	Proc. XIVth Int. Congr. on Rheology *Edited by:* Copyright 2004 – The Korean Society of Rheology	August 22-27, 2004 Seoul, Korea

A Physicists' View on Constitutive Equations

Harald Pleiner[a], Mario Liu[b], and Helmut R. Brand[c]

[a]Max Planck Institute for Polymer Research, D 55021 Mainz, Germany
[b]Institute for Theoretical Physics, University Tübingen, D 72676 Tübingen, Germany
[c]Theoretical Physics III, University Bayreuth, D 95440 Bayreuth, Germany

ABSTRACT

Nonlinear hydrodynamic equations for viscoelastic media are discussed. We start from the recently derived fully hydrodynamic nonlinear description of permanent elasticity that utilizes the (Eulerian) strain tensor. The reversible quadratic nonlinearities in the strain tensor dynamics are of the 'lower convected' type, unambiguously. Replacing the (often neglected) strain diffusion by a relaxation of the strain as a minimal ingredient, a generalized hydrodynamic description of viscoelasticity is obtained. This can be used to get a nonlinear dynamic equation for the stress tensor (sometimes called constitutive equation) in terms of a power series in the variables. The form of this equation and in particular the form of the nonlinear convective term is not universal but depends on various material parameters. A comparison with existing phenomenological models is given. In particular we discuss how these ad-hoc models fit into the hydrodynamic description and where the various non-Newtonian contributions are coming from.

INTRODUCTION

Hydrodynamics is a well established field to describe macroscopically simple fluids by means of the Navier-Stokes-, continuity, and heat conduction equations. However, it applies also to more complex fluids that are fully characterized by conservation laws and broken symmetries. This more general hydrodynamic method has been established in the 60s [1-3] and applied e.g. to superfluids [4] and liquid crystals [5]. It is based on (the Gibbsian formulation of) thermodynamics [6,7], symmetries and well-founded physical principles [8]. A detailed description of this method can be found in [5,9]. Somewhat related approaches have been used for liquid crystals [10-12] and more generally in [13,14].

On the other hand, non-Newtonian fluids are believed to show non-universal behavior and a host of different empirical models have been proposed [15-20] to cope with the flow rheology of such substances. Typically, these models are formulated as generalizations of the linear, Newtonian relation between stress and deformational flow allowing for additional time derivatives and nonlinearities. They are tailored to accommodate empiric findings or are based on principles [19] that are ad-hoc and generally insufficient.

Quite recently we have derived a nonlinear hydrodynamic description of elastic media [21,22] that is based on first principles, only, making use of thermostatics, linear irreversible thermodynamics, symmetries and broken symmetries, and invariance principles. It has been confirmed within the GENERIC formalism [23]. Allowing in this hydrodynamic description the strains to relax (and not only to diffuse) a generalized hydrodynamic description of nonlinear viscoelasticity is obtained in terms of a dynamic equation for the strain tensor [21,22]. We transform it into a description in terms of a dynamic equation for the stress tensor. This can only be done approximately in the form of a power expansion in the variables. Up to second order, a formulation is obtained that can directly be compared with many of the empirical models proposed to describe non-Newtonian rheology. The comparison reveals possible inconsistencies and connects the various ad-hoc additions of those models with physical relevant processes, like strain relaxation, elasticity and viscosity. A comparison with recent constitutive equations that refer to specific microscopic variables and processes, like convective constraint release, will not be done in the present paper. Here we rather concentrate on the simplest generalized hydrodynamic description of non-Newtonian rheology in terms of a relaxing strain field, while a detailed comparison with those theories requires the use of additional relaxing fields.

The present contribution is based on material presented and discussed in detail in [24].

RESULTS AND DISCUSSION

In an Eulerian description of elasticity deformations are described in terms of body frame coordinates that are viewed as functions of the laboratory frame coordinates. Since these two frames are completely independent and generally different in their origin and their orientation (this is a correct form of the 'frame indifference principle'), the dynamic equation for the (symmetric Eulerian) strain tensor $D\mathbf{U}=\mathbf{A}+\mathbf{X}$ contains the lower convected time derivative D [21,22], while in a Lagrangian picture it would be upper convected. $\mathbf{A}$ is the symmetric velocity gradient tensor, often called 'rate of strain' tensor, although in an Eulerian description it is *not* the time derivative of the strain tensor. The phenomenological current $\mathbf{X}$ describes strain diffusion and, in the case of a non-permanent elasticity, strain relaxation. The latter is expressed by the elastic stress tensor $\mathbf{Y}$. For an isotropic medium the most general expression within linear irreversible thermodynamics reads

