A study of the static yield stress in a binary Lennard-Jones glass

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The stress–strain relations and the yield behavior of a model glass (a 80:20 binary Lennard-Jones mixture) [W. Kob and H. C. Andersen, Phys. Rev. E 52, 4134 (1995)] is studied by means of molecular dynamics simulations. In a previous paper [F. Varnik, L. Bocquet, J.-L. Barrat, and L. Berthier, Phys. Rev. Lett. 90, 095702 (2003)] it was shown that, at temperatures below the glass transition temperature, $T_g$, the model exhibits shear banding under imposed shear. It was also suggested that this behavior is closely related to the existence of a (static) yield stress (under applied stress, the system does not flow until the stress $\sigma$ exceeds a threshold value $\sigma_y$). A thorough analysis of the static yield stress is presented via simulations under imposed stress. Furthermore, using steady shear simulations, the effect of physical aging, shear rate and temperature on the stress–strain relation is investigated. In particular, we find that at the yield point (the “peak”-value of the stress–strain curve) exhibits a logarithmic dependence both on the imposed shear rate and on the “age” of the system in qualitative agreement with experiments on amorphous polymers [C. Ho Huu and T. Vu-Khanh, Theoretical and Applied Fracture Mechanics 40, 75 (2003); L. E. Govaert, H. G. H. van Melick, and H. E. H. Meijer, Polymer 42, 1271 (2001)] and on metallic glasses [W. L. Johnson, J. Lu, and M. D. Demetriou, Intermetallics 10, 1039 (2002)]. In addition to the very observation of the yield stress which is an important feature seen in experiments on complex systems like pastes, dense colloidal suspensions [F. Da Cruz, F. Chevoir, D. Bonn, and P. Coussot, Phys. Rev. E 66, 051305 (2002)] and foams [G. Debrégeas, H. Tabuteau, and J.-M. di Meglio, Phys. Rev. Lett. 87, 178305 (2001)], further links between our model and soft glassy materials are found.

An example is the existence of hysteresis loops in the system response to a varying imposed stress. Finally, we measure the static yield stress for our model and study its dependence on temperature. We find that for temperatures far below the mode coupling critical temperature of the model ($T_c = 0.435$ in Lennard-Jones units), $\sigma_y$ decreases slowly upon heating followed by a stronger decrease as $T_c$ is approached. We discuss the reliability of results on the static yield stress and give a criterion for its validity in terms of the time scales relevant to the problem. © 2004 American Institute of Physics. [DOI: 10.1063/1.1636451]

I. INTRODUCTION

Despite the large diversity of their microstructures, the so-called soft glassy materials like pastes, dense colloidal suspensions, granular systems and foams exhibit many common rheological properties. Once in a glassy or “jammed” state, these systems do not flow, if a small shear stress is applied on them. For stresses slightly above a certain threshold value (the static yield stress, $\sigma_y$), however, they no longer resist to the imposed stress and a flow pattern is formed.2–5

On the other hand, in experiments upon imposed shear rate, shear thinning is observed.5,6 The apparent viscosity, defined as the average shear stress divided by the average overall shear rate, $\eta_{app} = \sigma / \dot{\gamma}_{tot}$, decreases with increasing $\dot{\gamma}_{tot}$ (in the case of a planar Couette-flow with wall velocity and separation $U_{wall}$ and $L_z$, for example, $\dot{\gamma}_{tot} = U_{wall}/L_z$). Furthermore, over some range of shear rates, the system separates into regions with different velocity gradients (shear bands).3,4,7

Whereas the shear thinning is commonly attributed to the acceleration of the intrinsic slow dynamics by the external flow (the new time scale, $1/\dot{\gamma}_{tot}$, is much shorter than the typical structural relaxation time of the system),1,8–11 the origin of the shear bands still remains to be clarified. In some cases, this shear-banding phenomenon can be understood in terms of underlying structural changes in the fluid, analogous to a first order phase transition. Examples are systems of rod like particles, entangled polymers or surfactant micelles where the constituents (rods, polymer or surfactant molecules) gradually align with increasing shear rate thus leading to a coupling between the local stress and the spatial variation of the velocity gradient.12,13 In the case of soft glassy materials, however, no such changes are evident, and coexistence appears between a completely steady region (zero shear rate) and a sheared, fluid region.4,7,14–16

Using molecular dynamics simulations, it was shown in a previous work17 that a model of 80:20 binary Lennard-Jones glass18 also exhibits the above-mentioned features.
Let us illustrate the existence of a static yield stress for our model, using results of simulations to be described in more detail in later sections. The system is confined between two parallel atomistic walls. A tangential force (stress) is then applied to the left wall and the resulting velocity profile in the inner part of the system is measured (see also Sec. II for more details on the model).

