Linear and nonlinear viscous flow in two-dimensional fluids

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We report on molecular dynamics simulations of shear viscosity η of a dense two-dimensional fluid as a function of the shear rate γ. We find an analytic dependence of η on γ, and do not find any evidence whatsoever of divergence in the Green-Kubo (GK) value that would be caused by the well-known long-time tail for the shear-stress autocorrelation function, as predicted by the mode-coupling theory. In accordance with the linear response theory, the GK value of η agrees remarkably well with nonequilibrium values at small shear rates.

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I. INTRODUCTION

The validity of the Green-Kubo (GK) formulas relating transport coefficients to equilibrium fluctuations, particularly in two dimensions (2D), has been a subject arousing considerable controversy. After the molecular dynamics (MD) simulations by Alder and Wainwright [1] that found the presence of long-time tails, or the persistence of memory in, for example, the velocity autocorrelation function (beyond the expected exponential decay on the order of a mean collision time), mode-coupling theory was developed [2,3] which predicts a power-law decay of the form $t^{-d/2}$ for the correlation functions, where d is the dimensionality of the system. This result leads to the divergence of 2D transport coefficients of the form $\ln N$, where N is the number of particles in the system. To be fair, Alder and Wainwright, in their original work, proposed a hydrodynamic argument (the so-called double vortex) for the diffusion of momentum, which leads to the $t^{-d/2}$ tail; mode-coupling theory simply puts dimensionality arguments on a more formal footing.

As pointed out by Zwanzig [4] the long-time tail in the stress autocorrelation function, whose time integral gives the GK formula for the shear viscosity η, could have the same origin as the nonanalytical dependence of η upon the shear rate γ, which in 2D would be $\eta(\gamma)\sim\ln\gamma$. Many MD simulations have been performed [5–9] to check these predictions, but the question is not completely clarified.

In this paper, we report the results of extensive MD simulations for viscous transport in a 2D fluid. In particular, we compute the shear viscosity by equilibrium MD (EMD), using the GK formula, and by nonequilibrium MD (NEMD), using the subtraction method of Ciccotti and co-workers [10]. This method allows us to study the dynamical response at very small gradients, so as to compare linear-regime results with the GK theory.

II. MODEL AND THEORY

We consider the 2D soft-disk system, whose particles interact by a pair potential of the form $\phi(r)=\epsilon(\sigma/r)^{12}$, at a mass density of $\rho\sigma^2/m=0.96$ and temperature $k_BT/\epsilon=1$. [For the remainder of this paper, we use as units of mass, distance, and energy, m, σ, and ϵ, from which the unit of time is obtained: $t_0=\sigma(m/\epsilon)^{1/2}$.] This thermodynamic state corresponds to a fluid very close to the freezing transition, but clearly outside the two-phase coexistence region [11]. Among possible choices [6,9], we have chosen this one at the highest density because it has the longest persistence of memory (see Fig. 1), though if mode-coupling theory is to be believed, a much lower density might be preferable, since the tail is predicted to be entirely kinetic in origin [12]. (However, low-density MD simulations, especially for continuous potentials, are very difficult because of the long times between collisions.)

The soft-disk potential is truncated at $r=1.51$, with a quadratic-polynomial smoothing between 1.50 and 1.51 in such a way that both potential and force go continuously to zero. The average error incurred in this way, as a pair of particles with relative velocity equal to the thermal velocity $(k_BT/m)^{1/2}$ suddenly come into range of each other, is approximately the error in the integration method, which we have chosen to be the velocity-Verlet form of Stoermer's finite central-difference method (the time step is $\delta t=0.005$).

