ON THE VISCOSITY OF COLLOIDS

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A previous paper [6] presented a linear thermodynamic theory of deformation and flow. The Onsager theory of non-equilibrium processes was shown to suit describing processes recorded as typical non-linear ones in mechanics. The method worked out there is rather abstract, and ignores the microstructure of the bodies studied. Essentials of the method will be illustrated on an example of some practical importance where the internal variable have an evident meaning. This problem is the flow of globular colloids. For the sake of simplicity, the body is supposed to be fluid, and to have two phases. The continuous phase is a Newtonian fluid, while the dispersed one consists of elastic spheres of uniform size. Because of their practical importance, only isochoric (i.e. steady-volume) motions will be concerned with. The condition of homodispersity facilitates the calculations nevertheless the final statements can be generalized for any dispersity.

The equilibrium states of the medium outlined above are characterized by the specific internal energy. If the medium is out of equilibrium the deformation of the particles has to be taken into consideration. During motion the spheres are deformed while a part of the internal energy is stored as restoring energy. As soon as the body is returned to equilibrium state the particles recover their original shape and the elastic energy stored in them is dissipated.

In accordance with what was said above, the specific internal energy and the deformation tensor of the particles are needed as state variables for describing any momentary state. All the other properties are given as functions of these, among others, the specific entropy:

$$s = s(u, \epsilon) \tag{1}$$

According to the presumption upon the structure of the body, the entropy depends on the undissipated part of the internal energy alone, and the form of the function is the same both in and out of equilibrium:

$$s = s\left(u - \frac{\varphi\mu}{\varrho}\,\epsilon : \epsilon\right) \tag{2}$$

Here s stands for the specific entropy, u for the specific internal energy ϱ is the density, φ means the volume fraction of the dispersed phase, while μ is the shear modulus of the spheres. The strain tensor ϵ of the particles, is symmetric and has zero trace. Moreover ϵ, equals zero in any equilibrium state, i.e. in any case where the particles are real spheres.

For the sake of thermodynamic treatment, let us determine the actual form of the entropy production. Substituting the material time derivative of function (2) into the general form of the entropy balance equation:

$$\sigma_s = \varrho\dot{s} + \mathrm{div}\frac{\vec{J}_q}{T} = \frac{\varrho}{T}\left(\dot{u} - \frac{2\varphi\mu}{\varrho}\epsilon : \dot{\epsilon}\right) + \frac{1}{T}\mathrm{div}\vec{J}_q + \vec{J}_q\,\mathrm{grad}\frac{1}{T} \qquad (3)$$

Here σ_s is the entropy production density, T is the temperature, $\vec{J}_q$ is the heat flux density.

Making use of the balance of internal energy:

$$\varrho\dot{u} + \mathrm{div}\,\vec{J}_q = \mathbf{t} : \overset{\circ}{\mathbf{d}} \qquad (4)$$

where $\mathbf{t}$ is the deviatoric part of the Cauchy stress tensor and $\overset{\circ}{\mathbf{d}}$ is the symmetric part of the velocity gradient tensor, the entropy production gets

$$\sigma_s = \frac{1}{T}\mathbf{t} : \overset{\circ}{\mathbf{d}} - \frac{2\varphi\mu}{T}\epsilon : \dot{\epsilon} - \vec{J}_q\frac{\mathrm{grad}\,T}{T^2} \qquad (5)$$

A still more expedient from of the entropy production can be obtained by multiplying (5) by the temperature T:

$$T\sigma_s = \mathbf{t} : \overset{\circ}{\mathbf{d}} - 2\varphi\mu\,\epsilon : \dot{\epsilon} - \vec{J}_q\frac{\mathrm{grad}\,T}{T} \qquad (6)$$

At a first glance the constitutive equations seem to result from here, making use of Onsager's law. It would be so, if any of the time derivatives in Eq. (6) ment the velocity of some material process. This is so in the case of $\overset{\circ}{\mathbf{d}}$ and $\vec{J}_q$ but not for $\dot{\epsilon}$. Namely, $\dot{\epsilon}$ can be non-zero even if nothing happens to the body but the frame of reference rotates.

