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Non-Newtonian behavior in simple fluids

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Using nonequilibrium molecular dynamics simulations, we study the non-Newtonian rheology of a microscopic sample of simple fluid. The calculations were performed using a configurational thermostat which unlike previous nonequilibrium molecular dynamics or nonequilibrium Brownian dynamics methods does not exert any additional constraint on the flow profile. Our findings are in agreement with experimental results on concentrated “hard sphere”-like colloidal suspensions. We observe: (i) a shear thickening regime under steady shear; (ii) a strain thickening regime under oscillatory shear at low frequencies; and (iii) shear-induced ordering under oscillatory shear at higher frequencies. These results significantly differ from previous simulation results which showed systematically a strong ordering for all frequencies. They also indicate that shear thickening can occur even in the absence of a solvent. © 2004 American Institute of Physics.
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I. INTRODUCTION

Shear induced ordering as well as shear induced phase transitions are problems of fundamental as well as of technological interest. These phenomena are extremely complex and a large variety of unexpected shear induced structures and behaviors can be observed. Experiments on “hard sphere”-like colloidal suspensions show that these suspensions order when submitted to oscillatory shear.¹ Other experiments on such concentrated suspensions show a shear thickening regime (i.e., the apparent viscosity increases with the applied shear rate) under steady shear flow² and a strain thickening regime (i.e., the complex viscosity increases with the amplitude of the applied shear rate) under oscillatory shear at low or very high frequencies.^{3,4} Much more exotic structures such as shear banding can also be observed in complex systems undergoing shear flow. Using molecular simulation to study these phenomena is an intriguing perspective since it would allow us to understand how these phenomena occur at the microscopic level.

It has been known for some time that simple fluids exhibit some non-Newtonian rheological features,⁵ e.g., shear thinning (the shear viscosity of simple fluids decreases with an increase in shear rate). This is due to the small size of systems studied by simulation. These systems consist typically of several hundred particles in periodic boundary conditions. This imposes a lower limit on the wave vector describing collective motion and prevents large-scale instabilities. The Reynolds number is low even for extremely high shear rates, and one observes non-Newtonian instead of turbulent behavior. However, despite the strongly non-Newtonian nature of the flow, most studies postulate that the simple flow form valid for a Newtonian fluid (a linear profile

in the flow direction for a fluid undergoing shear flow) correctly describes the actual motion in a non-Newtonian fluid. This is the case for the two atomistic simulation methods used to describe these phenomena, i.e., nonequilibrium molecular dynamics (NEMD) and nonequilibrium Brownian dynamics. All these studies report a systematic and strong ordering at high shear rates for simple fluids undergoing either steady^{6–17} or oscillatory shear flow.^{18–22} Experiments on non-Newtonian fluids such as concentrated colloidal suspensions of “hard sphere”-like colloidal particles show that ordering can occur under oscillatory shear.^{1,23,24} However, under steady shear (or under oscillatory shear at low frequencies), no such ordering is observed. Indeed, the viscosity of these suspensions is shown to increase with an increase in shear rate, i.e., in rheological terms, the suspensions exhibit shear thickening.^{2–4,25} This discrepancy between simulation and experimental results is usually attributed to the absence of lubrication interactions, the so-called “squeeze” mode, in the simulation methods.²⁶

It can be argued that assuming a simple Newtonian flow profile is going to stabilize (and possibly create) ordering in a sheared fluid. In particular, the fact that no secondary flow profile, perpendicular to the flow direction,²⁷ is allowed to develop in these simulations seems to be a key factor in the onset of ordering under steady shear.¹⁶ Several attempts have been made in the past to devise simulation methods to alleviate this problem and to determine with greater accuracy the flow profile. However, all these methods require making some assumption about the spatial or time dependence of the flow profile and have led to contradictory results.^{28–32} In previous work on simple fluids flowing past a frictionless wall, we showed that a simulation method postulating a linear profile systematically destroyed the expected plug flow profile even at very low shear rates. The simulation algorithm was also shown to enforce a linear flow profile and to

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induce ordering throughout the fluid.³³ All these results cast doubts on the reality of the ordering phenomena as observed in previous simulation studies.

