Viscoelastic and non-Newtonian effects in shear flow

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The time-correlation functions characterizing linear viscoelasticity and nonlinear transport in shear flow are compared for a low-density gas of Maxwell molecules. It is shown that the relationship between viscoelasticity and nonlinear transport given by the Goddard-Miller rheological equation of state does not apply, and the principle of objectivity on which this equation is based is not valid.

I. INTRODUCTION

Recent applications of mode-coupling theory to nonlinear transport in uniform shear flow suggest that the nonlinear shear viscosity is not an analytic function of the shear rate.[1,2] The predicted dependence on shear rate has the same form as the nonanalytic frequency dependence of the *linear* shear viscosity.[3] A similar relationship between frequency and shear rate nonanalyticities has been observed in nonequilibrium computer simulations of shear flow.[4] Since the anomalous frequency dependence is associated with the asymptotic behavior of equilibrium time-correlation functions for linear transport (the "long-time tails"), it is of some interest to see if there is a simple connection to the anomalous shear rate dependence for nonlinear transport. Such a connection would imply a close relationship, for example, between viscoelasticity and shear thinning. In the study of rheological fluids, models have been proposed on the basis of the principle of objectivity that directly relate the frequency and shear rate dependence of the shear viscosity.[5] The simplest of these is the Goddard-Miller "rheological equation of state."[5,6] Zwanzig has noted[7] that the implications of the Goddard-Miller model in fact agree with those of mode-coupling theory in two dimensions, although they do not agree in three dimensions. In a related context[8] (nonlinear diffusion in shear flow), the mode-coupling theory for both finite frequency *and* shear rate has been studied in three dimensions. Although qualitatively similar, it was found that the Goddard-Miller and mode-coupling results are quantitatively different. The purpose here is to show that this failure of the Goddard-Miller equation of state is not limited to the peculiar nonanalytic features above, but also occurs under simpler circumstances where such features are suppressed. Specifically, the Boltzmann limit for a low-density gas of Maxwell molecules (r^{-5} force law) is chosen, since the nonequilibrium statistical mechanics can be carried out exactly.[9,10] Again, it is found that the Goddard-Miller model fails. More generally, the principle of objectivity does not apply in this case.[11]

The linear viscoelastic properties of a fluid may be described in terms of local equilibrium time-correlation functions using the methods of linear response. In particular, for small velocity gradients the linear relationship of the irreversible stress tensor $t_{ij}^*(t)$ to the strain tensor $\gamma_{ij}(t)$ is (for simplicity, only incompressible flow is described)

$$t_{ij}^*(t) \sim -\int_0^t d\tau\, G_{ijkl}^{(0)}(t,\tau)\gamma_{kl}(\tau) \ , \tag{1}$$

$$\gamma_{ij}(t) \equiv \frac{1}{2}\left(\frac{\partial U_i}{\partial r_j}+\frac{\partial U_j}{\partial r_i}\right) \ .$$

Here $G_{ijkl}^{(0)}(t,\tau)$ is the local equilibrium autocorrelation function for a microscopic volume stress tensor, and $U_i(\vec{r},t)$ is the macroscopic velocity field. In general, Eq. (1) must be replaced by a nonlinear relationship of $t_{ij}^*(t)$ to both the strain tensor $\gamma_{ij}(t)$ and the vorticity w_{ij}:

$$t_{ij}^*(t) = -\int_0^t d\tau\, G_{ijkl}(t,\tau)[\gamma_{kl}(\tau)+w_{kl}(\tau)] \ , \tag{2}$$

$$w_{ij} \equiv \frac{1}{2}\left(\frac{\partial U_i}{\partial r_j}-\frac{\partial U_j}{\partial r_i}\right) \ ,$$

where now $G_{ijkl}(t,\tau)$ is a functional of the velocity field gradients. In continuum mechanics, explicit models are introduced for $G_{ijkl}(t,\tau)$ to characterize the viscoelastic and non-Newtonian properties of complex fluids. One such model is that of Goddard and Miller, which relates $G_{ijkl}(t,\tau)$ to the linear-response function $G_{ijkl}^{(0)}(t,\tau)$ in a simple way. The basic idea is that the linear relationship (1) holds in the corotating frame, from the principle of objectivity (invariance under the Euclidean group). The corotating frame is that for which the local vorticity vanishes and consequently the linear approximation (1) is presumably more reasonable. The resulting expression for $G_{ijkl}(t,\tau)$ is then found to be

$$[G_{ijkl}(t,\tau)]_{\rm GM} = G_{ijmn}^{(0)}(t,\tau)R_{mk}(t-\tau)R_{nl}(t-\tau) \ , \tag{3}$$

where $R_{ij}(t)$ is the rotation tensor for transformation to the corotating frame.