Planar Couette shear flow is imposed using the sliding Lees-Edwards periodic boundary conditions [13] and the so-called Sllod (homogeneous adiabatic deformation) equations of motion [14] (the name "Sllod" is used because of its close relationship to the Dolls tensor algorithm). Constant temperature is achieved (removing the heat generated by shearing) with Nosé-Hoover thermostatting [15]:

$$
\begin{aligned}
\dot{x}_i &= p_{xi}/m+\gamma y_i ,\\
\dot{y}_i &= p_{yi}/m ,\\
\dot{p}_{xi} &= F_{xi}-\nu\zeta p_{xi}-\gamma p_{yi} ,\\
\dot{p}_{yi} &= F_{yi}-\nu\zeta p_{yi} ,\\
\dot{\zeta} &= \nu\left[\sum_{i=1}^{N} p_i^2/2Nmk_BT-1\right] ,
\end{aligned}
\qquad (1)
$$

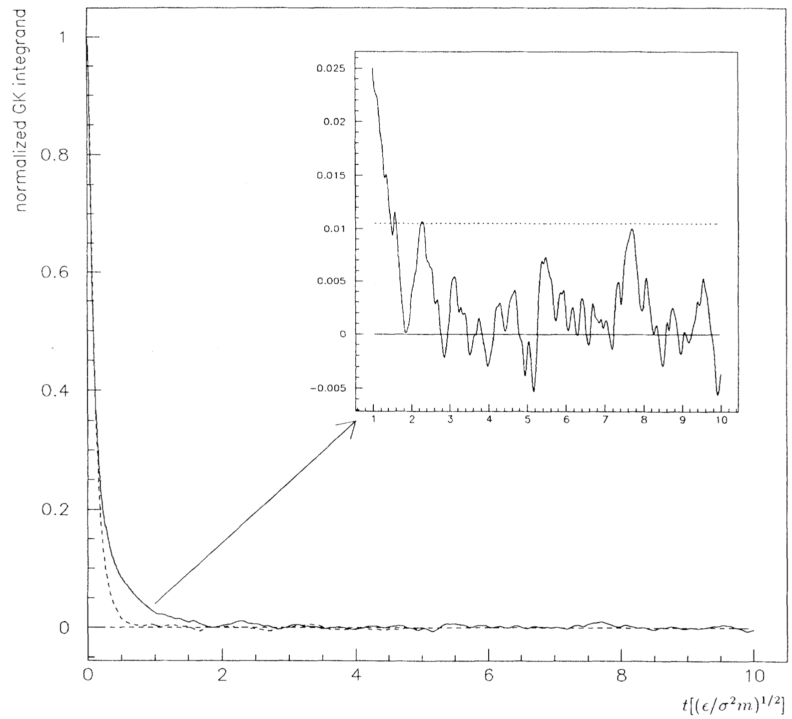

FIG. 1. Normalized equilibrium stress autocorrelation function (Green-Kubo integrand) for the 2D soft-disk fluid at $T=1$ for two densities: $\rho=0.69$ ($N=400$ and $t_{\max}=13\,000t_0$, dashed line) and $\rho=0.96$ ($N=10{,}000$ and $t_{\max}=50\,000t_0$, solid line and inset). N is the number of atoms, $t_{\max}$ is the maximum length of time for the equilibrium trajectory, and t is the time in reduced units $t_0=\sigma(m/\epsilon)^{1/2}$. The Maxwell relaxation time is $\tau_{\text{Maxwell}}=0.12\simeq\tau_{\text{collision}}$.

where ζ is the heat-flow variable (connecting the N atoms with the thermal reservoir) and ν is the rate of thermostatting. The velocity gradient in the nonequilibrium shearing trajectory is $\gamma=\partial u_x/\partial y$, for planar Couette flow in the x direction with shearing along the y axis.

Starting at a point selected from an equilibrium trajectory, the shear rate is switched on as a step function at time zero. A series of experiments is performed and an ensemble average is taken to obtain the instantaneous nonequilibrium shear viscosity η as a function of the shear rate γ and number of atoms N (at fixed number density $n=N/V$):

$$\eta(N,\gamma,t)=\frac{\langle\sigma_{xy}(t)\rangle_0}{\gamma} \tag{2}$$

where $\langle\cdot\rangle_0$ symbolizes the ensemble average over a canonical distribution of initial equilibrium states, sampled by Nosé-Hoover thermostatting; the nonequilibrium dynamics is implicit in the time dependence of the shear stress σ_{xy}, which is given as a function of time by

$$\sigma_{xy}=-(1/V)\sum_i(p_{ix}p_{iy}/m+F_{ix}y_i)\ , \tag{3}$$

where $V=Nm/\rho$ is the volume of the system. As $t\to\infty$, η approaches a plateau (steady-state) value.