We recently proposed a NEMD method which tackles this problem with a radically different approach, using the so-called configurational thermostat.³⁴ In usual NEMD methods, the reference to an assumed linear form for the flow profile is made in the thermostatting mechanism.³⁵ Deviations from the assumed flow profile are interpreted as thermal motion. They are consequently dampened to account for the dissipation of heat and to keep the temperature of the system constant. This prevents any significant deviation from the postulated profile from developing and destroys any secondary flow. When a configurational thermostat^{36,37} is used, temperature is evaluated only from the first and second spatial derivatives of the interaction energy^{38,39} and no reference to the flow profile (and therefore no assumption) is made. This approach was shown to allow a flow profile in agreement with the predictions of hydrodynamic stability theory⁴⁰ to develop: at high shear rates, the flow profile obtained in the steady state was a superposition of the linear profile and of a sinusoidal “secondary” flow along the flow direction. A sinusoidal secondary flow was also observed in directions perpendicular to the flow. Using a configurational thermostat, no ordering was observed under steady shear. On the contrary, we observed a shear thickening regime at high shear rates similar to experimental observations on colloidal suspensions. This finding is quite surprising since our method does not take into account any lubrication interaction. In this work, we pursue our ongoing investigation on the rheology of simple fluids using a NEMD method together with the configurational thermostat. The paper is organized as follows: In Sec. II, we describe the simulation method. We then present the results obtained by applying this method to study a simple fluid subjected to strong steady or oscillatory shear for a wide range of shear rate amplitudes and of frequencies. In particular, comparisons with experimental results on colloidal suspensions are made. We finally highlight the differences between the results obtained in this work and previous simulation results assuming a linear flow profile.

II. SIMULATION METHOD

We studied an atomic fluid modeled by the Lennard-Jones potential

$$\phi(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \quad \text{for } r < 2.5\sigma = 0 \quad \text{otherwise,} \quad (1)$$

where ϵ is the well depth of the pair potential and σ the particle exclusion diameter. In the remainder of the paper, we use a reduced system of units, where the unit of mass is m the mass of a particle, the unit of energy is ϵ , and the unit of length is σ . All simulations were carried out for a system of $N=1000$ particles at a reduced temperature $T=0.722$ and a reduced number density $n=N/V=0.844$.

The NEMD method used in this work is the homogeneous SLLOD algorithm³⁵ (so named because of its close relationship to the Dolls tensor algorithm) together with the appropriate Lees–Edwards periodic boundary conditions.⁴¹

Simulations were run with a configurational thermostat based on the following expression for the temperature:^{38,39}

$$\frac{1}{k_B T_{\text{conf}}} = \frac{\left\langle \sum_{i=1}^N \frac{\partial^2 \Phi_0}{\partial \mathbf{r}_i^2} \right\rangle}{\left\langle \sum_{i=1}^N \left(\frac{\partial \Phi_0}{\partial \mathbf{r}_i} \right)^2 \right\rangle}, \quad (2)$$

where k_B is Boltzmann’s constant and Φ_0 the potential energy of the system. In Eq. (2), temperature is estimated from configurational information only. Unlike the thermostatting schemes used in previous NEMD studies of these phenomena, using a configurational thermostat therefore does not require making any assumption about the streaming velocity profile. The configurationally thermostatted equations of motions are^{36,37}

$$\begin{aligned} \dot{\mathbf{r}}_i &= \frac{\mathbf{p}_i}{m} + \dot{\gamma} y_i \mathbf{e}_x + \frac{s}{T} \frac{\partial T_{\text{conf}}}{\partial \mathbf{r}_i}, \\ \dot{\mathbf{p}}_i &= \mathbf{F}_i - \dot{\gamma} p_{yi} \mathbf{e}_x, \\ \dot{s} &= -Q \frac{(T_{\text{conf}} - T)}{T}, \end{aligned} \quad (3)$$

where $\mathbf{r}_i$ and $\mathbf{p}_i$ are the position and “peculiar” momentum (i.e., with respect to linear streaming velocity profile $\dot{\gamma} y_i \mathbf{e}_x$) of particle i , $\mathbf{F}_i$ the Newtonian force exerted on i , and m its mass. T is the imposed temperature while T_{conf} is the value given by Eq. (2) (Q is a damping constant set to $10m\sigma^4/\epsilon$). $\dot{\gamma} = du_x(y)/dy$ is the imposed shear rate and $\mathbf{e}_x$ is a unit vector along the x axis. Simulations of steady shear flow were carried out at a constant value for the imposed shear rate $\dot{\gamma}$. In simulations of oscillatory shear flow, the imposed shear rate was a sinusoidal function of time $\dot{\gamma}(\omega) = \dot{\gamma}_0 \cos(2\pi\omega t)$.

