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Nanoscale simple fluid behavior under steady shear

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Abstract

In this study, we use two non-equilibrium molecular dynamics (NEMD) algorithms, boundary-driven shear and homogeneous shear, to explore the rheology and flow properties of a simple fluid undergoing steady simple shear. The two distinct algorithms are designed to elucidate the influences of nanoscale confinement. The results of rheological material functions, i.e. viscosity and normal pressure differences show consistent Newtonian behaviors at low shear rates from both systems. The comparison validates that confinements in the order of 10 nanometers is not strong enough to deviate the simple fluid behaviors from the continuum hydrodynamics. The non-Newtonian phenomena of the simple fluid is further investigated by the homogeneous shear simulations with much higher shear rates. We observe the “string phase” at high shear rates from both applying profile-biased and profile-unbiased thermostats. On the contrary to other findings where the string phase is found to be an artifact of the thermostats, we performed a thorough analysis on the fluid microstructures formed due to shear, which shows the possibility to have a string phase and second shear thinning for dense simple fluids.

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I. INTRODUCTION

Understanding shear rheology of dense fluids is of great importance for many fluid mechanics and chemical engineering applications. Low shear viscosity is generally desired to minimize pumping cost and to increase rate of mass transfer in processes such as chemical reactions and purifications. For other applications such as lubrication, higher viscosity may be favorable. Shear-induced structural orderings and phase transitions are also of fundamental and technological interests. These rheological phenomena may involve a large variety of unexpected fluid behaviors. The study of these subjects can be extremely complex at continuum scale and become even harder at microscale and nanoscale. Growing interests in miniaturized designs of micro- and nanofluidic systems and devices eagerly require a comprehensive understanding of the rheology of fluids in microscale and nanoscale confined geometries, e.g. nanochannel flows or shearing a thin film [1–3]. Highly confined nano-chambers or channels manifest predominant surface effects and finite-sized bulk effects, which could lead to fluid properties and behaviors significantly different from those at macroscale [4].

To facilitate the understanding of shear rheology, numerous theoretical, experimental and computational studies are focused on constructing the correlations between the rheology and microstructures for various fluids. In complex fluids such as colloidal suspensions and polymer solutions under a steady shear flow, both shear thinning and shear thickening were observed, along with different microstructures formed in the fluid [5–9]. These non-Newtonian behaviors, e.g. shear thinning, not only exist in complex fluids, but also observed in simple fluids under certain conditions [10]. More than one hundred years ago, Maxwell believed that all fluids have non-Newtonian properties. The reason for a simple fluid behaves Newtonian is that its characteristic time corresponding to non-Newtonian features (i.e., Maxwell relaxation time) is too short to be observed by the available analysis techniques. However, numerical simulations provide an effective way to investigate these non-Newtonian phenomena in simple fluids. One of the pioneers of this work is Erpenbeck [11], who observed shear thinning in a hard-sphere fluid at moderate shear rates ($\sim$ order of 0.1 reduced unit τ^{-1}) and an exotic “string phase” at high shear rates ($\sim$ order of 1), where particles arranged into strings in the flow direction with hexagonal symmetry in the plane normal

to the flow direction. Most studies using nonequilibrium molecular dynamics (NEMD) or nonequilibrium Brownian dynamics reported systematic and strong ordering in simple fluids undergoing either steady [12–15] or oscillatory shear flows [16, 17] when the shear rates are high. On the other hand, several groups have argued that the ordering in steady shear is caused artificially by the thermostat algorithms [18–21]. They, instead, showed amorphous particle distributions and observed shear thickening.

To obtain rheological material functions such as the shear viscosity and the normal pressure differences, the NEMD provides the ability to computing transport coefficients in a wide range of shear rates. There are two popular NEMD algorithms to generate a steady shear flow. One is the boundary-driven shear (Fig. 1(a)), where the simulation mimics realistic interactions between the walls and the fluid and observe the steady state of the closed system. The boundary-driven shear generates a shear flow in a physical way by moving either one of the walls or both walls. The other is the homogeneous shear (Fig. 1(b)), which ignores the surface effect by only simulating the fluid ensemble and focuses more on the “bulk” properties of the fluid under shear. Among homogeneous shear methods, the SLLOD and its related methods involving the Lees-Edwards boundary conditions are perhaps better known [22, 23]. These methods specify a shear field through a fictitious force term in the equations of motion and manipulate the simulation boundaries to preserve the flow. Liem et al. [24] showed that these two classes of methods gave similar results for key thermodynamics properties at sufficiently moderate shear rates. For both of these NEMD algorithms, the material functions are measured via appropriate components of the pressure tensor.

The objectives of this study are two folds: 1) To perform rheological studies of a simple fluid at nanoscale using the boundary-driven shear and the homogeneous shear. The flow velocity profiles and rheological quantities from both systems when they are under low shear rates ($\sim$ order of 0.01 and smaller) are compared. The results are expected to be similar at low shear rates since the confinement in this study is not strong enough to cause the breakdown of bulk hydrodynamics (usually $\sim 1\text{-}2$ nm). [3, 4] 2) To obtain the rheological quantities at high shear rates using homogeneous shear and correlate them with microstructural changes in the fluid. The corresponding non-Newtonian behaviors will be examined. To prevent the appearance of the artifacts induced from the thermostats, appropriate ther-

mostats are carefully applied in order to reduce viscous heating and allow the system to reach a steady state without imposing a bias onto the system.

