 0(\epsilon^3), \qquad [2.3]$$

$$\underline{v} = \overset{(0)}{\underline{v}} + \epsilon \overset{(1)}{\underline{v}} + \epsilon^2 \overset{(2)}{\underline{v}} + 0(\epsilon^3).$$

Furthermore, all quantities are evaluated on the initial sphere. Consequently, the continuity of velocity condition becomes:

$$\left[\overset{(0)}{\underline{v}}\right]_{r=1} + \epsilon \left[\overset{(1)}{\underline{v}} + \overset{(1)}{f} \frac{\partial \overset{(0)}{\underline{v}}}{\partial \underline{x}} \cdot \underline{x}\right]_{r=1} + \epsilon^2 \left[\overset{(2)}{\underline{v}} + \overset{(1)}{f} \frac{\partial \overset{(1)}{\underline{v}}}{\partial \underline{x}} \cdot \underline{x} + \overset{(2)}{f} \frac{\partial \overset{(0)}{\underline{v}}}{\partial \underline{x}} \cdot \underline{x}\right.$$

$$\left. + \frac{1}{2} \overset{(1)}{f}{}^2 \underline{x} \cdot \frac{\partial^2 \overset{(0)}{\underline{v}}}{\partial \underline{x}\, \partial \underline{x}} \cdot \underline{x}\right]_{r=1} = \left[\overset{(0)}{\underline{v}}{}^m + \epsilon \overset{(1)}{\underline{v}}{}^m + \epsilon^2 \overset{(2)}{\underline{v}}{}^m\right]_{r=1}, \qquad [2.4]$$

with a similar equation for $\underline{v}^*$.

For each iteration, the value of the membrane velocity is known. Consequently, the flow fields in D and D^* are uniquely determined from the velocity boundary conditions [2.1] and [2.2], and the load acting on the membrane follows readily.

Then the linearized membrane equations are solved for the new displacement vector. Owing to the Lagrangian formulation of the solid problem, the displacement is naturally expressed in terms of the coordinates of the material points before deformation occurs. It is obvious though, that this displacement consists of a solid body rotation (due to the vorticity of the flow) generating no deformation, and of pure strain due to the viscous load. Since the membrane is isotropic in the stress-free state, the solid body rotation of the points can be eliminated, and the displacement can be expressed in terms of the undeformed *Eulerian* coordinates, $\underline{y}$ in ($\mathscr{E}$), of the membrane points (see figure 2). The velocity of the membrane points is then obtained by superposing the displacement constant in space and the rotational motion. Then, if $\underline{x}$ represents the components of $\underline{A}$ in ($\mathscr{E}$)

$$\underline{x} = \underline{y} + \epsilon \overset{(1)}{\underline{A}}(\underline{y}) + \epsilon^2 \overset{(2)}{\underline{A}}(\underline{y}) + 0(\epsilon^3), \qquad [2.5]$$

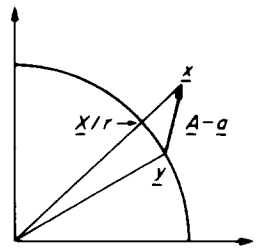

Figure 2. $\underline{y}$ is the Eulerian initial coordinate of a material point. After deformation, this point is a position $\underline{x}$ at time t. $r = \sqrt{(\underline{x} \cdot \underline{x})}$.

$$\frac{\mathrm{d}}{\mathrm{d}t}\underline{y} = \underline{\omega} \cdot \underline{y}, \tag{2.6}$$

$$\underline{v}^m(\underline{x}) = \underline{\omega} \cdot \underline{y} + \epsilon \frac{\mathrm{d}}{\mathrm{d}t}\overset{(1)}{\underline{A}}(\underline{y}) + \epsilon^2 \frac{\mathrm{d}}{\mathrm{d}t}\overset{(2)}{\underline{A}}(\underline{y}) + 0(\epsilon^3), \tag{2.7}$$

where $\underline{\omega}$ is the rotation rate of the membrane.