The equations of motion were integrated using a fourth-order Gear predictor–corrector algorithm with a time step $\tau=0.001$ for the steady shear simulations and with a time step $\tau=\pi/4000$ for the oscillatory shear simulations, except for the highest shear rates where a smaller time step had to be used. In simulations of steady shear flow, the shear viscosity η is evaluated as the ratio $\eta = \langle -P_{xy}/\dot{\gamma} \rangle$, where P_{xy} is the shear stress while under oscillatory shear, we define the complex viscosity $\eta(\omega)$ as $\eta(\omega) = \eta_r(\omega) + i\eta_i(\omega)$ with

$$\begin{aligned} \eta_r(\omega) &= \left\langle \frac{-2\pi}{\dot{\gamma}_0 \omega} \int_0^{2\pi/\omega} \cos(\omega s) P_{xy} ds \right\rangle \\ \eta_i(\omega) &= \left\langle \frac{-2\pi}{\dot{\gamma}_0 \omega} \int_0^{2\pi/\omega} \sin(\omega s) P_{xy} ds \right\rangle, \end{aligned} \quad (4)$$

where η_r and η_i are, respectively, the real part and the imaginary part of the complex viscosity and $\langle \dots \rangle$ denotes the ensemble average. These expressions only allow us to measure part of the response, i.e., the first harmonic in ω . The contribution from higher harmonics is negligible at high frequency, where shear induced ordering takes place. These expressions also provide estimates for the elastic modulus G'

FIG. 1. Shear viscosity against the imposed steady shear rate.

$=\omega\eta_i(\omega)$ and the viscous modulus $G''=\omega\eta_r(\omega)$. Finally, we define the strain amplitude $\gamma_0=\dot{\gamma}_0/\omega$ as the ratio of the shear rate amplitude over the frequency.

III. SIMULATION RESULTS: COMPARISON WITH EXPERIMENTS

We first present the results obtained for the rheological properties of simple fluids under steady shear. Figure 1 shows the variation in shear viscosity with the applied steady shear rate. For shear rates lower than 6, we observe a decrease in viscosity as shear rate increases. This non-Newtonian effect is referred to as shear thinning. This phenomenon is ubiquitous in nonequilibrium simulations of shear flow and has been reported on many occasions.⁵ We showed in previous work that a sinusoidal-like secondary flow profile developed on top of the linear primary flow profile in this shear thinning regime.³⁴ We also showed that a sinusoidal-like secondary flow profile also developed in directions perpendicular to the flow. For shear rates larger than 7, the fluid enters a shear thickening regime marked by a steep increase in viscosity with an increase in the applied shear rate. Again, in the shear thickening regime, the flow profile strongly departs from the linear form and exhibits strong fluctuations in directions parallel and perpendicular to the flow. We proposed a criterion to determine the critical shear rate beyond which thickening takes place. The onset of shear thickening occurs when the typical change in streaming velocities between nearest neighbors $|\Delta u_x|$ becomes comparable to the mean thermal velocity. This conjecture is in good agreement with the simulation results. The mean thermal velocity is equal to $\sqrt{k_B T_{\text{kin}}/m}$ where

$$T_{\text{kin}} = \left\langle \sum_{i=1}^N m(\mathbf{v}_i - \dot{\gamma} y_i \mathbf{e}_x)^2 \right\rangle / (3Nk_B) \quad (5)$$

(in this expression, $\mathbf{v}_i$ denotes the velocity of particle i). For the system studied in this work, the nearest neighbor distance is $N^{-1/3}=1.06$ and the mean change of streaming velocity between nearest neighbor layers is $|\Delta u_x|=N^{-1/3}\dot{\gamma}_c \approx 7.5$, where $\dot{\gamma}_c=7$ is the critical maximum shear rate associated with incipient shear thickening. We observe that $|\Delta u_x| \approx 2\sqrt{k_B T_{\text{kin}}/m}$ in good agreement with our conjecture.

