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Nonlinear Problems in Polymer Fluid Mechanics

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SUMMARY: The various approaches to modeling isotropic and anisotropic polymer fluids are discussed.

Introduction

In all problems of fluid mechanics, it is necessary to solve the general motion equations. These equations indicate how the mass, momentum, and angular momentum of the fluids change with position and time. For non-polar fluids the equation of change for angular momentum is reduced to a condition of symmetry of a stress tensor. The equations of change are well understood. They form the basis of the hydrodynamics of fluids.

For closing the basic equations of fluid mechanics one must formulate the constitutive equations establishing connection between the stress tensor and the kinematic quantities, taking into account the physical properties of liquids under consideration. This is the main problem of rheology. From this viewpoint, the rheology is a part of continuum mechanics.

The majority of rheological researches in the past five decades have been devoted to the study of polymer fluids. These fluids, partially or totally consisting of long macromolecules in the form of polymer solutions or polymer melts, have found a wide variety of industrial applications. Many experiments indicate that polymer fluids are capable to accumulate at flow the high recoverable strains. Due to this property such fluids engage an intermediate position between liquids and solids.

Nonlinear Constitutive Equations

The most essential properties of polymer fluids distinguishing them from the classical ones are the viscoelastic properties characterized by the relaxation spectrum. The main problem in

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rheology of polymer fluids is a description of strong nonlinearity that occurs due to a complex combination of elastic and viscous effects.

There are two fundamentally different approaches for constructing nonlinear constitutive equations of polymer fluids. The general principles of viscoelasticity are expounded in the purely phenomenological theories that issue from the basic ideas of mechanics and phenomenological irreversible thermodynamics, and certain assumptions concerning the properties of the fluid involved. The main obstacle in this approach is that of obtaining a nonlinear constitutive equation for polymer solutions and polymer melts, containing a small number of physically interpretable parameters. The most important achievements in this field, along with comparisons with experimental data , are given in books by Larson 1) and Leonov and Prokunin 2). In the phenomenological approach, no explicit consideration is given to the molecular structure of the polymer fluid. An appropriate constitutive equations are postulated.

The phenomenological theories do not establish the final results for the specific polymer fluids. The presentation of a unique quantitative description of the polymer fluid behavior calls for an account of their specificity. It is for this reason the molecular theories are built up which explicitly take into account the peculiarities of the structure and composition of the fluid. The polymer fluids are specific in that they consist of long flexible or rigid molecules.

All existing constitutive equations can be separated into two general categories: differential constitutive equations and integral constitutive equations. From the viewpoint of rheological modeling, the differential constitutive equations are more flexible than integral constitutive equations. They are usually presented as a set of independent nonlinear Maxwell modes with the invariant time derivatives for extra stress tensor.

The integral constitutive equations involve time integrals over the kinematic history of fluid elements. From a wide class of these equations, only the single integral equations were experimentally tested. For a large group of flow histories, the nonlinear polymer viscoelasticity can be described by the integral equation proposed by Bernstein, Kearsly and Zapas (BKZ equation). This equation has the potential form of a single integral equation. It is important to note that the non-potential single integral equations have been criticized by Larson 1) as being unphysical.

The problem of evaluating the macroscopic parameters in the constitutive equations is solved by molecular modeling or, more often, by experimental measurements.

Molecular Origins of Nonlinear Viscoelasticity

One of the principal objectives in the polymer physics is the development of a molecular theory of nonlinear viscoelasticity for polymer fluids with pronounced relaxation properties, typically concentrated solutions and melts of linear polymers. A substantial advance has been achieved in this field lately.

The existing molecular theories of nonlinear viscoelasticity for entangled polymer fluids are based on the one-molecular approximation. Within such an approach, the constraints imposed on the motion of single macromolecule are taken into account by introducing additional forces whose action is equivalent to the action of the real environment. Several molecular approaches to the study of nonlinear polymer viscoelasticity are summarized in review by Oakley et al. 3).