3. THE TWO FIRST ITERATIONS

A general solution of Stokes equations has been given by Lamb (1932) in terms of spherical harmonics. In particular, with respect to ($\mathscr{E}$), the velocity field in the external fluid can be written as:

$$\underline{v} = (\underline{e} + \underline{\Omega}) \cdot \underline{x} + \frac{6}{r^5}\underline{S} \cdot \underline{x} + \underline{x}^T \cdot \left(\frac{3}{2r^5}\underline{T} - \frac{15}{r^7}\underline{S}\right) \cdot \underline{x}\underline{x}$$

$$+ \frac{420}{r^9} \cdot \left(\underline{S}^{(iv)} - \frac{r^2}{28}\underline{T}^{(iv)}\right) \cdot (\underline{x}\underline{x}\underline{x}) - \frac{945}{r^{11}}\underline{x}^T \cdot \left(\underline{S}^{(iv)} - \frac{r^2}{18}\underline{T}^{(iv)}\right) \cdot (\underline{x}\underline{x}\underline{x})\underline{x} + \text{higher order terms}, \tag{3.1}$$

$$r^2 = \underline{x} \cdot \underline{x}, \quad \underline{x} \in D$$

where $\underline{T}$, $\underline{S}$, are symmetric, traceless second order tensors; $\underline{T}^{(iv)}$, $\underline{S}^{(iv)}$ are symmetric, traceless fourth order tensors.

The higher order terms have not been included since they do not enter the present problem. In fact, we are only interested in $\underline{T}$, the stresslet term, which alone contributes to the constitutive equation as was shown by Batchelor. But in order to compute $\underline{T}$ up to a given order in ϵ, the higher order tensors of all lower orders in ϵ must first be determined.

The 0(1) membrane velocity corresponds to a solid body rotation with the same vorticity as the undisturbed flow:

$$\overset{(0)}{\underline{v}}{}^m = \underline{\Omega} \cdot \underline{y}. \tag{3.2}$$

Using expression [3.1] for $\overset{(0)}{\underline{v}}$, boundary condition [2.4], and the fact that to this order of approximation $\underline{x} = \underline{y}$, yield the following expressions for the 0(1) spherical harmonics appearing in $\overset{(0)}{\underline{v}}$:

$$\overset{(0)}{\underline{T}} = -\frac{5}{3}\underline{e}, \quad \overset{(0)}{\underline{S}} = -\frac{1}{6}\underline{e}, \tag{3.3}$$

all other tensors being zero.

Since the membrane equations have all been linearized in the perturbation procedure, and since we are only seeking steady state solutions, it is obvious that the $0(\epsilon)$ displacement will depend linearly on $\underline{e}$. By analogy with the liquid droplet problem, we deduce that the first order displacement is given in general with respect to $(\mathscr{E})$ by:

$$\overset{(1)}{\underline{A}} = \underline{y}^T \cdot (\underline{J} - \underline{K}) \cdot \underline{yy} + \underline{K} \cdot \underline{y}, \qquad [3.4]$$

where $\underline{J}$ and $\underline{K}$ are both symmetric second order dyads depending only on $\underline{e}$. $\underline{J}$ specifies the radial displacement, and must be traceless to satisfy the incompressibility of the internal fluid. $\underline{K}$ measures the tangential displacement of material points, and can also be chosen traceless without any loss of generality. Consequently the equation of the deformed surface becomes:

$$r = 1 + \epsilon \underline{x}^T \cdot \underline{J} \cdot \underline{x} + 0(\epsilon^2),$$

$$\overset{(1)}{f} = \underline{x}^T \cdot \underline{J} \cdot \underline{x}.$$

The relationship between $\underline{x}$ and $\underline{y}$ is now

$$\frac{\underline{x}}{r} = \underline{y} + \epsilon(\underline{K} \cdot \underline{y} - \underline{y}^T \cdot \underline{K} \cdot \underline{yy}) + 0(\epsilon^2).$$

The dependence of $\underline{J}$ and $\underline{K}$ on $\underline{e}$ has been determined for the particular case of a simple shear flow in Ref. A where it is found that when $\underline{e}$ is given with respect to $(\mathscr{E})$ by

$$\underline{e}^{(ss)} = \begin{bmatrix} 0 & 1/2 & 0 \\ 1/2 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}, \qquad [3.5]$$

then

$$\underline{J}^{(ss)} = \frac{25}{2} \underline{e}^{(ss)} \text{ and } \underline{K}^{(ss)} = \frac{15}{2} \underline{e}^{(ss)}.$$

Consequently it follows from the previous remark on linearity that both $\underline{J}$ and $\underline{K}$ are given for any general linear shear flow by

$$\underline{J} = \frac{25}{2} \underline{e}, \quad \underline{K} = \frac{15}{2} \underline{e}.$$

