Time dependence of phase variables in a steady shear flow algorithm

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We study the periodic time dependence of shear stress that occurs in a low- and a high-density fluid in a molecular dynamics algorithm for simulation of constant shear flow. We present a generalization of the linear response theory for a case when the equilibrium relaxation function and the equilibrium shear stress depend on strain. The predictions of this generalization reveal that the time dependence at low densities is a completely nonlinear effect. At high densities the amplitude of equilibrium oscillations of shear stress with strain is modified by strain-dependent viscosity, causing a decrease in amplitude proportional to shear rate in the linear response regime.

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I. INTRODUCTION

In a previous paper [1], we pointed out a curious effect present in small systems undergoing thermostatted shear flow described by the "Sllod"[1] equations of motion [2] with constant shear rate, where the phase variables such as shear stress, hydrostatic pressure, and internal energy were found to be periodic in time, with a period equal to the inverse shear rate.

This time periodicity was investigated for a low-density two-dimensional Weeks-Chandler-Andersen (WCA) [3] fluid. We found that the amplitude of oscillations increased with the increase in shear rate, and disappeared quite rapidly with the increase in the number of particles in the system, so that for the investigated number density ($\rho = 0.396\,85$) it became virtually indistinguishable from the noise for $N \geqslant 8$. We showed that these oscillations can be reproduced using a time-dependent generalization of the transient time-correlation function formalism [4], but we did not explore the equilibrium linear response limit of this effect. We conjectured that the density has to be high enough so that it is impossible for a particle to traverse a distance L, equal to the side length of the periodic cell, in any direction without interacting with other particles. The investigated density was the limit density still satisfying this condition.

In a recent work [5], we established that this time three-dimensional, WCA fluid system at a high density would show finite unrelaxed shear stresses under strain, while retaining its liquid structure and diffusion, at much higher system sizes ($N \approx 256$). This effect is caused by a finite-, temperature-, and density-dependent "shear stress correlation length," related to the anisotropy in the pair distribution function induced by the strained periodic boundary conditions [6] (i.e., adjacent horizontal rows of periodic cells shifted by the same amount with respect to each other) and reflected in the angular dependence of the diffusion coefficient [7]. Here we show that this is another source of time dependence of phase variables in the Sllod description of shear flow at high density, but that in this case the amplitude decreases with shear rate.

In this work we investigate the time periodicity of shear stress under shear (assuming that the time dependence of the other phase variables is of the same origin) in the two limiting cases of low and high density from the point of view of the linear response theory. We show that the time periodicity of shear stress can be described by a generalization of the linear response theory that assumes strain dependence of both the equilibrium ensemble averages and the shear stress relaxation functions. The application of this theory to systems at low and high density shows that the periodic time dependence is caused by different mechanisms in these two cases. While the periodic behavior with the amplitude increasing with shear rate at low densities is a completely nonlinear effect, the decreasing amplitude at high densities can be described by linear response formalism, at least at low shear, provided that viscosity of the system has a weak strain dependence.

II. SIMULATION DETAILS

We have studied a three-dimensional fluid of N identical particles interacting through the short-range repulsive WCA potential, $\Phi_{ij} = 4\varepsilon[(\sigma/r_{ij})^{12} - (\sigma/r_{ij})^{6}] + \varepsilon$ if the distance r_{ij} between the particles i and j is less than $2^{1/6}\sigma$ and zero otherwise, where ε is the depth of the Lennard-Jones potential well, and σ is the particle exclusion diameter. The Lennard-Jones units [8] are used throughout the paper.

We investigated the systems of varying size at two state points. The first is at the temperature of $T = 1.0$ and the low-density limit of $\rho = 0.176\,78$ that still satisfies the same condition as the formerly studied two-dimensional system [1], i.e., that it is impossible for a particle to traverse the periodic cell in any direction without interacting with the other particle when $N = 2$. This is the limiting density at which the range of the WCA potential does not exceed half the simulation box length for $N = 2$.

The second state point is at the high density $\rho = 1.0$ at the temperature of $T = 1.2$ where the system still stays in the fluid

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[1]So named because of their close relationship to the Dolls tensor algorithm.

state even for sufficiently small system sizes for which the strained periodic boundary conditions can cause finite shear stress [7]. The smallest system size at this state point was $N=108$; systems smaller than this would crystallize because of the influence of periodic boundary conditions [9].

