Viscoelasticity Associated with Molecular Alignment

S. Hess

Institut für Theoretische Physik der Universität Erlangen-Nürnberg, Erlangen

Z. Naturforsch. **35a**, 915–919 (1980); received June 12, 1980

Viscoelasticity as it becomes apparent through the oscillatory motion in flow relaxation experiments is studied theoretically for liquids and liquid solutions containing nonspherical particles. The coupling between the viscous flow and the molecular alignment which underlies the flow birefringence gives rise to a viscoelastic behavior. The relevant time scale is determined by the orientational relaxation time rather than the (often much shorter) Maxwell relaxation time. The possible relevance of the present theory for the viscoelastic behavior of some dilute aqueous detergent solutions is discussed.

The coupling between the viscous flow and the molecular alignment which underlies the flow birefringence and the non-newtonian viscosity of molecular liquids and colloidal solutions also implies a viscoelastic behavior. The viscoelasticity associated with the molecular alignment is rather different from the viscoelasticity which follows from the Maxwell relaxation model [1]. In particular, the "elastic component" of the viscoelasticity shows up on a frequency scale determined by τ^{-1} where τ is the orientational relaxation time which can be many orders of magnitude larger than the Maxwell relaxation time τ_M. Thus the present theory may provide an explanation for the surprising viscoelastic behavior observed in some dilute detergent solutions [2] which have a viscosity comparable to that of water. The method of observation was to look for oscillatory motions in a simple flow relaxation experiment [2].

In this article the basic equations are stated which govern the friction pressure tensor $\bar{\mathbf{p}}$ and the alignment tensor $\mathbf{a}$. Then these equations are applied to an experimental situation where a liquid can reveal its viscoelasticity: the occurrence of a free oscillatory motion (which is damped) where an ordinary viscous fluid would just show an exponential relaxation.

Firstly, however, a remark on the alignment is in order. Consider a liquid containing (effectively) axisymmetric particles. Their orientation can be described by an orientational distribution function depending on the unit vector $\boldsymbol{u}$ which is parallel to the figure axis of a particle. The type of orientation which is of relevance for the present problem is characterized by the (2nd rank) alignment tensor [3] $\mathbf{a}=\zeta\langle\overline{\boldsymbol{uu}}\rangle$. The bracket $\langle\ldots\rangle$ indicates an average evaluated with the orientational distribution function. The symbol $\overline{\ldots}$ refers to the symmetric traceless part of a tensor, in particular, one has $\overline{\boldsymbol{uu}}=\boldsymbol{uu}-\frac{1}{3}\boldsymbol{\delta}$; $\boldsymbol{\delta}$ is the unit tensor. The quantity ζ is a numerical factor which can be chosen conveniently but need not be specified here.

Reprint requests to Prof. Dr. S. Hess, Inst. f. Theor. Physik, Glückstr. 6, D-8520 Erlangen.

The Basic Equations

The equations for the symmetric traceless part $\bar{\mathbf{p}}$ of the friction pressure tensor $\mathbf{p}$ and the alignment tensor are [4, 5]

$$-\left(1+\tau_M\frac{\mathrm{d}}{\mathrm{d}t}\right)\bar{\mathbf{p}} = 2\eta\overline{\boldsymbol{\nabla v}}+\sqrt{2}P_k\tau_{pa}\left(\frac{\mathrm{d}}{\mathrm{d}t}\mathbf{a}-2\overline{\boldsymbol{\omega}\times\mathbf{a}}\right), \tag{1}$$

$$-\boldsymbol{\Sigma}(\mathbf{a})=\sqrt{2}\tau_{ap}\overline{\boldsymbol{\nabla v}}+\tau_a\left(\frac{\mathrm{d}}{\mathrm{d}t}\mathbf{a}-2\overline{\boldsymbol{\omega}\times\mathbf{a}}\right) \tag{2}$$

where $\boldsymbol{v}$ is the flow velocity and the average rotational velocity $\boldsymbol{\omega}$ of the (stiff) particles is given by