Reptation theories

One of the first molecular theories of nonlinear viscoelasticity of entangled polymer fluids is the reptation theory developed by Doi and Edwards 4). The reptation model assumes that each macromolecule in the polymer melts and concentrated solutions moves along the tube made of the surrounding macromolecules. This assumption is not obviously true because the surrounding macromolecules are also moving. The Doi-Edwards theory considers the important fact that the large-scale motion of macromolecules in polymer fluids is anisotropic. This model describes the limit case of anisotropy when transverse (with respect to its contour) motion is absent.

A constitutive equation based on reptation concept has the form of a separable BKZ equation

$$\sigma_{ij} + p\delta_{ij} = \int_{-\infty}^{t} 2m(t-t')\left[\frac{\partial U}{\partial I_1}C_{ij} - \frac{\partial U}{\partial I_2}C_{ij}^{-1}\right]dt' \qquad (1)$$

where σ_{ij} is the extra stress tensor, $I_1 \equiv tr\mathbf{C}^{-1}$ and $I_2 \equiv tr\mathbf{C}$ are invariants of the Finger strain tensor $\mathbf{C}(t,t')$. The memory function is defined by

$$m(t) = \sum_{\alpha\,\mathrm{odd}}^{\infty} \frac{8}{\pi^2} \frac{1}{\alpha^2} \frac{1}{\lambda_\alpha} \exp(-t/\lambda_\alpha) \qquad (2)$$

Here $\lambda_\alpha = \lambda_1/\alpha^2$ are the relaxation times and λ_1 is the longest relaxation time. The potential function $U(I_1, I_2)$ is determined numerically. At present, the several analytical approximations have been proposed.

Apart from a success in describing polymer diffusion, a number of serious problems of linear and nonlinear viscoelasticity remain unsolved in the reptation theory. Various modifications of the Doi-Edwards model were summarized by Marrucci 5). The modified theories lead to some improvements in the comparison with experiments, but still contain many unresolved issues and conflicting viewpoints. There are some conceptual questions about the reptation approach 6).

Memory in Nonlinear Dynamics of Macromolecules

The theory of Markovian stochastic processes served for a long time as the fundamental basis for describing a wide range of statistical phenomena in physics and chemistry. At present, it is quite clear that the non-Markovian processes and the molecular memory play a great role in statistical physics of fluids. Being more general, they, however, are not so much theoretically elaborated. This seems to be the reason why in most applications the Markovian stochastic processes have been used. The investigation of non-Markovian stochastic system is of paramount importance for many branches of polymer science.

Volkov and Vinogradov 7) proposed the molecular theory of nonlinear viscoelasticity for entangled flexible-chain polymers based on the non-Markovian dynamics of macromolecules. It represents the entangled macromolecule as moving in a viscoelastic medium. The large–scale motions of the flexible polymer molecule is modeled by a linear chain of $N+1$ elastically coupled Brownian particles. The starting point of the theory is non-Markovian Langevin equation of motion for single macromolecule

$$m\frac{du_i^\alpha}{dt} = F_i^{1\alpha} + F_i^{2\alpha} + K_i^\alpha + \Phi_i^\alpha \qquad (3)$$

where m is the mass and u_i^α is the velocity of the α-th particle. The motion equation for each Brownian particle (3) includes, along with common elastic K_i^α and stochastic Φ_i^α forces, also two additional forces $F_i^{1\alpha}$ and $F_i^{2\alpha}$. These viscoelastic forces are defined by two equations of relaxation type with one relaxation time τ:

$$\tau \frac{D}{Dt} F_i^{1\alpha} + F_i^{1\alpha} = -\zeta B (u_i^\alpha - \nu_{ie} r_e), \qquad \tau \frac{D}{Dt} F_i^{2\alpha} + F_i^{2\alpha} = -\zeta E \frac{D r_i^\alpha}{Dt} \tag{4}$$

The first equation of set (4) describes a hydrodynamic friction of particle due to the action of the surrounding viscoelastic medium. The second equation represents the long-range medium-induced interaction along the chain due to the large-scale deformation of macromolecular coil. The segmental friction coefficient ζ determines the scale of relaxation motions. B and E are the dimensionless parameters of relaxation interactions of a macromolecule with polymer environment. D/Dt is the Jaumann vector derivative. ν_{ie} and ω_{ie} are respectively the velocity gradient and the vorticity tensor.

