Nonlinear-response theory for steady planar Couette flow

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We present a simplified derivation of the Yamada-Kawasaki formula for the nonlinear adiabatic response of the stress tensor to planar Couette flow. This formally exact expression is then used to prove the validity of two nonequilibrium molecular-dynamics algorithms that have been used to study fluids undergoing planar Couette flow, very far from equilibrium.

I. INTRODUCTION

Early attempts at computing transport coefficients using nonequilibrium molecular dynamics (NEMD) relied very heavily on simulating as closely as possible, actual experimental conditions relating to the transport process of interest. These simulation techniques employed, as in experiment, boundary conditions to sustain the nonequilibrium state.[1] Unfortunately, the use of moving, or thermal walls in these simulations, leads to difficulties due mainly to the extreme smallness of the simulated systems.

These difficulties lead to the development of synthetic algorithms which employ fictitious (i.e., not existing in nature) mechanical forces to sustain nonequilibrium states. Response theory is then used to relate the observed mechanical response to the required thermal transport coefficient. While this approach leads to dramatic improvements in efficiency it has until now been limited to the calculation of linear transport coefficients close to equilibrium.[2] This was because of difficulties in the theory of nonlinear processes.

In this Brief Report we derive a formally exact expression for the time-dependent adiabatic response of the stress tensor to a suddenly imposed $(t=0)$ constant strain rate. This derivation is essentially a simplified version of the Yamada-Kawasaki (YK)[3] result. This result is then used to comment on the validity of a number of NEMD algorithms for studying shear flow.

We find that the homogeneous shear or Lees-Edwards[4] algorithm and the recently proposed "Sllod" method[2] are exact. The Dolls tensor algorithm[5] on the other hand is found to give incorrect normal stress differences (Weissenberg effects) at second order in the strain rate.

II. THE NONLINEAR STRESS TENSOR FOR PLANAR COUETTE FLOW

Consider an initial canonical ensemble of systems characterized by the N-particle distribution function,

$$f_0=e^{-\beta H_0} \Big/ \int d\Gamma\, e^{-\beta H_0} \quad . \tag{1}$$

In this equation $\beta=1/k_B T$ and

$$H_0=\sum \frac{p_i^2}{2m}+\Phi \quad . \tag{2}$$

At time $t=0$ we change this distribution to the local distribution f_l, by transforming the x velocity of every particle

$$\dot{x}_i(0^+)=\dot{x}_i(0^-)+\gamma y_i \quad . \tag{3}$$

Such a system is simply a canonical ensemble with an imposed zero-wave-vector strain rate $\gamma=du_x/dy$.

If such a system evolves adiabatically under Newtonian equations of motion, the strain rate cannot change with time.[6] We calculate the strain rate dependent stress tensor by solving the Liouville equation for such a system. In fact this is essentially how Yamada and Kawasaki derived their result for the nonlinear stress tensor.[3]

Their derivation can be simplified however if we note that precisely the same distribution function $f(t)$ will be obtained if we consider the mechanical response of a canonical ensemble f_0 at $t=0$ to a fictitious strain rate field $\gamma(t)$ where instead of evolving under Newtonian equations, the system evolves as

$$\ddot{x}_i=\frac{F_{xi}}{m}+\dot{\gamma}(t)y_i \quad , \tag{4.1}$$

$$\ddot{y}_i=\frac{F_{yi}}{m} \quad , \tag{4.2}$$

$$\ddot{z}_i=\frac{F_{zi}}{m} \quad , \tag{4.3}$$

where

$$\gamma(t)=\gamma\Theta(t) \quad , \tag{5}$$

and Θ is the Heaviside step function. The equivalence of the two sets of trajectories is easily seen by integrating (4.1) in a small ϵ neighborhood of $t=0$ to obtain (3). From (4) we see that Newtonian dynamics will be followed for $t>0$.

It is convenient to work with first-order equations of motion rather than the second-order form (4). Equations (4) can be transformed to read

$$\dot{x}_i=\frac{p_{xi}}{m}+\gamma y_i \quad , \tag{5.1}$$

$$\dot{y}_i=\frac{p_{yi}}{m} \quad , \tag{5.2}$$

$$\dot{z}_i=\frac{p_{zi}}{m} \quad , \tag{5.3}$$

$$\dot{p}_{xi}=F_{xi}-\gamma p_{yi} \quad , \tag{5.4}$$

$$\dot{p}_{yi}=F_{yi} \quad , \tag{5.5}$$

$$\dot{p}_{zi}=F_{zi} \quad . \tag{5.6}$$

The equivalence of (5.1) and (5.6) with (4.1) and (4.3) is trivially seen by differentiating (5.1) and (5.3) and eliminating the momenta.