$$\boldsymbol{\omega}=\tfrac{1}{2}\,\mathrm{rot}\,\boldsymbol{v}\,. \tag{3}$$

The quantity $P_k=nk_BT$ is the kinetic pressure, n is the (total) number density, k_B the Boltzmann constant and T the temperature of the liquid. The (first newtonian) viscosity η can be written as $\eta=P_k\tau_p$. The relaxation time coefficients $\tau..$ have the properties

$$\tau_p>0\,,\ \tau_a>0\,,\ \tau_{ap}\tau_{pa}<\tau_a\tau_p\,, \tag{4}$$

0340-4811 / 80 / 0900-0915 $ 01.00/0. — Please order a reprint rather than making your own copy.

and the nondiagonal relaxation times obey the Onsager symmetry relation

$$\tau_{ap} = \tau_{pa} . \tag{5}$$

The Maxwell relaxation time τ_M is related to the viscosity η by $\eta = G_M \tau_M$ where G_M is the (Maxwell) shear modulus. For liquids without a network structure, one has $G_M \approx P_k$ and consequently $\tau_M \approx \tau_p$. The quantity $\boldsymbol{\Sigma}$ occurring on the left hand side of (2), in general, is a nonlinear function of the alignment tensor $\mathbf{a}$. For a liquid in the isotropic phase, it can be approximated by its linear term, viz.

$$\boldsymbol{\Sigma} = A\,\mathbf{a} \tag{6}$$

where the dimensionless coefficient A is of the form

$$A = A_0(1 - T^*/T) , \tag{7}$$

or

$$A = A_0[1 - g(c/c^*)] , \; g(x) \leq 1 \text{ for } x \leq 1 \tag{8}$$

for a thermotropic or lyotropic liquid crystal, respectively. The characteristic temperature T^* (concentration c^*) is somewhat smaller (larger) than the temperature (concentration) where the transition from the isotropic to the nematic phase takes place. The coefficient A_0 is only weakly dependent on the temperature T or the concentration c. Without loss of generality, the normalization of the alignment tensor $\mathbf{a}$ can be chosen such that $A_0 = 1$.

For $\tau_{pa} = 0$, i.e. no coupling between alignment and viscous flow, (1) reduces to the equation of the Maxwell relaxation model for viscoelasticity. The full equations (1, 2) have been derived within the framework of irreversible thermodynamics in Refs. [4, 5] and applied to flow alignment and viscous flow both in the isotropic and nematic phases of a liquid crystal; non-newtonian flow behavior was treated in Refs. [5, 6]. With the linear approximation (6, 7), Eqs. (1, 2) essentially reduce to the equations proposed by de Gennes [7] for pretransitional phenomena in the isotropic phase of a nematic liquid crystal. Analogous equations with $A = 1$ have been derived previously [8] from a generalized Boltzmann equation, viz. the Waldmann-Snider equation for molecular gases where, however, the alignment tensor has a different microscopic meaning. For an application to flow birefringence and viscous flow in the presence of an external magnetic field see [9, 10]. Equation (2) can also be derived from a generalized Fokker-Planck equation [11].

For the present applications, it is advantageous to eliminate the alignment tensor $\mathbf{a}$ from (1, 2). With $\boldsymbol{\Sigma}$ replaced by $A\,\mathbf{a}$, cf. (6, 7, 8), the equation

$$-\left(1 + \tau_M \frac{d}{dt}\right) \bar{\mathbf{p}} = 2\eta \overline{\nabla \boldsymbol{v}} + \tau\left(\frac{d}{dt} - 2\,\boldsymbol{\omega} \times\right)\left(\bar{\mathbf{p}} + 2\eta_\infty \overline{\nabla \boldsymbol{v}}\right) \tag{9}$$

is obtained, where the relaxation time τ is given by

$$\tau = \tau_a A^{-1} , \tag{10}$$

and

$$\eta_\infty = \eta\left(1 - \frac{\tau_{ap}\,\tau_{pa}}{\tau_a\,\tau_p}\right) < \eta \tag{11}$$

