

EFFECT OF THE ANISOTROPY OF MACROMOLECULAR TANGLES ON THE NONLINEAR PROPERTIES OF POLYMER LIQUIDS STRETCHED ALONG A SINGLE AXIS

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The most serious difficulty in mathematically treating the flow of solutions and melts of linear polymers is the inclusion of nonlinear effects. One often has to resort to theories which only qualitatively describe the behavior of the system. The insufficiently studied structure of experimentally measured quantities is a possible reason for this difficulty. In this context, we consider the example of steady-state viscosity of a stretched fluid.

1. Steady Flow of a Fluid Stretched along a Single Axis. In the case of steady flow the rheological equation of state of a liquid polymer can be written in the form of a relation between the velocity gradient tensor ν_{ij} and the deviator of the additional stress tensor τ_{ki} [1, 2]:

$$\nu_{ij} = \nu_{ij}(\tau_{kl}).$$

Using the Hamilton–Cayley theorem, this expression can be written as

$$\nu_{ij} = \lambda(\tau_{ij} - \alpha(\tau_{il}\tau_{lk})^d). \quad (1.1)$$

Here $\lambda = \lambda(J_2, J_3)$ and $\alpha = \alpha(J_2, J_3)$ are scalar functions of the invariants J_2 and J_3 of the tensor τ_{ik} and are called the slip and flow anisotropy coefficients, respectively [2]; $(s_{ik})^d$ denotes the operation of taking the deviator of the tensor s_{ik} .

For steady stretching in a single direction all tensors are diagonal:

$$[\nu_{ij}] = \begin{bmatrix} \dot{\epsilon} & 0 & 0 \\ 0 & -(1/2)\dot{\epsilon} & 0 \\ 0 & 0 & -(1/2)\dot{\epsilon} \end{bmatrix}, \quad [\tau_{kl}] = \begin{bmatrix} (2/3)\sigma & 0 & 0 \\ 0 & -(1/3)\sigma & 0 \\ 0 & 0 & -(1/3)\sigma \end{bmatrix} \quad (1.2)$$

($\dot{\epsilon}$ is the rate of stretching and σ is the tension) and α and λ are functions of the single argument σ .

In this case, defining the steady-state shear velocity η of the stretched fluid by the expression

$$\tau_{11} - \tau_{33} = \sigma = \eta(\sigma)\dot{\epsilon},$$

we find from (1.1) [2]

$$\eta(\sigma) = \frac{3}{2\lambda(\sigma)} \frac{1}{1 - (1/3)\alpha(\sigma)\sigma}. \quad (1.3)$$

We note that the dependence of the steady-state shear viscosity η of a stretched fluid on the tension σ is determined by the behavior of the two independent scalar functions $\lambda(\sigma)$ and $\alpha(\sigma)$. While the behavior of $\eta(\sigma)$ has often been studied experimentally, the author is aware of only one paper [2] discussing $\lambda(\sigma)$ and $\alpha(\sigma)$, where it is stated that

$$\lambda(\sigma) > 0, \alpha(\sigma) > 0 \text{ for small } \sigma, \alpha(\sigma) \leq 0 \text{ for large } \sigma. \quad (1.4)$$

Because of the lack of data on the behavior of $\lambda(\sigma)$ and $\alpha(\sigma)$, we attempt to determine a theoretical relationship between these parameters and the microscopic parameters of the polymer system. We use the rheological equation of state derived from a microstructural representation of the dynamics of linear polymer chains.

2. Nonlinear Theory of Microviscoelasticity of Solutions and Melts of Linear Polymers. The most successful theory of the viscoelasticity of concentrated polymer systems is presently the single-molecule approximation in which the macroscopic quantities are calculated by considering the dynamics of a single chain moving in an effective medium made up of the solvent and the other macromolecules. A detailed review of the literature in this field has been given in [3]. In this approximation to study comparatively slow motions one often uses the Karagin–Slonimskii–Rauz model (or the ball and spring model) in which the dynamical equations of the single macromolecule are written in terms of normal coordinates in the form [3-7]

$$\begin{aligned} m \frac{d}{dt} \psi_i^\alpha &= \Gamma_i^\alpha + T_i^\alpha - 2T\mu\lambda_\alpha \rho_i^\alpha + \Phi_i^\alpha, \\ \tau \frac{D}{Dt} \Gamma_i^\alpha + \Gamma_i^\alpha &= -\zeta B_{ij}^\alpha (\psi_j^\alpha - \nu_{ji} \rho_j^\alpha), \\ \tau \frac{D}{Dt} T_i^\alpha + T_i^\alpha &= -\zeta E_{ij}^\alpha (\psi_j^\alpha - \omega_{ji} \rho_j^\alpha). \end{aligned} \quad (2.1)$$