In order to deal with the next iteration, the $0(\epsilon)$ membrane velocity must be obtained by superposing the displacement [3.4] with the rotational motion [3.2]. This has been done by Barthes-Biesel who found that

$$\underline{v}^m = [\underline{\Omega} \cdot \underline{x}]_{r=1} + \epsilon[\underline{x}^T \cdot \underline{J} \cdot \underline{x}\, \underline{\Omega} \cdot \underline{x} + 2\, \underline{x}^T \cdot (\underline{J} - \underline{K}) \cdot \underline{\Omega} \cdot \underline{xx}$$

$$- \underline{\Omega} \cdot \underline{K} \cdot \underline{x} + \underline{K} \cdot \underline{\Omega} \cdot \underline{x}]_{r=1} + 0(\epsilon^2). \qquad [3.6]$$

Substituting in [2.4], for $\overset{(1)}{\underline{v}}$ an expression similar to [3.1], and replacing $\underline{v}^m$ by [3.6], it is possible

to identify the coefficients of the spherical harmonics appearing in $\overset{(1)}{\underline{v}}$ (the technique to do so has been presented in detail by Frankel & Acrivos 1970). Thus:

$$\overset{(1)}{\underline{T}} = -\frac{125}{7} Sd\,(\underline{e}\cdot\underline{e}) + \frac{95}{3} Sd\,(\underline{e}\cdot\underline{\Omega}),$$

$$\overset{(1)}{\underline{S}} = -\frac{125}{42} Sd\,(\underline{e}\cdot\underline{e}) + \frac{5}{2} Sd\,(\underline{e}\cdot\underline{\Omega}), \qquad [3.7]$$

$$\overset{(1)}{\underline{T}}^{(iv)} = 14\,\overset{(1)}{\underline{S}}^{(iv)} = -\frac{25}{18} Sd_4\,(\underline{e}\underline{e}),$$

where the symbols Sd and Sd_4 represent respectively symmetric deviators of order two and four, defined in index notation as:

$$Sd(A_{ij}) = \frac{1}{2}(A_{ij} + A_{ji} - \frac{2}{3}\delta_{ij} A_{ll}),$$

and

$$Sd_4(A_{ijab}) = \frac{1}{8}\{A_{ijab} + A_{iabj} + 22 \text{ other terms}$$

$$-\frac{2}{7}[\delta_{ab}(A_{ijll} + A_{illj} + 10 \text{ other terms})$$

$$+ 5 \text{ other terms}]$$

$$+\frac{8}{35}(\delta_{ij}\delta_{ab} + \delta_{ia}\delta_{bj} + \delta_{ib}\delta_{ja})(A_{llmm} + A_{lmlm} + A_{lmml})\}.$$

The expression for the internal velocity field is obtained in a similar fashion. It then appears that the membrane rotation rate is not altered but remains characterized by $\underline{\Omega}$.

The corresponding general expression for the stress force exerted at point $\underline{x}$ by the inner and outer fluids on the membrane has been given in Ref. A, where it is shown to be equal to:

$$\underline{q} = 5\,\underline{e}\cdot\underline{y} + \frac{25}{2}\epsilon\left\{\frac{2}{25}p^* + \frac{3}{5}\underline{e}:\underline{e} + 2\,\underline{y}^T\cdot\left[Sd(\underline{e}\cdot\underline{e}) - \frac{19\lambda+16}{5} Sd(\underline{e}\cdot\underline{\Omega})\right]\cdot\underline{y}\right\}\underline{y}$$

$$+\frac{25}{2}\epsilon\left\{-\left[\frac{5}{7} Sd(\underline{e}\cdot\underline{e}) + 2\,Sd(\underline{e}\cdot\underline{\Omega})\right]\cdot\underline{y} + \frac{7}{3} Sd_4(\underline{e}\underline{e})\cdot(\underline{y}\underline{y}\underline{y})\right\} + 0(\epsilon^2).$$

The $0(\epsilon)$ term of this load is then used in the perturbed membrane deformation equations to obtain the new $0(\epsilon^2)$ displacement vector. The perturbation procedure linearizes the equilibrium deformation equations. The non-linearities appear as products of $0(\epsilon)$ quantities, which have been shown to depend on $\underline{e}$. Consequently, keeping in mind that the solid body rotation of the particle was eliminated previously, the Eulerian displacement of each point can only depend quadratically on $\underline{e}$ and $\underline{\Omega}$ while each term must include $\underline{e}$. Thus, in its most general form, the