FIG. 2. Norm of the complex viscosity against the amplitude of the imposed shear rate and of the frequency. The arrow indicates the onset of shear induced ordering.

The norm of the complex viscosity, $|\eta(\omega)|$, is plotted against the imposed shear rate amplitude and against the imposed frequency in Fig. 2. We also plot in Fig. 3 the real and imaginary part of the complex viscosity against frequency and shear rate amplitude. We conducted numerical “strain sweep” experiments for frequencies ranging from 1 and 100. We can identify three different general types of behavior according to the relative value of the real and of the imaginary part of the complex viscosity in equilibrium for a given frequency (they can be obtained by calculating a Fourier transform of the equilibrium autocorrelation function of the shear stress). At low frequencies ($\omega < 10$), the real part of viscosity is larger than the imaginary part and the viscous modulus therefore dominates the elastic modulus. At intermediate frequencies ($10 \leq \omega \leq 20$), viscous and elastic moduli are comparable. At high frequencies ($\omega > 20$), the elastic modulus dominates. At low frequency, the real and imaginary part of viscosity exhibit a similar behavior with increasing shear rate amplitude. They both decrease with increasing shear rate amplitude $\dot{\gamma}_0$ until $\dot{\gamma}_0$ reaches approximately 7. For larger amplitudes, they both jump to higher values, indicating that the Lennard-Jones fluid exhibits strain thickening under those conditions. These results can be interpreted in view of our previous simulations of simple fluids undergoing steady shear flow:³⁴ the Lennard-Jones fluid underwent shear thinning for imposed shear rates lower than 7 and shear thickening for larger shear rates. Similarly, under oscillatory shear flow, $|\eta(\omega)|$ decreases with increasing shear rate amplitude for amplitudes lower than 7. For larger shear rate amplitudes, the fluid strain thickens, i.e., $|\eta(\omega)|$ increases with the amplitude. Shear or strain thickening take place for similar values of the imposed steady shear rate (approximately 7)³⁴ or of the imposed shear rate amplitude (in the range 7–8). Applying the same conjecture as for steady shear, we note that for oscillatory shear flow $|\Delta u_x| \approx 3\sqrt{k_B T_{\text{kin}}/m}$ for all frequencies where strain thickening is observed. These results show that the conjecture proposed for the onset of shear thickening is also valid for the onset of strain thickening.

We note that there is a remarkable similarity between the simulation results and the experimental observations on con-

FIG. 3. Real and imaginary part of the complex viscosity against the frequency and the shear rate amplitude. The arrow indicates the onset of ordering.

centrated colloidal suspensions.^{3,4} First, colloidal suspensions that exhibit shear thickening are generally observed to exhibit strain thickening under oscillatory shear at high shear rate amplitudes and low frequencies. Colloidal suspensions which strain thicken are characterized by larger values for the viscous modulus (or for the real part of viscosity) than for the elastic modulus (or for the imaginary part of viscosity). The onset of strain thickening at a critical maximal shear rate, equal to the product of the strain amplitude by the frequency in experiments, is associated with rapid increases in both the elastic and the viscous moduli. Finally, experiments show that shear and strain thickening occur for similar values of the critical maximal shear rate.⁴ All these observations are consistent with our simulation results.