Based on the relaxation macromolecular dynamics (3, 4) a theory of nonlinear viscoelasticity for the entangled monodisperse polymers within the range of slow relaxation processes has been developed. The main result is the nonlinear constitutive equation of differential type. The stress tensor σ_{ik} is separated in two parts

$$\sigma_{ik} + p\delta_{ik} = nT \sum_{\alpha=1}^{N} (\sigma_{ik}^{1\alpha} + \sigma_{ik}^{2\alpha}) \tag{5}$$

where T is the temperature in energy units and n is the number of macromolecules per unit volume. The sub-stress tensors $\sigma_{ik}^{1\alpha}$ and $\sigma_{ik}^{2\alpha}$ are described by coupled nonlinear equations of Maxwell type

$$\tau_\alpha^1 \frac{D_1}{Dt} \sigma_{ik}^{1\alpha} + \sigma_{ik}^{1\alpha} = 2B\tau_\alpha^R \gamma_{ik}, \qquad \tau_\alpha^2 \frac{D_2}{Dt} \sigma_{ik}^{2\alpha} + \sigma_{ik}^{2\alpha} = E\tau_\alpha^R \frac{\tau_\alpha^2}{\tau} \frac{D}{Dt} \sigma_{ik}^{1\alpha}$$

with nonaffine convective derivatives $D_d \sigma_{ik}^{d\alpha} / Dt = D\sigma_{ik}^{d\alpha} / Dt - d_{d\alpha}\left(\gamma_{ie}\sigma_{ek}^{d\alpha} + \gamma_{ke}\sigma_{ei}^{d\alpha}\right)$. Here D/Dt is the Jaumann tensor derivative and γ_{ik} is the strain rate tensor. $a_{d\alpha} = B\tau_\alpha^R / d\tau_\alpha^1$, $d = 1,2$ is the measure of non-affinity. The theory predicts for monodisperse polymers the two sets of long relaxation times

$$\tau_\alpha^1 = \frac{\tau}{2} + (B+E)\tau_\alpha^R, \qquad \tau_\alpha^2 = 2\tau\tau_\alpha^1 / (\tau + 2\tau_\alpha^1) \tag{6}$$

where $\tau_\alpha^R = \tau_1^R / \alpha^2$ is the Rouse relaxation time. In the self–consistent case the τ_α^2 are automatically reduced to the relaxation time of the surroundings $\tau \sim M^{3.4}$. The relaxation times τ_α^1 have the Rouse-like form with the maximum relaxation time $\tau_1 \sim M^{4.4}$. There are some experimental evidences of the existence of such very slow relaxation processes in high molecular weight polymers. Some tests demonstrate that the model can properly describe the nonlinear dynamics of monodisperse polymers with high values of M/M_c in a slow relaxation region. M_c is the critical molecular weight for a given polymer.

Additionally, the approach based on non-Markovian dynamics of macromolecules might help in explaining the high frequency viscoelasticity of polymer fluids [8)].

Anisotropic Viscoelasticity

The appearance of liquid crystalline (LC) polymers has given rise to a new splash of interest in the study of rheological properties of the anisotropic fluids. The dual nature of LC polymers leads to the fact that from the macroscopic viewpoint they represent anisotropic viscoelastic liquids. The experimental and theoretical investigations of LC polymers are discussed in reviews [9-11)].

Several fluid mechanical theories have been formulated which take into account the microstructure of complex fluids [12)]. The simplest continual theory for oriented fluids was developed by Ericksen [13)]. He defined a class of fluids with a single orientation vector $\mathbf{n}$, called the director. This unit vector characterizes the preferred orientation of fluid particles during flow. Ericksen's concept of transversely isotropic fluid was further used to develop a structural-continuum theory for suspensions of ellipsoidal particles. It is worth mentioning that this theory is widely used to describe blood flow and developed turbulent flows.