The direct, or even approximate, calculation of $G_{ijkl}(t,\tau)$ from its formal definition in nonequilibrium statistical mechanics is a formidable problem, except in isolated limiting cases. One such limit is a low-density gas, for which $G_{ijkl}(t,\tau)$ can be determined from a solution to the nonlinear Boltzmann equation. This equation can be solved exactly for the special case of Maxwell molecules and uniform shear flow.[12] The latter is defined in terms of a flow field of the form

$$U_i(\vec{r},t) = U_{i0} + a_{ij}r_j \ , \tag{4}$$

where U_{i0} is a constant vector and a_{ij} is a constant tensor with the properties $a_{ij}a_{jk} = a_{ji}a_{kj} = 0$. To be more specific, the x axis is chosen along the direction of shear and the y axis is taken along the direction of the gradient. Then a_{ij} has the representation

$$a_{ij} = a\delta_{ix}\delta_{jy} \ , \tag{5}$$

where a is the magnitude of the shear rate. The linear-response function $G_{ijkl}^{(0)}(t,\tau)$ is particularly simple in this

limit:[9,10]

$$G^{(0)}_{ijkl}(t,\tau)=e^{-\nu(t-\tau)}p(\tau)\Delta_{ijkl} \ , \tag{6}$$

$$\Delta_{ijkl}=(\delta_{il}\delta_{jk}+\delta_{ik}\delta_{jl}-\tfrac{2}{3}\delta_{ij}\delta_{kl}) \ .$$

Here ν is an eigenvalue of the Boltzmann operator and $p(t)$ the pressure at time t. The pressure increases due to viscous heating and is determined from the energy conservation law for uniform shear flow:

$$\frac{\partial p(t)}{\partial t}=-\tfrac{2}{3}a_{ij}t^{*}_{ij}(t) \ , \tag{7}$$

where use has been made of the low-density equation of state $\epsilon=3p/2$.

The Goddard-Miller model for $G_{ijkl}(t,\tau)$ is now easily determined from Eqs. (3) and (6). To simplify the notation, define the time difference $s\equiv t-\tau$; the results are then

$$[G_{ijkl}(t,\tau)]_{\rm GM}=\cos(as)G^{(0)}_{ijkl}(t,\tau)+a^{-1}\sin(as) \times[G^{(0)}_{ijkm}(t,\tau)\gamma_{ml}-G^{(0)}_{ijlm}(t,\tau)\gamma_{nk}] \ . \tag{8}$$

The first term in Eq. (8) is symmetric in the indices (k,l) and therefore only couples the strain rate in Eq. (2). The second term is antisymmetric and couples to the vorticity.

The exact expression for $G_{ijkl}(t,\tau)$ based on the Boltzmann equation is easily identified from the analysis in Appendix A2 of Ref. 10. The result is

$$G_{ijkl}(t,\tau)=\cos(\alpha as)G^{(0)}_{ijkl}(t,\tau)-(\alpha a)^{-1}\sin(\alpha as)[G^{(0)}_{ijkm}(t,\tau)(\gamma_{ml}+w_{ml})-G^{(0)}_{ijlm}(t,\tau)(\gamma_{mk}+w_{mk})] \ . \tag{9}$$

Here $\alpha^{-2}\equiv(\partial\epsilon/\partial p)_n=\frac{3}{2}$.

Although Eqs. (8) and (9) are surprisingly similar, their qualitative differences are significant. The additional factor of α in the Boltzmann result is due to a dependence of the correlation function on the heating rate beyond that which occurs through $G^{(0)}_{ijkl}(t,\tau)$. This is missing in the Goddard-Miller model since the rotation tensors introduce only the vorticity of the flow field, and the heating rate is independent of voriticity. Uniform shear flow consists of both a rotation and a dilation, but the nonlinear effects due to dilation are not included in the Goddard-Miller model. The second difference between Eqs. (8) and (9) is the additional dependence on the vorticity in the second term of Eq. (9). This represents a nonlinear dependence of the stress tensor on the vorticity that cannot be removed by transformation to the corotating frame, and therefore constitutes a violation of the principle of objectivity. This principle has been criticized in Ref. 11 where it is pointed out that the symmetry group associated with the underlying microscopic dynamics is the Galileo group. The Boltzmann equation is invariant under Galilean transformations, but not under the larger group of Euclidean transformations required by the principle of objectivity. A third difference is the overall sign of the second term in (9). Although this does not affect the nonlinear shear viscosity, it leads to a different sign for the first viscometric function $\Psi_1(a)$, as compared to the Goddard-Miller model. The sign in Eq. (9) and functional form agrees with the independent Chapman-Enskog solution of the Boltzmann equation to Burnett order.[11]

Although the viscometric functions implied by Eqs. (8) and (9) are quite different, the associated nonlinear shear viscosities are more similar. From Eq. (8) one finds

$$[\eta(a)]_{\rm GM}=\int_0^t d\tau e^{-\nu s}\cos(as)p(\tau) \ , \tag{10}$$

whereas the Boltzmann equation gives

$$\eta(a)=\int_0^t d\tau e^{-\nu s}\cos(\alpha as)p(\tau) \ . \tag{11}$$

The only difference here is the thermodynamic factor, $\alpha^2=(\partial p/\partial\epsilon)_n$. It is interesting to note that this factor is unity for two dimensions, which could explain the accidental agreement of the Goddard-Miller model with mode-coupling calculations for two dimensions.[7] Clearly there is no fundamental significance to this agreement since there is no relationship of the parameters of the corotating frame to the thermodynamic properties of the fluid.

The conclusion is that the qualitative features of models like that of Goddard and Miller which relate viscoelastic and non-Newtonian properties of a fluid, while often useful in practice, are phenomenological rather than fundamental. Their application for the interpretation of nonequilibrium computer simulation should be considered also as phenomenological.

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