$$\mathbf{X} = a_1 \mathbf{Y} + a_3 \mathbf{I}\, \mathrm{tr}\mathbf{Y} + \sum a_{2n} (\mathbf{U}_n\bullet\mathbf{Y} + \mathbf{Y}\bullet\mathbf{U}_n) \quad (1)$$
$$+ \sum a_{4n} (\mathbf{I}\, \mathbf{U}_n : \mathbf{Y} + \mathbf{U}_n\, \mathrm{tr}\mathbf{Y}) + \sum a_{5nm} (\mathbf{U}_n \mathbf{U}_m : \mathbf{Y} + \mathbf{U}_m \mathbf{U}_n : \mathbf{Y}) + \sum a_{6nm} (\mathbf{U}_n\bullet\mathbf{Y}\bullet\mathbf{U}_m + \mathbf{U}_m\bullet\mathbf{Y}\bullet\mathbf{U}_n)$$

with $\mathbf{U}_n$ the second rank tensor $\mathbf{U}\bullet\mathbf{U}\bullet \ldots \bullet\mathbf{U}$ that follows from a (n-1)-fold scalar contraction of n factors $\mathbf{U}$, $\mathbf{I}$ is the unity tensor, and tr is the trace. The sums $\sum$ in (1) run from n,m = 1 to infinity. The coefficients a_x are arbitrary functions of the scalar state variables, like density, temperature, and the three independent scalar invariants of the strain tensor $\mathrm{tr}\mathbf{U}$, $\mathrm{tr}\mathbf{U}_2$, and $\mathrm{tr}\mathbf{U}_3$. The explicit form of (1) up to quadratic order is listed in [24]. If $\mathbf{U}$ is uniaxial and traceless, then the traceless part of $\mathbf{U}_n$ is proportional to $\mathbf{U}$ and the sums in (1) are finite. By allowing a nonlinear dependence of $\mathbf{X}$ on $\mathbf{Y}$ one would leave the solid grounds of well-established statistical physics, since not very much is known on the validity range of 'non linear irreversible thermodynamics', where the currents depend nonlinearly on the forces. A second phenomenological process describes the connection between the viscous part of the stress tensor σ_v and $\mathbf{A}$. Generally, this relation has the same form as Eq.(1), with viscosities ν_1, ν_{2n}, ν_3, ν_{4n}, ν_{5nm}, ν_{6nm} that depend on $\mathrm{tr}\mathbf{U}$, $\mathrm{tr}\mathbf{U}_2$, and $\mathrm{tr}\mathbf{U}_3$, while in the incompressible case ν_3, ν_{4n} are zero. The elastic part of the stress tensor $\sigma_e = -\mathbf{X} + \mathbf{X}\bullet\mathbf{U} + \mathbf{U}\bullet\mathbf{X}$ is nonlinear due to the lower convected time derivative for $\mathbf{U}$. Finally, static elasticity is described by a suitable energy density function $\varepsilon = \varepsilon(\mathrm{tr}\mathbf{U}, \mathrm{tr}\mathbf{U}_2, \mathrm{tr}\mathbf{U}_3)$, from which $\mathbf{X} \equiv \partial\varepsilon / \partial\mathbf{U}$ follows.

Having set up the dynamic equation for the strain tensor and the strain tensor dependence of the material tensors, one can derive from that a description in terms of the stress tensor. This can only be done in an approximate way (as a power series expansion up to second order in the old and new variables), since the equations are nonlinear. Of course, the resulting equations are less general than the starting ones and only applicable, if quadratic nonlinearities are sufficient for the problem at hand. The final equation for the stress tensor is listed and discussed in detail in [24], and is not shown here, since it is too complicated for the required Word format of this abstract. It contains σ, its convected time derivative (which is neither of the upper nor of the lower type, but depends on a certain combination of material parameters) describing stress relaxation, $\mathbf{A}$ the effective viscosity part, and the convected time derivative of $\mathbf{A}$ (again material dependent, but generally different from that for σ) as well as nonlinearities in the stress tensor, and in σ and $\mathbf{A}$ with $\partial\mathbf{A}/\partial t$. The material parameters that occur at different places in this equation are not completely independent from each other and are combinations of the underlying physical parameters due to strain relaxation, viscosity and elasticity. It is in the form that many empirical constitutive models have and a direct comparison is possible. By putting to zero some of the material parameters involved one can either recover those constitutive models or show their intrinsic inconsistency. Among the first are (for the Eulerian description) the lower convected Maxwell [19] and Oldroyd A [15] models, as well as the Giesekus model [18], if for the latter a suitably chosen material dependent convective time derivative is used. The models with a corotational time derivative, Johnson-Segalman [25] and Jeffries [26] are inconsistent, since this special form of the convective time derivative is incompatible with other approximations and omissions made in these models. A corotational time derivative is more suitable for those descriptions that use an orientational order parameter tensor to describe viscoelasticity [27]. The 'second order fluid' [19] contains a contribution $\mathbf{A}\bullet\mathbf{A}$ to the stress tensor, which, by comparison with our general equation, turns out to be related to the material dependent part of the convected time derivative of $\mathbf{A}$, originating from the strain dependence of elasticity, viscosity and strain relaxation. This quadratic $\mathbf{A}\bullet\mathbf{A}$ contribution to the stress tensor cannot be obtained by a quadratic extension of linear irreversible thermodynamics. Even when no convective derivatives are considered, very often nonlinear phenomenological relations $\sigma = \sigma(\mathbf{A})$

are used. Examples are 'power law fluids', but much more complicated forms are used [26]. The problem with all these models is the compliance with thermodynamics. The expansion for the viscosity tensor in terms of **U** avoids this problem and can be carried on to any order desired. However, similar contributions to the stress tensor originate from the other phenomenological expansions and change quite considerably the structure of the dynamic equation for the stress tensor rendering inconsistent any model that uses a power law description of the shear viscosity, only.