The disturbances will be eliminated by some kinematical considerations. Denote by $\bar{R}$ a position which identifies a given material point of the body. Let $\bar{r}$ represent a position fixed in space, then for the place of any particular material point $\bar{R}$ of the body

$$\bar{r} = \bar{r}(\bar{R}, t) \qquad (7)$$

The deformation gradient is defined as a linear transformation operator $\mathbf{X}$ mapping the material point from $\bar{r}$ onto $\bar{R}$:

$$d\bar{r} = \mathbf{X}d\bar{R} \qquad (8)$$

According to the polar decomposition theorem of linear algebra, the tensor **X** can be uniquely decomposed into the product of two tensors, namely

$$\mathbf{X} = \mathbf{Q} \cdot \mathbf{D} \tag{9}$$

where **Q** is an orthogonal tensor, and **D** is a positive definite tensor, i.e. **D** is symmetric $\mathbf{D} = \mathbf{D}^T$ and has positive eigenvalues. Introduce a local frame marked by *, that the relationships

$$d\bar{r}^* = \mathbf{Q}^T d\bar{r} \quad \text{and} \quad \mathbf{X}^* = \mathbf{Q}^T \mathbf{X} = \mathbf{Q}^T \mathbf{Q} \mathbf{D} = \mathbf{D} \tag{10}$$

hold in. This local frame of reference corotates with the neighbourhood of the material point in consideration. The strain tensor of the colloid particles with respect to this new frame is given by

$$\epsilon^* = \mathbf{Q}^T \epsilon \mathbf{Q} \tag{11}$$

The changes of ϵ^* join real deformations, and the time derivative of ϵ^* describes a real material process:

$$\dot{\epsilon}^* = \mathbf{Q}^T(\dot{\epsilon} + \epsilon\dot{\mathbf{Q}}\mathbf{Q}^T - \mathbf{Q}\dot{\mathbf{Q}}^T\epsilon)\mathbf{Q} \tag{12}$$

The quantity in parentheses — let it be denoted by $\overset{\circ}{\epsilon}$ —

$$\overset{\circ}{\epsilon} = \dot{\epsilon} + \epsilon\omega - \omega\epsilon \tag{13}$$

has quite a clear physical meaning [8]. Here the notation

$$\omega = \overset{\bullet}{\mathbf{Q}}\mathbf{Q}^T \tag{14}$$

has been introduced for the spin tensor ω, which is antisymmetric:

$$\omega = -\omega^T \tag{15}$$

in accordance with the identities

$$\mathbf{Q}\mathbf{Q}^T = \delta \quad \text{and} \quad \dot{\mathbf{Q}}\mathbf{Q}^T = -\mathbf{Q}\dot{\mathbf{Q}}^T. \tag{16}$$

The spin tensor ω equals the antisymmetric part of the velocity gradient if the present configuration is used as a reference one. In this case, the time derivative of Eq. (8) is

$$d\bar{v} = \dot{\mathbf{X}}dr = (\dot{\mathbf{Q}} + \dot{\bar{\mathbf{D}}})\,d\bar{r} \tag{17}$$

which proves the statement above.

Making use of (13), we get

$$T\sigma_s = \mathbf{t} : \overset{\circ}{\mathbf{d}} - 2\varphi\mu\epsilon : \overset{\circ}{\epsilon} - \bar{J}_q \frac{\text{grad } T}{T} \tag{18}$$

This is the form of the entropy source strength that can be applied for getting the constitutive equations [1, 2, 3]. Onsager's linear laws result in the following equations:

$$\overset{\circ}{\mathbf{d}} = L_{11}\mathbf{t} - 2\varphi\mu L_{12}\boldsymbol{\epsilon} \tag{19}$$

$$\overset{\circ}{\boldsymbol{\epsilon}} = L_{12}t - 2\varphi\mu L_{22}\boldsymbol{\epsilon} \tag{20}$$

$$\overline{J}_q = -L_{qq}\frac{\text{gard } T}{T} \tag{21}$$

The last one is Fourier's law, which becomes obvious by introducing the notation

$$\lambda = \frac{L_{qq}}{T} \tag{22}$$

As the body is isotropic, the equation concerning heat conduction is independent of the others. Hence we confine ourselves to isothermal motions and omit the heat conduction. The Eqs (19) and (20) give a good account of the colloid particles influencing macroscopic motions.

Two special applications will be treated of next. The first of them concerns small amplitude oscillations.