The systems were studied in equilibrium and under shear. In equilibrium, static strain was imposed in the periodic boundary conditions [1,5,7] by shifting each horizontal layer of periodic cells by the distance Δ ($0<\Delta<L$, where L is the periodic box length) in the x direction with respect to the layer just below it. The dimensionless strain thus introduced is $\varepsilon=\Delta/L$.

Shear is simulated using the Sllod [2] homogeneous constant shear rate algorithm in conjunction with the Lees-Edwards sliding periodic boundary conditions [10]. The Sllod equations of motion with shear applied in the x direction are

$$\dot{\mathbf{r}}_i = \mathbf{p}_i/m + \mathbf{e}_x \gamma r_{yi},$$
$$\dot{\mathbf{p}}_i = \mathbf{F}_i - \mathbf{e}_x \gamma p_{yi} - \alpha \mathbf{p}_i, \tag{1}$$

where $\mathbf{r}_i$ and $\mathbf{p}_i$ are the atomic positions and momenta, $\mathbf{F}_i$ is the total interaction force acting on the atom i, γ is the constant strain rate, $\mathbf{e}_x$ is the unit vector in the x direction, and α is the Gauss thermostat multiplier,

$$\alpha = \sum_{i=1}^{N} \mathbf{F}_i \cdot \mathbf{p}_i - \gamma p_{xi} p_{yi} \Bigg/ \sum_{i=1}^{N} p_i^2, \tag{2}$$

used to remove viscous heat and keep the kinetic temperature, $T=(\Sigma p_i^2/m)/[k_B(3N-4)]$ constant. The number of degrees of freedom $3N$ in the expression for temperature is reduced by 4 because of the conservation of total momentum and the constraint on kinetic energy. Shear rate varied from 0.0 (equilibrium) to 1.0. Thermostat was used even in equilibrium (when $\gamma=0$) in order to ensure that the properties of the equilibrium and sheared systems were compared at the same state point.

The equations of motion (1) were integrated using the fifth order Gear predictor-corrector method with the time step of 0.001. In the equilibrium simulations, the system was first equilibrated for 10^6 time steps at the desired static strain ε in the periodic boundary conditions. After that, we collected the average values of the shear stress,

$$P_{xy}(\varepsilon)V = \left\langle \sum_{i=1}^{N} \frac{p_{xi}p_{yi}}{m} + \sum_{i,j>i} F_{xij} \cdot r_{yij} \right\rangle, \tag{3}$$

and computed the strain-dependent "modified" viscosity [7] using the Green-Kubo relations,

$$\eta^*(\varepsilon) = \frac{V}{k_B T}\int_0^\infty dt \langle [P_{xy}(\varepsilon,0) - P_{xy0}(\varepsilon)][P_{xy}(\varepsilon,t) - P_{xy0}(\varepsilon)] \rangle, \tag{4}$$

where V is the volume of the simulation cell, k_B is the Boltzmann constant, and $P_{xy0}(\varepsilon)$ is the ensemble average of the equilibrium shear stress at the strain ε. The modified viscosity η^* coincides with the conventional Green-Kubo viscosity when the equilibrium shear stress P_{xy0} vanishes. Equilibrium production runs were 10^8 time steps at low density and 10^7 time steps at high density, and the time window for the integration of the shear stress autocorrelation function (4) was five time units (i.e., 5000 time steps).

In the nonequilibrium runs, the system was brought to the steady state after 100 periods $1/\gamma$. The steady-state averages were then collected over 10^6 periods in the low-density runs, and in the high-density systems over 50 000 periods for $N=108$ and for 5000 periods for the largest system size $N=500$.

III. LINEAR RESPONSE THEORY

First, we briefly review the line of reasoning leading to finite shear stress proportional to strain rate in fluids under shear. If all fluid particles are instantaneously displaced at time $t=0$ in x direction by $\delta_{\mathbf{r}}=\mathbf{e}_x\varepsilon r_y$ (where $\mathbf{e}_x$ is the unit vector in the x direction), so that the total dimensionless deformation or strain is equal to ε, this creates instantaneous shear stress $P_{xy}(0)=G_\infty\varepsilon$ proportional to strain in the fluid. The constant of proportionality G_∞ is the "infinite frequency shear modulus." In time, this shear stress decays to zero according to some relaxation function $f_R(t)$,

$$P_{xy}(t) = G_\infty \varepsilon f_R(t). \tag{5}$$

The relaxation function is such that $f_R(0)=1$, $f_R(t)\to 0$ as $t\to\infty$, and that the integral $\int_0^\infty f_R(t)dt$ exists and is finite.

