Linear rheology of viscoelastic emulsions with interfacial tension

J. F. Palierne

Institut Charles Sadron, Strasbourg, France

Abstract: Emulsions of incompressible viscoelastic materials are considered, in which the addition of an interfacial agent causes the interfacial tension to depend on shear deformation and variation of area. The average complex shear modulus of the medium accounts for the mechanical interactions between inclusions by a self consistent treatment similar to the Lorentz sphere method in electricity. The resulting expression of the average modulus includes as special cases the Kerner formula for incompressible elastic materials and the Oldroyd expression of the complex viscosity of emulsions of Newtonian liquids in time-dependent flow.

Key words: Emulsions; blends; interfacial tension; linear viscoelasticity; mechanical polarisation

Introduction

Einstein's work on the viscosity of dilute suspensions of rigid spheres in a Newtonian liquid opened an active field of research on macroscopic mechanical properties of heterogeneous media. His result was extended to the case of elastic spheres by Fröhlich and Sack [2] and to dilute emulsions of one Newtonian liquid into another by Taylor [3], who assumed that the interfacial tension is strong enough to keep the drops spherical. Oldroyd [4, 5] derived the complex viscosity of emulsions of Newtonian liquids in time-dependent flow for any value of the interfacial tension, and Kerner [6] gave the elastic modulus of composites made of Hookean spheres embedded at arbitrary concentration in a Hookean matrix. These two authors treated the effect of interactions between inclusions in the same manner as [2]: each inclusion is considered alone, surrounded by the matrix up to a given distance, beyond which the medium has the properties of the average medium. A refined treatment of the interactions was given by Batchelor and Green [7] for rigid inclusions in a Newtonian matrix, and nonlinear effects in emulsions of Newtonian liquids have been described by Schowalter et al. [8, 9].

The scope of this paper is to derive the linear viscoelastic modulus at arbitrary concentration and polydispersity of spherical inclusions. Matrix and inclusions are supposed to be viscoelastic, and we consider the most general behavior of the interface: dependence of the interfacial tension on variation of area and resistance to shear, both effects being time-dependent. Such complications arise when an interface agent is introduced in the system in order to lower the interfacial tension. We shall not (yet) try to treat non-linear phenomena [8, 9], nor consider the modifications of the inclusion distribution by the flow [7]. Going from local to averaged quantities parallels the treatment of the macroscopic polarizability of dense media in electricity. We believe this allows a more transparent formalism than the usual stress averages [10, 11].

1. Single inclusion problem

An infinite matrix containing an inclusion of radius R, centered at the origin of the coordinate frame, is subjected to a harmonic strain, uniform at infinity. The strain γ at point $\boldsymbol{r}$ and time t

$$\gamma_{ij}(\boldsymbol{r}, t) = \partial_i u_j + \partial_j u_i \tag{1.1}$$

derives from the deformation field $\boldsymbol{u}(\boldsymbol{r}, t)$, and approaches a uniform value $\gamma^h(t) = \gamma^h(0) \exp(i\omega t)$ far away from the inclusion. Throughout this paper, all quantities proportional to the deformation have a complex amplitude; and their time-dependence through a factor $\exp(i\omega t)$ will be left implicit.

For the sake of simplicity we shall restrict our attention to incompressible media and to linear viscoelastic regime, in which case the stress-strain relationship is written

$$\sigma(r) = -p(r)\delta + \tau(r) \ , \quad \tau(r) = G^*(\omega)\gamma(r) \ , \quad (1.2)$$

where the frequency dependent complex shear modulus G^* relates the stress deviator τ to the strain γ. The value of this modulus is G_M^* in the matrix and G_I^* in the inclusion. G^* constant and real corresponds to elastic solids, and $G^* = i\omega\eta$ describes Newtonian fluids of viscosity η.

The length scale under consideration (the radius R) is assumed to be small enough for bulk forces (gravitation and inertia) to be negligible. The dynamics equation simplifies then to

$$\partial_j \sigma_{ij} = 0 \ . \quad (1.3)$$

As the inertial forces play no role, uniform translation and rotation about the origin can be subtracted from the displacement field. It can thus be written without loss of generality:

$$\boldsymbol{u}(\boldsymbol{r}) = \tfrac{1}{2}\gamma^h \cdot \boldsymbol{r} + \boldsymbol{v}(\boldsymbol{r}) \ , \quad (1.4)$$

where tensor γ^h is the uniform strain which would exist if the matrix was homogeneous, and $\boldsymbol{v}(\boldsymbol{r})$ is the perturbation due to the inclusion, vanishing at infinity.

As a consequence of incompressibility, $\gamma(\boldsymbol{r})$ and γ^h are symmetric traceless tensors, and $\boldsymbol{v}$ and $\boldsymbol{u}$ are divergenceless vectors.

The polar vector $\boldsymbol{v}$ can be expressed as the curl of an axial vector. Owing to the rotational symmetry of the medium, the most general axial vector linear in γ^h is $f(r)\boldsymbol{r} \times (\gamma^h \cdot \boldsymbol{r})$, and writing $\boldsymbol{r} f(r) = \nabla g(r)$ gives

$$\boldsymbol{v} = \operatorname{curl}\operatorname{curl}(g(r)\gamma^h \cdot \boldsymbol{r}) \ , \quad r = |\boldsymbol{r}| \ . \quad (1.5)$$

Inserting Eq. (1.2) into Eq. (1.3) yields

$$G^* \Delta \boldsymbol{u} = \nabla p \ , \quad (1.6)$$

and taking the curl of this equation results in an equation for g alone

$$\operatorname{curl} \Delta\Delta (g(r)\gamma^h \cdot \boldsymbol{r}) = 0 \ , \quad (1.7)$$

which has the solution

$$g = ar^4 + br^2 + cr^{-1} + dr^{-3} \quad (1.8)$$

to within an irrelevant additive constant. Constants c and d must vanish inside the inclusion, as do a and b in the matrix. The inner and outer displacement fields write thus, respectively,

$$r<R: \ \boldsymbol{u} = (\tfrac{1}{2} - 20ar^2 - 6b)\gamma^h \cdot \boldsymbol{r} + 8a\gamma^h : \boldsymbol{rrr} \quad (1.9)$$

and

$$r>R: \ \boldsymbol{u} = (\tfrac{1}{2} - 6dr^{-5})\gamma^h \cdot \boldsymbol{r} + (3cr^{-5} + 15dr^{-7})\gamma^h : \boldsymbol{rrr} \ . \quad (1.10)$$

Inserting these expressions for $\boldsymbol{u}$ into Eq. (1.6) gives the pressure to within a constant

$$r<R: \ p = -84 G_I^* a \gamma^h : \boldsymbol{rr} \quad (1.11)$$

$$r>R: \ p = 6 G_M^* c r^{-5} \gamma^h : \boldsymbol{rr} \ . \quad (1.12)$$

By symmetry, a uniform pressure term linear in deformation should be proportional to the scalar $sp(\gamma^h)$, which is zero. Static Laplace pressure will be considered later.

In the inclusion, the components of the stress deviator read, calling r_i the i-component of vector $\boldsymbol{r}$,

$$\tau_{ij}/G_I^* = (1 - 40ar^2 - 12b)\gamma_{ij}^h - 24a(\gamma_{ik}^h r_j r_k + \gamma_{jk}^h r_i r_k) + 16a\gamma^h : \boldsymbol{rr}\delta_{ij} \ , \quad (1.13)$$

and in the matrix

$$\tau_{ij}/G_M^* = (1 - 12dr^{-5})\gamma_{ij}^h + (6cr^{-5} + 60dr^{-7})(\gamma_{ik}^h r_j r_k + \gamma_{jk}^h r_i r_k) + (6cr^{-5} + 30dr^{-7})\gamma^h : \boldsymbol{rr}\delta_{ij} - (30cr^{-7} + 210dr^{-9})\gamma^h : \boldsymbol{rr} r_i r_j \ . \quad (1.14)$$

Interfacial tension plays a major role in the mechanics of emulsions. The tension of many systems of practical interest is lowered by addition of an interfacial agent, such as soap in oil-water systems, or an $A-B$ copolymer in an emulsion of polymer A into polymer B. An important feature of such interfaces is that, as the concentration of interfacial agent varies in a change of surface area, the mechanical tension is area-dependent [12]. The corresponding relaxation time is of the order $\lambda_d = R^2/D$, where D is a mean diffusion coefficient of the interfacial agent into matrix and inclusion. A further mechanism may act in systems comprising a polymeric interface agent. If this compound reticulates, or if its molecular mass is high enough for its chains to entangle, the interface can resist a shear deformation by opposing a shear stress. The response time, infinite in the first case, is in the second case the disentanglement time.