displacement becomes

$$\begin{aligned}\overset{(2)}{\underline{A}} = \{&C_0\,\underline{e}:\underline{e} + \underline{y}^T\cdot[C_1\,Sd(\underline{e}\cdot\underline{\Omega}) + C_2\,Sd(\underline{e}\cdot\underline{e})]\cdot\underline{y}\\ &+ C_3\underline{y}^T\cdot Sd_4(\underline{e}\underline{e})\cdot(\underline{y}\underline{y}\underline{y})\}\underline{y}\\ &+ C_4 Sd(\underline{e}\cdot\underline{\Omega})\cdot\underline{y} + C_5 Sd(\underline{e}\cdot\underline{e})\cdot\underline{y} + C_6 Sd_4(\underline{e}\underline{e})\cdot(\underline{y}\underline{y}\underline{y}).\end{aligned} \tag{3.8}$$

For the case of a simple shear flow this displacement has been computed by Barthes-Biesel (1980). Expressed in ($\mathscr{E}$) its components become:

$$\begin{aligned}\overset{(2)}{A}{}^{(ss)}_{\alpha} = y_\alpha\frac{25}{4}\Big[&-\frac{5801}{840}-\frac{79}{60}\Psi'-(-1)^\alpha\frac{3}{20}(19\lambda+26)+y_3^2\left(\frac{29}{42}-\frac{3}{4}\Psi'\right)\\ &+(20+4\Psi')\,y_1^2\,y_2^2-\left(\frac{1}{6}+\frac{1}{4}\Psi'\right)[-3+3\,y_3^2+4\,y_\alpha^2)\\ &+\frac{19\lambda+24}{8}(y_1^2-y_2^2)\Big],\end{aligned} \tag{3.9a}$$

$$\overset{(2)}{A}{}^{(ss)}_{3} = \frac{25}{4}\left[-\frac{5941}{840}-\frac{47}{30}\Psi'+y_3^2\left(\frac{3293}{168}+\frac{7}{2}\Psi'\right)+\left(\frac{64}{3}+6\Psi'\right)y_1^2\,y_2^2+\frac{209\lambda+276}{40}(y_1^2-y_2^2)\right], \tag{3.9b}$$

where Ψ' measures the non linearity of the membrane material and is defined by

$$\Psi' = \frac{\Psi}{\Phi+\Psi}\cdot$$

By identification between [3.9a, b] and [3.8], evaluated for a simple shear flow [3.5], the coefficients C_i are uniquely determined as functions of λ and of the elastic properties of the membrane. It is found that

$$C_0 = \frac{265}{24},\quad C_1 = -\frac{25}{16}(19\lambda+24),\quad C_2 = -\frac{1500}{7}-\frac{625}{14}\Psi',$$

$$C_3 = \frac{125}{3}+\frac{25}{3}\Psi',\quad C_4 = -\frac{15}{8}(19\lambda+26),\quad C_5 = -\frac{11175}{56}-\frac{150}{7}\Psi',$$

$$C_6 = \frac{25}{9}+\frac{25}{6}\Psi'. \tag{3.10}$$

4. DETERMINATION OF THE $0(\epsilon^2)$ STRESSLET STRENGTH

The stresslet $\overset{(2)}{\underline{T}}$ is obtained from the $0(\epsilon^2)$ boundary condition [2.4], where $\overset{(2)}{\underline{v}}$ is given by [3.1]. The first step consists in computing the membrane velocity to $0(\epsilon^2)$, as indicated by [2.6] and [2.7]. Correspondingly $\underline{v}^m$ at position $\underline{x}$ in naturally expressed as a function of $\underline{y}$, the initial

coordinate of the material point

$$\begin{aligned} \underline{v}^m = {} & \underline{\Omega}\cdot\underline{y} + \epsilon\left[\underline{y}^T\cdot 5\underline{e}\cdot(2\,\underline{\Omega}\cdot\underline{yy} + \underline{y}\,\underline{\Omega}\cdot\underline{y}) + \frac{15}{2}\,\underline{e}\cdot\underline{\Omega}\cdot\underline{y}\right] \\ & + \epsilon^2\{\underline{y}^T\cdot[C_1 Sd(\underline{e}\cdot\underline{\Omega}) + C_2 Sd(\underline{e}\cdot\underline{e})]\cdot(2\underline{\Omega}\cdot\underline{yy} + \underline{y}\,\underline{\Omega}\cdot\underline{y}) \\ & + C_3\underline{y}^T\cdot Sd_4(\underline{ee})\cdot[(3\,\underline{\Omega}\cdot\underline{yyy})\underline{y} + (\underline{yyy})\,\underline{\Omega}\cdot\underline{y}] \\ & + C_4 Sd(\underline{e}\cdot\underline{\Omega})\cdot\underline{\Omega}\cdot\underline{y} + C_5\,Sd(\underline{e}\cdot\underline{e})\cdot\underline{\Omega}\cdot\underline{y} + 3\,C_6\,Sd_4(\underline{ee})\cdot(\underline{yy}\underline{\Omega}\cdot\underline{y})\} \\ & + 0(\epsilon^3). \end{aligned} \tag{4.1}$$