When the system is sheared at a constant strain rate $\gamma=d\varepsilon/dt$, new deformations are constantly imposed while shear stresses due to the previous deformations did not have time to fully relax. Thus after dt we have

$$P_{xy}(dt) = G_\infty \gamma dt f_R(dt).$$

After $2dt$ the shear stress is

$$P_{xy}(2dt) = G_\infty \gamma dt f_R(2dt) + G_\infty \gamma dt f_R(dt),$$

where the first term on the right hand side is the shear stress due to the deformation imposed at $t=0$, which has now been relaxing for $2dt$, and the second term is the shear stress imposed at $t=dt$, which has been relaxing for dt. After ndt,

$$P_{xy}(ndt) = G_\infty \gamma dt \sum_{i=0}^{n-1} f_R((n-i)dt), \tag{6}$$

or with the substitution $t=ndt$ and $s=idt$,

$$P_{xy}(t) = \gamma \int_0^t G_\infty f_R(t-s)ds. \tag{7}$$

The steady-state value of P_{xy} under constant shear rate γ is then equal to the infinite-time limit of the Eq. (7), and is proportional to shear rate as long as the relaxation function and shear modulus do not get modified due to structural changes under shear. The coefficient of proportionality

$$\eta = P_{xy}(\infty)/\gamma = \int_0^\infty G_\infty f_R(t)dt \tag{8}$$

is the "linear response" viscosity of the system. In the Maxwell model of viscoelasticity, the relaxation function is assumed to have exponential form, $f_R(t)=\exp(-t/\tau)$, where τ is the "Maxwell relaxation time," and viscosity is equal to $G_\infty\tau$. In practice, the relaxation is rarely exponential. Green-Kubo theory gives the linear response viscosity in terms of correlations of the shear stress fluctuations in equilibrium,

$$\eta = \frac{V}{k_B T}\int_0^\infty dt \langle P_{xy}(0)P_{xy}(t)\rangle . \tag{9}$$

Comparing Eqs. (8) and (9), we can identify the infinite frequency shear modulus as

$$G_\infty = \frac{V}{k_B T}\langle P_{xy}^2(0)\rangle , \tag{10}$$

and the relaxation function as

$$f_R(t) = \frac{\langle P_{xy}(0)P_{xy}(t)\rangle}{\langle P_{xy}^2(0)\rangle} . \tag{11}$$

In a more general case both G_∞ and the relaxation function f_R depend on strain. We denote $F_R(\varepsilon,t)\equiv G_\infty(\varepsilon)f_R(\varepsilon,t)$, where $F_R(\varepsilon,t)$ corresponds to the equilibrium correlation function in the strained system,

$$F_R(\varepsilon,t) = \frac{V}{k_B T}\langle [P_{xy}(\varepsilon,0) - P_{xy0}(\varepsilon)][P_{xy}(\varepsilon,t) - P_{xy0}(\varepsilon)]\rangle . \tag{12}$$

$F_R(\varepsilon,t)$ is continuous in both ε and t, vanishes in the infinite time limit and has a finite infinite time integral equal to the "modified viscosity" $\eta^*(\varepsilon)$ at the strain ε [Eq. (4)].

In addition, we assume that the shear stress relaxes to a strain-dependent equilibrium value $P_{xy0}(\varepsilon)$. The equilibrium shear stress must be an odd periodic function of strain with the period equal to unity.

After instantaneous deformation from the initial strain ε_0 to $\varepsilon_0+\Delta\varepsilon$, shear stress relaxes according to

$$P_{xy}(\varepsilon_0 + \Delta\varepsilon,t) - P_{xy0}(\varepsilon_0 + \Delta\varepsilon) = \Delta\varepsilon F_R(\varepsilon_0 + \Delta\varepsilon,t).$$

Let us assume that initially, at $t=0$, the boundary strain is equal to ε_0, and that the system is sheared at a constant rate γ. At the end of each time increment dt, the shear stress will relax to the value determined by the relaxation function at the instantaneous value of strain. All terms of shear stress on the right-hand side relax towards the value of P_{xy0} corresponding to the instantaneous value of strain.