The outline of the paper is as follows: the details of the simulation models, system geometries, and thermostats to be used are presented in Section II. They are followed by the results and discussions in Section III. In this section, we will closely examine the surface effects by comparing the fluid behaviors from the two NEMD systems. The non-Newtonian behaviors such as shear thinning, second shear thinning, and microstructures in the fluid will be analyzed. Their relationships with the rheological material functions will also be studied. Finally, the conclusions are drawn in Section IV.

II. NUMERICAL MODELING AND SETUP

A. Material Functions

Rheological material functions are functions characterizing the rheological behaviors of a fluid. They depend on the stress responses $\boldsymbol{\tau}$ of a material when undergoing shear and elongational flows. The material functions, in general, are functions of time and kinematic parameters, e.g. strain or strain rate, that correspond to the type of flow imposed on the material.

Shear viscosity, η , is a material function that is the most commonly sought after as a rheological quantity in a steady shear flow. It is the primary material property that distinguishes a non-Newtonian fluid from a Newtonian fluid. For a Newtonian fluid, the shear viscosity η is a constant that is independent of the shear rate $\dot{\gamma}$, whereas for a non-Newtonian fluid η could be a function of the shear rate, $\eta = \eta(\dot{\gamma})$. Shear thinning and shear thickening are the two most common phenomena that are associated with varying viscosity in a non-Newtonian fluid. For steady simple shear flows, η is typically defined as the ratio of the steady-state shear stress to the shear rate $\dot{\gamma}$:

$$\eta(\dot{\gamma}) = \lim_{t \rightarrow \infty} \frac{\tau_{xz}(t)}{\dot{\gamma}} = - \lim_{t \rightarrow \infty} \frac{P_{xz}(t)}{\dot{\gamma}}. \quad (1)$$

As shown in the equation, the shear stress can also be related to the pressure tensor, $\mathbf{P}$, in the fluid. The shear rate $\dot{\gamma}$ is a gradient of one component of the fluid velocity, say the x direction (flow direction), with respect to another direction, say the z direction (gradient direction), $\frac{\partial v_x}{\partial z}$. The corresponding shear stress τ_{xz} represents the collinear momentum flux j_{xz} of the x component of the momentum p_x transported in the z direction per given time per unit area.

Another two important rheological material functions are the normal pressure differences. They are defined as,

$$p_- = \frac{1}{2}(P_{xx} - P_{zz}); \quad p_0 = \frac{1}{2} \left[P_{yy} - \frac{1}{2}(P_{xx} + P_{zz}) \right]. \quad (2)$$

p_- is associated with rotation of the distorted microstructure and p_0 reflects the nonlinear bulk deformation [25, 26]. For a Newtonian fluid, both p_- and p_0 are expected to be zero. In macroscopic non-Newtonian fluids, these normal pressure differences are responsible for a wide variety of interesting phenomena such as the Weissenberg effect [27]. The non-zero values of these two normal pressure differences are the key quantities associated with a non-Newtonian fluid.

As we have shown, these three rheological material functions all involve the computing of the pressure tensor, $\mathbf{P}$. In molecular dynamics simulations, several different methods have been used to calculate the pressure tensor. The popular zeroth-order approximation of Irving-Kirkwood expression [28] (same as the virial expression) calculates the pressure tensor in the domain of interest as:

$$P_{\alpha\beta} = \frac{1}{V} \left(\sum_i^N m_i v_{i\alpha} v_{i\beta} + \frac{1}{2} \sum_i^N \sum_{j \neq i}^N r_{ij\alpha} f_{ij\beta} \right). \quad (3)$$

α and β represent the directional indices. i and j are the atom indices. V is the volume of the domain of interest. m_i and $\mathbf{v}_i$ are the particle mass and velocity, respectively. $\mathbf{r}_{ij}$ and $\mathbf{f}_{ij}$ are the distance and force vectors between a pair of particles. The first term in Eq. (3) is the kinetic part and the second one is the virial part. Noting that for shear flows, $\mathbf{v}_i$ is the *thermal* or *peculiar* velocity with respect to the streaming velocity of the flow. This

approach of computing the pressure tensor can be used for both boundary-driven shear and homogeneous shear NEMD.

In the boundary-driven shear, the existence of the real solid walls provides an alternative way to compute P_{xz} directly from the shear forces of the fluid atoms exerted on the wall atoms, $\mathbf{F}$:

$$P_{xz} = \sum_i^{N_{wall}} \sum_j^{N_{fluid}} F_{ij}^x / A_z, \quad (4)$$

where F_{ij}^x is the x component of force exerted on atom i due to atom j . $A_z = L_x \times L_y$ is the area of the wall normal to the z direction. We will employ the results of both methods in calculating the viscosity in the boundary-driven shear simulations. Both methods are expected to yield the same statistical results at the steady state equilibrium, when the shear stress at the interface is the same as the internal fluid stress. For the normal pressure differences, only the Irving-Kirkwood expression is used since the diagonal components of the pressure tensor in Eq. (2) refer to the fluid-fluid interactions.

B. Computational Details

1. Molecular potential

In our molecular dynamics simulations of a simple fluid, only the short-range pairwise interactions between atoms are considered such that all atoms are treated as Lennard-Jones (LJ) particles. The interactions are modeled using the LJ potential:

$$V_{ij}(r) = 4\varepsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r} \right)^{12} - \left(\frac{\sigma_{ij}}{r} \right)^6 \right], \quad (5)$$

where r is the distance between any two atoms; ε_{ij} and σ_{ij} define the characteristic energies and length scales of the potential, respectively. A cutoff radius $r_c = 3.0 \sigma_{ff}$ for LJ potential is applied to all interactions to reduce computational time.