We now turn to the results obtained for the second frequency domain $10 \leq \omega \leq 20$, where the real and imaginary part of the viscosity at zero shear rate are comparable. For $\omega = 10$, the real (viscous) part of viscosity is still larger than the imaginary (elastic) part. The fluid successively shear thins, then strain thickens—again in the range 7–8 for the critical maximum shear rate—and finally shear thins upon increasing the shear rate amplitude. Again strain thickening is caused by a rapid increase in both the real and imaginary part of viscosity. For $\omega = 20$, the imaginary part of viscosity is now the larger of the two. In this case, there is no evidence

of strain thickening (just a shoulder in $|\eta(\omega)|$ for an imposed shear rate of amplitude of 8) and the fluid shear thins almost monotonically. At $\omega = 20$, the behaviors of the real and imaginary part of viscosity with increasing shear rate strongly differ. The imaginary part of viscosity monotonically decreases with increasing shear rate amplitude. On the other hand, the real part first increases, reaches a maximum for an imposed shear rate amplitude of 7, and decreases afterwards. These results for both the elastic and viscous part of viscosity are typical of nonthickening colloidal suspensions.⁴

No strain thickening is observed for larger frequencies. On the contrary, we start to observe drops in $|\eta(\omega)|$. For $\omega = 50$, a pronounced drop in $|\eta(\omega)|$ can be observed for a shear rate amplitude of 10, which corresponds to a strain amplitude of 0.2. It is associated with drops in the potential energy as well as in the hydrostatic pressure. This drop indicates shear induced ordering, i.e., the formation of an ordered structure that we will refer to as the “low strain” structure in the remainder of the paper. Upon further increase of the imposed shear rate amplitude, we observe another discontinuity in $|\eta(\omega)|$ and the onset of another ordered phase (the “high strain” structure) for a shear rate amplitude of 40, which corresponds to a strain amplitude of 0.8. The same succession of onsets of ordered structures is also observed

FIG. 4. Low strain ($\gamma=0.24$) and high strain ($\gamma=0.4$) structure obtained for a frequency of 50 and amplitudes of 12 and 40, respectively. A slab of fluid around the plane $y=0$ is shown in both cases.

for higher frequencies. In all cases, the “low strain” structure appears when the strain amplitude exceeds approximately 0.2 and the “high strain” structure takes over when the strain amplitude is larger than 0.8. Again, these results are very similar to those obtained in experimental studies, either from

scattering experiments^{1,23} or from direct microscope imaging.²⁴ Those studies also report the successive onset of a low strain structure and of a high strain structure.

In Fig. 4 we show a slab of fluid around the plane $y=0$ in the low and high strain regimes. This plot allows us to clearly identify the structures obtained in both regimes. In the low strain regime, the close-packed direction in the hexagonally ordered planes is perpendicular to the imposed velocity. This observation is in agreement with the findings of scattering experiments¹ and direct microscope imaging.²⁴ The high strain structure is very different from the low strain structure since ordering takes place along the flow velocity rather than perpendicularly to it. Indeed, the close-packed direction in the hexagonally ordered planes is now parallel to the imposed velocity. Direct microscope imaging yields exactly the same features: in particular, the shear induced hexagonal planes are also found to be oriented with a close-packed direction along the flow velocity.²⁴

IV. ARTIFACTS ARISING FROM ASSUMPTIONS ABOUT THE FLOW PROFILE

In this section, we compare the results obtained in this work to those from previous NEMD studies. We have therefore conducted the numerical “strain sweep” experiments described in the previous section using the kinetic thermostat of Refs. 20–22. In this scheme, Eq. (5) is used to evaluate and fix the temperature through a Gaussian constraint mechanism.³⁵ This method therefore assumes that, despite the strong non-Newtonian features observed for these systems, a linear profile describes accurately the form of the fluid flow. This thermostat is often termed as a profile biased thermostat (PBT).

The norm of the complex viscosity $|\eta(\omega)|$ so obtained is plotted against the imposed shear rate amplitude and against the imposed frequency in Fig. 5. For frequencies smaller than 35, we observe a sharp drop in the complex viscosity for shear rate amplitudes of approximately 4. This behavior is very similar to that observed for the onset of a strong ordering, the so-called string phase, under steady shear. Not surprisingly, the underlying explanation is also the same. Under steady shear at high shear rates, we showed that, accord-

FIG. 5. Norm of the complex viscosity against the amplitude of the imposed shear rate and of the frequency. Results obtained using a PBT.