In analogy to Eq. (6), after n steps of duration dt of shearing with the shear rate γ, shear stress is

$$\begin{aligned} &P_{xy}(\varepsilon_0 + n\gamma dt, ndt) - P_{xy0}(\varepsilon_0 + n\gamma dt) \\ &\quad = \gamma \sum_{i=0}^{n-1} dt F_R(\varepsilon_0 + n\gamma dt, (n-i)dt), \end{aligned}$$

or in integral form obtained by substitution $\varepsilon=\varepsilon_0+n\gamma dt$, $t=ndt$, $s=idt$,

$$P_{xy}(\varepsilon,t) - P_{xy0}(\varepsilon) = \gamma\int_0^t F_R(\varepsilon,t-s)ds.$$

In the infinite-time limit the "steady state" shear stress at the strain ε is

$$P_{xy}(\varepsilon,t) - P_{xy0}(\varepsilon) = \gamma\int_0^\infty F_R(\varepsilon,t)dt = \gamma\eta^*(\varepsilon). \tag{13}$$

If the equilibrium shear stress P_{xy0} vanishes for all values of strain and viscosity is strain independent, then there is no periodic dependence of shear stress in the linear response (low strain rate) regime. Note that viscosity can be strain independent even if the relaxation function F_R depends on strain, as long as its infinite time integral is strain independent.

If $P_{xy0}(\varepsilon)$ has a nonvanishing amplitude, but the modified viscosity η^* does not depend on strain, the periodic form $P_{xy0}(\varepsilon)$ under shear will be shifted by $-\gamma\eta^*$ without any deformation or phase lag, and the amplitude of $P_{xy}(\varepsilon,t)$ will be strain independent.

If the modified viscosity depends on strain, the equilibrium periodic form $P_{xy}(\varepsilon)$ gets deformed under shear even in the linear range of shear rates. However, the period-averaged shear stress $\overline{P_{xy}}$ stays proportional to strain rate in the range where the response is linear for all strains, $\overline{P_{xy}}=\gamma\overline{\eta^*}$ ($\overline{\eta^*}$ is the period-averaged modified viscosity).

In the previous paper [1], we have used the time-dependent generalization of the transient time-correlation function formalism [4] to obtain the strain dependence of shear stress in the two-particle system in the nonlinear regime,

$$P_{xy}(\gamma,\varepsilon) = \gamma\frac{V}{k_B T}\int_0^\infty dt\langle P_{xy}(\varepsilon,0)_{\mathrm{EQ}}P_{xy}(\gamma,\varepsilon,t)_{\mathrm{NEQ}}\rangle, \tag{14}$$

where $P_{xy}(\varepsilon,0)_{EQ}$ is the instantaneous equilibrium value of shear stress at the strain ε, connected to the value of shear stress at the same strain after time t by a nonequilibrium trajectory with strain rate γ. Equation (13) represents the linear limit of Eq. (14) with the substitution $P_{xy}(\varepsilon,0)_{\mathrm{EQ}} \to [P_{xy}(\varepsilon,0)-P_{xy0}(\varepsilon)]_{\mathrm{EQ}}$. The reasoning behind Eqs. (12) and (13) provides the physical interpretation for Eq. (14) as

$$P_{xy}(\gamma,\varepsilon) - P_{xy0}(\varepsilon) = \gamma\eta^*(\gamma,\varepsilon),$$

where η^* is the nonlinear modified viscosity,

$$\eta^*(\gamma,\varepsilon) = \frac{V}{k_B T}\int_0^\infty dt\langle [P_{xy}(\varepsilon,0) - P_{xy0}(\varepsilon)]_{\mathrm{EQ}}P_{xy}(\gamma,\varepsilon,t)_{\mathrm{NEQ}}\rangle,$$

which depends both on strain and on strain rate.