In homogeneous shear simulations, subscriptions i and j are the indices for any two fluid atoms. In boundary-driven shear simulations, these indices represent either fluid or wall

atoms. Parameters for interactions between different atom types are calculated using the geometric mixing rules,

$$\varepsilon_{wf} = \sqrt{\varepsilon_{ww}\varepsilon_{ff}}, \quad \sigma_{wf} = \sqrt{\sigma_{ww}\sigma_{ff}}. \quad (6)$$

The mass, potential and size of all the wall atoms are the same as the fluid atoms, which lead to a relatively strong wall-fluid interaction $\varepsilon_{wf} = 1.0 \varepsilon_{ff}$ that makes the walls very hydrophilic [29, 30]. It is expected to yield no-slip condition at low wall shearing velocity. LJ reduced units are used in the simulations that are non-dimensionalized with respect to the fluid parameters. All the subscripts in the parameters hereon are dropped.

2. System setups

The boundary-driven shear model uses an orthogonal simulation cell. As shown in Fig. 1(a), x is the flow or the shearing velocity direction, z is the velocity gradient direction, and y is called the neutral or vorticity direction. Periodic boundary conditions are imposed in the x and y directions. The steady simple shear flow is generated by moving the upper wall at a uniform velocity U_0 along the positive x direction while keeping the lower wall stationary. This NEMD simulation mimics a realistic experimental setup. The atomic sites are on the [001] plane of a fcc lattice with a lattice constant of 1.01σ . The two walls are rigid walls without thermal motion, where the forces on wall atoms are zeroed out in order to maintain a perfect lattice structure during the simulation. The purpose of imposing rigid walls is to simplify the analysis by decoupling the dynamics of the fluid flow from the thermal effects generated from the viscous heating in the fluid and heat conduction at the fluid-solid contact. Each wall consists of 1800 atoms that form four layers. The wall has a thickness of $\delta = 1.51 \sigma$ and the fluid is confined in a channel with height $h \approx 40 \sigma$. The fluid slab contains 7614 fluid atoms and has a density of $\rho_f \approx 0.844 \sigma^{-3}$. The density ratio between the wall and the fluid is $\rho_w/\rho_f = 4.62$, which produces a highly incommensurable interface. The entire simulation cell $L_x \times L_y \times L_z$ is about $15.13 \times 15.13 \times 44.88 \sigma^3$.

In the homogeneous shear simulations, we employ a non-orthogonal system with the deforming cube representation of the Lees-Edwards boundary conditions instead of the com-

monly used orthogonal coordinate system in the sliding brick representation. The images of the atoms are taken with respect to a skew coordinate system in which the z -axis forms an angle of $\theta = \cot^{-1}(\dot{\gamma}t)$ from the x -axis. Applying Lees-Edwards boundary conditions alone is capable of producing a shear flow. However, the shear motion induced purely by this boundary condition takes time to propagate to the interior of the system, typically with the speed of sound. To eliminate this time lag, a typical practice is to artificially superimpose a linear velocity profile at the start of the nonequilibrium simulation. We first let the system reach the equilibrium state and calculate the momentum of each particle $\mathbf{p}_i^0$. At the beginning of the nonequilibrium simulation, $t = 0$, we superimpose a linear velocity profile onto the particles in the equilibrated system by applying momentum $\mathbf{p}_i(t = 0) = \mathbf{p}_i^0 + \hat{\mathbf{i}}m_i\dot{\gamma}z_i(t = 0)$, where i is the particle index and $\hat{\mathbf{i}}$ denotes the unit vector in the x direction for the simple shear. We then let the system evolve by conventional Newtonian dynamics. Superimposing a profile immediately generates the shear flow, and the Lees-Edwards boundary conditions preserve the flow. The number of fluid atoms in the homogeneous shear simulations ranges from 1728 to 62208. The size of the simulation cell ranges from $20.16 \times 20.16 \times 5.04 \sigma^3$ to $120.94 \times 120.94 \times 5.04 \sigma^3$. The different simulation sizes are necessary to obtain enough statistics for each of the thermostats used. The details are explained in the next section.

All simulations initially assign fluid atoms with random velocities according to the Gaussian distribution that is scaled to produce a desired temperature with a mean of 0.0. The equations of motion is integrated using the velocity-Verlet algorithm with a time step of 0.005τ in LAMMPS Molecular Dynamics Simulator[31], where $\tau = (m\sigma^2/\varepsilon)^{1/2}$ is the characteristic time of the LJ potential. However, the time step may be reduced to 0.0003τ for homogeneous shear with very high shear rates. In all simulations, it takes 1×10^5 time steps for the system to first reach equilibrium. Boundary driven shear simulations typically require another 1×10^6 steps to reach steady state once shearing starts. The production period is at least another 5×10^5 steps to obtain statistical averages for stress, fluid velocity and density profiles. It may extend to 3×10^6 steps for low wall shearing velocity simulations to achieve better statistics. Homogeneous shear simulations require at least 5×10^5 steps to reach steady state after shearing, it is then followed by 5×10^5 to 5×10^6 production steps.