FIG. 6. Real and imaginary part of the complex viscosity against the amplitude of the imposed shear rate at a frequency of 20. Open (filled) circles are results obtained using a configurational thermostat (the PBT of Refs. 20–22, respectively).

ing to hydrodynamic stability theory⁴⁰ the flow profile obtained with a configurational thermostat was a superposition of the linear profile and of a sinusoidal “secondary” flow along the flow. We also showed that a sinusoidal secondary profile was allowed to develop in directions perpendicular to the flow. On the contrary, a simulation method postulating a linear profile was shown to prevent secondary flows from developing and to promote the onset of string phase. Under oscillatory shear, velocity profiles show similarly larger fluctuations and departures from the linear flow profile with a configurational thermostat. The constraint exerted by the kinetic thermostat of Refs. 20–22 on the flow profile translates into the onset of strong ordering. No thickening is observed under any circumstance. For larger frequencies, both methods seem to give results in qualitative agreement for $|\eta(\omega)|$. This is not unexpected since, as frequency increases, the real part of viscosity decreases much faster than the imaginary part, leading to little heat dissipation. In such a regime, it is not surprising that the way heat is removed from the system (i.e., the thermostatting scheme) has a smaller effect.

We now focus on the results obtained in Ref. 21 which were obtained for a simple fluid under oscillatory shear at a frequency of 20. This comparison is worthwhile since the authors also reported two successive ordered phases with increasing strain. The real and imaginary part of viscosity obtained with both thermostats for a frequency $\omega=20$, i.e., a system very similar to that studied in Ref. 21, are plotted in Fig. 6. The results we obtained using a kinetic thermostat for our system are in excellent agreement with those of Ref. 21. Indeed, both the real and imaginary part of the complex viscosity exhibit sharp drops just before the shear rate amplitude reaches 5, corresponding to a strain of 0.25. These drops are associated with the onset of a first ordered phase. Another drop in the imaginary part of viscosity can be seen for a shear rate amplitude slightly above 10, corresponding to a strain of 0.5. This drop indicates the onset of a second ordered phase. Results obtained at this frequency using a configurational thermostat strongly differ as shown in Fig. 6 and no ordering is observed at that frequency.

FIG. 7. Low strain structure obtained under oscillatory shear: (left) Using the PBT of Refs. 20–22; (right) using a configurational thermostat.

We compare the structures successively observed using a kinetic thermostat at $\omega=20$ or a configurational thermostat at $\omega=50$. Projections of the simulation cell on the x - y , y - z , and x - z planes are plotted in Fig. 7 for the low strain structure and in Fig. 8 for the high strain structure with the two thermostats. Structures obtained using a kinetic thermostat are significantly more ordered than those obtained using a configurational thermostat. Strong ordering can be seen in all directions of space with a kinetic thermostat even in the low strain structure. In particular, in the high strain regime, while ordering can only be clearly seen in the y - z plane when a configurational thermostat is used, all projections show lines along the x direction for the systems simulated with the kinetic thermostat. These plots emphasize again the constraint exerted by the kinetic thermostatting mechanism and its consequences on the microscopic mechanism underlying the ordering.

V. CONCLUSION

We have studied the non-Newtonian behavior of a simple fluid undergoing steady and oscillatory shear flow.

FIG. 8. High strain structure obtained under oscillatory shear: (left) using the PBT of Refs. 20–22; (right) using a configurational thermostat.

Unlike in previous simulation studies, the thermostatting method used in this work does not make any assumption on the form of the flow profile. Indeed, we showed in previous work that this method allowed for non-Newtonian flow profiles to develop.³⁴ Under steady shear as well as under oscillatory shear at low frequencies, a simple fluid is shown to exhibit thickening when the applied shear rate increases. At larger frequencies, shear induced ordering is observed when the applied shear rate increases. Ordering is shown to proceed first into a low strain structure, showing hexagonal planes with a closed packed direction perpendicular to the flow velocity, and then into a high strain structure, showing hexagonal planes with a closed packed direction parallel to the flow velocity. These phenomena are extremely similar to those experimentally observed in “hard sphere”-like colloidal suspensions. Many of the non-Newtonian effects observed in colloidal suspensions are attributed to the solvent. For instance, thickening is often explained invoking lubrication interactions through the squeeze mode. Our findings show that all these effects can take place even in the absence of a solvent, provided that the flow profile is not constrained to the Newtonian linear form. A more detailed analysis of the microscopic mechanism accounting for thickening is currently underway.

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