The transient fluid behavior is obtained by averaging nonequilibrium trajectories (called segments) of time from 0 to $t=2.5$ over many independent initial configurations sampled along an equilibrium trajectory. We can improve the statistics in the approach of $\eta(N,\gamma,t)$ to its asymptotic value by subtracting off the signal from the equilibrium trajectory which spawned the nonequilibrium trajectory [10]:

$$\eta'(N,\gamma,t)=\frac{\langle\sigma_{xy}(t)-\sigma^0_{xy}(t)\rangle_0}{\gamma}\ , \tag{4}$$

where $\sigma^0_{xy}(t)$ is the shear stress evaluated along the equilibrium trajectory that likewise began at time zero. The fluctuations in this subtraction-technique signal are inherently smaller at short times than the direct calculation [Eq. (2)], primarily because (especially for small γ) thermal fluctuations in σ_{xy} are removed, leaving a signal proportional to γ and noise proportional to γ^2. For small γ, the shear stress rises to a plateau value in a fashion that is almost identical to the GK result

$$\eta_0(N,t)=\frac{V}{k_BT}\int_0^t ds\,\langle\sigma^0_{xy}(0)\sigma^0_{xy}(s)\rangle_0\ . \tag{5}$$

The error in the subtraction plateau value near the end of time $t=2.5$ begins to grow exponentially, due to Lyapunov instability. At great expense, this error can be reduced by increasing the number of segments in the ensemble, because the error goes like $1/N_{\text{seg}}^{1/2}$. Thus there is a "window of opportunity" in the subtraction method: the time t must be larger than the initial decay time, so as to achieve the plateau value, yet not so large that the Lyapunov error makes the measurement meaningless.

The aim of these calculations is to see whether or not the NEMD subtraction results approach the EMD (GK) results analytically as a function of strain rate, and whether or not the limit exists as a function of system size N. The GK plateau value is

$$\eta_{\text{GK}}(N)=\lim_{t\to\infty}\eta_0(N,t)\stackrel{?}{=}\lim_{\substack{t\to\infty\\ \gamma\to0}}\eta(N,\gamma,t)=\lim_{\substack{t\to\infty\\ \gamma\to0}}\eta'(N,\gamma,t)\ . \tag{6}$$

[The question mark in Eq. (6) indicates an assertion to be proved, namely that the NEMD and EMD results converge to the same answer.] If a hydrodynamic limit exists in nonequilibrium statistical mechanics, similar to the thermodynamic limit at equilibrium, then as $N \to \infty$, with N/V fixed,

$$\eta_{\rm GK}(N \to \infty) \overset{?}{\leftarrow} \eta'(N \to \infty, \gamma = 0, t = \infty) \ . \qquad (7)$$

In the next section, we will present both EMD and NEMD results for the 2D soft-disk dense fluid.

III. RESULTS

The equilibrium stress autocorrelation function is calculated up to very long times, $t = 10$, to follow its long-time behavior. Therefore it is important to know at least two characteristic times, the mean collision time and the sound-wave traversal time in the finite periodic system. In either case, we need to know the speed of sound c in our dense fluid, since the mean collision time can be defined as the mean separation between particles r_0 (at density $\rho = 0.96$) divided by the sound speed ($\tau_{\rm collision} = r_0/c$), and the sound traversal time—a potential source of systematic error in time correlation functions—is the sidelength of the periodic box L divided by the sound speed, that is, the time for a sound-wave disturbance to propagate through the periodic sample ($\tau_L = L/c$).