is the 2nd newtonian viscosity which is reached for

$$\tau\,\omega = \tau\,\tfrac{1}{2}\,|\mathrm{rot}\,v| \gg 1$$

(cf. Ref. [6]). Here, it is assumed that the terms containing $\boldsymbol{\omega}$ can be disregarded. Then (9) reduces to

$$-\left[1 + (\tau_M + \tau)\frac{d}{dt}\right]\bar{\mathbf{p}} = 2\eta\left(1 + \tau' \frac{d}{dt}\right)\overline{\nabla \boldsymbol{v}} , \tag{12}$$

with

$$\tau' = \tau\,\eta_\infty \eta^{-1} < \tau . \tag{13}$$

Relation (13) is essentially the constitutive equation for the Burgers model [1], a combination of the Maxwell and Kelvin models [1]. Depending on the size of the nonspherical particles, the relaxation time τ_a can be larger than τ_p and τ_M by many orders of magnitude. To give an example, consider a liquid solution with a viscosity comparable to that of water which contains disolved nonspherical particles with a linear dimension of 10^{-5} cm (10^{-4} cm). Then one has $\tau_p \approx \tau_M \approx 10^{-11}$ s and $\tau_a \approx 10^{-2}$ s (10 s). The relaxation time τ as given by (10), in general, is still larger than τ_a due to the occurrence of the factor $A^{-1} > 1$, which takes into account that not single particles but cluster of interacting nonspherical particles are reoriented. This demonstrates that the relaxation times τ and τ' occurring in (12) can be drastically different from the Maxwell relaxation time τ_M.

Of course, (1, 2) or (12) has to be used together with the local conservation equation for the linear momentum, viz.

$$\varrho \frac{d}{dt} \boldsymbol{v} + \nabla P + \nabla \bar{\mathbf{p}} = 0 , \tag{14}$$

where $\varrho = \text{nm}$ is the mass density and P is the hydrostatic pressure.

Next, the application of (12, 14) to a flow relaxation problem is presented for a simple geometry.

Viscoelastic Flow Relaxation

Consider a plane Poiseuille flow in x-direction between two flat plates separated by the distance $2d$ which are parallel to the x-z plane. In this case one has $\boldsymbol{v} = v(t, y)\,\boldsymbol{e}^x$ and

$$\overline{\nabla \boldsymbol{v}} = \frac{\partial v}{\partial y}\,\overline{\boldsymbol{e}^x \boldsymbol{e}^y}$$

where $\boldsymbol{e}^{x,y}$ are unit vectors parallel to the x and y axes of the coordinate system. It is assumed that the pressure difference associated with

$$\nabla P = \frac{\partial P}{\partial x}\,\boldsymbol{e}^x$$

which pushes the liquid in a steady flow is suddenly removed at time $t = 0$. How does the flow field $\boldsymbol{v}$ relax ? To study this question, $\boldsymbol{v}$, for $t \geqq 0$ is written as

$$\boldsymbol{v} = V(t) \cos(k y)\,\boldsymbol{e}^x \tag{15}$$

where k is chosen such that $\boldsymbol{v}$ vanishes at the two planes corresponding to $y = \pm d$ (no slip boundary condition). It is understood that (15) is just one term of a Fourier series expansion. Its leading term has a k value given by

$$k = \pi (2d)^{-1}. \tag{16}$$

For $t = 0$, V is determined by the Fourier coefficient of the stationary velocity profile which is proportional to $1 - (y/d)^2$.

Insertion of the ansatz (15) into (12, 14) with $\nabla P = 0$, elimination of $\bar{\mathfrak{p}}$ and use of the incompressibility condition $\nabla \cdot \boldsymbol{v} = 0$ leads to anordinary differential equation for $V(t)$, viz.

$$\dot{V} + (\tau_{\mathrm{M}} + \tau)\,\ddot{V} + \nu k^2 (V + \tau' \dot{V}) = 0, \tag{17}$$

where

$$\nu = \eta/\varrho \tag{18}$$

is the kinematic viscosity.