It is interesting to note that these equations cannot be derived from a Hamiltonian. From (5.1) we see that p_{xl} is the peculiar rather than laboratory momentum. This observation shows that H_0 is the thermodynamic internal energy rather than the total energy. The observation also shows that the pressure tensor $\overleftrightarrow{P}$ can be obtained as

$$\overleftrightarrow{P}V=\sum_l\left[\frac{\vec{p}_l\vec{p}_l}{m}+\vec{r}_l\vec{F}_l\right] , \tag{6}$$

where V is the system volume. Differentiating the internal energy (2) using (5.1)–(5.6) we find that

$$\dot{H}_0=-\gamma P_{xy}V . \tag{7}$$

This is the mechanical analog of the first law of thermodynamics for adiabatic planar Couette flow.

Rather than studying the Newtonian evolution of f_l we can equivalently study the evolution of f_0, the canonical distribution, under the dynamics prescribed by (5.1)–(5.6). We shall call this dynamics, Sllod dynamics.[2]

If we denote the Liouville operator for Sllod dynamics by L, then at time t the distribution function is given exactly by the equation

$$f(t)=e^{-iLt}f_0=\tilde{f}_0(t) . \tag{8}$$

As we noted above, we could also write

$$f(t)=e^{-iL_0t}f_l=f_l(t) , \tag{9}$$

where L_0 is the Liouville operator derived from H_0. The tilde (8), denotes propagation under Sllod rather than Newtonian dynamics.

Substituting (1) into (8) we can write

$$f(t)=e^{-\beta\tilde{H}_0(-t)}\Big/\int d\Gamma\, e^{-\beta H_0} . \tag{10}$$

If (10) is substituted into the Liouville equation

$$\frac{\partial f(t)}{\partial t}=-iLf(t) ,$$

we find, using (7) that

$$\frac{\partial f(t)}{\partial t}=-\beta\gamma V\tilde{P}_{xy}(-t)f(t) . \tag{11}$$

This equation may be integrated to yield

$$f(t)=\exp\left[-\beta\gamma V\int_0^t ds\tilde{P}_{xy}(-s)\right]f_0 . \tag{12}$$

If we denote the viscous pressure tensor as $\overleftrightarrow{\Pi}$ $(=\overleftrightarrow{P}-p\overleftrightarrow{I})$ thus the time-dependent adiabatic response to the shear imposed at $t=0$ is

$$\langle\overleftrightarrow{\Pi}(t)\rangle=\sum_{n=1}^{\infty}(-\beta\gamma V)^n\int_0^t ds_1\cdots\int_0^t ds_n\langle\overleftrightarrow{\Pi}(0)\tilde{\Pi}_{xy}(-s_1)\cdots\tilde{\Pi}_{xy}(-s_n)\rangle_0 . \tag{13}$$

The brackets $\langle\ \rangle_0$ denote a canonical ensemble average. This is the Yamada-Kawasaki expression,[3] for the nonlinear response of the pressure tensor. The presence of γ in the Sllod Liouville operator means that (13) is not a simple power series expansion of the stress. Equation (13) is thus not a straightforward generalization of the Green-Kubo relation for shear viscosity.

III. NEMD ALGORITHMS

From the equivalence of the Newtonian response of the local distribution f_l and the Sllod dynamics response of the canonical ensemble f_0, we immediately derive two algorithms for studying adiabatic planar Couette flow. In fact the two algorithms described by Eqs. (4.1)–(4.3) and (5.1)–(5.6) are known, respectively, as the homogeneous shear or Lees-Edwards method[4] and the Sllod algorithm,[2,7] respectively.

The Lees-Edwards method or the homogeneous shear algorithm has been used extensively in shear flow simulations. The Sllod method was recently devised by Hoover and Ladd.[7] It is so named because of its close relationship to the Dolls tensor algorithm,[5] the equations of motion for which can be derived from the Dolls tensor Hamiltonian.

$$H=H_0+\gamma\sum_l y_lp_{xl} . \tag{14}$$

The equations of motion are very similar to the Sllod equations except for a permutation of indices in the momentum equation. Equations (5.4) and (5.5) are replaced by

$$\dot{p}_{xl}=F_{xl} , \tag{5.4$'$}$$

$$\dot{p}_{yl}=F_{yl}-\gamma p_{xl} . \tag{5.5$'$}$$

The other equations are unchanged.

Under Dolls tensor dynamics the momenta are still peculiar momenta and the dissipation is still given by (7). The Dolls tensor method of course yields precisely the same linear response as both the Lees-Edwards and Sllod methods. In the nonlinear domain the Dolls tensor method is found numerically, to produce statistically indistinguishable pressures and shear stresses but different normal stresses.[7,8] Since we now know that the other two methods are correct, the Dolls tensor method must therefore be incorrect.