The concept of a continuum with an inner structure appears to be very promising to advance a continuum theory for liquid crystals. Leslie [14)] modified Ericksen liquid to consider the dynamics of nematic liquid crystals. The popular Leslie-Ericksen theory describes the basic features of the rheological behavior of low molecular weight liquid crystals. However, this theory fails to describe the frequency dependence of dynamic moduli and nonlinear effects observed at flows of LC polymer fluids. This fact has stimulated the studies of general principles of anisotropic viscoelasticity [15-17)].

The relaxation processes depend on the rigid structure of macromolecules forming LC phase and are anisotropic. The total stress tensor of nematic fluid can be represented as

$$\sigma_{ij} + p\delta_{ij} = \sigma_{ij}^{e} + \sigma'_{ij} \tag{7}$$

where p is the pressure, σ_{ij}^{e} is the part of the stress tensor connected with the spatial inhomogeneity of the director field, and σ'_{ij} is the dissipative stress tensor. It is possible to propose the constitutive equation for viscoelastic fluid with single anisotropic relaxation time

$$\tau_{ijke}\frac{\nabla\sigma'_{ke}}{\nabla t} + \sigma'_{ke} = \eta_{ijke}\dot{\varepsilon}_{ke} \tag{8}$$

where τ_{ijke} is the relaxation time tensor, and η_{ijke} is the viscosity tensor. The invariant (tensor) time derivative can be represented as $\nabla\sigma'_{ij}/\nabla t = d\sigma'_{ij}/dt + A_{ijek}\sigma'_{ek}$ with $A_{ijek} = \delta_{ie}(\omega_{kj} + a\gamma_{kj}) + \delta_{jk}(\omega_{ei} + b\gamma_{ei})$ where a and b are the scalar parameters. In the special case $a = b = 0$, we have the corotational (Jaumann) tensor derivative.

For fluids where the internal rotational degrees of molecule freedom are essential, the non-symmetric strain rate tensor $\dot{\varepsilon}_{ke}$ is defined by

$$\dot{\varepsilon}_{ke} = \gamma_{ke} + \omega_{ke}^{r}, \quad \omega_{ke}^{r} = \omega_{ke} - \Omega_{ke} \tag{9}$$

Here $\gamma_{ke} = \mathrm{v}_{(k,e)}$ is the symmetric part of the velocity gradient of a fluid, and ω_{ke}^{r} is the relative rotation rate tensor; $\omega_{ke} = \mathrm{v}_{[k,e]}$ is the vorticity tensor, $\Omega_{ke} = \varepsilon_{kse}\Omega_{s}$ is the internal rotation rate tensor, ε_{kse} is the unit antisymmetric tensor, and Ω_{s} is the internal angular velocity. The antisymmetric part of the stress tensor arises as a consequence of the difference between fluid vorticity and spin.

For nematic (uniaxial) viscoelastic fluids, η_{ijke} and τ_{ijke} are transversely isotropic tensors relative to the director **n**. In this case, we have for the incompressible fluids

$$\begin{gathered}\eta_{ijke} = \eta_1\delta_{ik}\delta_{je} + \eta_2\delta_{ie}\delta_{jk} + \eta_3 n_{ijke} + \eta_4 n_{ik}\delta_{je} + \eta_5 n_{jk}\delta_{ie} + \eta_6 n_{ie}\delta_{jk} + \eta_7 n_{je}\delta_{ik} \\ \tau_{ijke} = \tau_1\delta_{ik}\delta_{je} + \tau_2\delta_{ie}\delta_{jk} + \tau_3 n_{ijke} + \tau_4 n_{ik}\delta_{je} + \tau_5 n_{jk}\delta_{ie} + \tau_6 n_{ie}\delta_{jk} + \tau_7 n_{je}\delta_{ik}\end{gathered} \tag{10}$$