At this order, the rotation rate of the particle may be modified. This leads to a extra term in $\underline{v}^m$ of the type $\epsilon^2\,\overset{(2)}{\underline{\omega}}\cdot\underline{y}$, which has not been included in [4.1], for it does not affect the value of $\overset{(2)}{\underline{T}}$.

Since $\underline{v}^m$ is to be matched with the fluid velocity at $\underline{x}$, it must be expressed in terms of $\underline{x}/r$. The relation between $\underline{x}$ and $\underline{y}$, given by [2.5], [3.4], [3.8], can be inverted by successive approximations.

$$\begin{aligned} \underline{y} = {} & \frac{\underline{x}}{r} - \epsilon\frac{15}{2}\left[\underline{e}\cdot\frac{\underline{x}}{r} - \frac{\underline{x}^T}{r}\cdot\underline{e}\cdot\frac{\underline{xx}}{r^2}\right] \\ & + \epsilon^2\left\{\left(\frac{\underline{xx}^T}{r^2} - \underline{I}\right)\cdot\left[C_4\,Sd(\underline{e}\cdot\underline{\Omega})\cdot\frac{\underline{x}}{r} + C_5\,Sd(\underline{e}\cdot\underline{e})\cdot\frac{\underline{x}}{r} + C_6\,Sd_4(\underline{ee})\cdot\left(\frac{\underline{xxx}}{r^3}\right)\right]\right. \\ & \left. + \frac{75}{4}\left[3\,\underline{e}\cdot\underline{e}\cdot\frac{\underline{x}}{r} + \frac{5}{2r^5}(\underline{x}^T\cdot\underline{e}\cdot\underline{x})^2\underline{x} - \frac{1}{r^3}(\underline{x}^T\cdot\underline{e}\cdot\underline{x})\underline{e}\cdot\underline{x} - \frac{9}{2r^3}\,\underline{x}^T\cdot\underline{e}\cdot\underline{e}\cdot\underline{xx}\right]\right\}. \end{aligned} \tag{4.2}$$

Then, combining [4.1] and [4.2], we find the correct expression of $\underline{v}^m$ to be used in boundary condition [2.4]. There remains now to compute the $0(\epsilon^2)$ term of the fluid velocity. The equation of the deformed surface of the capsule must be first determined to $0(\epsilon^2)$, in order to calculate the value of $\overset{(2)}{f}$ appearing in [2.4]. Correspondingly:

$$\begin{aligned} r = (\underline{A}\cdot\underline{A})^{1/2} = {} & 1 + \epsilon\frac{25}{2}\frac{\underline{x}^T}{r}\cdot\underline{e}\cdot\frac{\underline{x}}{r} + \epsilon^2\left\{C_0\,\underline{e}:\underline{e} + \frac{\underline{x}^T}{r}\cdot[(C_1+C_4)\,Sd(\underline{e}\cdot\underline{\Omega}) + (C_2+C_5)\,Sd(\underline{e}\cdot\underline{e})]\cdot\frac{\underline{x}}{r}\right. \\ & \left. + (C_3+C_6)\frac{\underline{x}^T}{r}\cdot Sd_4(\underline{ee})\cdot\left(\frac{\underline{xxx}}{r^3}\right) + \frac{1275}{8}\left[\left(\frac{\underline{x}^T}{r}\cdot\underline{e}\cdot\frac{\underline{x}}{r}\right)^2 - \frac{\underline{x}^T}{r}\cdot\underline{e}\cdot\underline{e}\cdot\frac{\underline{x}}{r}\right]\right\} + 0(\epsilon^3). \end{aligned} \tag{4.3}$$