The interface tension is a two-dimensional tensor α_{ab} defined in the plane tangent to the interface; indices a and b refer to an orthonormal basis ($\boldsymbol{e}_1$, $\boldsymbol{e}_2$) of this plane, relating the force df necessary to hold a segment dl of the boundary of a piece of interface to the orientation of this segment:

$$df = \boldsymbol{\alpha}\cdot\boldsymbol{m}\,dl = \alpha_{ab}\boldsymbol{e}_a(\boldsymbol{e}_b\cdot\boldsymbol{m})\,dl \ , \tag{1.15}$$

where $\boldsymbol{m}$ is a unit vector tangent to the interface, normal to dl and directed outwards. Summation of repeated indices a and b over the values 1 and 2 is implied. Since $\boldsymbol{e}_1$ and $\boldsymbol{e}_2$ are orthonormal, the two-dimensional divergence of a vector field $\boldsymbol{G} = G_b\boldsymbol{e}_b$ tangent to the interface reads $\mathrm{div}_{2D}\,\boldsymbol{G} = \boldsymbol{e}_c\cdot\partial_c\boldsymbol{G} = \partial_b G_b + G_b(\boldsymbol{e}_c\cdot\partial_c\boldsymbol{e}_b)$, where $\partial_c = \boldsymbol{e}_c\cdot\nabla$ is the gradient along the direction of $\boldsymbol{e}_c$. The last term compensates for the variation of the local basis ($\boldsymbol{e}_1$, $\boldsymbol{e}_2$) along the interface. Replacing G_b by $\alpha_{ab}\boldsymbol{e}_a$ gives the force the interface tension exerts per unit area as the divergence of the tensor $\boldsymbol{\alpha}$

$$\begin{aligned}\frac{df}{dS} &= \partial_c(\alpha_{ab}\boldsymbol{e}_a\boldsymbol{e}_b)\cdot\boldsymbol{e}_c \\ &= \boldsymbol{e}_a\partial_b\alpha_{ab} + \alpha_{ab}\{\partial_b\boldsymbol{e}_a + \boldsymbol{e}_a(\boldsymbol{e}_c\cdot\partial_c\boldsymbol{e}_b)\} \ . \end{aligned}\tag{1.16}$$

As no bulk torque is transmitted to the interface, either by the remainder of the interface or by the surrounding fluids, α_{ab} must be symmetric. At first order in deformation included, it is the sum

$$\alpha_{ab} = \alpha^0\delta_{ab} + \beta_{ab} \tag{1.17}$$

of a static part, the equilibrium tension $\alpha^0\delta_{ab}$, and of a part β_{ab} which is, in harmonic regime, proportional to the interface strain γ_{ab}, and consequently oscillates at frequency ω. The isotropic part of β_{ab}, proportional to γ_{aa}, is conjugate to the relative area variation; the traceless part, proportional to the strain deviator $\gamma_{ab} - \frac{1}{2}\delta_{ab}\gamma_{cc}$, is conjugate to shear without change of area. One has then

$$\beta_{ab} = \tfrac{1}{2}\beta'\gamma_{cc}\delta_{ab} + \beta''(\gamma_{ab} - \tfrac{1}{2}\delta_{ab}\gamma_{cc}) \ , \tag{1.18}$$

where $\beta'(\omega)$ is the complex, frequency-dependent surface dilatation modulus, and $\beta''(\omega)$ is the surface shear modulus. The interface strain is obtained from the three-dimensional strain $\gamma_{ij}(\boldsymbol{r})$ at a point $\boldsymbol{r}$ of the interface by projection on the plane tangent at this point. Its components, referred to the local basis $\boldsymbol{e}_1(\boldsymbol{r})$, $\boldsymbol{e}_2(\boldsymbol{r})$ of the tangent plane, read

$$\gamma_{ab}(\boldsymbol{r}) = e_{ai}e_{bj}\gamma_{ij} = e_{ai}\partial_b u_i + e_{bi}\partial_a u_i \ , \tag{1.19}$$

where e_{aj} is the j-component of vector $\boldsymbol{e}_a$ in the fixed three-dimensional frame. In such a mixed expression the summation convention applies either in the tangent plane, indices a and b taking the values 1 and 2, or in the three-dimensional space, indices i and j running over the values x, y and z.

As γ_{ab} is first order in $\boldsymbol{u}$, it can be evaluated with the same precision at the unperturbed position $\boldsymbol{\varrho}$ of the interface element we consider instead of its actual position $\boldsymbol{\varrho} + \boldsymbol{u}(\boldsymbol{\varrho})$, and in the plane tangent to the undeformed sphere rather than in the plane tangent to the actual, deformed, interface. The plane tangent to the sphere $|\boldsymbol{\varrho}| = R$ is normal to $\boldsymbol{\varrho}$, and is referred to two orthonormal basis vectors $\boldsymbol{\varepsilon}_1(\boldsymbol{\varrho})$ and $\boldsymbol{\varepsilon}_2(\boldsymbol{\varrho})$. Hereafter, $\boldsymbol{\varrho}$ designates a vector of modulus R, pointing to the undeformed interface.

By symmetry, the displacement $\boldsymbol{u}(\boldsymbol{\varrho})$ of any point of the interface is, at first order in γ^h, a linear combination

$$\boldsymbol{u}(\boldsymbol{\varrho}) = A\boldsymbol{u}^r + B\boldsymbol{u}^t \tag{1.20}$$

of the radial and tangential vector fields

$$\boldsymbol{u}^r = R^{-2}(\gamma^h : \boldsymbol{\varrho}\boldsymbol{\varrho})\boldsymbol{\varrho} \tag{1.21}$$

$$\boldsymbol{u}^t = \gamma^h\cdot\boldsymbol{\varrho} - \boldsymbol{u}^r \ , \tag{1.22}$$

both proportional to γ^h. The gradient of deformation in the plane tangent to the sphere reads then

$$\begin{aligned}\varepsilon_{ai}\varepsilon_{bj}\partial_j u_i = \varepsilon_{ai}\varepsilon_{bj}\{&(A-B) \\ &\times(2\gamma^h_{jk}\varrho_k\varrho_i + \gamma^h_{kl}\varrho_k\varrho_l\delta_{ij})R^{-2} + B\gamma^h_{ij}\}\end{aligned} \tag{1.23}$$

and, noting that $\boldsymbol{\varepsilon}_a\cdot\boldsymbol{\varrho} = \varepsilon_{ai}\varrho_i = 0$ and $\varepsilon_{ai}\varepsilon_{bi} = \boldsymbol{\varepsilon}_a\cdot\boldsymbol{\varepsilon}_b = \delta_{ab}$, one finds the surface strain at first order in the deformation

$$\gamma_{ab} = 2(A-B)\gamma^h_{kl}\varrho_k\varrho_l R^{-2}\delta_{ab} + 2B\gamma^h_{ij}\varepsilon_{ai}\varepsilon_{bj} . \tag{1.24}$$

The triad $\boldsymbol{\varrho}/R$, $\boldsymbol{\varepsilon}_1(\boldsymbol{\varrho})$, $\boldsymbol{\varepsilon}_2(\boldsymbol{\varrho})$ forms an orthonormal basis of the three-dimensional space, and the trace of tensor γ^h reads in this basis $\gamma^h_{ij}\varrho_i\varrho_j R^{-2} + \gamma^h_{ij}\varepsilon_{ai}\varepsilon_{aj}$