Figure 1 shows $U_{\text{max}}$, the maximum of the velocity profile (observed in the leftmost layer) as a function of the applied stress. The stress applied on the left wall is increased stepwise by an amount of $\Delta \sigma = 0.02$ (measured in LJ units) every 4000 LJ time units, and $U_{\text{max}}$ is measured between two subsequent stress increments. The horizontal dotted line marks the thermal velocity of the wall. Note the sharp increase in $U_{\text{max}}$ when changing the stress from $\sigma = 0.6$ to 0.62. Inset: rescaled velocity profiles, $U(z)/U_{\text{max}}$, measured during the same simulations for stresses in the flow regime (for which $U_{\text{max}} \approx U_{\text{thermal}}$). Obviously, once the flow sets in, a linear velocity profile is formed across the system.

![Graph showing maximum velocity vs. applied stress](image)

**FIG. 1.** The maximum velocity in the system, $U_{\text{max}}$, measured in the layer of closest approach to the left wall during simulations of a binary Lennard-Jones glass ($T = 0.2 (\sim T_c = 0.435)$) at imposed stress. The stress is increased by an amount of $\Delta \sigma = 0.02$ once in 4000 LJ time units and $U_{\text{max}}$ is measured between two subsequent stress increments. The horizontal dotted line marks the thermal velocity of the wall. Note the sharp increase in $U_{\text{max}}$ when changing the stress from $\sigma = 0.6$ to 0.62. Inset: rescaled velocity profiles, $U(z)/U_{\text{max}}$, measured during the same simulations for stresses in the flow regime (for which $U_{\text{max}} \approx U_{\text{thermal}}$). Obviously, once the flow sets in, a linear velocity profile is formed across the system.

Furthermore, in Ref. 17, a link was suggested between the occurrence of shear bands and the existence of a static yield stress, $\sigma_y$, in the system. It was found that (see Fig. 2) the yield stress, $\sigma_y$, is larger than the steady state stress measured in a steady shear experiment in the limit of the zero shear rate, $\sigma_y \approx \lim_{\dot{\gamma} \to 0} \sigma$ (the methods to measure these quantities are described in the next sections). It was then suggested that, a shear-banding could be expected for shear rates, for which $\sigma_y > \dot{\gamma}_{\text{tot}} < \sigma_\gamma$; as the flow is imposed externally (by moving, say, the left wall) the formation of a flow pattern is unavoidable. On the other hand, it follows from $\sigma_y (\dot{\gamma}_{\text{tot}}) < \sigma_\gamma$ that, some regions in the system are “rigid enough” to resist to the flow-induced stress whereas other regions undergo irreversible rearrangements more easily. Hence, whereas the details of the “nucleation” and growth of a heterogeneous flow pattern may depend on the initial heterogeneity in the “degree of jamming,” “free volume,” or “fluidity” at the beginning of the shear motion, its very origin lies in the possibility of resisting to the shear-induced stress, i.e., in the existence of a static yield stress.

Therefore, although it does not solve the problem of the selection between the two bands, the existence of a static yield stress is at least consistent with the coexistence of a jammed region and a fluidized band: once the yield stress $\sigma_y$ is added to the flow curve, shear rate becomes multivalued in a range of shear stresses, a situation encountered in several complex fluids. This phenomenon should thus be generic for many soft glassy materials.

In this paper we present an extensive study of the stress–strain relations and yielding properties of the present model. The report is organized as follows: After the introduction of the model in the next section, results on the system response to an imposed overall shear rate are presented, and the effects of physical aging, shear rate and temperature on the stress–strain curves are investigated. In Sec. IV, the response...
of the system to imposed stress is studied. The measurement of the static yield stress in the subject of Sec. V. A summary compiles our results.