IV. LOW DENSITY RESULTS AND DISCUSSION

In a low-density system under shear, the amplitude of the averaged shear stress oscillations as a function of instantaneous strain quickly decreases with system size. In Fig. 1 we show the amplitude of P_{xy} for increasing numbers of particles at the shear rate $\gamma=1.0$ at two densities, $\rho=0.176\,78$

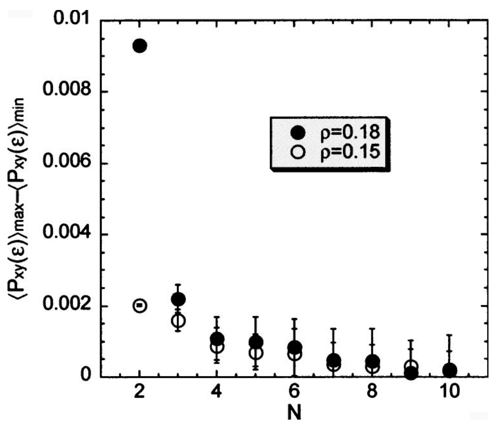

FIG. 1. Number dependence of the amplitude of shear stress oscillations at two low densities (ρ=0.18 is actually ρ=0.176 78) for the shear rate γ=1.0.

and ρ=0.15. Although the effect becomes reduced with the decrease in density, it still exists for small system sizes even at densities lower than that where the particles cannot traverse the periodic cell without interacting, proving that the conjecture in Ref. [1] was wrong.

Since the time periodicity of the shear stress is the most prominent for N=2, this is the system size we explore further. The amplitude of the shear stress oscillations increases with the increase in shear rate, as illustrated in Fig. 2. At the same time, the absolute value of the shear stress increases. From Fig. 3 it can be estimated that the magnitude of shear stress is proportional to shear rate (i.e., the response is linear) up to γ=0.4, after which shear thinning takes place. In the linear range of shear rates, Fig. 2 shows that the shear stress oscillations cannot be discerned within the accuracy of the signal.

The time correlation functions for this system, computed at different equilibrium strains ε imposed by the periodic boundary conditions, are shown in Fig. 4(a). As can be seen in the graph, the equilibrium shear stress vanishes for all strains and the relaxation function F_R found from Eq. (12) is a continuous function of strain ε as well as of the time,

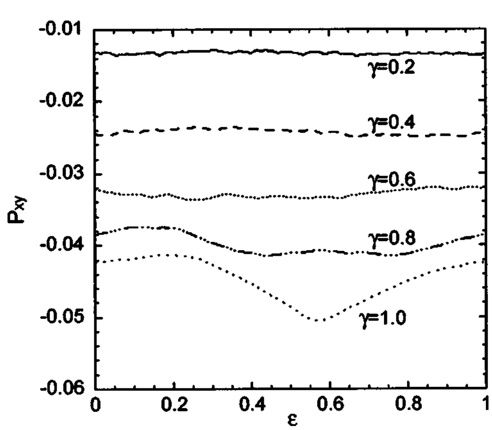

FIG. 2. Periodic form of shear stress under strain for increasing shear rates γ in a two-particle system at the density γ=0.176 78 under shear. The period of oscillations is $1/\gamma$ in time units, or 1 in terms of the instantaneous strain $\varepsilon=\gamma t$.

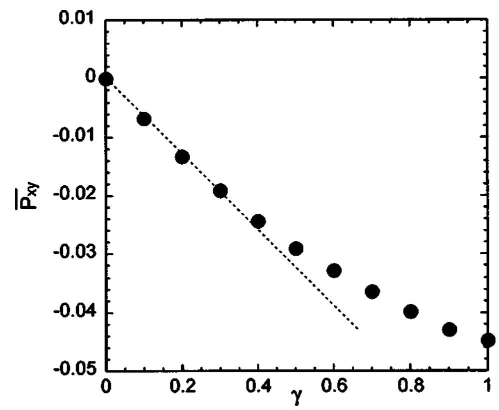

FIG. 3. Dependence of the shear stress averaged over a period of oscillation $\overline{P_{xy}}$ on shear rate for the two-particle system at ρ =0.176 78. From the dotted line, the response can be estimated to be linear for shear rates up to γ=0.4.

$$F_R(\varepsilon,t)=\frac{V}{k_BT}\langle P_{xy}(\varepsilon,0)P_{xy}(\varepsilon,t)\rangle. \tag{15}$$

The cause of the strain dependence of the correlation function Eq. (15) can be understood in the language of hard-