= 0. Using this identity yields the following expression of the linear part of the interface tension:

$$\beta_{ab} = \beta' \delta_{ab}(2A-3B)\gamma^h_{ij}\varrho_i\varrho_j R^{-2} + \beta'' B\gamma^h_{ij}(2\varepsilon_{ai}\varepsilon_{bj} - \delta_{ab}\varrho_i\varrho_j R^{-2}) \ . \qquad (1.25)$$

The difference between the gradient of any space-dependent quantity χ at point $\boldsymbol{r} = \boldsymbol{\varrho} + \boldsymbol{u}(\boldsymbol{\varrho})$ in the direction of $\boldsymbol{e}_a$, denoted $\partial_a\chi = \boldsymbol{e}_a\cdot\nabla\chi$, and the gradient at point $\boldsymbol{\varrho}$ along $\boldsymbol{\varepsilon}_a$, denoted $\partial'_a\chi = \boldsymbol{\varepsilon}_a\cdot\nabla\chi$, is first order in deformation. As $\boldsymbol{\beta}$ is itself a first-order quantity, one can replace ∂'_a by ∂_a and $\boldsymbol{\varepsilon}_a$ by $\boldsymbol{e}_a$ in the terms proportional to $\boldsymbol{\beta}$ in Eq. (1.16). Insertion of (1.25) into Eq. (1.16) can be made easy by chosing the field of tangent vectors $\boldsymbol{\varepsilon}_a(\boldsymbol{\varrho})$ locally geodetic, i.e., such that the gradient of $\boldsymbol{\varepsilon}_a(\boldsymbol{\varrho})$ along the $\boldsymbol{\varepsilon}_b$ direction is $\partial'_a\boldsymbol{\varepsilon}_a = -\delta_{ab}\boldsymbol{\varrho}/R^2$ (this condition is fulfilled, for instance, at the equator of the sphere if $\boldsymbol{\varepsilon}_1$ and $\boldsymbol{\varepsilon}_2$ are tangent to the meridians and the parallels respectively). One has then $\partial'_a\varepsilon_{bj} = -\delta_{ab}\varrho_j/R^2$ and $\boldsymbol{\varepsilon}_c\cdot\partial'_c\boldsymbol{\varepsilon}_b = 0$, and, of course, $\partial'_a\varrho_i = \varepsilon_{ai}$. This enables one to find

$$\partial'_b\beta_{ab} = 2\{\beta'(2A-3B) - 2B\beta''\}\gamma^h_{ij}\varepsilon_{ai}\varrho_j R^{-2} \qquad (1.26)$$

$$\beta_{ab}\{\partial'_b\boldsymbol{\varepsilon}_a + \boldsymbol{\varepsilon}_a(\boldsymbol{\varepsilon}_c\cdot\partial'_c\boldsymbol{\varepsilon}_b)\} = -2\beta'(2A-3B) \times\gamma^h_{ij}\varrho_i\varrho_j\boldsymbol{\varrho}R^{-4} \ . \qquad (1.27)$$

Noting that the expression $\gamma^h_{ij}\varepsilon_{ai}\varrho_j$ appearing in (1.26) is the a-component $u^t_a = \boldsymbol{u}^t\cdot\boldsymbol{\varepsilon}_a$ of the tangential vector $\boldsymbol{u}^t = u^t_a\boldsymbol{\varepsilon}_a$ defined in (1.22), one can write the contribution of β_{ab} to Eq. (1.16) as

$$\begin{aligned}\partial_b(\beta_{ab}\boldsymbol{e}_a) + \beta_{ab}\boldsymbol{e}_a(\boldsymbol{e}_c\cdot\partial_c\boldsymbol{e}_b) &= \partial'_b(\beta_{ab}\boldsymbol{\varepsilon}_a) + \beta_{ab}\boldsymbol{\varepsilon}_a(\boldsymbol{\varepsilon}_c\cdot\partial'_c\boldsymbol{\varepsilon}_b)\\ &= 2R^{-1}\{\beta'(2A-3B)(\boldsymbol{u}^t-\boldsymbol{u}^r) - 2B\beta''\boldsymbol{u}^t\}.\end{aligned} \qquad (1.28)$$

The contribution $\alpha^0\{\partial_a\boldsymbol{e}_a + \boldsymbol{e}_a(\boldsymbol{e}_c\cdot\partial_c\boldsymbol{e}_a)\}$ of the equilibrium interfacial tension to Eq. (1.16) must be evaluated by using a field of basis vectors $\boldsymbol{e}_1$, $\boldsymbol{e}_2$ that are tangent to the deformed interface at first order included (several quantities to appear in the remainder of this section, namely the vectors $\boldsymbol{r}(\boldsymbol{\varrho})$, its differential $d\boldsymbol{r}$, the tangent basis vectors $\boldsymbol{e}_1$ and $\boldsymbol{e}_2$, and the unit normal $\boldsymbol{n}$, are, as is $\boldsymbol{\alpha}$, made of static term and an oscillatory term proportional to the deformation γ^h. As we are interested in linear behavior, calculations involving any of these quantities have to be carried out at first order included in the deformation). It is first obvious that the tangential deformation does not alter (at first order) the shape of the interface, and cannot contribute to the α^0 term of Eq. (1.16). We shall thus consider a purely radial deformation $\boldsymbol{u}(\boldsymbol{\varrho}) = A\boldsymbol{u}^r(\boldsymbol{\varrho})$, which brings a point $\boldsymbol{\varrho}$ of the undeformed sphere to the position

$$\boldsymbol{r}(\boldsymbol{\varrho}) = \boldsymbol{\varrho} + A\boldsymbol{u}^r(\boldsymbol{\varrho}) = \boldsymbol{\varrho}(1 + AR^{-2}\gamma^h : \boldsymbol{\varrho}\boldsymbol{\varrho}) \ . \qquad (1.29)$$

An infinitesimal change $d\boldsymbol{\varrho} = d\varrho_a\boldsymbol{e}_a$ of $\boldsymbol{\varrho}$ results in a variation of $\boldsymbol{r}$

$$d\boldsymbol{r} = \boldsymbol{\varepsilon}_a d\varrho_a(1 + AR^{-2}\gamma^h : \boldsymbol{\varrho}\boldsymbol{\varrho}) + 2AR^{-2}\boldsymbol{\varrho}\, d\varrho_a\gamma^h : \boldsymbol{\varrho}\boldsymbol{\varepsilon}_a \ . \qquad (1.30)$$

This can be written at first order

$$d\boldsymbol{r} = dr_a\boldsymbol{e}_a \ , \qquad (1.31)$$

where

$$dr_a = d\varrho_a(1 + AR^{-2}\gamma^h : \boldsymbol{\varrho}\boldsymbol{\varrho}) \ , \qquad (1.32)$$

and

$$\boldsymbol{e}_a = \boldsymbol{\varepsilon}_a + 2\boldsymbol{\varrho}AR^{-2}\gamma^h : \boldsymbol{\varrho}\boldsymbol{\varepsilon}_a \ . \qquad (1.33)$$

As the relations $\boldsymbol{e}_a\cdot\boldsymbol{e}_b = \delta_{ab}$ and $dr^2 = dr_a dr_a$ are satisfied at first order included, the local basis $\boldsymbol{e}_1$, $\boldsymbol{e}_2$ is orthonormal, and dr_a is the a-component of $d\boldsymbol{r}$ in this basis. The normal to the deformed interface reads, at the same precision,

$$\begin{aligned}\boldsymbol{n} &= \boldsymbol{e}_1\times\boldsymbol{e}_2 = \boldsymbol{\varrho}/R - 2\boldsymbol{\varepsilon}_a AR^{-2}\gamma^h : \boldsymbol{\varrho}\boldsymbol{\varepsilon}_a \ ,\\ \boldsymbol{n}^2 &= 1 \ .\end{aligned} \qquad (1.34)$$