Here η_i and τ_i are the material constants with dimensions of viscosities and relaxation times; $n_{ie} = n_i n_e$, and $n_{ijke} = n_i n_j n_k n_e$. There are also two restrictions that follow from Onsager relations

$$\eta_5 = \eta_6 , \quad \tau_5 = \tau_6 \tag{11}$$

Thus we have an interpretation of Onsager relations as a special symmetry of $\eta_{ijke} = \eta_{keij}$ and $\tau_{ijke} = \tau_{keij}$. Using expressions (10), one easily shows that the constitutive equation (8) can be written as

$$\begin{gathered}
\tau_1 \frac{\nabla\sigma'_{ij}}{\nabla t} + \tau_2 \frac{\nabla\sigma'_{ji}}{\nabla t} + \tau_3 n_{ijek} \frac{\nabla\sigma'_{ek}}{\nabla t} + \tau_4 n_{ie} \frac{\nabla\sigma'_{ej}}{\nabla t} + \tau_5 n_{je} \frac{\nabla\sigma'_{ei}}{\nabla t} + \\
\tau_6 \frac{\nabla\sigma'_{je}}{\nabla t} n_{ei} + \tau_7 \frac{\nabla\sigma'_{ie}}{\nabla t} n_{ej} + \sigma'_{ij} = \mu_1 \gamma_{ij} + \mu_2 n_{ijke} \gamma_{ke} + \\
\mu_3 n_{ie} \gamma_{ej} + \mu_4 n_{je} \gamma_{ei} + \mu_5 \omega^r_{ij} + \mu_6 n_{ie} \omega^r_{ej} + \mu_7 n_{je} \omega^r_{ei}
\end{gathered} \tag{12}$$

Eq. (11) implies that $\mu_6 + \mu_7 = \mu_3 - \mu_4$. This relation reduces the number of independent viscosity coefficients to six. The case $\tau_4 = \tau_7$ and $\tau_5 = \tau_6$ is of special interest. This choice corresponds to the decoupled relaxation of symmetric and antisymmetric stresses.

We consider here particular cases for which Eq. (12) simplifies considerably. If $\tau_{ijke} = 0$ and the microstructure exhibits no preferred direction, i.e. if it is spherical, we obtain the simplest constitutive equation for the fluid with an internal rotation

$$\sigma_{ij} + p\delta_{ij} = 2\eta\gamma_{ij} + 2\eta_r \omega^r_{ij} \tag{13}$$

as first proposed by Born [18]. Here η_r is the rotational viscosity. When the local spin about the director is negligible, i.e. $\Omega_e n_e = 0$ and $\tau_{ijke} = 0$, Eq. (12) reduces to the form

$$\sigma'_{ij} = \alpha_1 n_{ijke} \gamma_{ke} + \alpha_2 n_i N_j + \alpha_3 N_i n_j + \alpha_4 \gamma_{ij} + \alpha_5 n_{ie} \gamma_{ej} + \alpha_6 \gamma_{ie} n_{ej} \tag{14}$$

where $N_i = \dot{n}_i - \omega_{ie} n_e = (\Omega_{ie} - \omega_{ie}) n_e$. This equation is identical with Leslie constitutive equation [14]. The α_i are commonly called the Leslie viscosity coefficients. More simple theory for anisotropic fluid has been proposed by Ericksen [13]. It can be obtained from Eqs. (7) and (14) by requiring that $\sigma^e_{ij} = 0$, $\alpha_2 = \alpha_3 = 0$ and $\alpha_5 = \alpha_6$.

The director **n**, which is included in the constitutive equations for nematic fluids, is defined using an additional equation describing the change in orientation induced by flow and external (magnetic or electric) field. This equation reflects unique properties of anisotropic fluids and has no analogue in the case of isotropic fluids.

Conclusion

All phenomenological approaches have resulted in a situation where more than ten popular nonlinear constitutive equations for flexible polymer fluids are in competition nowadays.

The molecular approach based on non-Markovian dynamics of macromolecules may gain more applications in polymer science because of the increasing interest in non-Markovian stochastic processes. We are still a long way from quantitatively understanding the molecular causes of strong nonlinear viscoelastic behavior in concentrated polymer fluids and polydisperse polymers.

The key problem is the experimental and theoretical study of the anisotropic relaxation processes in LC polymer systems under various mechanical actions.

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