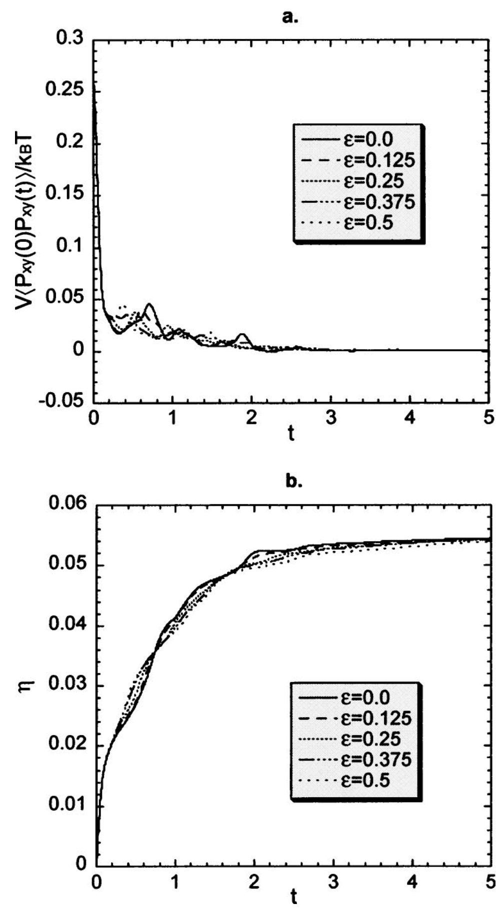

FIG. 4. Shear stress autocorrelation functions (a) and their integrals (b) in equilibrium two-particle system at different static strain ε. While the correlation functions depend on strain, viscosity does not.

sphere systems. In the equilibrium two-body periodic systems under different boundary-imposed strains, the collision frequency and the angular distributions of collisions remain the same, but the collision sequences are different, since when a particle leaves the minimum image box of the other particle after a collision, it re-enters it at a different position for different values of ε. This affects the time-correlation functions, but not the infinite-frequency shear modulus, which is a time-independent ensemble average. Viscosity does not depend on strain either [Fig. 4(b)]—as an infinite-time integral, it is again a time-independent ensemble average.

The linear response theory presented in Sec. III predicts the change in amplitude proportional to shear rate, but only if equilibrium viscosity depends on strain. Since this is not the case, the time periodicity of shear stress is a purely nonlinear effect.

Under strong shear, the angular probability distribution of collisions in a two-particle system becomes strain dependent [11,12], which causes the oscillations of shear stress. If the number of particles in the system increases, so does the number of possibilities of pair collisions, and the differences in the collision sequences in equilibrium and the angular distributions under shear disappear. If the density is lowered so that particles can move over the whole periodic cell length without interacting, the "noise" caused by missed collisions decreases the difference in the collision sequences and angular distributions.

V. HIGH DENSITY RESULTS AND DISCUSSION

At the high density of $\rho=1.0$ the smallest studied system size was $N=108$. This system size is large enough that the sequence of interactions does not influence the shear stress relaxation under strain. However, for sufficiently small system sizes (up to $N\sim500$) shear stress does not generally relax to zero, but to a strain-dependent finite value. The phase space distribution functions are strain dependent because the configurations that can reconcile different distributions of atoms on the opposite boundaries contain some shear stress dependent on the imposed boundary strain [5]. At the same time, the boundary strain does not affect the particle mobility—diffusion coefficient is the same under all strains within the simulation accuracy [7], but becomes slightly anisotropic. The eventual dependence of the modified viscosity on strain could not be discerned within the simulation accuracy.

The correlation functions for $N=108$ are presented in Fig. 5 for several values of strain. There are small differences in the infinite frequency shear moduli that are not in the same order as the unrelaxed stresses in the tails of correlation functions, but it is not clear if this is due to statistical errors. Viscosity calculated from the integral Eq. (4) at zero strain is $\eta=6.35$.

The magnitude of maximum ensemble-averaged shear stress under strain decreases with system size, albeit in an irregular, nonmonotonic way (crosses in Fig. 6). If the system is sheared very slowly, shear stress averaged at the same instantaneous strains oscillates periodically in time with the

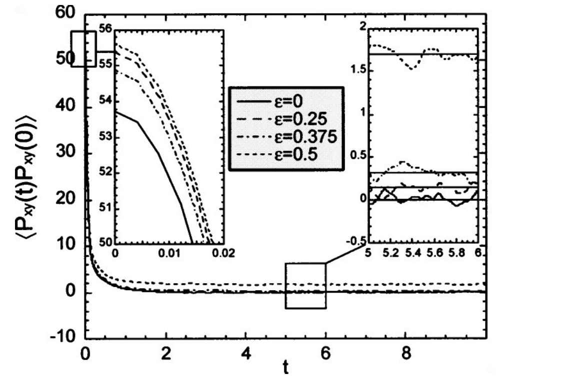

FIG. 5. Shear stress time-correlation function for different strains ε in a system of 108 particles at $T=1.2$, $\rho=1.0$. The inset on the left-hand side shows an enlargement of the shear modulus, the right-hand-side inset shows an enlargement of the tail.

period equal to the inverse shear rate, and the amplitude equal to the maximum ensemble-averaged shear stress under strain in equilibrium. Open circles in Fig. 6 represent the N-dependent amplitude of shear stress oscillations under the shear rate $\gamma=0.01$; they coincide (within the error bars) with the maximum equilibrium shear stress in the strained boundary conditions.