Let the velocity of the medium be

$$\overline{v}(\overline{r}, t) = \overline{v}_0(\overline{r})e^{pt} \tag{23}$$

where p is the complex frequency. The tensor $\boldsymbol{\epsilon}$ and the velocity are supposed to be small, hence the higher powers in (13) can be neglected.

$$\overset{\circ}{\boldsymbol{\epsilon}} \approx \dot{\boldsymbol{\epsilon}} = p\boldsymbol{\epsilon} \tag{24}$$

Making use of (24) and eliminating $\boldsymbol{\epsilon}$ from Eqs (19) and (20) results in the relationships between the speed of deformation and the stress tensor:

$$\overset{\circ}{\mathbf{d}} = \left(L_{11} - \frac{2\varphi\mu L_{12}^2}{p + 2\varphi\mu L_{22}}\right)\mathbf{t} \tag{25}$$

Hence, the complex viscosity is:

$$\frac{1}{2\eta} = L_{11} - \frac{2\varphi\mu L_{12}^2}{p + 2\varphi\mu L_{22}} \tag{26}$$

The body displays a viscoelastic behaviour and the mechanical model customary in rheology contains a spring and two dashpots. The two equivalent versions are seen in Figs 1 and 2. The values of the phenomenological coefficients are determined by comparing the complex viscosity given above with the formula derived by Oldroyd for the same model of globular colloids [7].
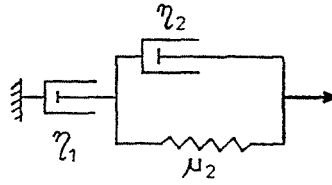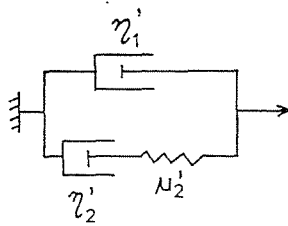
$$\eta_1 = \frac{L_{22}}{2(L_{11}L_{22}-L_{12}^2)}$$

$$\eta_2 = \frac{L_{22}}{2L_{12}^2}$$

$$\mu_2 = \varphi\mu\,\frac{L_{22}^2}{L_{12}^2}$$

Fig. 1

$$\eta_1' = \frac{1}{2L_{11}}$$

$$\eta_2' = \frac{L_{12}^2}{2L_{11}(L_{11}L_{22}-L_{12}^2)}$$

$$\mu_2' = \varphi\mu\,\frac{L_{12}^2}{L_{11}^2}$$

Fig. 2

The Oldroyd formula is explicit for the shear modulus:

$$\mu^* = \mu_\theta\,\frac{(2+3\varphi)\mu + 3(1-\varphi)\mu_0}{2(1-\varphi)\mu + (3+2\varphi)\mu_\theta} \tag{27}$$

where μ^*, μ and μ_0 are the shear moduli referring to the colloid, the dispersed material and the continuous phase, respectively. Introducing complex vis-

cosity, (27) turns to

$$\eta = \eta_0 \frac{(2 + 3\varphi)\mu + 3(1 - \varphi)\eta_0 p}{2(1 - \varphi)\mu + (3 + 2\varphi)\eta_0 p} \tag{28}$$

Hence, phenomenological coefficients are:

$$L_{11} = \frac{3 + 2\varphi}{6(1 - \varphi)\eta_0}$$

$$L_{22} = \frac{2 + 3\varphi}{6\varphi(1 - \varphi)\eta_0} \tag{29}$$

$$L_{12} = \frac{5}{6(1 - \varphi)\eta_0}$$

Remind that the sign of L_{12} was determined from Eq. (20).

Next, let us consider viscometric functions. According to the general theory of viscometric flows [4, 5], steady laminar shear flows will be dealt with. The velocity $\bar{\mathbf{v}}$ be of the form

$$v_x = \varkappa y, \quad v_y = 0, \quad v_z = 0 \tag{30}$$

It is simple to calculate the components of the velocity gradient tensor.

$$[\mathrm{Grad}\,\bar{v}] = \begin{bmatrix} 0 & \varkappa & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \tag{31}$$

For the tensors $\mathbf{d}$ and $\boldsymbol{\omega}$ we find

$$[\mathbf{\mathring{d}}] = \frac{\varkappa}{2} \begin{bmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \text{ and } [\boldsymbol{\omega}] = \frac{\varkappa}{2} \begin{bmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \tag{32}$$

