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On the Relation Between Complex Viscosity and Steady State Shearing in the Maxwell Orthogonal Rheometer

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Recent analyses of steady flow in the Maxwell Orthogonal Rheometer (MOR) have indicated that one can relate the complex viscosity $\eta = \eta' - i\eta''$ of a substance to measurements made with the MOR (*1, 2*). In particular, Bird and Harris (*2*) have employed an integral model [Bird and Carreau (*3*)] in which the stress $\boldsymbol{\tau}$ at time t is given by

$$\boldsymbol{\tau} = -\int_{-\infty}^{t} m[t-t', II(t')] \left[\left(1+\frac{\epsilon}{2}\right)\overline{\boldsymbol{\Gamma}} - \frac{\epsilon}{2}\boldsymbol{\Gamma}\right] dt' \quad (1)$$

with a memory function

$$m[t-t', II(t')] = \sum_{p=1}^{\infty} \frac{\eta_p}{\lambda^2_{2p}} \frac{e^{-(t-t')/\lambda_{2p}}}{\left[1+\frac{1}{2}\lambda^2_{1p} II(t')\right]} \quad (2)$$

to obtain the following results:

$$\lim_{\psi\to 0}\left[\frac{\tau_{xz}}{-\Omega\psi}\right] = \eta' \quad (3)$$

$$\lim_{\psi\to 0}\left[\frac{\tau_{yz}}{-\Omega\psi}\right] = \eta'' \quad (4)$$

In Equation (1), $\Gamma_{ij} = \delta_{ij} - (\partial x_\alpha'/\partial x_i)(\partial x_\alpha'/\partial x_j)$, $\overline{\Gamma}_{ij} = (\partial x_i/\partial x_\alpha')(\partial x_j/\partial x_\alpha') - \delta_{ij}$, ϵ is a scalar constant, and $II(t') = \dot\gamma_{ij}\dot\gamma_{ij}$, where $\dot\gamma_{ij} = \partial v_j/\partial x_i + \partial v_i/\partial x_j$. Cartesian tensor notation is employed, and repetition of subscripts implies summation over repeated indexes. x_i and x_i' refer to position coordinates at present time t and past time t', respectively. The reader is referred to Figure 1 of reference 2 for a schematic diagram showing relevant parameters for the MOR. Ω is the (constant) angular velocity of the rotating disks, and $\psi = a/b$ is the ratio of lateral displacement (eccentricity) a between disk centers to gap distance b between disks. A rectangular coordinate system is chosen in which y is taken parallel to the projection onto one of the disks of the line connecting the two disk centers, z is along the axis of one of the disks, and x is orthogonal to y and z.

We show below that reexamination of the assumptions inherent in the derivation of Equations (3) and (4) leads to somewhat different conditions for the equivalence of $\tau_{xz}/(-\Omega\psi)$ with η' and $\tau_{yz}/(-\Omega\psi)$ with η''. In addition, some comments are made concerning the application of Tanner's network rupture model (*4, 5*) to flow in the MOR. Finally, we note a correspondence between measurements in transversely superposed steady shear and oscillatory flow, and flow in the MOR.

The arguments presented below are valid for any memory function $m[t-t', II(t')]$ which fulfills the condition

$$m[t-t', II(t')] \cong m(t-t', 0) \quad (5)$$

as $II(t')$ approaches zero. This condition is consistent with the observed behavior of wide classes of polymer solutions and melts and also agrees with predictions made from rather general theories of the constitutive behavior of materials.

Equation (1) under the condition imposed by Equation (5) then becomes

$$\boldsymbol{\tau} \cong -\int_0^{\infty} m(\tau, 0)\left[\left(1+\frac{\epsilon}{2}\right)\overline{\boldsymbol{\Gamma}} - \frac{\epsilon}{2}\boldsymbol{\Gamma}\right] d\tau \quad (6)$$

STRESS COMPONENTS IN THE MOR

By using a constitutive equation of the form of Equation (1), it is a simple matter to show, with the aid of Equation (14) of (*2*), that steady flow in the MOR is described by $II(t') = 2(\Omega\psi)^2$ and stress components

$$\frac{\tau_{xz}}{-\Omega\psi} = \int_0^{\infty} m[\tau, 2(\Omega\psi)^2] \frac{\sin(\Omega\tau)}{\Omega} d\tau \quad (7)$$

$$\frac{\tau_{yz}}{-\Omega\psi} = \int_0^{\infty} m[\tau, 2(\Omega\psi)^2] \frac{[1-\cos(\Omega\tau)]}{\Omega} d\tau \quad (8)$$

Note that Equations (7) and (8) are not dependent upon a specific form of $m[t-t', II(t')]$, such as that given by Equation (2).