In further studies we use the system size of $N=108$. In Fig. 7 we compare (as full circles) the average shear stress under several strains in equilibrium and (the dashed-dotted line) the time-periodic form of the shear stress under shear rate of 0.01 as a function of instantaneous strain. If we subtract the shear stress averaged over the period of oscillation (which is equal to $-\gamma\eta$, where $\eta=6.35$ as calculated from zero strain equilibrium Green-Kubo integral), from the periodic form, the equilibrium shear stresses fall on the obtained (dotted) line.

The magnitude of period-averaged shear stress increases with shear rate, initially linearly for shear rates up to 0.3, after which the system starts to shear thin [Fig. 8(a)]. The amplitude of shear stress oscillations decreases with the in-

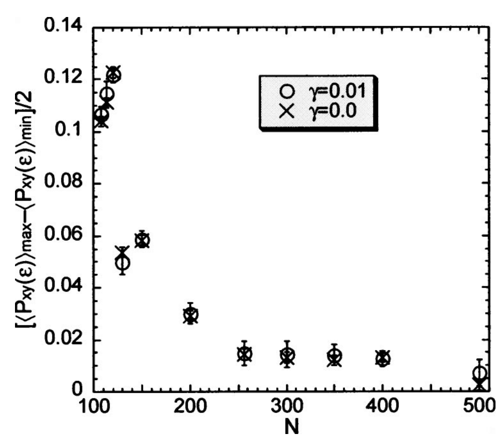

FIG. 6. Amplitude of the average shear stress as a function of system size in equilibrium under strained periodic boundary conditions ($\gamma=0.0$, crosses) and under low shear rate ($\gamma=0.01$, open circles) at $T=1.2$, $\rho=1.0$. The amplitudes are within each other's error bars.

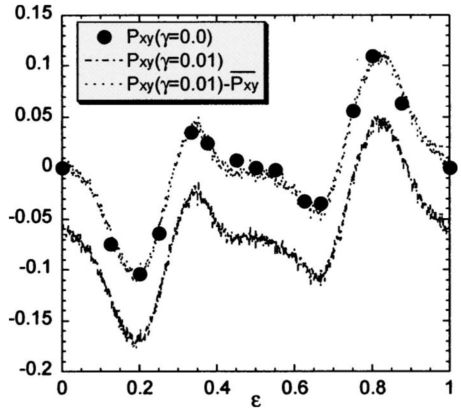

FIG. 7. Full circles represent equilibrium shear stress as a function of strain for the $N=108$ system at $T=1.2$, $\rho=1.0$. The dashed-dotted line is the strain-dependent periodic form of shear stress under shear rate $\gamma=0.01$. When this periodic form is shifted by $\overline{P_{xy}}=\gamma\eta$, where $\eta=6.35$ is the equilibrium zero-strain viscosity, it passes through the equilibrium shear stress values.