Now let us link the specification of the flow field to the constitutive equations. Keeping the stationarity in mind, we get

$$\mathring{d}_{ij} = L_{11}t_{ij} - 2\varphi\mu L_{12}\varepsilon_{ij} \tag{33}$$

$$\varepsilon_{ik}\omega_{kj} - \omega_{ik}\varepsilon_{kj} = L_{12}t_{ij} - 2\varphi\mu L_{22}\varepsilon_{ij} \tag{34}$$

First of all the value of ε_{33} will be determined by using (32), (33) and (34), leading to the system of equations

$$0 = L_{11}t_{33} - 2\varphi\mu L_{12}\varepsilon_{33}$$

$$0 = L_{12}t_{33} - 2\varphi\mu L_{22}\varepsilon_{33} \tag{35}$$

hence $\varepsilon_{33} = t_{33} = 0$. The equations for ε_{13} and ε_{23} are similar:

$$0 = L_{11}t_{13} - 2\varphi\mu L_{12}\varepsilon_{13}$$

$$\varepsilon_{1j}\omega_{j3} - \omega_{1j}\varepsilon_{j3} = -\frac{\varkappa}{2}\varepsilon_{23} = L_{21}t_{13} - 2\varphi\mu L_{22}\varepsilon_{13}$$

$$0 = L_{11}t_{23} - 2\varphi\mu L_{12}\varepsilon_{23} \tag{36}$$

$$\varepsilon_{2j}\omega_{j3} - \omega_{2j}\varepsilon_{j3} = \frac{\varkappa}{2}\varepsilon_{13} = L_{12}t_{23} - 2\varphi\mu L_{22}\varepsilon_{23}$$

This system of linear equations is also homogeneous with non-zero determinant, thus $\varepsilon_{13} = \varepsilon_{23} = t_{13} = t_{23} = 0$.

Now, Eqs (33) and (34) will be put down in matrix notation.

$$\frac{\varkappa}{2}\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} = L_{11}\begin{bmatrix} -\sigma_y & \tau \\ \tau & \sigma_y \end{bmatrix} - 2\varphi\mu L_{12}\begin{bmatrix} -\varepsilon_{22} & \varepsilon_{12} \\ \varepsilon_{12} & \varepsilon_{22} \end{bmatrix} \tag{37}$$

$$\frac{\varkappa}{2}\begin{bmatrix} -\varepsilon_{22} & \varepsilon_{12} \\ \varepsilon_{12} & \varepsilon_{22} \end{bmatrix}\begin{bmatrix} 0 & 1 \\ -1 & 0 \end{bmatrix} - \frac{\varkappa}{2}\begin{bmatrix} 0 & 1 \\ -1 & 0 \end{bmatrix}\begin{bmatrix} -\varepsilon_{22} & \varepsilon_{12} \\ \varepsilon_{12} & \varepsilon_{22} \end{bmatrix} =$$

$$= \frac{\varkappa}{2}\begin{bmatrix} -\varepsilon_{12} & -\varepsilon_{22} \\ -\varepsilon_{22} & \varepsilon_{12} \end{bmatrix} = L_{12}\begin{bmatrix} -\sigma_y & \tau \\ \tau & \sigma_y \end{bmatrix} - 2\varphi\mu L_{22}\begin{bmatrix} \varepsilon_{22} & \varepsilon_{12} \\ \varepsilon_{12} & \varepsilon_{22} \end{bmatrix} \tag{38}$$

The third rows and columns containing only zeros have been omitted. The matrices in (37) and (38) are defined uniquely by their second columns, hence the equations can be reformulated:

$$\frac{\varkappa}{2}\begin{bmatrix} 1 \\ 0 \end{bmatrix} = L_{11}\begin{bmatrix} \tau \\ \sigma_y \end{bmatrix} - 2\varphi\eta L_{12}\begin{bmatrix} \varepsilon_{12} \\ \varepsilon_{22} \end{bmatrix} \tag{39}$$

$$\begin{bmatrix} \overset{\circ}{\varepsilon}_{12} \\ \overset{\circ}{\varepsilon}_{22} \end{bmatrix} = \varkappa\begin{bmatrix} -\varepsilon_{22} \\ \varepsilon_{12} \end{bmatrix} = L_{12}\begin{bmatrix} \tau \\ \sigma_y \end{bmatrix} - 2\varphi\mu L_{22}\begin{bmatrix} \varepsilon_{12} \\ \varepsilon_{22} \end{bmatrix} \tag{40}$$