By comparing this expression with [2.3], the value of $\overset{(2)}{f}$ follows readily. By combining [3.1], [3.3], [3.7], [3.10] and [4.3], it is possible to evaluate all the known quantities appearing in the l.h.s. $0(\epsilon^2)$ bracket of [2.4]. In order to solve [2.4] for the unknown velocity $\overset{(2)}{\underline{v}}$, it is convenient to integrate the equation over a unit sphere and to make use of the orthogonality conditions. Correspondingly, if $d\Omega_s$ is the elementary solid angle

$$\frac{1}{4\pi}\int\left[\overset{(2)}{\underline{v}}\,\underline{x}\right]d\Omega_s = \frac{1}{5}\overset{(2)}{\underline{T}}, \tag{4.4}$$

$$\frac{1}{4\pi}\int\left[{}^{(1)}f\frac{\partial {}^{(1)}\underline{v}}{\partial \underline{x}}\cdot\underline{x}+{}^{(2)}f\frac{\partial {}^{(0)}\underline{v}}{\partial \underline{x}}\cdot\underline{x}+\frac{1}{2}{}^{(1)}f^{2}\underline{x}^{T}\cdot\frac{\partial^{2}{}^{(0)}\underline{v}}{\partial\underline{x}\partial\underline{x}}\cdot\underline{x}\right]d\Omega_{s}=\left(\frac{440}{147}-\frac{1645\,\Psi'}{294}\right)\underline{e}\,(\underline{e}:\underline{e})$$

$$-\left(\frac{3365}{84}-\frac{1045}{112}\lambda+\frac{185}{21}\Psi'\right)Sd\,(\underline{\Omega}\cdot\underline{e}\cdot\underline{e})$$

$$+\frac{(209\lambda+276)}{48}\left[Sd\,(\underline{\Omega}\cdot\underline{\Omega}\cdot\underline{e})-Sd\,(\underline{\Omega}\cdot\underline{e}\cdot\underline{\Omega})\right]. \qquad [4.5]$$

Similarly

$$\frac{1}{4\pi}\int\left[{}^{(2)}\underline{v}^{m}\right]_{r=1}d\Omega_{s}=-\left(\frac{551\lambda+744}{48}\right)\left[Sd(\underline{\Omega}\cdot\underline{\Omega}\cdot\underline{e})-Sd\,(\underline{\Omega}\cdot\underline{e}\cdot\underline{\Omega})\right]$$

$$+\left(\frac{1005}{7}+\frac{365}{21}\Psi'\right)Sd\,(\underline{\Omega}\cdot\underline{e}\cdot\underline{e}). \qquad [4.6]$$

Consequently from [4.4] to [4.6], we obtain the following expression for ${}^{(2)}\underline{T}$, where the fractions have been evaluated with an absolute precision of 5×10^{-4}.

$${}^{(2)}\underline{T}=(-14.966+27.976\,\Psi')\,\underline{e}(\underline{e}:\underline{e})+(918.155-46.652\,\lambda$$

$$+130.952\,\Psi')\,Sd\,(\underline{\Omega}\cdot\underline{e}\cdot\underline{e})-(106.250+79.167\lambda)\left[Sd(\underline{\Omega}\cdot\underline{\Omega}\cdot\underline{e})\right.$$

$$\left.-Sd\,(\underline{\Omega}\cdot\underline{e}\cdot\underline{\Omega})\right]. \qquad [4.7]$$

5. THE CONSTITUTIVE EQUATION

As shown by Batchelor (1970) the bulk properties of a suspension are defined as averages of the corresponding local quantities over a representative volume V_1 containing many particles but small with respect to the length scale of the flow. Consequently reverting to dimensional quantities the deviatoric bulk stress is expressed as

$$Sd(\langle\underline{\sigma}\rangle-2\,\mu\,\langle\underline{e}\rangle)=\frac{1}{V_1}\sum_{p}\int_{A_1}Sd\,(\underline{\sigma}\cdot\underline{n}\underline{x}-2\mu\,\underline{v}\underline{n})\,dA\,,$$

where the brackets $\langle\ \rangle$ denote bulk quantities, and where the summation is taken over all the particles present in V_1. The domain A_1 represents an arbitrary surface enclosing one particle. Then Batchelor showed that the overall contribution from the particles is contained in the stresslet term $\underline{T}$:

$$\langle\underline{\sigma}\rangle=-p\underline{I}+2\mu\left(\langle\underline{e}\rangle-\frac{3}{2V_1}\sum_{p}V_p\underline{T}\right), \qquad [5.1]$$

where V_p is the volume of one particle. In the case when all the capsules are identical, the equation involves the volume fraction ϕ of particles:

$$\langle\underline{\sigma}\rangle=-p\underline{I}+2\mu\left(\langle\underline{e}\rangle-\frac{3}{2}\phi\underline{T}\right). \qquad [5.2]$$