OSCILLATORY SHEAR FLOW

Let us apply Equation (1) to oscillatory shear flow, defined by the velocity field

$$\mathbf{v} = Re\,\{0, v_0(x_3)e^{i\omega t}, 0\} \tag{9}$$

where v_0 is a complex amplitude. The second invariant of $\dot{\boldsymbol{\gamma}}$ is

$$II(t') = 2[Re\{\kappa_0\, e^{i\omega t'}\}]^2 \tag{10}$$

where $\kappa_0 = dv_0/dx_3$. From Equation (10), we have

$$II(t') \leq 2\,|\kappa_0|^2 \tag{11}$$

If we employ Equation (1) and make the approximation of Equation (5) for sufficiently small $|\kappa_0|$, it is readily shown that

$$\eta'(\omega) \cong \int_0^\infty m(\tau, 0)\,\frac{\sin(\omega\tau)}{\omega}\,d\tau \tag{12}$$

$$\eta''(\omega) \cong \int_0^\infty m(\tau, 0)\,\frac{[1-\cos(\omega\tau)]}{\omega}\,d\tau \tag{13}$$

where η' and η'' are defined by

$$\tau_{23} = -Re\,\{(\eta' - i\eta'')\kappa_0\, e^{i\omega t}\} \tag{14}$$

In a similar manner, for small $\Omega\psi$, Equations (7) and (8) become

$$\frac{\tau_{xz}}{-\Omega\psi} \cong \int_0^\infty m(\tau, 0)\,\frac{\sin(\Omega\tau)}{\Omega}\,d\tau \tag{15}$$

$$\frac{\tau_{yz}}{-\Omega\psi} \cong \int_0^\infty m(\tau, 0)\,\frac{[1-\cos(\Omega\tau)]}{\Omega}\,d\tau \tag{16}$$

By comparing Equations (15) and (16) with Equations (12) and (13) it follows that

$$\left[\frac{\tau_{xz}}{-\Omega\psi}\right]_{\Omega\psi\to 0} = [\eta'(\Omega)]_{|\kappa_0|\to 0} \tag{17}$$

$$\left[\frac{\tau_{yz}}{-\Omega\psi}\right]_{\Omega\psi\to 0} = [\eta''(\Omega)]_{|\kappa_0|\to 0} \tag{18}$$

These results hold for any $m[t-t', II(t')]$ which fulfills the condition of Equation (5).

BIRD AND HARRIS MEMORY FUNCTION

In the development of Bird and Harris (2), it is stated that the memory function being used is that of Equation (2). However, in order to obtain their expressions for η' and η'' [their Equations (11) and (12)] in oscillatory shear flow, one must assume that the term $\frac{1}{2}\lambda^2_{1p}\,II(t')$ in Equation (2) is negligible with respect to unity; that is, one requires

$$\lambda^2_{1p}\,|\kappa_0|^2 << 1 \tag{19}$$

so that

$$m[t-t', II(t')] \cong \sum_{p=1}^{\infty} \frac{\eta_p}{\lambda^2_{2p}}\, e^{-(t-t')/\lambda_{2p}} \tag{20}$$

which is a special case of our Equation (5).

For steady shearing in the MOR, the memory function of Equation (2) becomes

$$m[t-t', II(t')] = \sum_{p=1}^{\infty} \frac{\eta_p}{\lambda^2_{2p}}\,\frac{e^{-(t-t')/\lambda_{2p}}}{[1+(\lambda_{1p}\,\Omega\psi)^2]} \tag{21}$$

If we make an assumption similar to that leading to Equation (19), namely

$$\lambda^2_{1p}(\Omega\psi)^2 << 1 \tag{22}$$

Equation (21) becomes

$$m[t-t', II(t')] \cong \sum_{p=1}^{\infty} \frac{\eta_p}{\lambda^2_{2p}}\, e^{-(t-t')/\lambda_{2p}} \tag{23}$$

which is identical to Equation (20) and is again a special case of Equation (5). In summary, under the conditions of Equations (19) and (22), the memory function used by Bird and Harris reduces to Equation (20). Equations (12), (13), (15), and (16) then apply with

$$m(\tau, 0) = \sum_{p=1}^{\infty} \frac{\eta_p}{\lambda^2_{2p}}\, e^{-\tau/\lambda_{2p}}$$

Thus, we see that the conditions under which the Bird-Harris Equations (1) and (2) admit association of η' with $\tau_{xz}/(-\Omega\psi)$, and η'' with $\tau_{yz}/(-\Omega\psi)$ are properly stated by

$$\begin{aligned} &\lambda^2_{1p}\,|\kappa_0|^2 << 1 \quad \text{in oscillatory shear} \\ &\lambda^2_{1p}\,|\Omega\psi|^2 << 1 \quad \text{in the MOR} \end{aligned} \tag{24}$$

These results are, of course, consistent with Equations (17) and (18), which were derived for the more general memory function.