The exponential ansatz $V \sim e^{-i\omega t} = e^{-i\Omega T}$ where the dimensionless time and frequency variables

$$T = t(\tau + \tau_{\mathrm{M}})^{-1},\ \Omega = \omega(\tau + \tau_{\mathrm{M}}) \tag{19}$$

are used, yields

$$\Omega_{1/2} = -\frac{i}{2}(1 + R K^2) \cdot [1 \pm \sqrt{1 - 4K^2(1 + R K^2)^{-2}}] \tag{20}$$

for the eigenfrequencies $\Omega_{1/2}$. The quantity K is a dimensionless wave vector defined by

$$K^2 = (\tau + \tau_{\mathrm{M}})\,\nu k^2, \tag{21}$$

and R stands for

$$R = \tau'(\tau + \tau_{\mathrm{M}})^{-1} = \eta_\infty \eta^{-1}(1 + \tau_{\mathrm{M}} \tau^{-1})^{-1} < 1. \tag{22}$$

The eigenfrequencies are purely imaginary (overdamped motion) or contain a real part (damped oscillations) depending on whether $4\,K^2$ is smaller or larger, respectively, than $(1 + R K^2)^2$. In the first case, the well-known result $V \sim e^{-K^2 T} = e^{-\gamma k^2 t}$ is recovered for $K^2 \ll 1$. Here, the main attention is focussed on the oscillatory solutions which immediately reveal the elastic component of the viscoelasticity. Solutions of this type only occur in a certain interval of K values which is determined by

$$K_1^2 < K^2 < K_2^2 \tag{23}$$

with

$$K_{1/2}^2 = R^{-2}[2 - R \pm 2\sqrt{1 - R}]. \tag{24}$$

For $R = 1 - \varepsilon^2$, $\varepsilon \ll 1$, (24) reduces to $K_{1/2}^2 \approx 1 \pm 2\varepsilon$; for $R \ll 1$, $K_1^2 \approx 1/4$, $K_2^2 \to \infty$ is obtained. Thus $K^2 \approx 1$ is a typical value where an oscillatory rather than a simple exponential relaxation can occur. This corresponds to

$$\tau + \tau_{\mathrm{M}} \approx \nu^{-1} d^2. \tag{25}$$

The relation (16) between k and the typical macroscopic length d has been used in (25). In other words, the elastic component of viscoelasticity becomes apparent in a flow relaxation esperiment only if the (effective) relaxation time $\tau + \tau_{\mathrm{M}}$ is large enough to match the macroscopic relaxation time $\nu^{-1} d^2$. The latter quantity is of the order of 1 s for a viscosity comparable to that of water and $d \approx 1$ mm.

The results pertaining to a pure Maxwell relaxation model (no coupling with the alignment) are recovered with $\tau = \tau' = 0$. Then of course, the relation (25) cannot be fullfilled for the case discussed above.

The damped oscillatory solution as it follows from (17) with the initial conditions $V = V_0$, $\dot{V} = 0$ for $t = 0$, is

$$V = V_0 e^{-\frac{1}{2}(1+RK^2)T} \cdot \left[\cos\frac{Q}{2}(1+RK^2)T + Q^{-1}\sin\frac{Q}{2}(1+RK^2)T\right], \tag{26}$$

with

$$Q = [4K^2(1+RK^2)^{-2} - 1]^{1/2}. \tag{27}$$

In Fig. 1. the quantity Q is plotted as function of K^2 for $R = 16/25 = 0.64$; 0.4; 0.3; 0.2.

The K intervall where the oscillatory solutions exist can also be inferred from this figure. Notice that the maximal value for Q pertaining to $RK^2 = 1$ is $(R^{-1} - 1)^{1/2}$.

In Fig. 2. V/V_0 as given by (26) is displayed graphically as function of $\frac{1}{2}(1+RK^2)\ T \sim t$ for $Q = 3/4 = 0.75$; 1.225; 1.528; 2.0. These are the maximal Q values pertaining to the values of R used in Figure 1.