Note the similarity to the complex numbers. Taking the first and second components of the matrices as the real and imaginary parts of complex numbers, respectively, the matrix equations are reduced the complex form

$$\frac{\varkappa}{2} = L_{11}t - 2\varphi\mu L_{12}\varepsilon \tag{41}$$

$$i\varkappa\varepsilon = L_{12}t - 2\varphi\mu L_{22}\varepsilon \tag{42}$$

Eliminating the complex number ε and introducing the notation $p = i\varkappa$:

$$\frac{\varkappa}{2} = \left(L_{11} - \frac{2\varphi\mu L_{12}^2}{p + 2\varphi\mu L_{22}}\right)\mathbf{t} \tag{43}$$

The formal analogy to (25) is complete, the complex viscosity being:

$$\frac{1}{2\eta} = L_{11} - \frac{2\varphi\mu L_{12}^2}{p + 2\varphi\mu L_{22}} \tag{44}$$

The complex stress is given by

$$t = \eta\varkappa \tag{45}$$

where the complex viscosity is the same function of the variable p as in the case of small-amplitude oscillations, the physical meaning of the complex variable p is, however, different. The real part of the complex stress means the shear stress

$$\tau = \mathrm{Re}\,\eta\varkappa \tag{46}$$

the imaginary part means normal stress difference

$$\sigma_y = -\sigma_x = \mathrm{Im}\eta \cdot \varkappa \tag{47}$$

The general relationships may be used to calculate the actual form of the viscometric functions. The complex viscosity is available by using (28)

$$\eta = \eta_0 \frac{(2 + 3\varphi)\mu + 3(1 - \varphi)\eta_0\varkappa i}{2(1 - \varphi)\mu + (3 + 2\varphi)\eta_0\varkappa i} \tag{48}$$

For the sake of shortness, introduce the notations

$$\varkappa_0 = \frac{2(1 - \varphi)\mu}{(3 + 2\varphi)\eta_0}; \quad \eta_s = \eta_0 \frac{2 + 3\varphi}{2(1 - \varphi)}; \quad \eta_f = \eta_0 \frac{3(1 - \varphi)}{3 + 2\varphi} \tag{49}$$

where η_s and η_f mean the limit viscosities for slow and fast motions, respectively.

$$\eta = \frac{\eta_s + i\eta_f \dfrac{\varkappa}{\varkappa_0}}{1 + i \dfrac{\varkappa}{\varkappa_0}} \tag{50}$$

Hence, the viscometric functions are

$$\tau = \left[\eta_f + \frac{\eta_s - \eta_f}{1 + \left(\dfrac{\varkappa}{\varkappa_0}\right)^2}\right]\varkappa \tag{51}$$

$$\sigma_y = -\sigma_x = -\varkappa_0(\eta_s - \eta_f)\frac{\left(\dfrac{\varkappa}{\varkappa_0}\right)^2}{1 + \left(\dfrac{\varkappa}{\varkappa_0}\right)^2} \tag{52}$$

These viscometric functions given by the linear Onsager theory describe the non-Newtonian features of colloid systems. Their non-linearity is not due to the non-linearity of constitutive equations but to rotations appearing during motions.

Finally, we mention that all the considerations above can be extended over emulsions. In that case, the effect of interface tension is taken into account by considering the stored energy and defining an apparent modulus of elasticity. Formulae become simple if the viscosity of the dispersed material is negligible e.g. in the case of foams.

In this case the apparent shear modulus is:

$$\mu = \frac{4}{5} \frac{\gamma}{r} \tag{53}$$

where γ is the interface tension and r the radius of the drops or bubbles. Its value depends on the size of the colloid particles, hence the heterodispersity causes some difficulty, to be overcome by defining several internal degrees of freedom.

Summary

On the ground of Onsagerian thermodynamics, the non-Newtonian behaviour of globular colloids is dealt with. The viscometric functions are established. In the case of emulsions, the effect of interface tension is taken into account.

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