NETWORK RUPTURE MODEL

Tanner and Simmons (4) have introduced an integral model similar to Equation (1), which includes the possibility of network rupture. Using this model in the form recently given by Tanner (5), we have

$$\boldsymbol{\tau} = -\int_{t-\tau_R}^{t} m(t-t')\left[\left(1+\frac{\epsilon}{2}\right)\overline{\boldsymbol{\Gamma}} - \frac{\epsilon}{2}\boldsymbol{\Gamma}\right]dt' \tag{25}$$

where $t-\tau_R$ is the age of the junctions at which rupture occurs. Tanner (5) has claimed that the strain required for rupture will not be reached if, at all times

$$\mathrm{tr}\left[\left(1+\frac{\epsilon}{2}\right)\overline{\boldsymbol{\Gamma}} - \frac{\epsilon}{2}\boldsymbol{\Gamma}\right] < (1+\epsilon)B^2 \tag{26}$$

where B is a number of order 10. For sufficiently small $|v_0|$ in the case of oscillatory shear or ψ in the MOR, the left-hand side of Equation (26) will always be less than $(1+\epsilon)B^2$, and in this case Equation (25) may be written as

$$\boldsymbol{\tau} = -\int_{-\infty}^{t} m(t-t')\left[\left(1+\frac{\epsilon}{2}\right)\overline{\boldsymbol{\Gamma}} - \frac{\epsilon}{2}\boldsymbol{\Gamma}\right]dt' \tag{27}$$

which is identical to Equation (6). For this model, we conclude that

$$\left[\frac{\tau_{xz}}{-\Omega\psi}\right]_{\psi\to 0} = [\eta'(\Omega)]_{|v_0|\to 0} \tag{28}$$

$$\left[\frac{\tau_{yz}}{-\Omega\psi}\right]_{\psi\to 0} = [\eta''(\Omega)]_{|v_0|\to 0} \tag{29}$$

Note that these conditions are somewhat different than those expressed in Equations (17) and (18) for the equivalence of η with the MOR measurements. The reason for these differences is immediately evident when we note that Equation (25) reduces to Equation (6) when the *strain* is small, while Equation (1) reduces to Equation (6) when the *rate of strain* is small.

According to Tanner's model, the stresses τ_{xz} and τ_{yz} in the MOR are linear functions of ψ, regardless of the values of Ω, over the range of validity of Equations (28) and (29). Similarly, for the general model of Equation (1), τ_{xz} and τ_{yz} are again predicted to be linear functions of ψ in the region where Equations (17) and (18) hold. However, in this case the extent of the linear region is a function of $\Omega\psi$, rather than ψ, as in Tanner's model. It would be of interest to compare results from the MOR in the limits of small $\Omega\psi$ and small ψ to see whether real materials correspond more closely to predictions based upon Equation (1) or upon Equation (25).

STEADY SHEAR FLOW WITH TRANSVERSELY SUPERPOSED OSCILLATORY FLOW

It has recently been pointed out (6) that the Bird-Harris Equations (1) and (2) lead to a correspondence between MOR flow and a large deformation steady shear flow with transversely superposed oscillatory motion of infinitesimal amplitude. This flow belongs to the class

$$\mathbf{v} = \{\kappa x_3,\ Re[v_0(x_3)e^{i\omega t}],\ 0\} \tag{30}$$

where κ is a constant. Correspondence between the two flows is not restricted to the Bird-Harris equations but holds for any fluid with a constitutive equation given by Equation (1) under the condition

$$|\kappa_0|^2 << \kappa^2 \tag{31}$$

where $\kappa_0 = dv_0/dx_3$. Then

$$II(t') = 2[\kappa^2 + (Re\{\kappa_0\ e^{i\omega t'}\})^2] \cong 2\kappa^2 \tag{32}$$

and

$$m[t-t',\ II(t')] \cong m(t-t',\ 2\kappa^2) \tag{33}$$

Straightforward computation by using Equations (1) and (30) then leads to

$$\tau_{23} = -Re\left\{\int_{-\infty}^{t} m(t-t',\ 2\kappa^2)\left[\frac{\kappa_0}{i\omega}\ (e^{i\omega t} - e^{i\omega t'})\right] dt'\right\} \tag{34}$$