3. Thermostats

As long as the system is off-equilibrium, there is viscous dissipation occurring. Since we intend to decouple the thermal effects from the dynamics of the fluid, a thermostat device is applied exclusively on fluid particles to enforce uniform temperature everywhere in both boundary-driven shear and homogeneous shear simulations. Nosé-Hoover chain (NHC) thermostat [32] is a time-reversible and deterministic thermostat generating a well-defined canonical ensemble. It can be easily coupled to the system equations as the following:

$$\begin{aligned}
\dot{\mathbf{r}}_i &= \frac{\mathbf{p}_i}{m_i}, \\
\dot{\mathbf{p}}_i &= \mathbf{F}_i - [\mathbf{p}_i - m_i \mathbf{u}_s(\mathbf{r}_i)] \frac{p_{\eta_1}}{Q_1}, \\
\dot{\eta}_i &= \frac{p_{\eta_i}}{Q_i}, \\
\dot{p}_{\eta_1} &= \left[\sum_i^N \frac{[\mathbf{p}_i - m_i \mathbf{u}_s(\mathbf{r}_i)]^2}{m_i} - N_f k_B T \right] - p_{\eta_1} \frac{p_{\eta_2}}{Q_2}, \\
\dot{p}_{\eta_j} &= \left(\frac{p_{\eta_{j-1}}^2}{Q_{j-1}} - k_B T \right) - p_{\eta_j} \frac{p_{\eta_{j+1}}}{Q_{j+1}}, \quad 1 < j < M \\
\dot{p}_{\eta_M} &= \left(\frac{p_{\eta_{M-1}}^2}{Q_{M-1}} - k_B T \right).
\end{aligned} \tag{7}$$

Here, $\mathbf{r}_i$ and $\mathbf{p}_i$ are the particle position and momentum in laboratory frame of reference, respectively. $\mathbf{F}_i$ is the total conservative force on particle i , M is the length of the thermostat chains, and Q_j , $1 \leq j \leq M$ are thermostat coupling coefficients. N_f is the number of degrees of freedom. $\mathbf{u}_s(\mathbf{r})$ is an important variable, which is the instantaneous local streaming velocity of the shear flow. The determination of $\mathbf{u}_s$ is not a trivial procedure because an incorrect evaluation could cause a thermostat to generate unphysical behaviors on the particles.

The thermostat can be classified into profile biased-thermostat (PBT) and profile-unbiased thermostat (PUT) based on the specific definition of $\mathbf{u}_s$. For planar simple shear flows, if we assume $\mathbf{u}_s(\mathbf{r}) = (\dot{\gamma} \times z, 0, 0)$, the corresponding thermostat is referred to as PBT. The PBT artificially maintains the linear velocity profiles, and any deviation from the linear profile is interpreted as the thermal fluctuation and is inhibited by the thermostat.

As pointed out by Evans and Morriss [18], the PBT could be a reasonable assumption for low shear rates. However, as shear rate increases, the Reynolds number increases and it is possible that a secondary flow due to turbulence may develop. An attempt to restore the linear profile at high shear rates is considerably dubious; the PBT might distort the dynamics of the system and cause artificial shear thinning.

On the other hand, if the streaming velocity profile is not assigned *a priori* but computed locally via simulations, the thermostat is categorized as PUT. In the past decades, the discussions of PUT have prompted different ways to compute the instantaneous local streaming velocity. Two notable ways are: 1) representing the streaming velocity by a finite Fourier series expansion and computing the Fourier coefficient [19, 20, 33], and 2) computing spatially averaged particle velocity within sub-domains of a simulation cell [14, 18, 34–36]. Here, we choose to calculate the streaming velocity using the latter for its robustness and easiness in implementation. The $\mathbf{u}_s$ of each sub-domain is evaluated by averaging the velocity of the particles within every time step. Similar to the notation introduced by Evans et al. [33], the simulation cell is divided into sub-domains: slabs for 1D coordinate dependences, bins for 2D coordinate dependences and bricks for 3D coordinate dependences. If $(x \times z)$ PUT is assumed, the simulation cell is divided into slabs with thickness D_z in the z direction. If $(xyz \times yz)$ PUT is assumed, slabs are further subdivided into bins along the y direction, which means that the streaming velocity has three (xyz) components and are functions of yz . A $(xyz \times xyz)$ PUT means three Cartesian components of the instantaneous local streaming velocity are allowed to be functions of the coordinates $(x, y$ and $z)$, $\mathbf{u}_s(\mathbf{r}) = u_{sx}(x, y, z)\hat{\mathbf{i}} + u_{sy}(x, y, z)\hat{\mathbf{j}} + u_{sz}(x, y, z)\hat{\mathbf{k}}$. It is well-known that PBT might dissipate heat and inhibit the form of secondary flow. PUT could underestimate the temperature because the thermal velocity could be mis-identified as the local streaming velocity while the particles remain un-thermostated. To correctly distinguish the thermal and streaming parts of the total velocity, the sub-domain dimensions, especially that of the directions with huge velocity gradient, e.g. the shear is imposed in the z -direction in this case, have to be chosen

with caution by the following criterion [34]:

$$\frac{\dot{\gamma} D_z}{v_{th}} \ll 1 \ll \rho V_{sd}. \quad (8)$$

ρ is the prescribed average particle density. $V_{sd} = D_x \times D_y \times D_z$ denotes the sub-domain volume. $v_{th} = \sqrt{k_B T / \min(m_i)}$ is the highest characteristic thermal velocity among particle species. This requirement means that the choices of D_x , D_y and D_z should be large enough to provide a reliable statistic in each sub-domain and small enough to ensure an accurate local description of streaming velocity even at high shear rates. In our simulations, it usually results in hundreds of slabs in the z direction.