The sound speed can be calculated by [16]

$$c = \left[\frac{C_P}{C_V} \left[\frac{\partial P}{\partial \rho} \right]_T \right]^{1/2} , \qquad (8)$$

where the ratio of heat capacities (constant pressure C_P vs constant volume C_V) is [17]

$$\frac{C_P}{C_V} = 1 + \frac{T[V^2(\partial P/\partial T)_V]^2}{NC_V(\partial P/\partial \rho)_T} \ . \qquad (9)$$

We find this ratio to be 1.59, so that $c = 9.08$. From this, we compute the mean collision time to be $\tau_{\rm collision} = 0.11$. To compare with this, the Maxwell relaxation time can be obtained from the time integral of the normalized shear-stress autocorrelation function [see the GK expression in Eq. (5)]:

$$\tau_{\rm Maxwell} = \frac{\int_0^\infty dt \langle \sigma_{xy}^0(0)\sigma_{xy}^0(t)\rangle_0}{\langle (\sigma_{xy}^0)^2\rangle_0} = \frac{k_B T}{V} \frac{\eta_{\rm GK}}{\langle (\sigma_{xy}^0)^2\rangle_0}$$
$$\simeq 0.18 \ . \qquad (10)$$

This agrees well with the $1/e$-fold time we read off of Fig. 1, namely, $\tau_{\rm Maxwell} = 0.12$. In Table I, we report the sound traversal time for different system sizes. We see no effect of this traversal time in our results. Perhaps this is to be expected, since giving a fluid element at the center of the periodic box a momentum pulse to the right sends a compressive longitudinal sound wave that passes horizontally through the box and kicks the element from the rear, while the vertical shear waves cancel at the periodic boundary.

EMD results for GK shear viscosity as a function of system size N are reported in Table I. These plateau values were obtained by averaging $\eta_0(N,t)$ over times $2.5 < t < 10$, weighted by the error $1/\delta\eta_0^2(N,t)$. The error given in Table I is $\delta\eta_0(N, t = 5)$, which is proportional to $1/t_{\rm max}^{1/2}$, where $t_{\rm max}$ is the maximum length of time for the equilibrium trajectory. In Fig. 2, we see that the GK shear viscosity depends upon system size [18] like $1/N$, but so weakly that the data are consistent with the hypothesis of no dependence. In any event, the infinite-system size limit can be obtained from a linear least-squares fit, weighted by $t_{\rm max}$: $\eta_0(N) = 5.86(1 - 17.6/N)$ (to be compared with the average value $\eta = 5.69 \pm 0.07$ obtained assuming N independence of the data and using as weight the length of the trajectory). Thus we find that the GK value in the hydrodynamic limit for 2D soft disks at $\rho = 0.96$ and $T = 1$ is finite: $\eta_{\rm GK} = 5.86$. A logarithmic divergence for $t \to \infty$ in $\eta_0(N,t)$ is not observed, since $\eta_0(N,t)$ remains largely within its statistical error beyond $t = 2.5$ and up to $t = 10$, as shown in Fig. 3.

NEMD results for the subtraction method are reported in Table II, where $\eta(N,\gamma)$ is calculated as the weighted average of $\eta(N,\gamma,t)$ for $1.8 < t < 2.5$ and $\delta\eta(N,\gamma) = \delta\eta(N,\gamma,t = 1.8)$. We see from Fig. 1 that the subtraction method is valid for the soft-disk system at this thermodynamic state, since beyond $t = 1.8$ the pla-

TABLE I. Equilibrium shear viscosity η_0 (Green-Kubo) in the 2D soft-disk fluid as a function of the number of atoms N; $t_{\rm max}$ is the maximum length of time in the equilibrium trajectory, L is the sidelength of the periodic box of volume $V = L^2$, and $\tau_L = L/c$ is the sound traversal time (c is the sound speed).