Following the lead of Bird and Harris (6), we define the real quantities $\eta'_\perp$ and $\eta''_\perp$ by

$$\tau_{23} = -Re\{(\eta'_\perp - i\eta''_\perp)\kappa_0\ e^{i\omega t}\} \tag{35}$$

where from Equations (34) and (35) we find

$$\eta'_\perp(\omega, \kappa^2) = \int_0^\infty m(\tau, 2\kappa^2)\ \frac{\sin(\omega\tau)}{\omega}\ d\tau \tag{36}$$

$$\eta''_\perp(\omega, \kappa^2) = \int_0^\infty m(\tau, 2\kappa^2)\ \frac{[1-\cos(\omega\tau)]}{\omega}\ d\tau \tag{37}$$

Upon comparison with the MOR Equations (7) and (8), we immediately see that

$$\frac{\tau_{xz}}{-\Omega\psi} = \eta'_\perp\ [\Omega,\ (\Omega\psi)^2] \tag{38}$$

$$\frac{\tau_{yz}}{-\Omega\psi} = \eta''_\perp\ [\Omega,\ (\Omega\psi)^2] \tag{39}$$

CONCLUSIONS

1. Equations (17) and (18) relate real and imaginary parts of the complex viscosity $\eta = \eta' - i\eta''$ in small amplitude oscillatory shear flow to the stress components in MOR flow if the fluid in question obeys a constitutive equation of the form of Equation (1) with $m[t-t',\ II(t')] \cong m(t-t',\ 0)$ as $II(t')$ approaches zero. Over the range of applicability of Equations (17) and (18), τ_{xz} and τ_{yz} are linear functions of ψ.

2. Equations (17) and (18) are valid for the model employed by Bird and Harris (2) [Equations (1) and (2)] if the conditions of Equations (24) are met.

3. Tanner's network rupture model, under the condition of Equation (26), also leads to an association between MOR flow and oscillatory flow. However, while the association holds in the limit $\Omega\psi \to 0$ for the model of Equation (1), the correct limit for the network rupture model is $\psi \to 0$.

4. Equations (38) and (39) apply to infinitesimal oscillatory motion transversely superposed upon large deformation steady shear if the fluid is described by a constitutive relation of the form of Equation (1) and the condition corresponding to Equation (33) is met.

ACKNOWLEDGMENT

Support of this research by the National Aeronautics and Space Administration through Grant NGR 31-001-025 is gratefully acknowledged. Helpful comments were supplied by R. B. Bird and R. I. Tanner.

NOTATION

$m[t-t',\ II(t')]$ = memory function
$t,\ t'$ = time
$\mathbf{v}$ = velocity vector
$x_i,\ x_i'$ = coordinates at times t and t', respectively
$x,\ y,\ z$ = coordinates for Maxwell orthogonal rheometer (MOR)
$\overline{\mathbf{\Gamma}},\ \mathbf{\Gamma}$ = strain tensors defined following Equation (4)
$\dot{\gamma}_{ij}$ = $\partial v_j/\partial x_i + \partial v_i/\partial x_j$
v_0 = complex amplitude in oscillatory shear
δ_{ij} = Kronecker delta
ϵ = constant in Equation (1)
η_p = constant in Equation (2)
$\eta',\ \eta''$ = real and imaginary parts of the complex viscosity
$\eta'_\perp,\ \eta''_\perp$ = real and imaginary parts of the complex viscosity for superposed steady and oscillatory shear [Equation (35)]
κ = shear rate defined by Equation (30)
κ_0 = dv_0/dx_3
$\lambda_{1p},\ \lambda_{2p}$ = constants in Equation (2)
$\boldsymbol{\tau}$ = stress tensor
τ_R = rupture time
$\tau_{xz},\ \tau_{yz}$ = stress components in MOR
ψ = ratio of displacement of disk axes to disk separation in MOR
Ω = angular speed of rotation in MOR
ω = oscillation frequency
$II(t')$ = $\dot{\gamma}_{ij}\dot{\gamma}_{ij}$, the second invariant of $\dot{\boldsymbol{\gamma}}$

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