For the boundary-driven shear, applying the NHC thermostat needs a choice of auxiliary algorithm PBT or PUT. As a result of the possible slip appearing at the fluid-solid interface, it is impractical to apply PBT by assuming an *a priori* linear velocity profile. Thus, the fluid temperature is controlled at $T = 1.1 \varepsilon / k_B$ using PUT by applying the thermostat every time step with a relaxation time of 0.05τ . In the homogeneous shear, $T = 1.1 \varepsilon / k_B$ is fixed by the NHC thermostat with either PBT or PUT assumption. The relaxation time of the thermostat is much smaller comparing to the boundary-driven shear, and is varied for each simulation.

III. RESULTS AND DISCUSSIONS

A. Boundary driven shear simulations

In boundary driven shear simulations, the fluid is confined between two solid walls. The bulk of the fluid has a large surface-to-volume ratio, where the interface may have a significant impact on the dynamic and structural properties of the bulk fluid. Previous simulation studies [1, 37–39] confirmed that a solid wall constrains the motion of fluid atoms in both directions parallel and perpendicular to the wall.

1. Velocity profiles vs. shear rates

Moving the upper wall shears the fluid slab and creates a steady simple shear flow (or planar Couette flow), which ideally should demonstrate a linear velocity profile. The time-averaged fluid velocity profiles for shearing velocities of $U_0 = 1.0 \sigma/\tau$ to $U_0 = 9.0 \sigma/\tau$ are plotted in Fig. 2(a). When the shearing velocity is low, e.g. $U_0 = 1.0 \sigma/\tau$, the velocity profiles are perfectly linear in the bulk fluid region away from the walls. The velocity profiles has small nonlinearities adjacent to the walls, which corresponds to the large wall-induced fluid density oscillations. This linear trend is consistent with the expectation for a Newtonian fluid under steady simple shear. When the applied shearing velocity is higher, i.e. $U_0 = 3.0, 5.0$ and $7.0 \sigma/\tau$, their velocity profiles are no longer linear even in the bulk region. This nonlinearity is also observed in previous MD studies on simple fluids [39, 40]. Figure 2(b) shows the deviations of these velocity profiles from a linear profile. In this shearing velocity range, the fluid still remains amorphous and homogeneous except near the interface.

The reason for this nonlinearity in the velocity profile is the temperature in the system. Even though we intend to disassociate the dynamic and structural behaviors from the thermal effect by enforcing a uniform fluid temperature, as the shear rate gets higher, the fluid temperature inside the system starts to deviate from the set temperature of $T = 1.1 \varepsilon/k_B$. This has also been observed in other studies [24, 40, 41]. To examine how the fluid temperature alters as a result of the shearing, a local fluid temperature (kinetic temperature) as a function of z for each slab of the simulation cell is computed by using the kinetic energy:

$$k_B T(z^j) = \frac{m_i}{3N^j - 3} \sum_{i=1}^{N^j} [\mathbf{v}_i - \mathbf{u}_s(\mathbf{r}_i)]^2, \quad (9)$$

where $\mathbf{v}_i$ is the particle velocity, $\mathbf{u}_s$ is once again the local streaming velocity, z^j and N^j are the center coordinate of the j th slab in the z direction and the number of fluid atoms in the j th slab, respectively. Three degrees of freedom are cautiously excluded when evaluating the local temperature because it is already involved in the evaluation of the local streaming velocity [34]. Figure 3 shows the time-averaged temperature profiles of the bulk fluid for

different wall shearing velocity U_0 . It is evident that the fluid starts to heat up near the walls when U_0 exceeds $3.0 \sigma/\tau$. The increase of the fluid temperature at both lower and upper interfaces have the same magnitude. The core reason of the heating up is that the rate of local viscous heating becomes significant when large slip velocities emerge. Simultaneously, the temperature around the center plane along the channel height exhibits a significant drop. This is to “maintain” the averaged temperature as the set temperature because the feedback mechanism of the NHC thermostat is based on the average temperature of the entire fluid.

As the shearing velocity reaches $U_0 = 9.0 \sigma/\tau$, the fluid forms a “layered” structure, referred to as the layer regime in the previous study [39]. The velocity profile has a segment with approximately constant velocity, representing the collective translational movement of the layers. In the region where the fluid remains amorphous, the velocity still increases monotonically to match up with the upper wall shearing velocity. With the appearance of these ordered layers, the temperature becomes totally nonuniform and asymmetric (see Fig. 3). The layer region has a temperature lower than the melting point corresponding to a solid-like structure. The emergence of the layer structures can be explained based on thermal instability associated with the global nature of the NHC thermostat: at the start of the nonequilibrium process, the top wall starts moving from stationary. This large shearing force between the interacting fluid and the wall generates a large friction that results in substantial heating up at the upper interface, which causes spontaneous symmetry breaking in the fluid system. The thermostat responds to that by significantly increasing a damping term which reduces the thermal motion of other fluid atoms besides those at the upper interface. Once the local temperature of certain part of the fluid drops below the melting point, the fluid is going to nucleate and the spacial-modulated fluid atoms in the first fluid layer serve as nuclei. This mechanism explains why the formation of the layers always start within the first fluid layer adjacent to the bottom wall and then propagate to the bulk.