Then, replacing $\underline{T}$ by its expansion given by [3.3], [3.7] and [4.7], the constitutive equation of

the suspension becomes:

$$\underline{\sigma} = -p\underline{I} + 2\mu\,\underline{e} + 2\,\mu\phi\Big\{\frac{5}{2}\,\underline{e} + \frac{\mu r_0}{Eh}\,[26.786\ Sd\ (\underline{e}\cdot\underline{e}) - 47.500\ Sd\ (\underline{e}\cdot\underline{\Omega})]$$

$$-\left(\frac{\mu r_0}{Eh}\right)^2\,[(-22.449 + 41.964\ \Psi')\underline{e}(\underline{e}:\underline{e})$$

$$+ (1377.232 - 69.978\lambda + 196.429\ \Psi')\ Sd(\underline{\Omega}\cdot\underline{e}\cdot\underline{e}) \qquad [5.3]$$

$$-(159.375 + 118.750\lambda)\,[Sd(\underline{\Omega}\cdot\underline{\Omega}\cdot\underline{e}) - Sd\,(\underline{\Omega}\cdot\underline{e}\cdot\underline{\Omega})]]\ + 0(\epsilon^3 G)\Big\} + 0(\mu G\phi^2)\,.$$

The brackets have been dropped to simplify the notation, but it is to be understood that [5.3] is expressed in terms of bulk quantities. The above constitutive equation should be compared to the one obtained for dilute emulsions to an equivalent order of approximation by Barthes-Biesel & Acrivos (1973). Their equation is more general since it applies to time dependent flows and involves the Jaumann derivative of the strain rate. However, for steady flows, this derivative reduces to the symmetric deviator.

$$\frac{\mathscr{D}\underline{e}}{\mathscr{D}t} = \underline{e}\cdot\underline{\Omega} - \underline{\Omega}\cdot\underline{e} = 2\ Sd\ (\underline{e}\cdot\underline{\Omega})\,, \qquad [5.4]$$

and consequently, it appears that the suspension of microcapsules and the emulsion have the same general viscoelastic behavior of the type suggested by Rivlin & Ericksen (1955).

The differences between the capsules and the droplets lie in the numerical values of the coefficients and in their dependency on the parameters of the problem. In particular the higher order coefficients are linear functions of the viscosity ratio λ for capsules, whereas they are rational fractions of λ for drops. It would seem that this difference is due mainly to the behaviour of the membrane interface as compared to the fluid one, and also to the mecanisms of shear stress transmission from the exterior to the interior fluid. Finally, [5.3] involves still another parameter Ψ' which is linked to the non-linear properties of the membrane material. Owing to the perturbation procedure, Ψ' enters the problem only to $0(\epsilon^2)$, and consequently, its influence on the behaviour of the suspension is somewhat damped.

Similarly, [5.3] is of the same type as the constitutive equation derived by Goddard & Miller (1967) for a dilute suspension of elastic spheres, and recomputed for weakly time dependent flows by Barthes-Biesel & Acrivos (1973). Again, the dependency of the coefficients of the equation on the microrheological parameters is different as should be expected.

The analogies between the constitutive equations obtained for liquid droplets, elastic spheres and microcapsules suspensions should not be surprising since the analysis which lead to these stress–strain relations was essentially the same for the three types of particles. Consequently, [5.3] which was derived for steady flows, can be generalized to weakly time dependent flows, such that $(\mathscr{D}\underline{e}/\mathscr{D}t)$ is of order 1. Indeed, in that case [5.3] can only be of the Rivlin–Ericksen type, then the occurrence of the vorticity tensor $\underline{\Omega}$ is linked in the generalized equation to Jaumann time derivatives. For example, in view of [5.4], $2Sd(\underline{e}\cdot\underline{\Omega})$ is the degenerate form of $(\mathscr{D}\underline{e}/\mathscr{D}t)$. Similarly, $Sd(\underline{\Omega}\cdot\underline{e}\cdot\underline{e})$ and $2\,[Sd(\underline{\Omega}\cdot\underline{\Omega}\cdot\underline{e}) - Sd(\underline{\Omega}\cdot\underline{e}\cdot\underline{\Omega})]$, can be considered as steady state representations of respectively $-Sd((\mathscr{D}\underline{e}/\mathscr{D}t)\cdot\underline{e})$ and $(\mathscr{D}^2\underline{e}/\mathscr{D}t^2)$. Consequently, the stress–strain relation of the capsule suspension, extended to weakly time