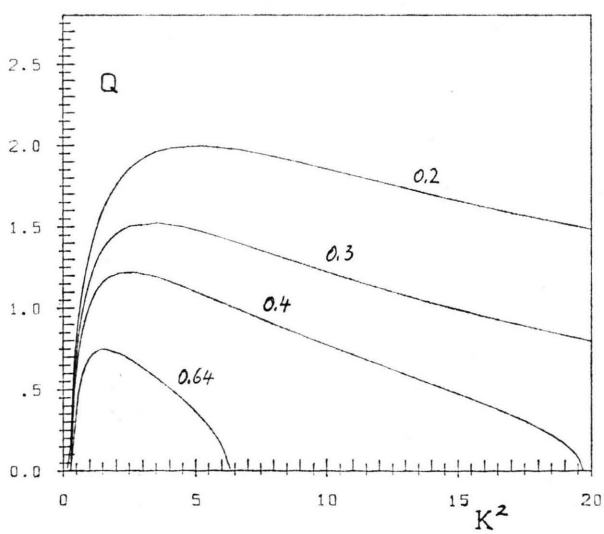

Fig. 1. The quantity Q defined in (27) as function of K^2. The curves are labelled with the pertaining values of the coefficient R, cf. (22).

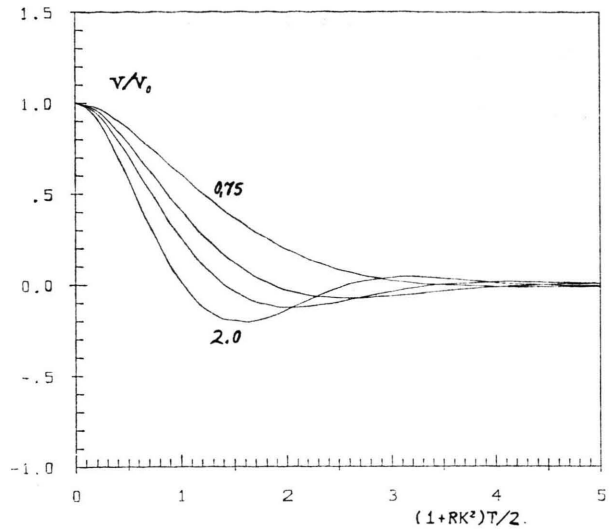

Fig. 2. The ratio V/V_0 of the velocity amplitude at time t divided by its value V_0 at $t = 0$ as function of the dimensionless time variable $\frac{1}{2}(1+RK^2)\,T$, cf. (26). The parameters Q used are the maximum values pertaining to the values of R chosen in Figure 1. The curve showing the most pronounced oscillatory behavior corresponds to $Q = 2.0$.

Concluding Remarks

In this article, it has been shown that oscillatory flow relaxation which reveals the viscoelasticity can occur in liquids with relatively small viscosity and without any network structure provided that the orientational relaxation time is large enough. This relaxation time which depends on the size of the disolved particles can be enhanced by cooperative effects. In particular, this occurs in the pretransitional range of concentrations in the isotropic phase of a lyotropic nematic liquid crystal. The mechanism which underlies the viscoelasticity as studied here is the flow alignment and its reciprocal phenomenon [4, 12]. Qualitatively, it can be understood as follows. A steady flow field induces an alignment $\mathbf{a} \sim \overline{\nabla \boldsymbol{v}}$ (flow birefringence). If the flow is suddenly stopped, the alignment will relax towards zero. In this nonequilibrium situation, a pressure tensor $\mathbf{p}$ is induced due to the effect reciprocal to the flow alignment. This pressure now "pushes" the liquid and gives rise to a flow in the opposite direction. Of course, the flow is not stopped suddenly in a flow relaxation experiment but the backward flow can be observed if the alignment relaxes at least as slowly as (or ever slowlier than) the flow velocity such that one has still $\mathbf{a} \neq 0$ for $\boldsymbol{v} \approx 0$. This corresponds to the condition (25).