N	$\eta_{\rm GK}$	$t_{\rm max}/t_0$	L	τ_L
400	5.58 ± 0.11	50 000	20.4	2.25
900	5.84 ± 0.16	24 000	30.6	3.37
1600	5.82 ± 0.16	24 000	40.8	4.49
2025	5.80 ± 0.30	6800	54.9	5.06
4900	5.60 ± 0.31	6250	71.4	7.86
10 000	5.81 ± 0.26	8750	102	11.23

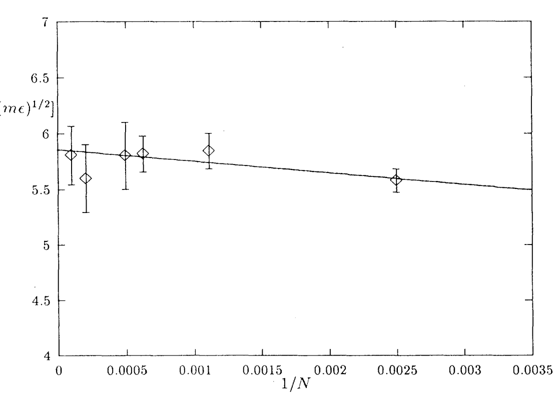

FIG. 2. Green-Kubo values of shear viscosity η_0 for the 2D soft-disk fluid as a function of the number of atoms N. The straight line is a linear least-squares fit, with weight to each point given by the length of its trajectory $t_{\rm max}$: $\eta_0 = 5.86(1 - 17.6/N)$, $\eta_{\rm GK} = \eta_0(N \to \infty) = 5.86$.

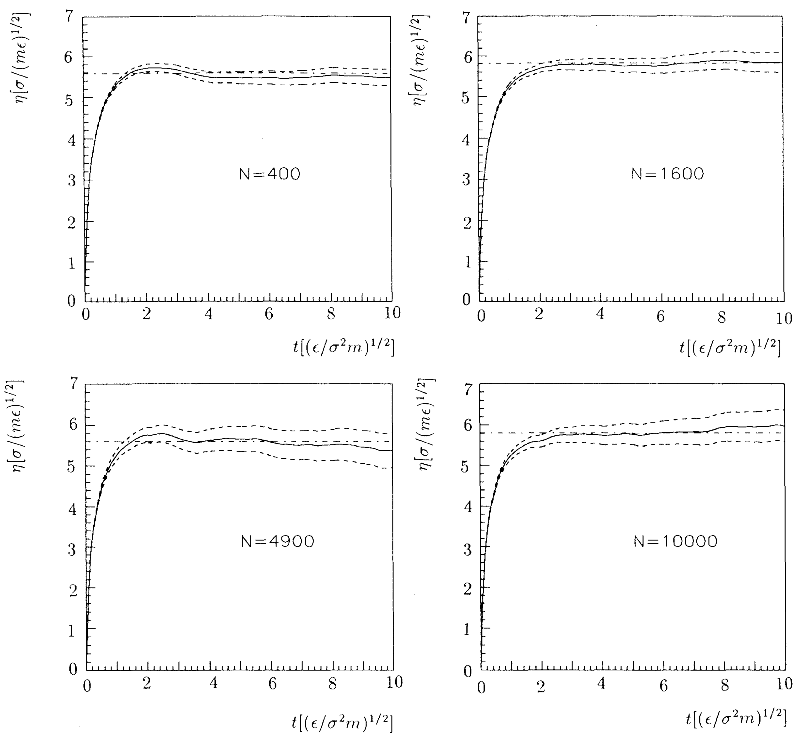

FIG. 3. Green-Kubo viscosity with its error and its average value for $N=400$, 1600, 4900, and 10 000 for the 2D soft-disk fluid. The number of time steps of the equilibrium trajectories are those with the largest statistic shown in Table I.

teau has been reached, and there is only noise in the correlation function. The statistical error reported in Table II for $\eta(N,\gamma)$ depends upon the number of segments and the size of the system, according to the relation [19] $\delta\eta(N,\gamma)\sim 1/(NN_{\rm seg})^{1/2}$.