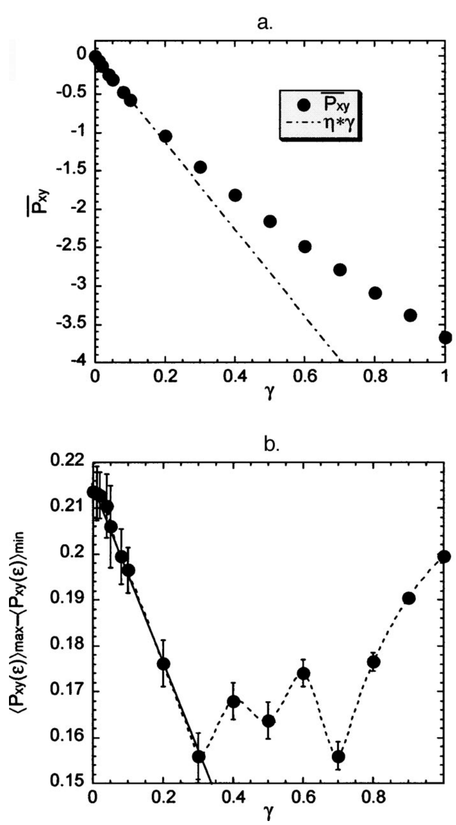

FIG. 8. (a) Dependence of the shear stress averaged over a period of oscillation $\overline{P_{xy}}$ on shear rate for $N=108$. The response can be estimated to be linear for shear rates up to $\gamma=0.3$. (b) Amplitude of oscillations of shear stress decreases linearly with the increase in shear rate in the linear response regime (full line). For higher shear rates it reaches a minimum and then increases nonmonotonically. The dashed line is a guide for the eye.

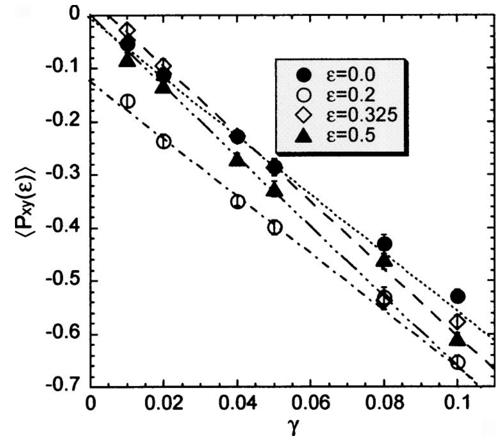

FIG. 9. For shear rates $\gamma\leqslant 0.1$, the magnitude of shear stress increases proportionally to shear rate, but with different slopes reflecting strain-dependent viscosities.

crease in shear rate up to $\gamma=0.4$. For higher shear rates it starts to increase in an irregular, nonmonotonic way.

In Fig. 8(b), the amplitude of shear stress oscillations decreases linearly for $\gamma<0.3$, i.e., in the range where the period-averaged shear stress is proportional to shear rate. A linear change (whether increase or decrease) of amplitude under shear is predicted by the linear response theory in Sec. III if the modified viscosity is strain dependent. We plot shear stress at four strains as a function of shear rate in this range in Fig. 9. For low shear rates the dependence is clearly linear with weakly strain-dependent slopes, showing that the modified viscosity is indeed dependent on strain. This strain dependence is responsible for the small decrease in amplitude in this range of strain rates.

Note that a linear decrease in amplitude according to Eq. (13) cannot go on indefinitely with increase in shear rate—eventually, some peaks in the form in Fig. 7 will disappear and then move to the other side of the period average. Until all the peaks change sides, the amplitude will change irregularly; afterwards it will increase linearly with the increase in shear rate, just as can be seen in Fig. 8(b) for $\gamma\geqslant 0.7$. However, for such high shear rates the increase is not linear because of shear thinning.

VI. CONCLUSION

We have studied the periodic time dependence of shear stress in the constant strain rate algorithm for computer simulation of bulk shear flow in the low and high fluid density limits.

We showed that the generalization of the linear response theory, where both the equilibrium shear stress relaxation function and the equilibrium shear stress are strain dependent, predicts that the periodic form of shear stress as a function of strain for different shear rates will be equal to the periodic strain-dependent form of shear stress shifted by the period-averaged viscosity multiplied by shear rate. The deformation of the signal will be determined by the strain dependence of equilibrium viscosity and proportional to strain rate.

In the case of very low density, the shear stress relaxation function depends on strain only for extremely low particle numbers ($N \sim 2$), where it is a consequence of the strain dependence of the sequence of collisions. Equilibrium shear stress vanishes and viscosity does not depend on strain. The dependence of the probability distribution of collisions on strain is a nonlinear effect, and generates the periodic time dependence of shear stress only in the nonlinear regime, for $\gamma > 0.4$.

In contrast, when the density is high, both the equilibrium shear stress and the modified viscosity (Green-Kubo viscosity calculated using the difference between the ensemble-averaged shear stress and its instantaneous value) depend on strain for sufficiently small systems ($N < 500$). The weak dependence of viscosity on strain causes the linear decrease of amplitude in the linear regime to a minimum value. For higher shear rates there is a nonlinear increase in amplitude accompanied by shear thinning in the period-averaged shear stress.

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