II. MODEL

We performed molecular dynamics simulations of a generic glass-forming system, consisting of a 80:20 binary mixture of Lennard-Jones particles (whose types we call A and B) at a total density of $\rho = \rho_A + \rho_B = 1.2$. A and B particles interact via a Lennard-Jones potential, $U_{LJ}(r) = 4\varepsilon_{ab}[\sigma_{ab}/r]^12 - (\sigma_{ab}/r)^6]$, with $\alpha, \beta = A, B$. The parameters $\varepsilon_{AA}$, $\sigma_{AA}$, and $m_A$ define the units of energy, length, and mass. The unit of time is then given by $\tau_{LJ} = \sigma_{AA}/\varepsilon_{AA}$. It must be emphasized at this stage that we do not intend an exact matching between the properties of our model and a specific experimental system. Rather, we wish to focus on generic aspects of the rheology of glassy systems like, e.g., shear thinning, existence of a static yield stress, shear banding, etc. As a consequence, the specific values of the length, time, and energy units of our model will in general depend on the properties of the experimental reference system. An example, we compare our system to metallic glasses. As metals usually melt at temperatures of about a few thousands Kelvin, we may estimate the LJ energy unit by $\varepsilon = k_B T = 1.38\times 10^{-23}$ J/K$\times 3000$ K$\approx 4\times 10^{-20}$ J. We now use the knowledge of the yield stress of metallic glasses, which is of the order of $10^8$ Pa. Setting this equal to the yield stress of our model in the glassy phase, $\sigma_{y} = 0.6$ (note that, at low temperatures, $\sigma_y$ does not vary much with $T$; see e.g. Fig. 17 below), gives an estimate of the length unit: $0.6\varepsilon/\sigma_{AA} \approx 10^9$ J/m$^3 \rightarrow \sigma_{AA} = 0.62$ nm. In order to estimate the time unit, we mention that the diffusion coefficient of metallic glasses at the melting point is of the order of $10^{-9}$ m$^2$/s.$^{24}$ Setting this equal to the diffusion coefficient of our model in the liquid state, $D(T=1) \approx 10^{-2}$ $\sigma_{AA}^2/\tau_{LJ}$, yields $\tau_{LJ} \approx 3.8 \times 10^{-12}$ s. Note that the range of shear rates we are going to study lies between $10^{-2}/\tau_{LJ}$ and $10^{-6}/\tau_{LJ}$ corresponding $2.6 \times 10^9$/s and $2.6 \times 10^5$/s. This lies by orders of magnitude beyond the experimentally accessible range. Despite this fact, we will see in the next sections that the present model fairly well reproduces the most salient features of the rheology of glassy systems.

Furthermore, we choose $\varepsilon_{AB} = 1.5\varepsilon_{AA}$, $\varepsilon_{BB} = 0.5\varepsilon_{AA}$, $\sigma_{AB} = 0.8\sigma_{AA}$, $\sigma_{BB} = 0.88\sigma_{AA}$, and $m_B = m_A$. The potential was truncated at twice the minimum position of the LJ potential, $r_c = 2.245$. Note that the density is kept constant at the value of 1.2 for all simulations whose results are reported here. This density is high enough so that the pressure in the system is positive at all studied temperatures. The present model system has been extensively studied in previous works.$^{8,10,18,25}$ and exhibits, in the bulk state, a computer glass transition (in the sense that the relaxation time becomes larger than typical simulation times) at a temperature of $T_c = 0.435$. Since our aim is to study the interplay between the yield behavior and the possible flow heterogeneities, we do not impose a constant velocity gradient over the system as done in Ref. 10, where a homogeneous shear flow was imposed through the use of Lees–Edwards boundary conditions. Rather, we confine the system between two solid walls, which will be driven at constant velocity. By doing so, we mimic an experimental shear cell, without imposing a uniform velocity gradient.