2. *Material functions vs. shear rates*

Besides the velocity profiles examined above, the material functions can also provide a clear and quantitative representation of the nature in simple LJ fluids. In the boundary

driven shear simulations, the viscosity for different fluid shear rates (up to the onset of layer regime) are calculated from both Irving-Kirkwood (Eq. (3)) and the shear force (Eq. (4)) approaches, shown in Fig. 4(a). When the layer appears, there is no physical definition of global shear viscosity in an inhomogeneous system. The fluid shear rate $\dot{\gamma}$ here is not directly proportional to the applied wall shearing velocity U_0 due to slippage at the interface. A high fluid shear rate cannot be produced due to the possible “overshear” of the fluid when a large wall shearing velocity is applied, which means that the fluid stays stagnant when the wall velocity is too high [42]. For a range of $U_0 = 0$ to $7.0 \sigma/\tau$, a range of fluid shear rates from 0 to $0.12 \tau^{-1}$ is produced. The approaches of calculating pressure tensor yield very close viscosity results. Therefore, the fluid viscosity hereafter is expressed using the average of the two results. Consistent with previous MD results [40, 43], the shear viscosity is found to be nearly constant at $\eta = 2.35 \pm 0.02 \varepsilon\tau\sigma^{-3}$, and remains independent of the shear rate. This value is slightly lower than the value obtained later by our homogeneous shear and previous report [44]. We believe that the small deviation is caused by the surface effects of the nanoscale confinement. We conduct a series of simulations with different channel heights, and the result shows that the shear viscosities of the confined systems converge slowly to the one of the homogeneous shear system when increasing the height.

Two normal pressure differences p_- and p_0 are also measured, shown in Fig. 4(b). Both are approximately zero in most of the simulated shear rates, up to $\dot{\gamma} = 0.1 \tau^{-1}$, but become slightly non-zero at higher shear rates $\dot{\gamma} > 0.1 \tau^{-1}$. This is a clear indication of the fluid transferring from Newtonian to non-Newtonian. However, if we trace back to the velocity profiles in Fig. 2, the nonlinearity starts to be significant at $U_0 = 3.0 \sigma/\tau$, corresponding to a fluid shear rate of $\dot{\gamma} = 0.06 \tau^{-1}$. At this shear rate, it still has a constant viscosity and zero normal pressure differences. Therefore, based on the quantitative studies of the material functions, it is clear that the nonlinearity in the velocity profile appears before the fluid transfers to non-Newtonian. This indicates that the nonlinearity is primarily induced by the viscous heating (from the temperature profiles), rather than the fluid transferring from Newtonian to non-Newtonian.

B. Homogeneous shear

In the homogeneous shear simulations, only the “bulk” of the fluid is modeled where the shear flow is driven by the initial perturbation with the Lees-Edwards periodic boundary conditions on the moving surface layer of the fluid atoms. The internal fluid is driven by its adjacent fluid in the shear flow. The fluid shear rate, therefore, can reach much higher values comparing to the boundary driven shear. Because the systems to be considered are at nanometer scales, the Reynolds numbers are maintained at low values even at extremely high shear rates. Therefore, the homogeneous shear simulation provides a unique approach to study non-Newtonian behaviors at high shear rates without turbulence complicating the analysis. Similar to the boundary driven shear simulations, we will first examine the non-Newtonian behaviors of simple fluids and thermostat influences by studying the velocity profiles of the system. Then the non-Newtonian behaviors will be examined quantitatively from the rheological material functions. The origin of these non-Newtonian phenomena will be revealed by investigating the microstructure formed in the fluid.

1. *Velocity profiles vs. shear rate*

A range of shear rates $\dot{\gamma}$ from 0.001 to 10.0 τ^{-1} is imposed on the fluid boundary. These shear rates are far beyond what the boundary driven shear can produce, but still have their corresponding Reynolds numbers to remain within laminar condition. Here, we examine two representative shear rates, $\dot{\gamma} = 1.0 \tau^{-1}$ and $\dot{\gamma} = 5.0 \tau^{-1}$. The velocity profile along the channel height direction z for these two shear rates are shown in Fig. 5(a). Three thermostats: PBT, 2D PUT ($xz \times z$), and 3D PUT ($xyz \times yz$) are used and their results are compared. At relatively lower shear rate, e.g. $\dot{\gamma} = 1.0 \tau^{-1}$, the V_x velocity profiles using the three different thermostats all show linear trend and yield nearly identical results. Linear profiles indicate that there is no significant secondary flow. The fluid is amorphous at this shear rate. At high shear rate, e.g. $\dot{\gamma} = 5.0 \tau^{-1}$, the velocity profile in Fig. 5(a) shows that ($xyz \times yz$) PUT yields substantially larger fluctuations of instantaneous profile in the y - z plane where the disturbance in y and z directions is not prohibited by the thermostat.

Secondary flows in the y - z plane is observed. Figure 5(b) shows the magnitude of the disturbance in the y - z plane, which is computed as $|V_{yz}|(z) = \sqrt{V_y(z)^2 + V_z(z)^2}$. Meanwhile, PBT prevents these behaviors and maintains a linear profile with no disturbance.

