A Molecular Interpretation of the Steady State Maxwell Orthogonal Rheometer Flow

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In a recent paper, Bird and Harris (*1*) showed that a certain limiting process is required to obtain the dynamic viscoelastic properties (η' and η'') from the thrust measurements in a Maxwell orthogonal rheometer. Since, however, the derivation made use of an empirical nonlinear viscoelastic model, it is advisable to supplement the previous work by reconsidering the problem from a molecular point of view.

For this purpose we choose to use the rigid dumbbell model which, although simple, has been shown to give a non-Newtonian viscosity (*2, 3*), a shear-dependent normal stress function (*4*), a frequency-dependent complex viscosity (*5*), and a host of other properties (*6*). For the velocity profile $v_x = -\Omega(y - \psi z)$, $v_y = \Omega x$, and $v_z = 0$ [see (*1*) for notation and coordinate system], the diffusion equation (*2, 3*) for the distribution function $\Upsilon(\theta, \phi)$ for the orientation of the dumbbells in the orthogonal-rheometer, steady state flow is

$$\frac{1}{S}\frac{\partial}{\partial\theta}\left(S\frac{\partial\Upsilon}{\partial\theta}\right) + \frac{1}{S^2}\frac{\partial^2\Upsilon}{\partial\phi^2} = 6\lambda\Omega\left[\frac{1}{S}\frac{\partial}{\partial\theta}\{\psi\, SC^2\, c\Upsilon\} + \frac{1}{S}\frac{\partial}{\partial\phi}\{S - \psi Cs)\,\Upsilon\}\right] \tag{1}$$

Here, $\lambda = \zeta L^2/12kT$ is a time constant, where L is the length of the dumbbell and ζ is the friction coefficient for the bead of the dumbbell; the abbreviations $S = \sin\theta$, $C = \cos\theta$, $s = \sin\phi$, and $c = \cos\phi$ are used. When $\Upsilon(\theta, \phi)$ is obtained from Equation (1), the stresses in the system are obtained from (*2, 3, 7*)

$$\tau_{xz} = -\eta_s\Omega\psi + \frac{n_0\zeta L^2\Omega}{4J}\langle CSs - \psi C^2\rangle \tag{2}$$

$$\tau_{yz} = -\frac{n_0\zeta L^2\Omega}{4J}\langle SCc\rangle \tag{3}$$

in which η_s is the solvent viscosity, n_0 is the number density of dumbbells, $J = \int\int \Upsilon S\, d\theta\, d\phi$, and $\langle Q\rangle = \int\int Q\Upsilon S\, d\theta\, d\phi$. The problem is thus reduced to solving Equation (1) for the distribution function and then using it to evaluate the integrals appearing in Equations (2) and (3).

It is not difficult to show that the solution to Equation (1) is

$$\Upsilon = 1 + 3SC\left[\frac{c + \lambda\Omega s}{1 + \lambda^2\Omega^2}\right]\lambda\Omega\psi + O(\lambda\Omega\psi)^2 \tag{4}$$

Substitution of this into Equations (2) and (3) gives

$$\tau_{xz} = -\left\{\eta_s + n_0kT\lambda\left[1 - \frac{3}{5}\frac{\lambda^2\Omega^2}{1 + \lambda^2\Omega^2}\right]\right\}\Omega\psi + O(\lambda\Omega\psi)^2 \tag{5}$$

$$\tau_{yz} = -\left\{\frac{3}{5}n_0kT\lambda\left[\frac{\lambda\Omega}{1 + \lambda^2\Omega^2}\right]\right\}\Omega\psi + O(\lambda\Omega\psi)^2 \tag{6}$$

The { } quantities in Equations (5) and (6) are $\eta'(\Omega)$ and $\eta''(\Omega)$, respectively, for the rigid dumbbell suspension (*5*). Hence, when the limit is taken as $\psi \to 0$, $\tau_{xz}/(-\Omega\psi) \to \eta'$ and $\tau_{yz}/(-\Omega\psi) \to \eta''$ as indicated in Equations (20) and (21) of Bird and Harris. This gives additional support to the argument that the Maxwell orthogonal rheometer flow provides the possibility of measuring the dynamic properties of fluids.

In order to examine further the connection between the orthogonal rheometer flow and the transversely superposed steady and oscillatory flows [see (*7*)], we have compared the rigid dumbbell suspension kinetic theory results for these two systems. The calculation of even the first few terms is quite lengthy; the main results are:

Maxwell orthogonal rheometer:

$$\frac{\tau_{xz} - \eta_s\Omega\psi}{(-\Omega\psi)} = n_0kT\lambda\left[\left(1 - \frac{3}{5}\frac{\lambda^2\Omega^2}{1 + \lambda^2\Omega^2}\right) - \frac{18}{35}(\lambda\Omega\psi)^2\left(1 - \underline{\frac{119}{30}}\lambda^2\Omega^2 + \ldots\right) + \ldots\right] \tag{7}$$

Transversely superposed flow:

$$\eta'_{\perp} - \eta_s = n_0kT\lambda\left[\left(1 - \frac{3}{5}\frac{\lambda^2\omega^2}{1 - \lambda^2\omega^2}\right) - \frac{18}{35}(K^2)\left(1 - \underline{\frac{797}{300}}\lambda^2\omega^2 + \ldots\right) + \ldots\right] \tag{8}$$

It is evident that the dashed underlined terms are different. From this we conclude that the similarity in material functions found by Bird and Harris is a fortuitous result depending on the choice of rheological model and hence not a general result.

The details of the techniques used here as well as an extensive summary of dumbbell kinetic theories will be presented elsewhere (*6*).

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