Because of the exponential divergence of the perturbed and unperturbed trajectories, the subtraction method does not give the response at long times, though the appearance of the noise can be delayed by increasing the number of segments. Calling $t=\min(t\colon \delta\eta(N,\gamma,t)>0.1\eta(N,\gamma))$, i.e., the time to reach an error of about 10%, we show values of t in Fig. 4 as a function of the number of segments $N_{\rm seg}$, demonstrating that the cost of reducing the error becomes exponentially high. The good agreement between $\eta_0(N,t)$ and $\eta(N,\gamma,t)$ for times well beyond $\tau_{\rm Maxwell}$, as shown in Fig. 5, justifies extrapolation to the plateau times and beyond. The results of Ref. [8], which were obtained with an analogous technique, confirm our expectation.

In Table II, our results are compared with those of Ref. [6], which were obtained with the method of large-gradient steady-state NEMD [see Eq. (2), where the average is taken over a long time at the plateau value]. Our results compare very well with these, which suggests that the relation $\eta\sim\ln\gamma$ might only hold over a fixed range of γ, though certainly not down to $\gamma=0$. From Fig. 6, we see that in the range $0<\gamma<0.56$, $\eta(N,\gamma)$ can be well approximated by a Lorentzian, whose characteristic time is

TABLE II. Nonequilibrium shear viscosity $\eta(N,\gamma)$ in the 2D soft-disk fluid as a function of strain rate γ and the number of atoms N; $N_{\rm seg}$ is the number of segments in the subtraction-method ensemble; the results of direct NEMD simulation of Ref. [6] are labeled [6].

		$N=400$		$N=900$		$N=1600$		$N=2025$		$N=4900$		$N=10\,000$	
γ	[6]	η	$N_{\rm seg}$	η	$N_{\rm seg}$	η	$N_{\rm seg}$	η	$N_{\rm seg}$	η	$N_{\rm seg}$	η	$N_{\rm seg}$
10^{-8}				5.11±2.43	500	5.72±0.63	4000	4.80±1.59	500				
10^{-6}				5.09±2.26	500	5.81±1.76	500	6.59±1.55	500				
10^{-4}				5.82±0.55	9000	5.94±0.51	6000	5.22±1.37	700			5.63±0.34	2100
0.01	5.3	5.58±0.33	10 000	5.12±0.98	500	5.44±0.71	500	5.48±0.68	500	5.86±0.19	2500	5.87±0.22	990
0.03	5.3	5.63±0.28	2000										
0.06	5.3	5.34±0.10	4000										
0.1	4.9	5.02±0.12	1000					5.10±0.09	500			5.06±0.04	400
0.18	4.3	4.44±0.07	1000	4.51±0.07	501								
0.32	3.9	3.81±0.04	1000										
0.56	3.3	3.27±0.04	500	3.34±0.02	500	3.30±0.02	500						
1.0	2.8	2.79±0.02	500	2.80±0.01	500	2.80±0.01	500	2.78±0.02	200			2.82±0.02	10

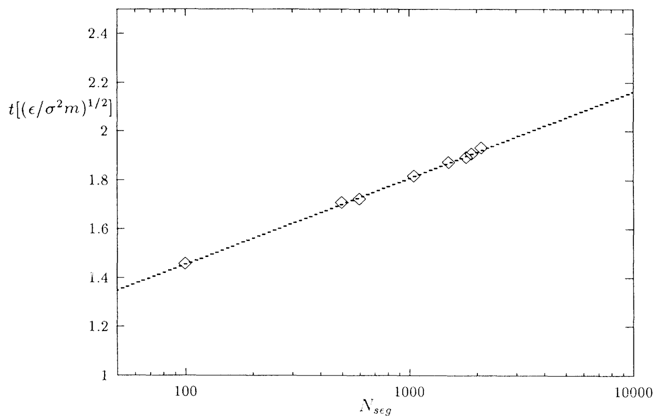

FIG. 4. Dependence of the error in the response upon the number of segments with the subtraction method for $N=10\,000$ and $\gamma=10^{-4}$. Time equals $\min(t: \delta\eta_s(t)>0.5)$.