An infinitesimal change $d\boldsymbol{\varrho}$ of $\boldsymbol{\varrho}$ makes $\boldsymbol{r}$ change by $d\boldsymbol{r} = (1 + AR^{-2}\gamma^h : \boldsymbol{\varrho}\boldsymbol{\varrho})d\boldsymbol{\varrho}$, the vector $\boldsymbol{\varepsilon}_a$ changes by $d\boldsymbol{\varepsilon}_a = -\boldsymbol{\varrho}R^{-2}d\varrho_a = -\boldsymbol{\varrho}R^{-2}dr_a + 0(\gamma^h)$, and consequently, $\boldsymbol{e}_a$ changes by

$$d\boldsymbol{e}_a = -\boldsymbol{\varrho}R^{-2}dr_a(1 + AR^{-2}\gamma^h : \boldsymbol{\varrho}\boldsymbol{\varrho}) + 2dr_c AR^{-2}(\boldsymbol{\varepsilon}_c\gamma^h : \boldsymbol{\varrho}\boldsymbol{\varepsilon}_a + \boldsymbol{\varrho}\gamma^h : \boldsymbol{\varepsilon}_a\boldsymbol{\varepsilon}_c) \ . \qquad (1.35)$$

Dividing by dr_c gives the gradient $\partial_c\boldsymbol{e}_a = (\boldsymbol{e}_c\cdot\nabla)\boldsymbol{e}_a$ at point $\boldsymbol{r}$, along the $\boldsymbol{e}_c(\boldsymbol{r})$ direction,

$$\partial_c\boldsymbol{e}_a = -\delta_{ac}\boldsymbol{\varrho}R^{-2}(1 + AR^{-2}\gamma^h : \boldsymbol{\varrho}\boldsymbol{\varrho}) + 2AR^{-2}(\boldsymbol{\varepsilon}_c\gamma^h : \boldsymbol{\varrho}\boldsymbol{\varepsilon}_a + \boldsymbol{\varrho}\gamma^h : \boldsymbol{\varepsilon}_a\boldsymbol{\varepsilon}_c) \ . \qquad (1.36)$$

The contribution of the constant part of the interface tension eventually reads, at the required precision,

$$\alpha^0 \delta_{ab}\{\partial_b \boldsymbol{e}_a + \boldsymbol{e}_a(\boldsymbol{e}_c \cdot \partial_c \boldsymbol{e}_b)\} = -2\boldsymbol{n}\alpha^0 R^{-1} - 4\alpha^0 A R^{-2} \boldsymbol{u}^r . \quad (1.37)$$

The first term of the right member is a static force-per-unit area of constant magnitude, normal to the deformed interface. It is the source of the equilibrium Laplace pressure inside the inclusion. The second term of the right member of (1.37) is a first-order oscillatory term, coming from the increase of curvature due to the deformation.

Adding Eq. (1.28) and Eq. (1.37) gives the force-per-unit area of interface:

$$\begin{aligned}\frac{df}{dS} &= \boldsymbol{e}_a \partial_b \alpha_{ab} + \alpha_{ab}\{\partial_b \boldsymbol{e}_a + \boldsymbol{e}_a(\boldsymbol{e}_c \cdot \partial_c \boldsymbol{e}_b)\} \\ &= 2(2A-3B)\beta'/R^2(\gamma^h \cdot \varrho - 2(\gamma^h : \varrho\varrho)\varrho/R^2) \\ &\quad -4A\alpha^0(\gamma^h : \varrho\varrho)\varrho/R^4 \\ &\quad -4B\beta''/R^2(\gamma^h \cdot \varrho - (\gamma^h : \varrho\varrho)\varrho/R^2) \\ &\quad -2\alpha^0 \boldsymbol{n} R^{-1} . \end{aligned} \quad (1.38)$$

The balance of forces acting on the interface is eventually written

$$\sigma_M \cdot \varrho/R - \sigma_I \cdot \varrho/R + p_L \boldsymbol{n} + \frac{df}{dS} = 0 , \quad (1.39)$$

where σ_I and σ_M are the stress on the inclusion and on the matrix side of the interface, and $p_L \boldsymbol{n}$ is the Laplace pressure term. It is directed along the normal $\boldsymbol{n}$, which is the sum of a constant part ϱ/R and a first order part $\boldsymbol{n} - \varrho/R$ due to the tilt of the interface with respect to its equilibrium orientation. The constant terms $p_L \varrho/R$ and $-2\alpha^0 \varrho R^{-2}$ of Eq. (1.39) cancel if the Laplace pressure has the value

$$p_L = 2\alpha^0/R . \quad (1.40)$$

One has then $p^0 \boldsymbol{n} = 2\alpha^0 \boldsymbol{n}/R$, and these terms cancel in Eq. (1.39) at first order included. All constants a, b, c, d, A, B appearing in Eqs. (1.8), (1.11), and (1.18) can now be determined. Continuity of the displacement at the interface requires that the inner and outer coefficients of $\gamma^h \cdot \boldsymbol{r}$ and $(\gamma^h : \boldsymbol{rr})\boldsymbol{r}$ in Eqs. (1.9) and (1.10) match that $|\boldsymbol{r}| = R$:

$$\tfrac{1}{2} - 20aR^2 - 6b = \tfrac{1}{2} - 6dR^{-5} \quad (1.41)$$

$$8a = 3cR^{-5} + 15dR^{-7} . \quad (1.42)$$

This corresponds to $B = \frac{1}{2} - 6dR^{-5}$ and $A = \frac{1}{2} + 3cR^{-3} + 9dR^{-5}$. The force balance (1.39) gives two more equations, the first one for the $\gamma^h \cdot \varrho/R$ term;

$$\begin{aligned} &G_M^*(1 + 6cR^{-3} + 48dR^{-5}) \\ &+ G_I^*(-1 + 64aR^2 + 12b) \\ &+ \beta'/R(-1 + 12cR^{-3} + 72dR^{-5}) \\ &+ 4\beta''/R(-\tfrac{1}{2} + 6dR^{-5}) = 0 , \end{aligned} \quad (1.43)$$

and the second for the $(\gamma^h : \varrho\varrho)\varrho/R^3$ term:

$$\begin{aligned} &-24G_M^*(cR^{-3} + 5dR^{-5}) - 76G_I^* aR^2 \\ &-\beta'/R(-2 + 24cR^{-3} + 144dR^{-5}) \\ &-\alpha^0/R(2 + 12cR^{-3} + 36dR^{-5}) \\ &-4\beta''/R(-\tfrac{1}{2} + 6dR^{-5}) = 0 . \end{aligned} \quad (1.44)$$

The solution to Eqs. (1.41) to (1.44) reads

$$a = \frac{5R^{-3}}{8D} G_M^*(4\beta' - 4\alpha^0 + 4\beta'') , \quad (1.45)$$

$$\begin{aligned} b = \frac{1}{6D}\{&(G_I^* - G_M^*)(19G_I^* + 16G_M^*) + 24\beta'\alpha^0/R^2 \\ &+ 16\beta''(\alpha^0 + \beta')/R^2 + 10\alpha^0/R(2G_I^* + 5G_M^*) \\ &+ \beta'/R(23G_I^* - 58G_M^*) \\ &+ 26\beta''/R(G_I^* - G_M^*)\} , \end{aligned} \quad (1.46)$$

$$\begin{aligned} c = -\frac{5R^3}{6D}\{&(G_I^* - G_M^*)(19G_I^* + 16G_M^*) + 24\beta'\alpha^0/R \\ &+ 16\beta''(\alpha^0 + \beta')/R^2 + 4\alpha^0/R(5G_I^* + 2G_M^*) \\ &+ \beta'/R(23G_I^* - 16G_M^*) \\ &+ 2\beta''/R(13G_I^* + 8G_M^*)\} , \text{ and} \end{aligned} \quad (1.47)$$

$$\begin{aligned} d = \frac{R^5}{6D}\{&(G_I^* - G_M^*)(19G_I^* + 16G_M^*) + 24\beta'\alpha^0/R^2 \\ &+ 16\beta''(\alpha^0 + \beta')/R^2 + 20\alpha^0/R\, G_I^* \\ &+ \beta'/R(23G_I^* - 8G_M^*) \\ &+ 2\beta''/R(13G_I^* + 12G_M^*)\} , \end{aligned} \quad (1.48)$$

where the common denominator reads

$$\begin{aligned} D = &(2G_I^* + 3G_M^*)(19G_I^* + 16G_M^*) + 48\beta'\alpha^0/R^2 \\ &+ 32\beta''(\alpha^0 + \beta')/R^2 + 40\alpha^0/R(G_I^* + G_M^*) \\ &+ 2\beta'/R(23G_I^* + 32G_M^*) \\ &+ 4\beta''/R(13G_I^* + 12G_M^*) . \end{aligned} \quad (1.49)$$