In the simulations performed we chose a rather large integration time step, $dt = 0.02$. When simulating a Lennard-Jones liquid at high temperatures, this time step might appear to be too large. However, at temperatures under consideration, the system’s mobility is practically zero and larger integration time steps are less problematic. Nevertheless, we have also performed comparative simulations with a much smaller time step of $dt = 0.001$. For both choices of $dt$, identical results are obtained for all quantities of interest.

We first equilibrate a large simulation box with periodic boundary conditions in all directions, at $T = 0.5$. The system is then quenched to a temperature below $T_c$, where it falls out of equilibrium, in the sense that structural relaxation times are by orders of magnitude larger than the accessible simulation times. On the time scale of computer simulation, the system is in a glassy state, in which its properties slowly evolve with time towards the (unreachable) equilibrium values (aging, see Fig. 5 below). After a time of $t = 4 \times 10^4$ (2 $\times 10^6$ MD steps), we create two parallel solid boundaries by freezing all the particles outside two parallel $xy$-planes at positions $z_{wall} = \pm L_z/2$ ($L_z = 40$) (see Fig. 4 below). For each computer experiment, ten independent samples (each containing 4800 fluid particles) are prepared using this procedure. Note that the system is homogeneous in the $xy$-plane ($L_x = L_y = 10$). We thus compute local quantities like the velocity profile, the temperature profile, etc. as an average over particles within thin layers parallel to the wall.

The amorphous character of our model is clearly seen by an analysis of the packing structure, i.e., the radial pair distribution function. Figure 3 shows the various kinds of radial pair distribution functions which can be defined for a binary mixture: $g_{\alpha \beta}$ is the probability (normalized to that of an ideal
gas) of finding a particle of type α at a distance \( r \) of a β-particle \((\alpha, \beta \in \{A, B\})\). In order to demonstrate that the system keeps its amorphous structure at temperatures far below the glass transition temperature of the model, we show the mentioned pair distribution functions at two characteristic temperatures, one in the supercooled state \((T = 0.5 > T_c = 0.435)\) and one at \( T = 0.2 \). As seen from Fig. 3, the maxima of \( g_{\alpha\beta} \) are more pronounced at lower \( T \). However, no sign of crystallization or long range positional order is observed as the temperature is lowered through the glass transition.

The mentioned insensitivity of the static structure to the glass transition must be contrasted to the fact that, at temperatures slightly above \( T_c \), the system can be equilibrated within the time accessible to the simulation whereas this is no longer the case for temperatures significantly below \( T_c \).

At \( T = 0.5 \), for example, the time necessary for an equilibration of the system is of order of a few hundred Lennard-Jones time units (not shown). For \( T = 0.45 \), the equilibration time rises to a few thousand, whereas at \( T = 0.2 \) the system is not equilibrated even after \( 2 \times 10^5 \) LJ time units. At this temperature, time translation invariance does not hold and the dynamical quantities depend on \( \Delta \) times: the actual time, \( t \), and the waiting time \( t_w \). Here, \( t_w \) is the time elapsed after the temperature quench (from \( T = 0.5 \) to \( T = 0.2 \)) and the beginning of the measurement (see Fig. 5).

This behavior is illustrated in Fig. 5, where the mean square displacement (MSD) of a tagged particle is shown at a temperature \( T_c \) \((T = 0.45)\) and at \( T = 0.2 \) (far below \( T_c \)) for various waiting times. The figure nicely demonstrates the establishment of time translation invariance (TTI) at \( T = 0.45 \). Here, \( t_w = 0 \) corresponds to a change of temperature from \( T = 0.5 \) to \( T = 0.45 \). As expected from the fact that \( T = 0.45 \) belongs to the supercooled (liquid) state, with increasing waiting time, the MSD converges towards the equilibrium curve reaching it after about 4000 Lennard-Jones time units. It is worth noting that the waiting time at which the TTI is recovered roughly corresponds to the time needed for the MSD to reach the size of a particle.

At \( T = 0.45 \), the equilibrium curve for the MSD exhibits the well-known two step relaxation characteristic of a supercooled liquid: for short times \((t \ll 1)\), free particle motion with thermal velocity is observed \((\langle r(t + t_w) - r(t_w) \rangle^2 = \langle v^2 \rangle t = k_B T \langle v^2 \rangle t \)). The free (ballistic) motion ends up in a plateau thus indicating the (temporal) arrest of the tagged particle in the cage formed by its neighbors. Already after a few hundred LJ time units, the plateau is gradually left and the MSD crosses over towards a linear dependence on time (diffusive regime). This is indicative of cooperative relaxation processes leading to the final release of the tagged particle from the cage (cage relaxation).