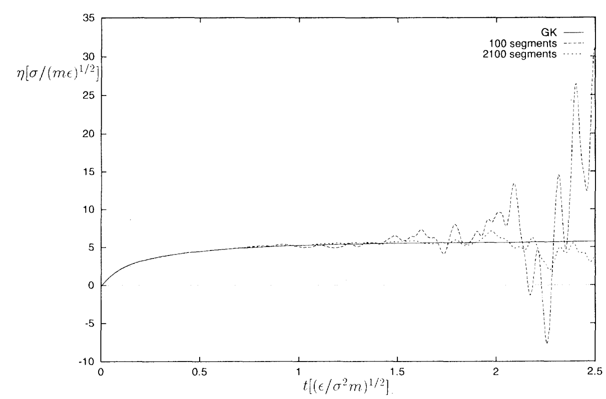

FIG. 5. Comparison between Green-Kubo and subtraction shear viscosity with 100 and 2100 segments for $N=10\,000$, $\gamma=10^{-4}$.

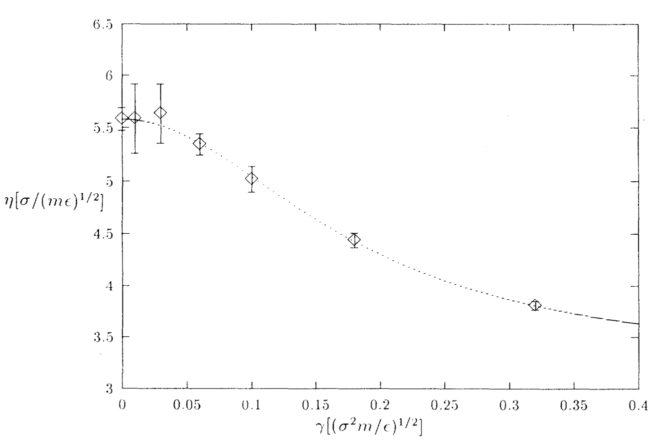

FIG. 6. Fit of $\eta(\gamma)$ with a Lorentzian for several NEMD results ($N=400$); Green-Kubo value at $\gamma=0$ is also included. The fit function is $\eta(\gamma)=a+b/(1+c\gamma^2)$ and the result to the fit is $a=3.22$, $b=2.36$, $c=29.3$ for $0<\gamma\leq 0.32$; thus $\eta_0(N=400)=5.58$, $\tau_{\text{Lorentzian}}=3.5\sim 30\tau_{\text{collision}}$.

3.5, or about 30 collision times. This characteristic time is eminently reasonable, since we might imagine that the shear-thinning behavior as a function of shear rate would take many collision times to manifest itself. At small γ, as one expects in the Newtonian regime, $\eta(N,\gamma)$ becomes independent of γ, and agrees well with $\eta_0(N)$. If nonanalytic behavior with γ were observed, linear response theory would be cast into doubt; clearly, these results confirm its validity. Nonanalyticity of this kind has already been disproved for 3D shearing fluids [20,21]. Therefore we may remove the question marks from Eqs. (6) and (7).

IV. CONCLUSION

In the range of times and system sizes accessible to our MD simulations, we find no evidence whatsoever of the long-time tail in dense 2D fluids subjected to planar Couette shear flow. The tail can well exist but seems numerically irrelevant. By this we mean that divergence effects, which are sensible only on a time scale of the age of the universe, are irrelevent to transport behavior.

Moreover, we find no evidence of nonanalytic behavior of the shear viscosity as a function of shear rate, just as in the 3D case [20,21]. We conclude that η, either the Green-Kubo limit $\gamma=0$ or the dynamical response $\gamma>0$, exists and reaches an asymptotic limit as a function of system size N in 2D; the dynamical transport coefficient is also analytic in γ, reaching the linear response limit as γ^2.