The amplitudes of the radial and tangential displacement of the interface are, respectively,

$$A = \frac{5}{2D} G_M^*(19G_I^* + 16G_M^* + 24\beta'/R + 8\beta''/R) \tag{1.50}$$

$$B = \frac{5}{2D} G_M^*(19G_I^* + 16G_M^* + 8\alpha^0/R + 16\beta''/R) \ . \tag{1.51}$$

An infinite value of α^0 causes the coefficient A to vanish, the only possible motion of the interface being tangential. The total area is then conserved, but it varies locally. Conversely, an interface with infinite shear modulus β'' can stand only radial deformations, in which case B vanishes. The effect of an infinite value of β' is to allow a motion proportional to the vector $3\boldsymbol{u}^r + 2\boldsymbol{u}^t = R^{-2}(\gamma^h : \boldsymbol{\varrho\varrho})\boldsymbol{\varrho} + 2\gamma\cdot\boldsymbol{\varrho}$, in which case the local area variation $\frac{1}{2}\gamma_{aa} = (2A-3B)\gamma^h : \boldsymbol{\varrho\varrho}$ is second order in $\boldsymbol{u}$. If at least two among the coefficients α^0, β', and β'' are infinite, no motion of the interface is possible and both A and B vanish. The same thing arises, of course, when the inner modulus G_I^* is infinite.

The condition of linearity stated at the beginning of this section can now be made more quantitative. It is first necessary, for the boundary conditions at the interface to hold, that the departure from the spherical shape of the inclusions, i.e., the radial deformation, be small. The relative radial deformation is of order $A\gamma^h/R$, where A is given by Eq. (1.50). If G_I^* is greater than G_M^*, the relative deformation is of order $G_M^*\gamma^h/G_I^*$, whereas if α^0/R has a greater modulus than G_M^*, the deformation amounts to $\gamma^h G_M^* R/\alpha^0$. In other cases the inclusions undergo a shape variation of order γ^h. A further condition is that the rheological behavior of the matrix and inclusion materials be linear viscoelastic, i.e., that the deformation taking place during the relaxation time of the considered material be small. The strain γ to be considered is γ^h for the matrix and for "soft" inclusions. For a "hard" one, such that G_I^* is greater than G_M^*, this strain is of order $\gamma_I = \gamma^h G_M^*/G_I^*$. The rigidity of the interface can also reduce the inner strain magnitude to $\gamma_I = G_M^* R/\alpha$ if at least two among the coefficients α^0, β', and β'' are of order α greater than $G_M^* R$. The linearity of the relation between interface tension and surface deformation must eventually be secured. The surface motion must, therefore, be small (with respect to the radius) during the relaxation time λ of the tension coefficients β' and β''. As the ratio of surface motion over the radius is of order γ_I, the relative departure from linearity in the interfacial tension is of order of the smallest of γ_I and $\gamma_I\omega\lambda$.

2. Mechanics of dilute emulsions

The outer perturbation of the deformation field (1.10)

$$\begin{aligned} v &= u - \tfrac{1}{2}\gamma^h \cdot r \\ &= 3cr^{-5}(\gamma^h : rr)r \\ &\quad + 3d\{5r^{-7}(\gamma^h : rr)r - 2r^{-5}\gamma^h . r\} \end{aligned} \tag{2.1}$$

splits into two contributions. The first one, varying like r^{-2}, identifies outside the inclusion with the displacement, due to a point dipole $\boldsymbol{\pi}$ acting on an homogeneous matrix (A.9):

$$\boldsymbol{\pi} = 8\pi G_M^* c\gamma^h \ , \tag{2.2}$$

(π without subscript or double bar is the number 3.14..., otherwise it denotes the dipole moment). The polarizability of the inclusion is thus $8\pi G_M^* c$, where the constant c is given in (1.47). The second contribution, enclosed in {}, varies like r^{-4}. This characterizes the deformation field of an octupole, which gives no contribution to the induction $\boldsymbol{\Theta}$ defined in the appendix. Calling N_I the number concentration of inclusions of kind I, and c_I the corresponding value of coefficient c (1.47), we have for the macroscopic polarization density

$$\boldsymbol{\Pi} = 8\pi \sum_I N_I c_I G_M^* \gamma^h \ . \tag{2.3}$$

The viscoelastic induction defined in (A.21) reads

$$\boldsymbol{\Theta} = \left(1 - 8\pi \sum_I N_I c_I\right) G_M^* \gamma^h - P\delta \ , \tag{2.4}$$

where P is the average pressure. At lowest order in concentration, the unperturbed strain γ^h at the location of an inclusion (if this inclusion was not present) is the macroscopic strain $\boldsymbol{\Gamma}$. The macroscopic modulus (A.22) of the emulsion is then, at linear order in concentration,

$$\begin{aligned} G^* &= G_M^*\left(1 - 8\pi \sum_I N_I c_I\right) \\ &= G_M^*\left(1 + \frac{5}{2}\sum_I \Phi_I \frac{E_I}{D_I}\right) \ , \end{aligned} \tag{2.5}$$

where $\Phi_I = \frac{4}{3}\pi N_I R_I^3$ is the volume fraction of kind I, and

$$E_I = 2(G_I^* - G_M^*)(19G_I^* + 16G_M^*) + 48\beta'\alpha^0/R^2 + 32\beta''(\alpha^0+\beta')/R^2 + 8\alpha^0/R(5G_I^* + 2G_M^*) + 2\beta'/R(23G_I^* - 16G_M^*) + 4\beta''/R(13G_I^* + 8G_M^*) \ , \quad (2.6)$$

and

$$D_I = (2G_I^* - 3G_M^*)(19G_I^* + 16G_M^*) + 48\beta'\alpha^0/R^2 + 32\beta''(\alpha^0+\beta')/R^2 + 40\alpha^0/R(G_I^* + G_M^*) + 2\beta'/R(23G_I^* + 32G_M^*) + 4\beta''/R(13G_I^* + 12G_M^*) \quad (2.7)$$

are such that $E_I/D_I = -12c_I/5R_I^3$, which takes into account the radius, the viscoelastic modulus, and interfacial tension coefficients of each kind I of inclusion (subscript I on all these quantities has been omitted for brevity). The ratio E_I/D_I is normalized to unity for rigid inclusions.