dependent flows becomes:

$$\underline{\sigma} = -p\underline{I} + 2\mu\,\underline{e} + 2\mu\phi\left\{\frac{5}{2}\underline{e} + \frac{\mu r_0}{Eh}\left[26.786\,Sd(\underline{e}\cdot\underline{e}) - 23.750\frac{\mathscr{D}\underline{e}}{\mathscr{D}t}\right]\right.$$

$$-\left(\frac{\mu r_0}{Eh}\right)^2\left[(-22.449 + 41.964\,\Psi')\,\underline{e}\,(\underline{e}:\underline{e}) - (1377.232 - 69.978\lambda\right.$$

$$\left.\left. + 196.429\,\Psi')\,Sd\left(\frac{\mathscr{D}\underline{e}}{\mathscr{D}t}\cdot\underline{e}\right) - (79.688 + 59.375\lambda)\frac{\mathscr{D}^2\underline{e}}{\mathscr{D}t^2} + 0\,(\epsilon^3 G)\right]\right\} + 0(\mu G\phi^2)\,. \tag{5.5}$$

The validity of this equation is limited to slowly varying flows and to small values of the parameter ϵ, or correspondingly for a given system, to small values of the shear rate. Furthermore, λ should be 0(1), since the coefficient of the $0(\epsilon^2)$ term is a linear function of the viscosity ratio. It should be noted that a similar restriction applies for dilute emulsions as well, since when λ is large, the analysis becomes somewhat different.

Two easily measurable quantities are the shear viscosity and the normal stress difference. Equation [5.3], when evaluated for the simple shear flow [3.5], yields the following value for the apparent shear viscosity μ_a:

$$\mu_a = \mu\left\{1 + \phi\left[\frac{5}{2} - \left(\frac{\mu G r_0}{Eh}\right)^2 (68.463 + 20.982\,\Psi' + 59.375\lambda) + 0(\epsilon^3)\right]\right\}. \tag{5.6}$$

This model predicts that the suspension exhibits a shear thinning behaviour as was observed experimentally by Bredimas (1980) for interfacially polymerized emulsions. The advantage of [5.6] is that it shows explicitely how the apparent viscosity depends on the relevant microscopical parameters of the suspension, namely λ, r_0, Eh and Ψ'.

Similarly the normal stress difference may be computed for simple shear flow

$$\sigma_{11} - \sigma_{33} = 37.143\,\mu G\phi\epsilon + 0(\epsilon^3 G\phi, \phi^2)\,. \tag{5.7}$$

There is no presently available experimental measure of this quantity which can be used to check at least qualitatively the prediction of the model.

In conclusion, a dilute suspension of microcapsules has a specific rheological behaviour, which nevertheless presents some similarities with that of emulsions or that of suspensions of elastic spheres. For weakly time dependent flows, the stress–strain relation is of the Rivlin–Ericksen type, where the coefficients depend on the physical properties of the suspended capsules. The present model can be used, within its range of validity, to interpret experimental macroscopic measurements in terms of the microrheological parameters of the suspension. Such a study is feasible for interfacially polymerized emulsions, and its results will be published in a forthcoming paper.

REFERENCES

BARTHES-BIESEL D. 1980 Motion of a spherical microcapsule freely suspended in a linear shear flow. *J. Fluid Mech.* **100**, 831–853.

BARTHES-BIESEL D. & ACRIVOS A. 1973 The rheology of suspensions and its relation to phenomenological theories for non-Newtonian fluids. *Int. J. Multiphase Flow* **1**, 1–24.

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

BREDIMAS M. 1980 Polymérisation bidimensionnelle à l'interface eau-huile. Application aux émulsions. Thèse de Doctorat d'Etat. Université Pierre et Marie Curie (Paris–France).

BRENNEN C. 1975 A concentrated suspension model for the Couette rheology of blood. *Can. J. Chem. Engng* **53**, 126–133.

FRANKEL N. A. & ACRIVOS A. 1970 The constitutive equation for a dilute emulsion. *J. Fluid Mech.* **44**, 65–78.

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

GREEN A. E. & ADKINS J. E. 1960 *Large Elastic Deformations.* Oxford Univ. Press.

LAMB H. 1932 *Hydrodynamics*, 6th Edn. Cambridge Univ. Press.

RIVLIN R. S. & ERICKSEN J. L. 1955 Stress-deformation relations for isotropic materials. *Arch. Rat. Mech. Anal.* **4**, 323–425.