Stress Relaxation in Solutions of Linear Macromolecules

R. Byron Bird, Harold R. Warner, Jr., and William R. Ramakka
Chemical Engineering Department and Rheology Research Center, University of Wisconsin, Madison, Wisconsin 53706

(Received 20 October 1969)

The rigid dumbbell model has been used to derive expressions for the relaxation of shear and normal stresses after the cessation of steady shearing flow. It is found that the shear stresses relax more rapidly than the normal stresses, and that all stresses relax more rapidly as the velocity gradient during the prior steady state shearing flow increases; this behavior is in qualitative agreement with experimental data. The results further show that the integral under the shear-stress relaxation curve is simply related to the normal stress in steady flow. The elastic dumbbell model, with a Gaussian spring, gives results inconsistent with experiment.

The mechanical behavior of a suspension of rigid dumbbells with Brownian motion has been calculated for several flows: steady shearing,[1–4] for which shear-rate dependent viscosity and normal stresses are found; small-amplitude oscillatory motion,[5,6] for which the frequency-dependent dynamic properties are obtained; large-amplitude oscillatory motion,[1,7] where a reduction in the dynamic properties is found with increasing shear-rate amplitude; elongational flow,[2,8] for which the elongational viscosity is found to increase slightly with increasing elongational rate; and the Maxwell orthogonal rheometer flow.[9] For all of these systems the rigid dumbbell model gives results which are qualitatively similar to those obtained experimentally in dilute and moderately concentrated polymer solutions.

We here consider another flow system, namely the sudden cessation of a steady shearing flow, with the resultant time decay of the shear and normal stresses. For $t<0$, the flow is $v_x=\kappa_0 y$, and the observed stresses are

$$\tau_{yx}^{-},\ (\tau_{xx}-\tau_{yy})^{-},$$

and

$$(\tau_{yy}-\tau_{zz})^{-},$$

which are functions of κ_0. For $t>0$, the fluid is motionless, and the observed stresses are

$$\tau_{yx}^{+},\ (\tau_{xx}-\tau_{yy})^{+},$$

and

$$(\tau_{yy}-\tau_{zz})^{+},$$

which depend on κ_0 and the time t.

For unsteady-state shearing flows with $v_x=\kappa(t)y$, the equation for the orientational distribution function $\psi(\theta,\phi,t)$ for rigid dumbbells is[1,2]

$$6\lambda\frac{\partial\psi}{\partial t}=\frac{1}{S}\frac{\partial}{\partial\theta}\left(S\frac{\partial\psi}{\partial\theta}\right)+\frac{1}{S^2}\frac{\partial^2\psi}{\partial\phi^2}-6\lambda\kappa\left(\frac{sc}{S}\frac{\partial}{\partial\theta}(S^2C\psi)-\frac{\partial}{\partial\phi}(s^2\psi)\right),\quad(1)$$

where $S=\sin\theta$, $C=\cos\theta$, $s=\sin\phi$, $c=\cos\phi$. The time constant $\lambda=\zeta L^2/12kT$ contains ζ, the friction factor of one bead of the dumbbell, and L, the length of the dumbbell. The stresses in the suspension are then given by[2,3,4]

$$\tau_{yx}-\tau_{yx,s}=(n_0\zeta L^2/4J)[(\partial/\partial t)\langle S^2sc\rangle-\kappa\langle S^2s^2\rangle],\quad(2)$$

$$\tau_{xx}-\tau_{yy}=(n_0\zeta L^2/4J)[(\partial/\partial t)\langle S^2(c^2-s^2)\rangle-2\kappa\langle S^2sc\rangle],\quad(3)$$

$$\tau_{yy}-\tau_{zz}=(n_0\zeta L^2/4J)[(\partial/\partial t)\langle S^2s^2-C^2\rangle].\quad(4)$$

Here

$$\langle Q\rangle=\int\int Q(\theta,\phi)\psi(\theta,\phi,t)\,Sd\theta d\phi$$

and

$$J=\int\int\psi\,Sd\theta d\phi;$$

also $\tau_{yx,s}=-\eta_s\kappa$, where η_s is the solvent viscosity and n_0 is the number density of dumbbells.

For $t<0$ in the stress-relaxation problem one solves Eq. (1) with $\partial\psi/\partial t=0$ and $\kappa(t)=\kappa_0$ to obtain

$$\psi^{-}=1+(6\lambda\kappa_0)(\tfrac{1}{4}S^2s_2)+(6\lambda\kappa_0)^2\times(-\tfrac{1}{120}+\tfrac{1}{64}S^4+\tfrac{1}{24}S^2c_2-\tfrac{1}{64}S^4c_4)+(6\lambda\kappa_0)^3\times[(-\tfrac{13}{1440}S^2+\tfrac{1}{512}S^6)s_2+\tfrac{1}{240}S^4s_4-\tfrac{1}{1536}S^6s_6]+\cdots,\quad(5)$$

where $s_k=\sin k\phi$, $c_k=\cos k\phi$. From Eqs. (2)–(5) one gets[1–4]

$$(\tau_{yx}-\tau_{yx,s})^{-}=-n_0kT(\lambda\kappa_0)\times[1-\tfrac{18}{35}(\lambda\kappa_0)^2+\tfrac{1326}{1925}(\lambda\kappa_0)^4-\cdots],\quad(6)$$

$$(\tau_{xx}-\tau_{yy})^{-}=-\tfrac{6}{5}n_0kT(\lambda\kappa_0)^2[1-\tfrac{38}{35}(\lambda\kappa_0)^2+\cdots],\quad(7)^{10}$$