3. Nondilute emulsions

The effect of finite concentrations is that the local strain "seen" by an inclusion is no longer the macroscopic strain $\boldsymbol{\Gamma}$, but is modified by the deformation field of neighboring inclusions (the local strain is the strain which would exist at the location of an inclusion if this inclusion was replaced by the matrix). In order to account for this effect we shall borrow from electricity the Lorentz sphere method, where the effect of other inclusions is taken into account within a sphere of radius R_L, large enough to contain many inclusions and concentric with the inclusion under consideration, whereas the medium outside is treated as an average continuum. If R_L is chosen to be of sufficient magnitude with respect to the interparticular distance, the effect of averaging the interactions with inclusions outside the sphere can be made negligible (as the strain (1.14) varies as r^{-3}, the error is, at most, of order $(l/R_L)^4$, where l is the separation between neighboring inclusions). The local strain γ^{loc} at the center of the Lorentz sphere is thus obtained by substituting the continuum polarization $\boldsymbol{\Pi}$ inside the sphere for the discrete dipoles created by the inclusions effectively present, the polarization outside the sphere being held constant in this process. More precisely, in a reference frame which originates at the center of the Lorentz sphere,

$$\gamma_{ij}^{\mathrm{loc}} = \Gamma_{ij} - \Gamma_{ij}^d(\mathbf{0}) + \sum_{r_A<R_L} (\partial_i v_j(-\boldsymbol{r}_A) + \partial_j v_i(-\boldsymbol{r}_A)) \ , \quad (3.1)$$

where $\boldsymbol{\Gamma} = (\boldsymbol{\Theta} + P\boldsymbol{\delta})/G^*$ is the regularized strain of the continuous medium of macroscopic modulus G^*, according to Eq. (A.22), $\boldsymbol{\Gamma}^d(\mathbf{0})$ is the depolarization strain, i.e., the strain created at the origin by a polarization $\boldsymbol{\Pi}$ uniform into the sphere and zero outside, and the terms under the summation sign represent the strain at $\boldsymbol{r} = \mathbf{0}$ due to the inclusion present at $\boldsymbol{r} = \boldsymbol{r}_A$. Self-consistency will be achieved by requiring that the force dipole

$$\boldsymbol{\pi}_I = 8\pi c_I G_M^* \gamma^{\mathrm{loc}} \quad (3.2)$$

of the particular inclusion at the center of the Lorentz sphere has the right magnitude to create a macroscopic polarization density

$$\boldsymbol{\Pi} = \sum_I N_I \boldsymbol{\pi}_I \quad (3.3)$$

identical with the continuum polarization $\boldsymbol{\Pi} = \boldsymbol{\Sigma} - \boldsymbol{\Theta}$ we started from. This statement leads to exact results if all inclusions have the same environment, i.e., are regularly stacked. If the inclusions are randomly distributed, this leads to the mean field approximation. The depolarization field $\boldsymbol{\Gamma}^d(\boldsymbol{r})$ results from a polarization prescribed to be uniform and equal to $\boldsymbol{\Pi}$ inside the Lorentz sphere, and to vanish outside. The induction is then

$$\boldsymbol{\Theta} = \boldsymbol{\Sigma} - \boldsymbol{\Pi} = G_M^*\boldsymbol{\Gamma} - P\boldsymbol{\delta} - \boldsymbol{\Pi} \quad \text{for} \quad |\boldsymbol{r}| < R_L \quad (3.4)$$

$$\boldsymbol{\Theta} = \boldsymbol{\Sigma} = G_M^*\boldsymbol{\Gamma} - P\boldsymbol{\delta} \quad \text{for} \quad |\boldsymbol{r}| > R_L \ . \quad (3.5)$$

As no external macroscopic forces are applied, $\boldsymbol{\Theta}$ satisfies the relation

$$\partial_j \Theta_{ij} = 0 \ . \quad (3.6)$$

The discontinuity of the polarization at the surface of the Lorentz sphere induces an equal discontinuity of the macroscopic stress: calling $\boldsymbol{\Sigma}^{\mathrm{out}}(\boldsymbol{r})$ and $\boldsymbol{\Sigma}^{\mathrm{in}}(\boldsymbol{r})$ the stress on the outer and inner side of this sphere, relation (3.6) is written at a point $\boldsymbol{R}$ such that $|\boldsymbol{R}| = R_L$,

$$(\boldsymbol{\Sigma}^{\mathrm{out}} - \boldsymbol{\Sigma}^{\mathrm{in}} + \boldsymbol{\Pi}) \cdot \boldsymbol{R}/R_L = 0 \ . \quad (3.7)$$

Everywhere else, relation (3.6) results in

$$G_M^* \Delta \xi = \nabla P \ , \quad (3.8)$$

where the macroscopic displacement $\xi(r)$ is everywhere continuous.

Equations (3.6) and (3.8) are in formal analogy with Eqs. (1.3) and (1.6). The treatment of Sect. 1 may then be used, through the substitution of the spherical inclusion by the Lorentz sphere. The microscopic displacement v and pressure p must be replaced by the corresponding macroscopic quantities ξ and P, and there is no homogeneous deformation at infinity. γ^h as the cause of the deformation is replaced here by the inner macroscopic polarization $\boldsymbol{\Pi}$, and the solution can be expected to be of the form

$$\xi = \mathbf{curl\,curl}\,(h(r)\boldsymbol{\Pi}\cdot\boldsymbol{r}) \ , \tag{3.9}$$

where function h reads

$$h(r) = a'r^4 + b'r^2 + c'r^{-1} + d'r^{-3} \ . \tag{3.10}$$

As for the function g defined in (1.8), the constants c' and d' are zero inside the sphere, and a' and b' vanish outside (the primed constants of Eq. (3.10) have the dimension of the corresponding unprimed constants of Eq. (1.8) divided by a stress). The conditions of continuity for ξ take the same form as Eqs. (1.41) and (1.42):

$$20a'R_L^2 + 6b' = 6d'R_L^{-5} \tag{3.11}$$

$$8a' = 3c'R_L^{-5} + 15d'R_L^{-7} \ . \tag{3.12}$$

Eq. (3.7) has the same form as the force balance (1.39) with the interfacial tension term replaced by the polarization force $\Pi_{ij}R_j/R_L$, and where both the inner and the outer modulus is G_M^*, because of Eqs. (3.4) and (3.5). Equations (1.43) and (1.44) transform, therefore, into

$$G_M^*(6c'R_L^{-3} + 48d'R_L^{-5} + 64a'R_L^2 + 12b') + 1 = 0 \tag{3.13}$$

$$-24(c'R_L^{-3} + 5d'R_L^{-5}) - 76a'R_L^2 = 0 \ . \tag{3.14}$$

The solution to Eqs. (3.11 – 14) reads

$$\begin{aligned} a' &= 0 \ ; & b' &= -1/(30G_M^*) \ ; \\ c' &= R_L^3/(6G_M^*) \ ; & d' &= -R_L^5/(30G_M^*) \ , \end{aligned} \tag{3.15}$$

and from Eq. (1.9) we get the deformation field and the depolarization strain inside the Lorentz sphere:

$$\xi(r) = \frac{1}{5G_M^*}\boldsymbol{\Pi}\cdot\boldsymbol{r} \quad \text{for} \quad |\boldsymbol{r}| < R_L \tag{3.16}$$

$$\boldsymbol{\Gamma}^d(r) = \frac{2}{5G_M^*}\boldsymbol{\Pi} \quad \text{for} \quad |\boldsymbol{r}| < R_L \ . \tag{3.17}$$

$\boldsymbol{\Gamma}^d$ is homogeneous inside the sphere. The corresponding depolarization factor is 2/5, to be contrasted with its value 1/3 for electric field, of vectorial character.