SUMMARY

In this manuscript we have shown that the hydrodynamically derived model for non-Newtonian fluids in terms of the Eulerian strain tensor contains most of the standard rheological models as special cases and discards a few of them. Our approach is more general, as it contains powers of the relevant fields of arbitrary order when written in terms of the stress tensor. The hydrodynamic framework automatically ensures the resulting equations to conform with the appropriate physical principles (e.g. Galilean invariance), thermodynamic laws (e.g. energy conservation and dissipative entropy production), as well as with other applicable symmetry properties. The hydrodynamic method also allows to discriminate those pieces of the dynamics that are due to general principles from the unavoidable phenomenological part. The latter is given here in the form of truncated power series in the strain tensor that can systematically be generalized when necessary. For the phenomenological part we stick to the well-established 'linear irreversible thermodynamics', which, being linear in the generalized forces, nevertheless leads to equations highly nonlinear in the variables like the strain tensor.

REFERENCES

1. N. N. Bogoljubov, Phys.Abhandl.SU **6**, 229 (1962).
2. L. P. Kadanoff and P. C. Martin, Ann. Phys. **24**, 419 (1963).
3. P. Hohenberg and P. C. Martin, Ann. Phys. **34**, 291 (1965).
4. I. M. Khalatnikov, *Introduction to the Theory of Superfluidity*, Benjamin, New York (1965).
5. P. C. Martin, O. Parodi, and P. S. Pershan, Phys. Rev. A **6**, 2401 (1972).
6. H. B. Callen, *Thermodynamics*, John Wiley, New York, 1st ed.(1960) and 2nd ed.(1985).
7. L. E. Reichl, *A Modern Course in Statistical Physics*, Texas University Press, Austin (1980).
8. D. Forster, *Hydrodynamic Fluctuations, Broken Symmetry and Correlation Functions*, Benjamin, Reading, Mass. (1975).
9. H. Pleiner and H. R. Brand, in *Pattern Formation in Liquid Crystals*, eds. A. Buka and L. Kramer, Springer, New York, p.15 (1996).
10. F. M. Leslie, Arch. Rat. Mech. Anal. **28**, 265 (1968).
11. J. L. Ericksen, Arch. Rat. Mech. Anal. **4**, 231 (1960) and **9**, 371 (1962).
12. S. Hess, Z. Naturforsch. **30a**, 728 and 1224 (1975).
13. M. Grmela, Phys. Lett. A **102**, 355 (1984); **111**, 36 and 41 (1985).
14. A. N. Beris and B. J. Edwards, *Thermodynamics of flowing systems with internal microstructure*, University Press, Oxford (1994).
15. J. G. Oldroyd, Proc. Roy. Soc. A **200**, 523 (1950).
16. B. D. Coleman and W. Noll, Rev. Mod. Phys. **33**, 239 (1961).
17. C. Truesdell and W. Noll, *The non-linear field theories of mechanics*, Springer, Berlin/New York (1965).
18. H. Giesekus, Rheol. Acta **5**, 29 (1966) and J. Non-Newt. Fluid Mechanics **11**, 69 (1982).
19. R. B. Bird, R. C. Armstrong, and O. Hassager, *Dynamics of Polymeric Liquids*, Vol.1, John Wiley & Sons, New York (1977).
20. R. G. Larson, *Constitutive equations for polymer melts and solutions*, Butterworths, Boston (1988).
21. H. Temmen, H. Pleiner, M. Liu, and H. R. Brand, Phys. Rev. Lett. **84**, 3228 (2000) and **86**, 745 (2001).
22. H. Pleiner, M. Liu, and H. R. Brand, Rheol. Acta **39**, 560 (2000).
23. M. Grmela, Phys. Lett. A **296**, 97 (2002).
24. H. Pleiner, M. Liu, and H. R. Brand, Rheol. Acta **xx**, xxx (2004); DOI 10.1007/s00397-004-0365-8.
25. M. W. Johnson and D. Segalman, J. Non-Newt. Fluid Mechanics **2**, 255 (1977) and J. Rheol. **22**, 445 (1978).
26. G. Boehme, *Stroemungsmechanik nichtnewtonscher Fluide*, Teubner, Stuttgart, 2nd edition, (2000).
27. H. Pleiner, M. Liu, and H. R. Brand, Rheol. Acta **41**, 375 (2002).