At the high shear rate of $\dot{\gamma} = 5.0 \tau^{-1}$, a string phase appears for all three thermostats. The string phase is where atoms form hexagonal pattern in the y - z plane (i.e. vorticity-velocity gradient plane) as shown in Fig. 6. It is usually associated with significant instantaneous fluctuations and shear localization. They appear in the form of discontinuities in the velocity profile [45], as we also see in Fig. 5(a). Unlike the layered structures we found in the boundary driven shear simulations, which are the artifacts of the thermostats, the string phase appears most likely because of the non-Newtonian nature of the fluid. Unfortunately, this cannot be verified by the experiment with the current available techniques. However, it is able to draw similarity of the string phase with the observation from colloidal suspensions [7, 46]. Following section on material functions analysis will discuss further on the possible microstructures appearing in simple fluids.

2. Material functions vs. shear rate

The shear viscosity of shear rates from 0.001 to $10.0 \tau^{-1}$ is first studied, shown in Fig. 7(a). The results from the three thermostats yield nearly the same result and showed consistent shear rate dependency. Noting that the quality of the data obtained at very low shear rates is quite poor, especially for the shear viscosity. It appears that the fluctuation at low shear rates makes a large noise-to-signal ratio, which makes it difficult to measure. The shear viscosity can be separated into three regions by two characteristic shear rates, the non-Newtonian transition shear rate $\dot{\gamma}_{nt}$ and the critical shear rate $\dot{\gamma}_{cr}$. The non-Newtonian transition shear rate $\dot{\gamma}_{nt}$ locates at $\dot{\gamma}_{nt} \approx 0.1 \tau^{-1}$, which separates the viscosity from constant (Newtonian) to shear-thinning region (non-Newtonian). The shear-thinning region can be fitted well by the three-parameter Carreau model [47]. This transition shear rate has a magnitude that is consistent with the result we obtained in the boundary-driven shear. The critical shear rate $\dot{\gamma}_{cr}$ defines the transition from the shear-thinning region to a third region which is separated by a sudden drop in the viscosity at $\dot{\gamma}_{cr} \approx 3.0 \tau^{-1}$. The third region is normally named

as the second shear-thinning region because of the rapid decrease in viscosity. The fluid remains amorphous until the shear rate reaches $\dot{\gamma}_{cr}$, and the string phase emerges along with the second shear thinning above $\dot{\gamma}_{cr}$. The viscosity drop associated with the string phase was analyzed by previous studies [13, 48]. When strings appear, the fluid particles are more widely spaced within a string than between the strings, which leads to a higher self-diffusion coefficient component in the x direction. Consequently, the viscosity decreases.

The two normal pressure differences as functions of the shear rates are shown in Fig. 7(b). At low shear rates, p_- and p_0 are approximately zero, which is associated with the constant viscosity confirming the atomistic fluid is Newtonian at low shear rates. In the shear thinning region, both normal pressure differences decrease monotonically until reaching $\dot{\gamma}_{cr}$. For $\dot{\gamma} > \dot{\gamma}_{cr}$, p_- and p_0 scatter without any obvious trend, which is related to the appearance of the string phase. In this range of shear rates, the string phase contains large fluctuations of flow properties and shear localization, therefore the material functions resulted from different thermostats in the second shear thinning region are shown to be more sporadic.

Stability analysis and direct numerical simulations [49, 50] found that the linear velocity profile for simple shear flow is stable upon arbitrary infinitesimal perturbations for $Re < 125$. For the systems in this work, the critical shear rate $\dot{\gamma}_{cr} \approx 3.0 \tau^{-1}$ corresponds to $Re \approx 9.8$. Therefore, rheological behaviors, such as the viscosity and the pressure differences observed above are truly due to the non-Newtonian nature of the simple fluid preventing the possible onset of turbulence.

The consistent non-Newtonian behavior and the appearance of the string phase we observe from all three thermostats contradict with other studies [18, 51], where McWhirter showed that a $(xyz \times xyz)$ PUT prevents the onset of the string phase because of large vortices exist in the y - z plane [51]. On the contrary, the PUT thermostats we have simulated still sustain the string phase as long as the spatial average of particle velocity is statistically reliable.

A possible physical interpretation of the string phase is proposed as the following by an analogy to colloidal suspensions. In a comprehensive discussion on colloidal suspensions [9, 52], Foss et al. stated that the string phase forms in colloidal suspensions when there are repulsive forces among colloidal particles. The repulsive forces prevent particles from getting close enough for the build-up of short-range lubrication forces which disrupt any

order that may form. For simple fluids, the absence of solvent means there is no lubrication force to prevent the onset of string phase and the shear thinning continues. Thus, based on the similarities in the formation of string phase, we believe that the string phase we observe is likely not an artifact and it is possible to have second shear thinning and string phase to occur in simple fluids. To investigate whether the string phase is possibly a physical behavior induced by high shear rates, we further look into the pattern of the fluid structural change due to different shear rates.

3. Shear induced microstructures

The shear-induced distortion of fluid particle distribution is believed to be responsible for the non-Newtonian phenomenon in simple fluids [10]. The behavior is similar to colloidal suspensions [53]. To qualitatively investigate the structural change, the projections of pair distribution function $g(\mathbf{r})$ on different planes are measured. The pair distribution function describes the distribution of distances between pairs of particles contained within the simulation cell. The projection of it on the x - y plane is defined as

$$g(x, y) = \frac{N(x, y, \Delta x, \Delta y)}{N_t \rho_{xy} A(x, y, \Delta x, \Delta y)}, \quad (10)$$

where $N(x, y, \Delta x, \Delta y)$ is the number of particles found in a square area $A(x, y, \Delta x, \Delta y)$ located at (x, y) with respect to the sampled center particle, N_t is the total number of particles within the simulation cell and ρ_{xy} is the planar number density in the x - y plane. Other projections can be obtained in the same manner.