The short scale properties of the distribution of inclusions are accounted for by the last term of Eq. (3.1). The dipole $\boldsymbol{\pi}^A$ of the inclusion at point $\boldsymbol{r}_A$ is proportional to the local strain at this point (Eq. (3.2)), it is thus symmetric and traceless. Equation (A.9) gives the local strain at the origin

$$\begin{aligned} &\sum_{r_A<R_L} \{\partial_i v_j(-\boldsymbol{r}_A) + \partial_j v_i(-\boldsymbol{r}_A)\} \\ &= \frac{3}{8\pi G_M^*}\sum_{r_A<R_L} \{(r_i^A r_k^A \pi_{jk}^A + r_j^A r_k^A \pi_{ik}^A) r_A^{-5} \\ &\qquad - 5 r_i^A r_j^A r_k^A r_l^A \pi_{kl}^A r_A^{-7}\} \ . \end{aligned} \tag{3.18}$$

Evaluation of this sum requires some knowledge about the distribution of inclusions, or some hypotheses to compensate for the lack of knowledge. We assume first that all inclusions have the same environment, which is rigorously true when they are regularly stacked, and otherwise constitutes the mean field approximation. They have then the same dipole, which can be factored out of expression (3.18). The task is now to compute the average of $r_i^A r_j^A r_A^{-5}$ and $r_i^A r_j^A r_k^A r_l^A r_A^{-7}$ over all positions $\boldsymbol{r}_A$ in the Lorentz sphere. Our second assumption will be that the distribution is isotropic, in which case averaging over all positions $\boldsymbol{r}_A$ at the same distance r_A of the origin results in

$$\langle r_i^A r_j^A \rangle = \frac{1}{3} r_A^2 \delta_{ij} \tag{3.19}$$

$$\langle r_i^A r_j^A r_k^A r_l^A \rangle = \frac{1}{15} r_A^4 (\delta_{ij}\delta_{kl} + \delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk}) \ . \tag{3.20}$$

These relations simplify Eq. (3.18) to

$$\sum_{r_A<R_L} (\partial_i v_j(-\boldsymbol{r}_A) + \partial_j v_i(-\boldsymbol{r}_A)) = 0 \ . \tag{3.21}$$

The effect of the short-range distribution averages then to zero. It must be noted that, although Eq.

(3.18) is still valid in cubic lattices, relations (3.20) and (3.21) fail.

Insertion of Eqs. (3.17) and (3.21) into Eq. (3.1) gives the local strain, inside the Lorentz sphere,

$$\gamma^{\mathrm{loc}} = \boldsymbol{\Gamma} - \frac{2}{5G_M^*}\boldsymbol{\Pi} \ . \tag{3.22}$$

The dipole of the inclusion at the center of the Lorentz sphere is taken from Eq. (2.2), where the local strain γ^{loc} replaces γ^h, and thus the macroscopic polarization density (3.3) can be written

$$\boldsymbol{\Pi} = \chi^* \boldsymbol{\Gamma} = 8\pi \sum_I c_I N_I \left(\boldsymbol{\Gamma} - \frac{2}{5G_M^*}\boldsymbol{\Pi}\right) \ . \tag{3.23}$$

The average polarizability is then

$$\chi^* = G_M^* \frac{8\pi \sum\limits_I c_I N_I}{1 + \frac{16\pi}{5} \sum\limits_I c_I N_I} \ , \tag{3.24}$$

and we eventually get the average modulus (A.22)

$$G^* = G_M^* - \chi^* \tag{3.25}$$

$$G^* = G_M^* \left(\frac{1 + \frac{3}{2}\sum\limits_I \frac{\Phi_I E_I}{D_I}}{1 - \sum\limits_I \frac{\Phi_I E_I}{D_I}} \right) \ , \tag{3.26}$$

where E_I and D_I are given by (2.6) and (2.7).

4. Discussion

Special cases of expression (3.26) of the average modulus have been given in the literature. Setting $\alpha^0 = \beta' = \beta'' = 0$ yields

$$G^* = G_M^* \frac{1 + \frac{3}{2}M}{1 - M} \text{ where } M = \sum_I \Phi_I \frac{2(G_I^* - G_M^*)}{2G_I^* + 3G_M^*} , \tag{4.1}$$

which is the Kerner result in the case of incompressible media [6] (although Kerner considered elastic media, it generalizes readily to linear viscoelasticity). In the monodisperse case, and at first order in Φ, putting G_I^* constant and real and $G_M^* = i\omega\eta$ in (4.1) gives the formula Fröhlich and Sack [2] derived for emulsion of Hookean spheres in a Newtonian liquid. If both the matrix and the inclusions are Newtonian liquids (such that $G_M^* = i\omega\eta_M$ and $G_I^* = i\omega\eta_I$), Eq. (3.26) reads

$$G^* = i\omega\eta_M \frac{1 + \frac{3}{2}\sum\limits_I \Phi_I \frac{E_I}{D_I}}{1 - \sum\limits_I \Phi_I \frac{E_I}{D_I}} \tag{4.2}$$

$$\begin{aligned} E_I &= 2i\omega(\eta_I - \eta_M)(19\eta_I + 16\eta_M) + 48\beta'\alpha^0/i\omega R^2 \\ &\quad + 32\beta''(\alpha^0 + \beta')/i\omega R^2 + 8\alpha^0/R(5\eta_I + 2\eta_M) \\ &\quad + 2\beta'/R(23\eta_I - 16\eta_M) + 4\beta''/R(13\eta_I + 8\eta_M) \end{aligned}$$

$$\begin{aligned} D_I &= i\omega(2\eta_I + 3\eta_M)(19\eta_I + 16\eta_M) + 48\beta'\alpha^0/i\omega R^2 \\ &\quad + 32\beta''(\alpha^0 + \beta')/i\omega R^2 + 40\alpha^0/R(\eta_I + \eta_M) \\ &\quad + 2\beta'/R(23\eta_I + 32\eta_M) \\ &\quad + 4\beta''/R(13\eta_I + 12\eta_M) \ . \end{aligned}$$

This gives the result of Oldroyd [4, 5] in the monodisperse case if the factor $i\omega$ is identified with his operator Δ and $G^*/i\omega$ with his viscosity operator η^*, and legitimates his formulas beyond the first order in concentration. The identity of the Kerner [6] and Olroyd [4, 5] equations with formulas (4.1) and (4.2) at arbitrary concentration comes from the fact that the effect of interactions between neighbors (3.19) and (3.20), which is ignored by these authors, averages to zero under the mean field hypothesis.

Different results would be obtained if the inclusion distribution showed a particular structure, to be introduced into Eq. (3.20). This equation fails also for inclusions so close to each other that their interaction is not just dipole-dipole.

If coefficients β' and β'' have a finite relaxation time (whereas α^0 remains constant), the zero frequency limit of Eq. (4.2) takes the same form, with

$$\begin{aligned} E_I &= 48\zeta'/R + 32\zeta''/R + 8(5\eta_I + 2\eta_M) \\ D_I &= 48\zeta'/R + 32\zeta''/R + 40(\eta_I + \eta_M) \ , \end{aligned} \tag{4.3}$$

where ζ' and ζ'' are the limits of $\beta'/i\omega$ and $\beta''/i\omega$, respectively, as $\omega \to 0$ (only the terms varying like ω, involving α^0, have survived; all other terms vary like ω^2 in the limit $\omega \to 0$). The Taylor formula is recovered in the low concentration limit if ζ' and ζ'' are set to zero.

Appendix: Theory of viscoelastic polarization

Let a linear viscoelastic incompressible medium be submitted to a harmonic point force $\boldsymbol{F}(t) = \boldsymbol{F}(0)\exp(i\omega t)$, concentrated at the origin. The corresponding force density f writes

$$f(r) = F\delta(r) \quad (A.1)$$

with an implied time factor $\exp(i\omega t)$. The displacement field is related to F by the Green tensor U

$$u(r) = U(r)\cdot F \ . \quad (A.2)$$

At a frequency ω low enough for inertia to play no role at the length scale of interest, and in the case of an infinite, incompressible, and isotropic medium, U takes the form

$$U_{ij}(r) = \frac{1}{8\pi G^*(\omega)}(\delta_{ij}r^{-1} + r_i r_j r^{-3}) \ , \quad (A.3)$$

where the viscoelastic modulus G^* is complex and function of the frequency ω. The Green tensor of elasticity corresponds to G^* constant and real [13], and the Oseen tensor [14] for incompressible Newtonian fluid of viscosity η is recovered by setting $G^* = i\omega\eta$.