Note added. Recently Bill Hoover kindly shared with us a manuscript that he and Harald Posch had written [22], showing very similar results to ours and to a previous recent paper by Hood, Evans, and Cui [9]. The Hoover results were for a shorter-range repulsive potential, also in 2D. Their results for $\eta(N,\gamma)$ can also be fitted to a Lorentzian in γ, whose time constant is several collision times, though they studied only two strain rates. Nevertheless, the stationary plateau values they observed—for much larger systems (up to 2.5×10^5 atoms)—showed similar limiting behavior of shear viscosity as a function of system size, that is to say, they saw absolutely no evidence, either, for a divergence of η with N. In their case (error bars of less than 1%), the asymptotic approach was best fitted by the form $\eta(N,\gamma)=\eta(\gamma)(1-\text{const}/N^{1/2})$ with a goodness of fit of 0.97, though a $1/\ln(N)$ behavior gave an equally good fit. In our case (error bars of about 5%), the goodness of fit for $1/N$ was 0.8, vs 0.5 for $1/N^{1/2}$.

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[1] B. J. Alder and T. E. Wainwright, Phys. Rev. **1**, 18 (1970).
[2] K. Kawasaki and J. D. Gunton, Phys. Rev. A **8**, 2048 (1973).
[3] M. H. Ernst, B. Cichocki, J. R. Dorfman, J. Sharma, and H. van Beijeren, J. Stat. Phys. **18**, 237 (1978).
[4] R. Zwanzig, Physica A **118**, 427 (1983).
[5] D. J. Evans, Phys. Rev. A **22**, 290 (1980).
[6] D. J. Evans and G. P. Morris, Phys. Rev. Lett. **51**, 1776 (1983).
[7] G. P. Morris and D. J. Evans, Phys. Rev. A **32**, 2425 (1985).
[8] G. P. Morris and D. J. Evans, Phys. Rev. A **39**, 6335 (1989).
[9] L. M. Hood, D. J. Evans, and S. T. Cui, Mol. Simulation **9**, 307 (1992).
[10] G. Ciccotti and G. Jacucci, Phys. Rev. Lett. **35**, 789 (1975); G. Ciccotti, G. Jacucci, and L. R. McDonald, J. Stat. Phys. **21**, 1 (1979).
[11] D. J. Evans, Phys. Lett A **88**, 48 (1982) corrects the results of F. van Swol, L. V. Woodcock, and J. N. Cape, J. Chem. Phys. **73**, 913 (1980).
[12] M. H. Ernst, E. H. Hauge, and J. M. J. van Leeuwen, Phys. Rev. A **4**, 2055 (1971).
[13] A. W. Lees and S. F. Edwards, J. Phys. C **5**, 1921 (1972).
[14] D. J. Evans and G. P. Morris, Comput. Phys. Rep. **1**, 299 (1984).
[15] S. Nosé, J. Chem. Phys. **81**, 511 (1984); Mol. Phys. **52**, 255 (1984); W. G. Hoover, Phys. Rev. A **31**, 1695 (1985); S. Nosé, Mol. Phys. **57**, 187 (1986); D. J. Evans and B. L. Holian, J. Chem. Phys. **83**, 4069 (1985).
[16] L. D. Landau and E. M. Lifshitz, *Fluids Mechanics* (Pergamon, London, 1959), p. 247.
[17] L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Pergamon, London, 1958), p. 51.
[18] J. L. Lebowitz, J. K. Percus, and L. Verlet, Phys. Rev. **153**, 250 (1967).
[19] J. P. Ryckaert, A. Bellemans, G. Ciccotti, and G. V. Paolini, Phys. Rev. A **39**, 259 (1988).
[20] M. Ferrario, G. Ciccotti, B. L. Holian, and J. P. Ryckaert, Phys. Rev. A **44**, 6939 (1991).
[21] J. P. Ryckaert, A. Bellemans, G. Ciccotti, and G. V. Paolini, Phys. Rev. Lett. **60**, 128 (1988).
[22] W. G. Hoover and H. A. Posch, Phys. Rev. E **51**, 273 (1995).