It should be mentioned that terms nonlinear in $\mathbf{a}$ were disregarded in $\boldsymbol{\Sigma}$, cf. (2). These terms are of importance for strong alignment and if a transition into a nematic phase can occur. A detailed analysis of the non-linear Eq. (2) for a stationary situation revealed [13] that the velocity gradient can induce

a transition into an orientationally ordered phase which is essentially of nematic type under certain conditions where the fluid is in the isotropic phase in the absence of shear. The shear induced transition observed in dilute viscoelastic detergent solutions [2, 14] may be of this type.

Finally, however, a few qualifying remarks on the application of the present theory to the aforementioned detergent solutions are in order. In this case, the nonspherical (rod like) particles are micelles or vesicles which cannot be expected to be stiff. Thus, firstly, the angular velocity of the long axis of the micelle can be smaller than $\frac{1}{2}$ rot $\boldsymbol{v}$ due to the possible occurrence of a rotatory flow of the outer layer of a micelle or vesicle. This can even provide a better justification of the neglect of terms containing $\boldsymbol{\omega}$ in Eq. (9) which is, strictly speaking, only a good approximation for $|\boldsymbol{\omega}|\,\tau \leqq 1$. Secondly, the velocity gradient may directly deform the particles or change their size by affecting the chemical equilibrium between the monomers and the micelles. As a consequence, the quantity c^* which is related to the interaction energy between the nonspherical micelles and their excluded volume, as well as the relaxation times $\tau_a, \tau_{ap}, \ldots$ will become functions of the velocity gradient. In lowest order, correction terms proportional to the scalars $\mathbf{a}: \overline{\nabla \boldsymbol{v}}$ and $(\overline{\nabla \boldsymbol{v}}) : (\overline{\nabla \boldsymbol{v}})$ can be expected. Effects of this type have been disregarded here.

In conclusion, however, it can be stated that oscillatory flow relaxation revealing viscoelasticity and velocity gradient induced phase transitions are obtained for practically stiff particles. Thus the present investigation and the results of Ref. [13] may already contain the basic physics underlying some of the surprising flow properties of the viscoelastic detergent solutions. The conjectures put forward in [15] aimed in the same direction. Further measurements, where the viscoelasticity is studied in forced rather than free oscillations, are desirable.

[1] M. Reiner, Rheologie in elementarer Darstellung, Hauser, München 1960; in Handbuch der Physik, ed. S. Flügge, vol. VI, p. 434, Springer, Berlin 1958.
[2] S. Gravsholt, J. Colloid Interface Sci. **57**, 575 (1976); **69**, 358 (1979).
[3] I. Pardowitz and S. Hess, Physica **100A**, 540 (1980).
[4] S. Hess, Z. Naturforsch. **30a**, 728, 1224 (1975).
[5] S. Hess, Physica **87A**, 273 (1977).
[6] S. Hess, Physica **86A**, 383 (1977).
[7] P. G. de Gennes, Phys. Lett. **30A**, 454 (1969).
[8] S. Hess and L. Waldmann, Z. Naturforsch. **21a**, 1529 (1966); H. Raum and W. E. Köhler, Z. Naturforsch. **25a**, 1178 (1970).
[9] S. Hess, Phys. Lett. **30A**, 239 (1969); F. Baas, Phys. Lett. **36A**, 107 (1971).
[10] A. G. St. Pierre, W. E. Köhler, and S. Hess, Z. Naturforsch. **27a**, 721 (1972).
[11] S. Hess, Z. Naturforsch. **31a**, 1034 (1976); in "Electro-Optics and Dielectrics of Macromolecules and Colloids", p. 321 ed. B. R. Jennings, Plenum Press, New York 1979.
[12] S. Hess, Z. Naturforsch. **23a**, 1531 (1973).
[13] S. Hess, Z. Naturforsch. **31a**, 1507 (1976).
[14] S. Gravsholt, Physico-chemical properties of viscoelastic highly dilute aqueous detergent solutions; Report presented at the conference on Viscoelastic solutions, Bayreuth, 1979.
[15] H. Wennerström, Anisotropic repulsive forces as a source of the viscoelastic behaviour of some micellar solutions; Talk presented at the conference on Viscoelastic solutions, Bayreuth 1979.