At \( T = 0.2 \), however, the situation is completely different. Here, TTI is not reached on the simulation time scale. Even after a waiting time of \( 10^5 \) LJ time units, the MSD continues slowing down without reaching a steady state. The slowing down of the dynamics with \( t_w \) also has a direct consequence on the lifetime of the cage. Figure 5 shows that, as \( t_w \) increases, so also does the width of the plateau. Hence, the time necessary for the cage relaxation increases continuously with \( t_w \). However, in the case of \( t_w = 3.9 \times 10^4 \), one can observe the very beginning of the cage relaxation around \( t \approx 2 \times 10^5 \). As will be discussed in Sec. III, this has an important consequence for the shear rate dependence of \( \sigma^\text{break} \), the stress at the maximum of stress–strain curves.

### III. RESULTS AT IMPOSED SHEAR RATE

An overall shear rate is imposed by moving in the \( x \)-direction, say, the left wall \((z_{\text{wall}} = -20)\) with a constant velocity of \( U_{\text{wall}} \). This defines the total shear rate \( \dot{\gamma}_{\text{tot}} = U_{\text{wall}}/L_z \). The motion of the wall is realized in two different ways. One method used in our simulations is to move all wall atoms with strictly the same velocity. In this case, wall
atoms do not have any thermal motion. As a consequence, the only way to keep the system temperature constant, is to thermostat the fluid atoms directly. A different kind of wall motion is realized by coupling each wall atom to its equilibrium lattice position via a harmonic spring. In this case, the lattice sites are moved with a strictly constant velocity while each wall atom is allowed to move according to the forces acting upon it (the harmonic forces ensure that the wall atoms follow the motion of the equilibrium lattice sites). In such a situation, we can thermostat the wall atoms while leaving the fluid particles unperturbed. The temperature of the inner part of the system is then a result of the heat exchange with the walls (which now act as a heat bath). This method has the advantage of leaving the fluid dynamics unperturbed by the thermostat.

The drawback of thermostating the system through the heat exchange with the walls is that, depending on the shear rate and the stiffness of the harmonic spring, measured by the spring constant \( k_h \), a temperature profile can develop across the system. Note that the smaller the harmonic spring constant, the better the heat exchange with the walls and thus the more efficient the system is thermostated (the imposed shear rate having the opposite effect). On the other hand, if \( k_h \) is too small, the fluid particles may penetrate the walls. We find that \( k_h = 25 \) is a reasonable choice for our model. However, even with this value of the harmonic spring constant, we observe a temperature profile as the shear rate exceeds \( \dot{\gamma}_{\text{wall}} = 10^{-4} \). For \( \dot{\gamma}_{\text{tot}} = 10^{-3} \), for example, the maximum temperature in the fluid is by about 3% higher than the prescribed value.

In order to prevent such uncontrolled temperature increases, we have therefore decided to apply direct thermostating to the inner particles at all shear rates, independently of the possibility of the heat exchange with the walls. For this purpose, we divide the system into parallel layers of thickness \( \Delta z = 0.25 \) and rescale (once every ten integration steps) the \( \gamma \)-component of the particle velocities within the layer, so as to impose the desired temperature \( T \). Such a local treatment is necessary to keep a homogeneous temperature profile when flow profiles are heterogeneous. To check for a possible influence of the thermostat, we compared, for low shear rates (\( \dot{\gamma}_{\text{tot}} = 10^{-4} \)), these results with the output of a simulation where the inner part of the system was unperturbed and the walls were thermostated instead. Both methods give identical results, indicating that the system properties are not affected by the thermostat.

