Nonlinear shear viscosity and long time tails

(statistical mechanics/mode-coupling/rheology/Goddard–Miller model)

R. Zwanzig

Institute for Physical Science and Technology, University of Maryland, College Park, Maryland 20742

Contributed by Robert Zwanzig, March 9, 1981

ABSTRACT A theoretical connection between nonlinear shear viscosity and the long time tail of the equilibrium stress–stress correlation function is pointed out. The connection is a consequence of the Goddard–Miller rheological equation of state which takes into account the angular rotation of a fluid in steady uniform shear.

Recently, several theoretical arguments have been advanced (1–3) that the shear viscosity $\eta_s(X)$ of a fluid in steady uniform shear flow is not an analytic function of the shear rate $X$. The functional form that has been predicted (for small $X$) is

$$\eta_s(X) = -B \log X + O(1)$$  \[1a\]

in two dimensions or

$$\eta_s(X) = \eta(0) - BX^{1/2} + O(X)$$  \[1b\]

in three dimensions.

I call attention here to a connection between this nonanalytic behavior of $\eta_s(X)$ and the asymptotic long time behavior of the equilibrium stress–stress correlation function. This connection, which appears very reasonable but is probably not exact, is a direct consequence of the Goddard–Miller (GM) rheological equation of state (4). An excellent discussion of the GM model and its basis has been given by Bird et al. (5).

Consider first a small, and divergenceless, shear flow. The strain rate tensor is

$$\varepsilon = \nabla \vec{v} + (\nabla \vec{v})^T$$  \[2\]

According to linear response theory, the stress tensor $\sigma(t)$ is related to $\varepsilon$ by

$$\sigma(t) = \int_0^\infty ds \, G(s) \varepsilon(t - s),$$  \[3\]

where $G(s)$ is the viscoelastic memory function. The frequency-dependent viscosity for a small shear flow varying in time with frequency $\omega$ has the real and imaginary parts

$$\eta'(\omega) = \int_0^\infty ds \, G(s) \cos \omega s,$$  \[4\]

$$\eta''(\omega) = \int_0^\infty ds \, G(s) \sin \omega s.$$

Various theoretical arguments, summarized by Pomeau and Resibois (6), predict that $G(s)$ decays asymptotically as $s^{-1}$ in two dimensions and as $s^{-3/2}$ in three dimensions. This is the "long time tail" of $G(s)$. The corresponding frequency dependence of the real part $\eta'(\omega)$ of the viscosity is

$$\eta'(\omega) = -A \log \omega + O(1)$$  \[5a\]

in two dimensions and

$$\eta'(\omega) = \eta(0) - A \omega^{1/2} + O(\omega)$$  \[5b\]

in three dimensions.

These functional forms have exactly the same structure as the predicted shear-dependent viscosity $\eta_s(X)$. In the GM model, $\eta(Z)$ and $\eta'(Z)$ are identical functions of $Z$, which may be either $X$ or $\omega$.

The GM model is based on a simple idea: any rheological equation of state should be invariant to rigid-body rotations of the fluid with respect to an observer. The linear response equation (Eq. 3) does not have this invariance; the GM equation is a generalization of Eq. 3 which does have this invariance.

Consider a steady uniform shear flow for which the velocity is $\vec{v} = X i y$, so that $\varepsilon = X (ij + ji)$. This flow has vorticity, and the corresponding angular velocity is $\vec{\omega} = (\text{curl} \, \vec{v})/2 = -(X/2)k$. As in the theory of rigid-body rotation, the matrix $\Omega$ is introduced:

$$\frac{d}{dt} \vec{A} = \vec{\omega} \times \vec{A} = \Omega \cdot \vec{A}.$$  \[6\]

The matrix $\text{exp}(t\Omega)$ describes the transformation from a coordinate system fixed in the laboratory to a coordinate system fixed in the moving fluid—the "corotating frame." Any tensor $\phi$ in the laboratory frame is related to another tensor $\phi^{(c)}$ in the corotating frame by

$$\phi(t) = \text{exp}(t\Omega) \cdot \phi^{(c)}(t) \cdot \text{exp}(-t\Omega).$$  \[7\]