If we formally expand our exact expression for the viscous pressure tensor to quadratic order in γ we find that

$$\langle\overleftrightarrow{\Pi}(t)\rangle=-\beta V\int_0^t ds_1\langle\overleftrightarrow{\Pi}(0)\Pi_{xy}(-s_1)\rangle_0\gamma-\beta V\int_0^t ds_1\langle\overleftrightarrow{\Pi}(0)(\tilde{\Pi}_{xy}(-s_1)-\Pi_{xy}(-s_1))\rangle_0\gamma$$
$$+\frac{(\beta V)^2}{2}\int_0^t ds_1\int_0^t ds_2\langle\overleftrightarrow{\Pi}(0)\Pi_{xy}(-s_1)\Pi_{xy}(-s_2)\rangle_0\gamma^2+O(\gamma^3) . \tag{15}$$

As before the tilde denotes propagation with the full γ-dependent propagator.

If we use the well known result[9] that

$$e^{iLt}-e^{iL_0t}=\int_0^t ds\, e^{iL(t-s)}i\Delta L e^{iL_0 s} , \tag{16}$$

Eq. (15) can be written entirely in terms of Newtonian propagators.

$$\langle\overleftrightarrow{\Pi}(t)\rangle = -\beta\gamma V\int_0^t ds_1\langle\overleftrightarrow{\Pi}(0)\Pi_{xy}(-s_1)\rangle_0+\frac{(\beta\gamma V)^2}{2}\int_0^t ds_1\int_0^{s_1} ds_2\langle\overleftrightarrow{\Pi}(0)\Pi_{xy}(-s_1)\Pi_{xy}(-s_2)\rangle_0$$
$$+\beta\gamma^2 V\int_0^t ds\, s\left\langle\overleftrightarrow{\Pi}(s)\sum_i\left(y_i\frac{\partial}{\partial x_i}-p_{yi}\frac{\partial}{\partial p_{xi}}\right)\Pi_{xy}\right\rangle_0+O(\gamma^3) . \tag{17}$$

The first term on the right-hand side of (17) is the familiar Green-Kubo expression for the pressure tensor. The quadratic terms could have been derived applying Kubo's power series representation of the mechanical response,[10] to the Sllod equations of motion. We did not use this approach here because a proof of the validity of the NEMD algorithms would require a formal summation of the nonlinear response. Furthermore, it is expected that in three-dimensional fluids the coefficient of γ^2 in (17) is infinite due to long-time tail effects.[11]

We can employ the same Dyson decomposition of propagators to examine the error in the Dolls tensor expression for the viscious pressure tensor. If that error is denoted as $\langle\Delta\overleftrightarrow{\Pi}(t)\rangle$ we see that to $O(\gamma^2)$ it arises from the differences between the Sllod and Dolls tensor propagators appearing in the second term in (15).

$$\langle\Delta\overleftrightarrow{\Pi}(t)\rangle = +\beta\gamma^2 V\int_0^t ds\, s\left\langle\overleftrightarrow{\Pi}(s)\sum_i\left(\frac{p_{xi}p_{xi}}{m}-\frac{p_{yi}p_{yi}}{m}\right)\right\rangle_0 . \tag{18}$$

Thus we find that to second order in γ, the Dolls tensor method correctly describes the shear stress, the hydrostatic pressure, and the *zz* component of the normal stress. In agreement with computer simulation results, it gives incorrect normal stresses $\Pi_{xx}\Pi_{yy}$.

IV. SUMMARY

We have produced a simple rederivation of Yamada and Kawaskai's formal expression for the nonlinear adiabatic response of a fluid to planar Couette flow. In contrast to the YK derivation, ours shows the intimate relationship of Sllod equations of motion used in computer simulations and the adiabatic response observed in nature. This relationship is so close that the proof of validity of both the Sllod and homogeneous shear NEMD algorithms is trivial.

The errors in the Dolls tensor algorithm, which first show up at $O(\gamma^2)$, indicate that extreme care must be exercised in interpreting the results of NEMD simulations in the nonlinear regime. The correct linear response is simply insufficient to guarantee the correct nonlinear behavior.

A major issue that we have not discussed in this paper is the steady-state response to shear flow. We have restricted ourselves to a discussion of the time-dependent adiabatic response.

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[9]D. J. Evans and G. P. Morriss, Chem. Phys. **87**, 451 (1984).

[10]See Eq. (2.29) in R. Kubo, J. Phys. Soc. Jpn. **12**, 570 (1957).

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