Here ρ_i^α and ψ_i^α are the generalized coordinate and velocity, m is the mass of the ball, ζ is the coefficient of friction of the ball, Φ_i^α is the random force, Γ_i^α is the hydrodynamic force, T_i^α is the force due to internal viscosity, $2T\mu\lambda_\alpha$ is the elastic coefficient, τ is the relaxation time of the surroundings, B_{ij}^α and E_{ij}^α are the tensor coefficients of friction, ω_{ij} is the antisymmetrized velocity gradient tensor, D/Dt is the Jauman tensor derivative, $\alpha = 1, 2, \dots, N$ is the number of the mode of motion of the macromolecule, where N is large for long macromolecules. Then the following expression for the stress tensor σ_{ik} of the system follows from statistical mechanics [4]:

$$\sigma_{ik} = -nT\delta_{ik} + 3nT \sum_\alpha [x_{ik}^\alpha - (1/3)\delta_{ik} - (1/2)(u_{ik}^\alpha + u_{ki}^\alpha)], \quad (2.2)$$

where $x_{ik}^\alpha = 2\mu\lambda_\alpha \langle \rho_i^\alpha \rho_k^\alpha \rangle / 3$, $u_{ik}^\alpha = \langle \rho_i^\alpha T_k^\alpha \rangle / (3T)$ and the averages are calculated over all possible values of the random phase Φ_i^α , whose statistical properties are determined by the appropriate fluctuation–dissipation relation.

Following [5], if we assume that the anisotropy of the surroundings of the single chain is determined by the shape and orientation of the macromolecular tangles and is characterized by the tensor

$$\begin{aligned} a_{ij} &= \frac{\langle s_i s_j \rangle}{\langle s^2 \rangle} - \frac{1}{3} \delta_{ij} \\ \langle \langle s_i s_j \rangle \rangle &= \frac{1}{N} \sum_\alpha \langle \rho_i^\alpha \rho_j^\alpha \rangle, \end{aligned} \quad (2.3)$$

then we can write

$$\begin{aligned} B_{ij}^\alpha &= B(\delta_{ij} + 3\beta a_{ij} + a_{ij} - \beta a_{ij} \delta_{ij})^{-1}, \\ E_{ij}^\alpha &= E(\delta_{ij} + 3\varepsilon a_{ij} + \nu a_{ij} - \varepsilon a_{ij} \delta_{ij})^{-1}. \end{aligned} \quad (2.4)$$

These expressions generalize the series expansions of B_{ij}^α and E_{ij}^α in powers of the applied anisotropy tensor a_{ij} given in [4] to the case of large velocity gradients and, as shown in [5], correspond to the condition of self-consistency. Multiplying the dynamical equations (2.1) of the macromolecule successively by ρ_i^α and T_i^α and using (2.3) and (2.4), we obtain the relaxation equations for the correlation functions x_{ik}^α and u_{ik}^α in the form [5, 6]

$$\frac{D}{Dt} x_{ik}^\alpha - \frac{B\tau_\alpha^\alpha}{\tau_\alpha} (x_{ij}^\alpha \nu_{jk}^\alpha + x_{kj}^\alpha \nu_{ji}^\alpha) = -\frac{1}{2\tau_\alpha} \left(\left(x_{ij}^\alpha - \frac{1}{3} \delta_{jk} \right) \delta_{ij}^\alpha + \left(x_{kj}^\alpha - \frac{1}{3} \delta_{kj} \right) \delta_{ji}^\alpha \right),$$

$$\begin{aligned} & \frac{D}{Dt} u_{ik}^\alpha + \frac{1}{\tau} u_{ik}^\alpha + \frac{1}{2\tau_\alpha} b_{ij}^\alpha u_{jk}^\alpha - \frac{B\tau_\alpha^R}{\tau_\alpha} e_{ij}^\alpha \gamma_{ik}^\alpha u_{ik}^\alpha \\ & = \psi \frac{B\tau_\alpha^R}{\tau_\alpha} \left(\left(x_{ii}^\alpha - \frac{1}{3} \delta_{ii} \right) a_{ik}^\alpha - 2B\tau_\alpha^R x_{ij}^\alpha \gamma_{jk}^\alpha \right), \end{aligned} \quad (2.5)$$