The GM model is linear response in the corotating frame:

$$\sigma^{(c)}(t) = \int_0^\infty ds \, G(s) \varepsilon^{(c)}(t - s).$$  \[8\]

When transformed back to the laboratory frame, this becomes (for steady flow)

$$\sigma = \int_0^\infty ds \, G(s) \exp(s\Omega) \cdot \varepsilon \cdot \exp(-s\Omega).$$  \[9\]

When the rotational transformations are worked out, a shear dependent viscosity is obtained,

$$\eta_s(X) = \int_0^\infty ds \, G(s) \cos (Xs).$$  \[10\]

This is evidently the same function as $\eta'(\omega)$ in Eq. 4. In particular, the coefficients $B$ in Eq. 1 are predicted to be identical with the coefficients $A$ in Eq. 5.

Abbreviation: GM, Goddard–Miller.

3296
In any shear flow, the tensor \( \nabla \vec{v} \) has a symmetric part \( \epsilon/2 \) and an anti-symmetric part \( \Omega/2 \). The GM model takes full account of the anti-symmetric part but is still linear in the symmetric part. Therefore, it cannot be regarded as exact, and its validity must be investigated.

Bird et al. (5) quoted data on polymeric fluids which show that \( \eta_0(X) \) and \( \eta(\omega) \) are not identical functions but are numerically close. However, polymer systems are much more sensitive to shear flow than are simple liquids because a polymer molecule is long, flexible, and easily deformed. There is considerable information concerning \( \eta(\omega) \) for supercooled organic liquids (7), but I am not aware of corresponding data on \( \eta_0(X) \) for these materials.

Recently, several groups (8–11) have obtained "experimental data" by numerical molecular dynamics simulation of shear flow in simple liquids. The results can be fit, at least approximately, to equations of the form of Eqs. 1b and 5b. Numerically, \( B \) appears to be roughly twice as large as \( A \); the computer results, so far, are not accurate enough to say more than this. Also, the coefficients \( A \) and \( B \) appear to be considerably larger than theoretical predictions.

Is the GM model consistent with currently available statistical mechanical theory? In two dimensions, the theoretical expressions for \( A \) (long time tails) and \( B \) (shear dependence) are identical, and the GM model works.

In three dimensions, the situation is not so clear, because there are several calculations of \( B \). These all have the general form

\[
B = kT \left[ \frac{M^{\eta \eta}}{(2\nu)^{3/2}} + \frac{M^{++}}{(\Gamma)^{3/2}} \right],
\]

where \( \nu \) is the kinematic viscosity, \( \Gamma \) is the sound damping coefficient, and \( M^{\eta \eta} \) and \( M^{++} \) are numerical coefficients. The theoretical \( A \) has the same structure, so only the factors \( M^{\eta \eta} \) and \( M^{++} \) need be compared. The comparison is made in Table 1.

In distinction to the two-dimensional case, the agreement is not so good; but refs. 1, 2, and 3 are not in agreement either.

What can be concluded from this? Most evidence indicates that the GM model is not exact but nevertheless is qualitatively reasonable. Statistical mechanicians should take it seriously because it provides a simple way to obtain at least part of the shear dependence of this viscosity. The remarkable agreement of the theoretical \( A \) and \( B \) in two dimensions should be looked into further, because the calculations appear to be very different.

I thank J. R. Dorfman for valuable discussions. This work was supported by National Science Foundation Grant CHE 77-16308.


<table>
<thead>
<tr>
<th>Source</th>
<th>( M^{\eta \eta} )</th>
<th>( M^{++} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ref. 1</td>
<td>1.4</td>
<td>—</td>
</tr>
<tr>
<td>Ref. 2</td>
<td>0.86</td>
<td>—</td>
</tr>
<tr>
<td>Ref. 3</td>
<td>0.259</td>
<td>0.406</td>
</tr>
<tr>
<td>TAIL</td>
<td>2.63</td>
<td>0.375</td>
</tr>
</tbody>
</table>

*TAIL* is the result obtained by using the GM model and the theoretical \( A \). (All numbers are to be multiplied by \( 10^{-2} \).)