In accordance with Maxwell's theory of multipoles, we define a force dipole as a system of two opposite point forces of equal strength, applied to two different points with separation d. If, for simplicity, one of these points is chosen as the origin, the force density of the dipole reads

$$f(r) = F\delta(r-d) - F\delta(r) \ . \quad (A.4)$$

Let the dipole moment of this force distribution be the second rank tensor

$$\pi_{jk} = F_j d_k \ . \quad (A.5)$$

The torque of the dipole is the vector $\varepsilon_{ijk}\pi_{jk}$ associated with the antisymmetric part. In the limit of vanishing separation d, keeping constant the dipole moment π, this system of forces becomes a point dipole generating a displacement

$$u_i(r) = \lim_{d\to 0}(U_{ij}(r-d) - U_{ij}(r))F_j \quad (A.6)$$

$$= -\pi_{jk}\partial_k U_{ij}(r) \ . \quad (A.7)$$

The Green tensor of a dipole is thus the third rank tensor

$$U_{ijk}(r) = -\partial_k U_{ij}(r) \ , \quad (A.8)$$

leading to

$$u_i(r) = \pi_{jk}U_{ijk}(r)$$
$$= \frac{1}{8\pi G^*}\{(\pi_{ij} - \pi_{ji})r_j r^{-3} + (3\pi_{jk} - \pi_{ll}\delta_{jk})r_i r_j r_k r^{-5}\} \ . \quad (A.9)$$

Because of incompressibility, the isotropic part of π does not contribute to u.

A point quadrupole can be built in the same way with two point dipoles, π_{jk} at point d' and $-\pi_{jk}$ at the origin; and by making d' to vanish, keeping constant the quadrupole moment $q_{jkl} = \pi_{jk}d'_l$. The same process, applied L times, generates the 2^L-pole. The associated Green tensor is of order L + 1, and is a homogeneous function of r, of degree $-L-1$.

The continuum mechanics used here is valid at a macroscopic scale, and the limiting processes must stop before reaching the atomic scale. On the other hand, some problems involve a "microscopic, but large compared to atomic" scale at which the force distribution f is defined (and continuum mechanics is valid), and a coarse, "macroscopic" scale at which the deformation is observed. In what follows, this intermediate length scale will be called microscopic. The concept of viscoelastic multipole allows to describe the macroscopic mechanical behavior by averaging the effect of the microscopic force distribution $f(r)$, in analogy with the Lorentz procedure in electricity. The mechanical analogues of the polarized atoms in vacuum are here the inclusions into the matrix. If the force density f can be resolved into an equivalent distribution of point dipoles, the macroscopic dipole density $\Pi(r)$ is obtained by averaging the microscopic distribution of dipoles over a distance s around the point r. We use, therefore, a regularizing function $\Psi(r)$ which has appreciable value within a distance s around the origin, and such that

$$\int \Psi(r)dv = 1 \ . \quad (A.10)$$

In addition, Ψ will be required to be differentiable at least once, and to vanish beyond a given finite radius (of order s). It permits to introduce the macroscopic dipole density

$$\Pi(r) = \sum_A \pi^A \Psi(r - r_A) \ , \quad (A.11)$$

where r_a is the location of dipole π^a, and the summation extends over the whole distribution. The macroscopic pressure and stress deviator read, respectively,

$$P(r) = \int p(r')\Psi(r-r')dv' \ ,$$
$$T(r) = \int \tau(r')\Psi(r-r')dv' \ , \quad (A.12)$$

and regularization of the total stress $\sigma = \tau - p\delta$ yields the macroscopic stress $\Sigma = T - P\delta$.

The macroscopic displacement is accordingly,

$$\xi(r) = \int u(r')\Psi(r-r')dv' \quad (A.13)$$

and the macroscopic deformation tensor $\Gamma_{ij} = \partial\xi_j/\partial r_i + \partial\xi_i/\partial r_j$ results, after integration by parts, in

$$\Gamma(r) = \int \gamma(r')\Psi(r-r')dv' \ , \quad (A.14)$$

where $\gamma_{ij}(r') = \partial u_j/\partial r'_i + \partial u_i/\partial r'_j$ is the microscopic deformation tensor. If γ is traceless, so is Γ. Consequently, the stress-strain relation holds unmodified by the averaging:

$$\Sigma = G^*\Gamma - P\delta \ . \quad (A.15)$$

Inserting the displacement field created by the distribution of dipoles:

$$u_i(r) = -\sum_A \pi^A_{jk}\partial_k U_{ij}(r - r_A) \quad (A.16)$$

into Eq. (A.13) yields

$$\xi_i(r) = -\int \Pi_{jk}(r')\partial_k U_{ij}(r-r')dv' \ . \tag{A.17}$$

Assuming, for simplicity, that the dipole distribution vanishes at infinity, one gets after integration by parts

$$\xi_i(r) = -\int U_{ij}(r-r')\partial'_k \Pi_{jk}(r')dv' \ , \tag{A.18}$$

where $\partial_k = \partial/\partial r_k$ and $\partial'_k = \partial/\partial r'_k$. This identifies with the displacement created by a polarization force distribution φ^{pol}

$$\varphi_j^{\text{pol}}(r) = -\partial_k \Pi_{jk}(r) \ . \tag{A.19}$$

The isotropic part of $\boldsymbol{\Pi}$ is irrelevant, since the pressure is undetermined in an incompressible medium. The macroscopic viscoelastic force density acting on the medium is thus the divergence of a stress induction $\boldsymbol{\Theta}$ (named in analogy with the electric induction)

$$\varphi_j = \partial_k \Theta_{jk} \ . \tag{A.20}$$

Θ accounts for both the stress Σ generated by the macroscopic distortion in the unpolarized medium and the average effect of the force dipoles:

$$\Theta = \Sigma - \Pi \ . \tag{A.21}$$

If the dipole density is proportional to the strain $\boldsymbol{\Pi} = \chi^* \boldsymbol{\Gamma}$, the medium behaves at the macroscopic scale as a continuum of viscoelastic modulus $\tilde{G}^*$

$$\boldsymbol{\Theta} = \tilde{G}^* \boldsymbol{\Gamma} - P\boldsymbol{\delta} \ , \quad \text{where} \quad \tilde{G}^* = G^* - \chi^* \ . \tag{A.22}$$

For the regularized quantities to be smooth, the length s must be large enough to cover an appreciable number of dipoles $\boldsymbol{\pi}^a$, but small with respect to the macroscopic length scale. All developments of this appendix hold however for any value of s, and setting $\Psi(r) = \delta(r)$ makes the regularized equations identical with the microscopic ones. A meaningful macroscopic length scale comes out only from the constitutive equation, which determines the macroscopic polarizability χ^*.

The results presented here are independent of the particular form (A.3) of the Green tensor, which is known to be wrong at long distance [11, § 24]. When form (A.3) is assumed, the force dipole (A.5) is consistent with the definition given by Batchelor [10].

References

1. Einstein A (1906/1911) Ann Phys 19:289; 34:591
2. Fröhlich H, Sack R (1946) Proc Roy Soc A185:415
3. Taylor GI (1932) Proc Roy Soc A138:41
4. Oldroyd JG (1953) Proc Roy Soc A218:122
5. Oldroyd JG (1955) Proc Roy Soc A232:567
6. Kerner EH (1956) Proc Roy Soc B69:808
7. Batchelor GK, Green JT (1972) J Fluid Mech 56:401
8. Schowalter WR, Chaffey CE, Brenner H (1968) J of Colloid and Interface Sci 26:152
9. Choi SJ, Schowalter WR (1972) Phys of Fluids 18:420
10. Batchelor GK (1969) J Fluid Mech 41:545
11. Landau L, Lifshitz EM (1959) Fluid mechanics, § 22. Addison Wesley, Reading MA
12. Lucassen J, van der Tempel M (1972) Chem Eng Sci 27:1283
13. Love AEH (1893/1954) Mathematical theory of elasticity. Cambridge University Press
14. Oseen CW (1927) Neure Methoden und Ergebnisse in der Hydrodynamic. Akad Verlag, Leipzig

(Received December 18, 1989; accepted April 9, 1990)

Author's address:

J.F. Palierne
Institut Charles Sadron (E.A.H.P.)
4, rue Boussingault
67083 Strasbourg Cedex, France