where

$$\begin{aligned} b_{ik}^\alpha &= \left(\delta_{ik} - \frac{B\tau_\alpha^R}{\tau_\alpha} (\beta_{ik} + \psi \varepsilon_{ik}) \right)^{-1}; \\ c_{ik}^\alpha &= (\delta_{ij} - \beta_{ij}) b_{jk}^\alpha; \quad e_{ik}^\alpha = b_{ij}^\alpha (\delta_{jk} - \beta_{jk}); \\ d_{ik}^\alpha &= b_{ij}^\alpha (\delta_{kj} - \varepsilon_{kj}); \quad f_{ik}^\alpha = c_{ij}^\alpha (\delta_{kj} - \varepsilon_{jk}); \\ \beta_{ik} &= 3\beta \left(a_{ij} + \frac{1}{3} \left(\frac{\kappa}{\beta} - 1 \right) a_{ij} \delta_{ij} \right) \\ & \times \left(\delta_{jk} + 3\beta \left(a_{jk} + \frac{1}{3} \left(\frac{\kappa}{\beta} - 1 \right) a_{jk} \delta_{jk} \right) \right)^{-1}; \\ \varepsilon_{ik} &= 3\varepsilon \left(a_{ij} + \frac{1}{3} \left(\frac{\nu}{\varepsilon} - 1 \right) a_{ij} \delta_{ij} \right) \\ & \times \left(\delta_{jk} + 3\varepsilon \left(a_{jk} + \frac{1}{3} \left(\frac{\nu}{\varepsilon} - 1 \right) a_{jk} \delta_{jk} \right) \right)^{-1}; \end{aligned}$$

and γ_{jk} is the symmetrized velocity gradient tensor.

The system of equations (2.5) involves the relaxation times

$$\tau, \tau_\alpha^R = \tau^*/\alpha^2, \quad \tau_\alpha = \chi + B\tau^*(1 + \psi)/\alpha^2,$$

and therefore the solution of this system is determined by one dimensional parameter $B\tau^*$ and six dimensionless parameters

$$\psi = E/B, \quad \chi = \tau/(2B\tau^*), \quad \beta, \quad \varepsilon, \quad \kappa, \quad \nu.$$

Steady flows for simple shear and stretching along a single axis were calculated in [5] using the system of rheological equations (2.2) and (2.5) with $\kappa = \beta$ and $\nu = \varepsilon$.

These results do not contradict the known experimental data, but the resulting system of equations is quite complicated and therefore a simpler model was suggested in [6] which uses the smallness of the parameters χ and ψ . This model was used in [7] to study unsteady effects in a liquid under simple shear.

3. Nonlinear Effects Resulting from Anisotropy of the Macromolecules. To calculate the slip λ and anisotropy α coefficients introduced in Sec. 1, we consider (2.2) and (2.5) in the case of steady stretching along a single axis, when the velocity gradient tensor has the form (1.2). In this case $u_{ik}^\alpha = 0$ and all matrices appearing in (2.5) are diagonal. Then (2.2) and (2.5) take the form [5]:

$$\begin{aligned} \tau_{ii} &= \sigma_{ii} - \frac{1}{3} \sigma_{ii}, \quad \sigma_{ii} - nT = 3nT \sum_\alpha \left(x_{ii}^\alpha - \frac{1}{3} \right), \\ x_{ii}^\alpha - \frac{1}{3} &= \frac{2}{3} B\tau_\alpha^R \gamma_{ii} (1 + 3\beta a_{ii})^{-1} \\ &+ 2B\tau_\alpha^R \left(x_{ii}^\alpha - \frac{1}{3} \right) (1 + 3\beta a_{ii})^{-1}. \end{aligned} \quad (3.1)$$

Here there is no summation over i and $\gamma_{11} = \dot{\varepsilon}$; $\gamma_{22} = \gamma_{33} = -1/3\dot{\varepsilon}$. It is evident that the solution of (3.1) is determined by the single dimensionless parameter β introduced in (2.4) and used to take into account the shape and orientation of the macromolecular tangles in the dynamical equations (2.5) of the macromolecule. To first order in the velocity gradients we obtain from (3.1)

$$x_{\bar{u}}^{\alpha} - \frac{1}{3} = \frac{2}{3} B\tau_{\alpha}^R \gamma_{\bar{u}}, \quad (3.2)$$

$$\tau_{\bar{u}} = \frac{\pi^2}{3} nT B\tau^* \gamma_{\bar{u}}, \quad l = 1, 2, 3,$$

since $a_{ii} = 0$ for zero velocity gradients. Using (1.3), we then have

$$\lambda_0 = \lambda(0) = \frac{3}{\pi^2 nT B\tau^*}. \quad (3.3)$$

We solve (3.1) to second order in the velocity gradients γ_{ij} and to first order in the anisotropy parameter β . It follows from (2.3) and (3.2) that

$$a_{\bar{u}} = \frac{2\pi^2}{15} B\tau^* \gamma_{\bar{u}}, \quad (3.4)$$

and therefore we find from (3.1)