However, for wall velocities close to 1 or larger (corresponding to overall shear rates of \( \dot{\gamma}_{\text{tot}} \approx 2.5 \times 10^{-2} \)), a nonuniform temperature profile develops across the system even if the velocities are rescaled extremely frequently. This can be rationalized as follows. The heat created by the shear motion needs approximately \( t_c = c/L_z \) to transverse the system (\( c \) is the sound velocity). We can estimate the sound velocity from a knowledge of the shear modulus, \( G \), and the density of the system, \( c = \sqrt{G/\rho} \). At \( T = 0.2 \) we find \( G \approx 15 \) (see Fig. 6) thus obtaining \( c \approx 3.54 \). A time of \( t_c \approx 11.3 \) is therefore needed for a signal to transverse the whole system. Note that the heat creation rate is given by \( dQ/dt = \sigma \dot{\gamma}_{\text{tot}} \) (neglecting inhomogeneities in the local shear rate). An amount of energy equal to \( k_B T \) is thus generated within \( t_c = k_BT/\dot{\gamma}_{\text{tot}} \). The requirement \( t_c \geq t_c \) now means that the heat creation must be slow enough so that the created energy can be dissipated in the whole system efficiently. This gives \( \dot{\gamma}_{\text{tot}} \approx k_B T/\sigma t_c \), which, after setting \( T = 0.2 \) and \( \sigma = 0.6 \), yields \( \dot{\gamma}_{\text{tot}} \approx 3 \times 10^{-2} \).

Figure 6 shows a typical set of (transient) stress–strain curves at a temperature of \( T = 0.2 \) and for a waiting time of \( t_w = 4 \times 10^4 \) LJ time units. The varying parameter is the overall shear rate \( \dot{\gamma}_{\text{tot}} = U_{\text{wall}}/L_z \) (the strain is simply computed as \( \gamma = \dot{\gamma}_{\text{tot}} t_w \)). First, an elastic regime is observed at small shear deformations (\( \gamma \approx 0.02 \)). The stress then increases up to a maximum, \( \sigma_{\text{peak}} \), before decreasing towards the steady state stress at large deformations. Therefore, this maximum is sometimes referred to as the yield point or dynamical yield stress. In the following, we will simply refer to this quantity as \( \sigma_{\text{peak}} \), since plastic (irreversible) deformation actually sets in before the corresponding value of the strain is reached. Moreover, as will be seen below, \( \sigma_{\text{peak}} \) depends on strain rate and waiting time in a nontrivial way, so that it is difficult, in our simulations, to define a yield stress value from such dynamical stress/strain curve.

As commonly observed in experiments on polymers and on metallic glasses, the stress overshoot \( \sigma_{\text{peak}} \) decreases and is observed at smaller strains as the shear rate is lowered (see also Fig. 8 below). Note also that all curves in Fig. 6 show the same elastic response at small strains. As also shown in the figure, a linear fit to \( \sigma = G \gamma \) with a shear modulus of \( G \approx 15 \) describes well the data at small deformations.

In order to understand the rather strong deviation from linearity at small strains in the case of \( \dot{\gamma}_{\text{tot}} = 10^{-2} \), we recall that, once the (left) wall starts its motion, a time of approximately \( t_c = 11.3 \) must elapse before the deformation field comprises the whole system. This is nicely borne out in the inset of Fig. 7 where, for a wall velocity of \( U_{\text{wall}} = 0.1, \) “snapshots” of the layer resolved displacement of center of
temperatures of 5 of Fig. 7. Region reaches the immobile wall only after t and have found t for 5. This can be rationalized as follows. The total strain at main part of Fig. 7, at higher wall velocities, the deformation ~U\_\text{wall} is observed, whereas at higher wall velocities this is no longer the case. The inset shows, for a (low) wall velocity of \( U_{\text{wall}} = 0.1, \) how the deformation field propagates towards the immobile wall (placed at \( z = 20 \)). The speed with which the boundary of the deformed region extends towards the immobile wall is found to be indeed very close to the estimated value of the sound velocity \( c \sim 3.54. \) The stars in the inset correspond to \( U_{\text{wall}} = 0.4 \) at \( t = 5 \) demonstrating that, at a time corresponding to a smaller strain, the local response of the system is elastic (see also the text for more discussion).