$$(\tau_{yy}-\tau_{zz})^{-}=0.\quad(8)$$

For $t>0$ we solve Eq. (1) with $\kappa=0$, and require that $\psi^{+}=\psi^{-}$ at $t=0$ and $\psi^{+}\rightarrow 1$ as $t\rightarrow\infty$. This gives

$$\psi^{+}=1+(6\lambda\kappa_0)[\tfrac{1}{4}S^2s_2e^{-t/\lambda}]+(6\lambda\kappa_0)^2\times[-\tfrac{1}{84}(1-\tfrac{3}{2}S^2)e^{-t/\lambda}+\tfrac{1}{280}(1-5S^2+\tfrac{35}{8}S^4)e^{-10t/3\lambda}+\tfrac{1}{24}S^2c_2e^{-t/\lambda}-\tfrac{1}{64}S^4c_4e^{-10t/3\lambda}]+(6\lambda\kappa_0)^3\times[-\tfrac{19}{2520}S^2s_2e^{-t/\lambda}-\tfrac{3}{1232}(S^2-\tfrac{7}{6}S^4)s_2e^{-10t/3\lambda}+\tfrac{1}{1056}(S^2-3S^4+\tfrac{33}{16}S^6)s_2e^{-7t/\lambda}+\tfrac{1}{240}S^4s_4e^{-10t/3\lambda}-\tfrac{1}{1536}S^6s_6e^{-7t/\lambda}]+\cdots.\quad(9)$$

From Eqs. (2)–(4), and (9), we find

$$(\tau_{yx}-\tau_{yx,s})^{+}=(\tau_{yx}-\tau_{yx,s})^{-}\cdot[\tfrac{3}{5}-\tfrac{12}{35}(\lambda\kappa_0)^2+\cdots]e^{-t/\lambda}, \tag{10}$$

$$(\tau_{xx}-\tau_{yy})^{+}=(\tau_{nx}-\tau_{yy})^{-}\cdot[1-\tfrac{8}{35}(\lambda\kappa_0)^2+\cdots]e^{-t/\lambda}, \tag{11}$$

$$(\tau_{yy}-\tau_{zz})^{+}=\tfrac{12}{35}n_0kT(\lambda\kappa_0)^2\cdot[1-\tfrac{157}{110}(\lambda\kappa_0)^2+\cdots]e^{-t/\lambda}. \tag{12}$$

Equations (10) and (11) are qualitatively similar to experimental data[11–13] which indicate that (a) shear stresses relax more quickly than normal stresses [note appearance of $\frac{3}{5}$ in Eq. (10)], and (b) all stresses relax more quickly as κ_0 increases. No data are available to test Eq. (12).

Note that, from Eqs. (7) and (10), the relation

$$(\tau_{xx}-\tau_{yy})^{-}=2\kappa_0\int_0^\infty(\tau_{yx}-\tau_{yx,s})^{+}dt \tag{13}$$

holds up to terms in $(\lambda\kappa_0)^4$. This relation has not been tested experimentally over the full range of κ_0.

It is interesting to note that for an elastic dumbbell (two beads joined by a Hookean spring with spring constant H), λ is replaced by a time constant $\zeta/4H$, and the bracketed quantities in Eqs. (10) and (11) are both unity. Hence the bead-spring model cannot describe the observed properties (a) and (b) mentioned above.

Note added in proof: (8 Jan. 1970) Dr. H. Giesekus has called our attention to his prior work on this problem [Rheol. Acta **1**, 2 (1958)] and pointed out that the constant terms in the brackets in Eqs. (10)–(12) are identical with his results. The quadratic terms in these brackets are, however, different from his; Dr. Giesekus has informed us that his results are incorrect because of an error in his fourth approximation to the distribution function. We wish to thank Dr. Giesekus for his very helpful comments.

ACKNOWLEDGMENT

The authors wish to acknowledge financial support received from National Science Foundation Grant GK-1275 and Petroleum Research Fund Grant 1758-C of the American Chemical Society. They also wish to thank Professor T. Kotaka and Dr. H. Giesekus for correspondence in connection with Eq. (7).

[1] J. G. Kirkwood and R. J. Plock, J. Chem. Phys. **24**, 665 (1956).
[2] S. Prager, Trans. Soc. Rheol. **1**, 53 (1957).
[3] T. Kotaka, J. Chem. Phys. **30**, 1566 (1959).
[4] H. Giesekus, Kolloid-Z. **147**, 29 (1956); see erratum in Footnote 18 of Rheol. Acta **1**, 404 (1961).
[5] J. G. Kirkwood and P. L. Auer, J. Chem. Phys. **19**, 281 (1951).
[6] G. K. Fraenkel. J. Chem. Phys. **20**, 642 (1952).
[7] E. Paul. J. Chem. Phys. **51**, 1271 (1969).
[8] R. B. Bird, M. W. Johnson, Jr., and J. F. Stevenson, Proceedings of the 5th International Congress on Rheology, October 1968.
[9] H. R. Warner, Jr. and R. B. Bird, A.I.Ch.E. J. (to be published).
[10] In Kotaka's expression[3] there is a misprint: 128/175 should be 228/175.
[11] F. W. Schremp. J. D. Ferry, and W. W. Evans, J. Appl. Phys. **22**, 711 (1951).
[12] J. J. Benbow and E. R. Howells, Polymer **2**, 429 (1961).
[13] J. D. Huppler, I. F. Macdonald, E. Ashare, T. W. Spriggs, R. B. Bird, and L. A. Holmes, Trans. Soc. Rheol. **11**, 181 (1967).