$$x_{\bar{u}}^{\alpha} - \frac{1}{3} = \frac{2}{3} B\tau_{\alpha}^R \gamma_{\bar{u}} (1 + 3\beta a_{\bar{u}})^{-1} + \frac{4}{3} B\tau_{\alpha}^R \left(B\tau_{\alpha}^R - \frac{\pi^2}{5} B\tau^* \beta \right) \gamma_{\bar{u}}^2, \quad (3.5)$$

$$\sigma_{\bar{u}} - nT = \frac{\pi^2}{3} nT B\tau^* \gamma_{\bar{u}} + \frac{2\pi^4}{15} nT \left(\frac{1}{3} - \beta \right) (B\tau^*)^2 \gamma_{\bar{u}}^2$$

or

$$\gamma_{\bar{u}} = \lambda_0 (\sigma_{\bar{u}} - nT) - \frac{2\pi^2}{15} (1 - 3\beta) B\tau^* \gamma_{\bar{u}}, \quad l = 1, 2, 3.$$

Taking into account the diagonal form of the tensors γ_{ik} , σ_{ik} , τ_{ik} for stretching along a single axis, the last expression reduces to the form

$$\gamma_{ik} = \lambda_0 \tau_{ik} - \frac{2\pi^2}{15} (1 - 3\beta) B\tau^* (\gamma_{il} \gamma_{lk}).$$

Using the method of successive approximations to second order in τ_{ik} , we obtain from the preceding equation the function $\gamma_{ik} = \gamma_{ik}(\tau_{ik})$ in the form (1.1), which gives

$$\alpha(0) = \alpha^* (1 - 3\beta), \quad (3.6)$$

$$\alpha^* = \frac{2\pi^2}{15} \lambda_0 B\tau^*.$$

The next terms in the expansions of α and λ in powers of the tension σ are obtained in the same way:

$$\frac{\lambda(\bar{\sigma})}{\lambda_0} = 1 - \frac{16}{525} \left(\frac{4}{3} - 11\beta \right) \bar{\sigma}^2 + \frac{32}{7875} \left(\frac{4}{3} + 97\beta \right) \bar{\sigma}^4; \quad (3.7)$$

$$\frac{\alpha(\bar{\sigma})}{\alpha^*} = \frac{\lambda_0}{\lambda(\bar{\sigma})} \left(1 - 3\beta - \frac{4}{5} \left(\frac{8}{105} + 7\beta \right) \bar{\sigma}^2 \right). \quad (3.8)$$

Here $\bar{\sigma} = \sigma/(nT)$; λ_0 and α^* are determined by (3.3) and (3.6).

Equations (3.7) and (3.8) are graphed in Figs. 1 and 2 (curves 1-5 correspond to the values $\beta = 0, 0.05, 0.1, 0.25, 0.3$). We see from Fig. 1 that the slip coefficient $\lambda(\bar{\sigma})$ is an increasing function of both the tension $\bar{\sigma}$ (when $\beta \neq 0$) and the anisotropy parameter β , and large β corresponds to large $\lambda(\bar{\sigma})$. We see from Fig. 2 that the flow anisotropy coefficient $\alpha(\bar{\sigma})$ becomes independent of the tension at small $\bar{\sigma}$ and is determined by (3.6). With increasing $\bar{\sigma}$, the coefficient $\alpha(\bar{\sigma})$ at first decreases and becomes negative, then increases. These results do not contradict the experimental data of [2] and the statement (1.4).

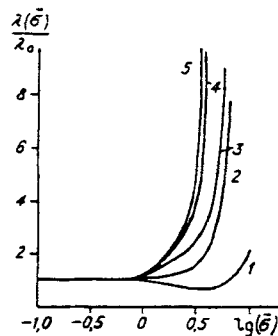


Fig. 1

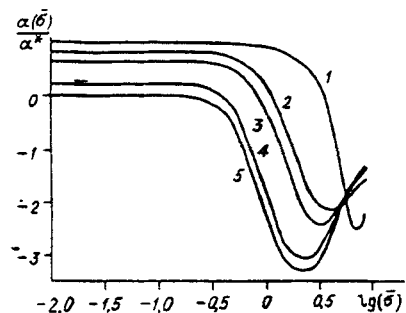


Fig. 2

In summary with the help of the microstructural approach we have found a relationship between the nonlinear characteristics of solutions and melts of linear polymers stretched along a single axis and the anisotropy parameter β characterizing the effect of the shape and orientation of the macromolecular tangles in the flow on the dynamics of the single macromolecule. More detailed experimental data for the slip λ and anisotropy α coefficients could be used with our results to determine the anisotropy parameter β , which is a fundamental parameter of the nonlinear theory of microviscoelasticity [4-7].

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