

Slow Relaxational Dynamics and Rheology in Complex Fluids

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Abstract. We discuss how slow relaxational degrees of freedom – arising from transient internal structures – can influence the rheological behavior of complex fluids.

Introduction: Complex Fluids can be characterized as fluids that obey hydrodynamic equations more complicated than the usual Navier-Stokes equations. A prominent example are polymers showing visco-elasticity, shear-thinning (or thickening) and other non-Newtonian features. The origin of such a behavior is thought to stem from transient mesoscopic structures, like entanglements, orientational correlations etc. Although it is rather simple to incorporate linear visco-elasticity into hydrodynamics, it is far from clear how a reasonable and physically valid description of nonlinear effects should look like. As a first attempt nonlinear hydrodynamic equations are given for polymers including transient elastic, orientational, and rotational degrees of freedom described by ϵ_{ij} , a symmetric second rank tensor [1], by Q_{ij} the traceless mass quadrupolar momentum [2], and by Ω_{ij} an antisymmetric tensor [3], respectively, in addition to the usual variables, energy density ϵ , mass density ρ , and momentum density g_i . This is a purely phenomenological treatment, where the connection to a mesoscopic description and the identification of the additional degrees of freedom still have to be done. Implications for shear flow are sketched. A basic introduction to the hydrodynamic method is given in [4].

Basic Equations: The various hydrodynamic variables are linked to the entropy density σ by the Gibbs relation thus defining the conjugate quantities (e.g. the temperature T , the chemical potential μ , the velocity $v_i = g_i/\rho$)

$$Td\sigma = d\epsilon - \mu d\rho - v_i dg_i - W_{ij} dQ_{ij} - \Psi_{ij} d\epsilon_{ij} - L_i d\nabla_j \Omega_{ji} \quad (1)$$

Neglecting the thermal degree of freedom for lack of space the dynamic equations

$$\dot{\epsilon}_{ij} + v_k \nabla_k \epsilon_{ij} - A_{ij} + A_{il}(\epsilon_{jl} + \Omega_{jl}) + A_{jl}(\epsilon_{il} + \Omega_{il}) = -(1/\tau)_{ijkl} \Psi_{kl} \quad (2)$$

$$\dot{Q}_{ij} + v_k \nabla_k Q_{ij} + a_{ijkl} A_{kl} - \omega_{il} Q_{lj} - \omega_{jl} Q_{il} = -(1/\gamma)_{ijkl} W_{kl} \quad (3)$$

$$\dot{H}_i + v_k \nabla_k H_i - \nabla_j \omega_{ji} = -(1/\kappa)_{ij} L_j \quad (4)$$

together with mass $\dot{\rho} + \nabla \cdot \rho \mathbf{v} = 0$ and momentum conservation $\dot{g}_i + \nabla_j \sigma_{ij} = 0$ describe the system. Some dissipative cross-couplings have been neglected on the right hand sides of (2-4). We have used the abbreviations for elongational flow $2A_{ij} \equiv \nabla_j v_i + \nabla_i v_j$ and for the vorticity tensor $2\omega_{ij} \equiv \nabla_j v_i - \nabla_i v_j$. The nonlinearities in (2) are chosen such that in the limit of permanent crosslinking ($\tau \rightarrow \infty$) elasticity is described by the displacement vector (\mathbf{u}) via $2\epsilon_{ij} \equiv \nabla_i u_j + \nabla_j u_i - (\nabla_k u_i)(\nabla_k u_j)$ [5]. Since the internal rotations Ω_{ij} occur in (2) we also need their dynamic equations (4), which however enter hydrodynamics only in the inhomogeneous case with $H_i \equiv \nabla_j \Omega_{ij}$. The nonlinearities in (3) are dictated by Q_{ij} describing local orientations. Thermodynamics leads to the following form of the stress tensor (p is the pressure), which can be brought into the required symmetric form $\nabla_j \sigma_{ij} = \nabla_j \sigma_{ji}$ by the standard procedure [6]

$$\begin{aligned} \sigma_{ij} = & \delta_{ij} p + v_i g_j - \Psi_{ij} + a_{ijkl} W_{kl} + (1/2)(\nabla_i L_j - \nabla_j L_i) - W_{jl} Q_{il} + W_{il} Q_{jl} \\ & + \Psi_{jl}(\epsilon_{li} + \Omega_{li}) + \Psi_{il}(\epsilon_{lj} + \Omega_{lj}) - \nu_{ijkl} A_{kl} \end{aligned} \quad (5)$$

The system of equations is closed by the constitutive equations relating the conjugate quantities to the variables. Neglecting cross-couplings one finds $\Psi_{ij} = c_{ijkl} \epsilon_{kl}$, $W_{ij} = K_{ijkl} Q_{kl}$ and $L_i = r_{ij} \nabla_k \Omega_{kj}$.

Shear Flow: If an external shear flow is imposed, both A_{ij} and ω_{ij} are non-zero and as a consequence of (2,3) also ϵ_{ij} and Q_{ij} . Then the stress tensor depends strongly on the shear rate first directly through (5) and additionally by expanding the viscosity tensor with respect to the variables

$$\begin{aligned} \nu_{ijkl} = & \nu_{ijkl}^{(0)} + \mu_{ijklpqrs}^{(2A)} A_{pq} A_{rs} + \mu_{ijklpq}^{(2H)} H_p H_q + O(4) + \mu_{ijklpq}^{(Q)} Q_{pq} \\ & + \mu_{ijklpq}^{(\epsilon)} \epsilon_{pq} + \mu_{ijklpqrs}^{(2Q)} Q_{pq} Q_{rs} + \mu_{ijklpqrs}^{(2\epsilon)} \epsilon_{pq} \epsilon_{rs} + \mu_{ijklpqrs}^{(Q\epsilon)} Q_{pq} \epsilon_{rs} + O(3) \end{aligned} \quad (6)$$

Both effects lead to a complicated dependence of the 'effective' viscosities **and** moduli on the shear rate as well as on the frequency. In addition the flow profile is no longer linear and thus H_i is non-zero and has therefore been inserted into the expansion (6), too (while Ω_{ij} is not allowed there for thermodynamic reasons).

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(appeared in the Proceedings of the 8th Tohwa University Conference, p.160, 1999)