Figure 8 shows $g(\mathbf{r})$ been projected onto three different planes (x - z , y - z and x - y) when the fluid is sheared at shear rates $\dot{\gamma} = 0.0, 0.5, 2.0, 5.0 \tau^{-1}$. Column “eqm” is a reference and depicts the equilibrium particle distribution for the fluid at rest, i.e. $\dot{\gamma} = 0.0 \tau^{-1}$. The intensity of the distribution corresponds to the probability of finding a particle in a given region and is measured by the darkness of the shading: the lighter, the greater the probability. Since the fluid is isotropic at equilibrium, $g(\mathbf{r})$ has no directional dependence. The intensity pattern is radially symmetric in all three planes as expected. For Newtonian

flow regime when “ $\dot{\gamma} = 0.5$ ”, the microstructure distortion is mainly limited in the x - z plane, i.e. velocity-velocity gradient plane, where the circular pair distribution function becomes a biaxial ellipsoid with the long principal axis aligning with the extensional axes at $\pi/4$ and the short principal axis aligning with the compressive axes at $3\pi/4$. The intensity becomes higher along the compressive axes in the second and fourth quadrants. The projection of $g(\mathbf{r})$ on the y - z plane still preserves to be radially symmetric. When shear thinning occurs, e.g. “ $\dot{\gamma} = 2.0$ ”, the deformation of $g(\mathbf{r})$ is so large that the long axis rotates away from the extensional axes in the x - z plane and distortion is introduced even in the y - z plane. These microstructure distortions in fluid atoms closely relate to the shear thinning with negative p_- and p_0 . Based on these observations, the shear thinning can be explained such that as the shear rate rises, shear stress rises correspondingly, the particles diffuse against the flow trying to recover to their un-stressed equilibrated distribution. The particle diffusion eventually can no longer keep up with the flow and the microstructure distortion saturates, and shear thinning starts. As the shear rate further increases, e.g. $\dot{\gamma} = 5.0$, the ordered structures for the string phase appears. A hexagonal pattern is clearly found in the y - z plane.

PUT thermostat is used in this simulation. The system with PBT yields very similar pair distribution function as the one in the system with PUT, which confirms that different thermostats do not influence the essential behaviors of the systems. This study shows that it is possible the formation of the string phase is due to the high shear rate, not the choices of thermostats.

IV. CONCLUSIONS

In this study, we simulated a simple fluid using two different NEMD approaches: the boundary-driven shear and homogeneous shear algorithms. Our rheological results of the simple fluid validated the confinement used in this work was not strong enough to deviate from the bulk hydrodynamics. At low shear rates, the simple fluid showed its Newtonian nature, e.g. constant shear viscosity and zero normal pressure differences, consistently in the boundary-driven shear simulations and homogeneous shear simulations. The nonlinearities

of the velocity profiles in the bulk fluid region found in the boundary-driven shear simulations were due to the temperature variations caused by interfacial friction generated at the surfaces. The layer structures formed in the fluid are also an artifact due to the thermostat.

The non-Newtonian behaviors of simple fluids at high shear rates were further studied by the homogeneous shear simulations. The PBT and PUT essentially yielded identical non-Newtonian phenomena for simple fluids when applying NHC thermostat. The minor differences between PBT and PUT were only revealed in the velocity profiles and small discrepancies in the material function after the onset of the string phase. By relating the first shear thinning to the shear-induced fluid microstructure distortion and the particle pair distribution function, we discussed a rational hypothesis on the formation of string phase. Our results suggest that the second shear thinning and the string phase are possibly physical behaviors due to the high shear rates rather than purely thermostat artifacts for dense simple fluids. Taking into account the global and local natures of different thermostat algorithms may also be required for a better understanding of non-Newtonian behaviors of simple fluids at high shear rates.

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FIGURES

FIG. 1. Schematics of the: (a) boundary-driven shear and (b) homogeneous shear.

(a)

(b)

FIG. 2. Time-averaged (a) velocity profiles and (b) deviations of the velocity profiles from their corresponding linear forms along the z direction.

FIG. 3. Time-averaged temperature profiles as a function of z for the tabulated shearing velocities.

(a)

(b)

FIG. 4. (a) Shear viscosity of the fluid in the channel using the Irving-Kirkwood expression (open circles) and the shear force expression (stars), (b) normal pressure difference p_- (crosses) and p_0 (open prisms) at various shear rates.

(a)

(b)

FIG. 5. (a) Time-averaged fluid velocity profiles along the z direction and (b) magnitude of the disturbance in the $y-z$ plane in systems with different thermostats at $\dot{\gamma} = 1.0 \tau^{-1}$ and $\dot{\gamma} = 5.0 \tau^{-1}$.

FIG. 6. A snapshot of the string phase on $y - z$ plane view when $\dot{\gamma} = 5.0 \tau^{-1}$.

(a)

(b)

FIG. 7. (a) Fluid viscosity and (b) normal pressure differences as functions of shear rate with different thermostats.

FIG. 8. Projections of the pair distribution function in all three planes at $\dot{\gamma} = 0, 0.5, 2.0$ and $5.0 \tau^{-1}$.