mass (normalized to the displacement of the wall) are shown for \( t = 1, 5, \) and 11. Indeed, the boundary of the deformed region reaches the immobile wall only after \( t = 11 \) LJ time units. We have verified this behavior for other wall velocities and have found \( t \approx 11 \) in all cases. However, as shown in the main part of Fig. 7, at higher wall velocities, the deformation field is no longer linear at the time it reaches the immobile wall. This can be rationalized as follows. The total strain at \( t = t_0 \) is given by \( \gamma = \gamma_{\text{yield}} \) yielding \( \gamma = 11% \) for \( L_y = 0.4/40 = 10^{-2}. \) Hence, the elastic regime is left already before the whole system is affected by the motion of the wall. Putting it the other way, one can estimate the time for which a locally elastic response can still be observed at a given wall velocity: \( t_{\text{d,el}} = \gamma_{\text{d}} / \gamma_{\text{tot}}. \) Assuming an elastic response at a strain of a few percent one obtains for \( t_{\text{d,el}} \) a time of a few Lennard-Jones units at \( \gamma_{\text{tot}} = 10^{-2} \) (see the stars in the inset of Fig. 7).

Note, however, that in a real experiment, the situation we discussed above would correspond to extremely high deformation rates: a strain of a few percent must be reached before the sound travels across the system, a case not encountered in a typical experiment.

The dependence of \( \sigma_{\text{peak}} \) on \( \gamma_{\text{tot}} \) is depicted in Fig. 8 for temperatures of \( T = 0.2 \) and \( T = 0.4. \) For the lower temperature, data are shown for two system sizes \( L_x = L_y = 10, L_z = 40 \) (averaged over ten independent runs) and \( L_x = L_y = L_z = 40 \) (a sole run). As seen from Fig. 8, for both system sizes, results on \( \sigma_{\text{peak}} \) are practically identical. Note that the computation of \( \sigma_{\text{peak}} \) at \( \gamma_{\text{tot}} = 2.5 \times 10^{-6} \) for the large system required about 25 days of simulation on a 1.8 GHz Athlon CPU. The data point corresponding to \( \gamma_{\text{tot}} = 10^{-6} \) has therefore been computed using the average over many small systems only. As the results are not sensitive to the system size, we have used the smaller system size also in the case of \( T = 0.4 \) (again averaging over ten independent runs). For \( T = 0.2, \) a change in the slope of \( \sigma_{\text{peak}} - \gamma_{\text{tot}} \) curve is observed at a shear rate of approximately \( \gamma_{\text{co}} = 2.5 \times 10^{-5}. \) Note that the stress overshoot \( \sigma_{\text{peak}} \) shown in Fig. 8 is typically observed at strains lower than 5%. This indicates that the subsequent (partial) release of the stress is induced by rather small rearrangements. This, in turn, suggests a link between the stress response and the (inherent) structural re-arrangements on a length scale much smaller than the particle size. If the shear rate is so low that inherent structural re-arrangements can keep pace with the imposed deformation, the stress would increase more slowly and the resulting stress overshoot would be smaller.

The slower increase of the stress response at lower shear rates is nicely born out in Fig. 6. On the other hand, an investigation of the mean squared displacement shown in Fig. 5 reveals that the MSD departs from the plateau for \( \tau_{\text{co}} = 2 \times 10^4. \) This time is of the same order as the inverse of the cross over shear rate thus suggesting that the cross over in the \( \gamma_{\text{tot}} \) dependence of \( \sigma_{\text{peak}} \) is indeed related to an enhancement of the stress release due to inherent structural relaxation (the beginning of the cage relaxation). While at higher overall shear rates the system response is dominated by the (shorter) time scale imposed by the shear motion, the contribution of the inherent system dynamics seems to become non-negligible and progressively more important as \( \gamma_{\text{tot}} \) is decreased below \( \gamma_{\text{co}}. \)
Although not so pronounced, a similar crossover is seen also in the case of $T = 0.4$ at a higher shear rate in agreement with the observation that, compared to $T = 0.2$, the MSD at $T = 0.4$ leaves the plateau at a shorter time [see the MSD ($T = 0.4$) in Fig. 18]. Note that, as the structural relaxation time is approximately proportional to the age of the system, $\tau_{co}$ is of the order of $t_w$. The system response below the crossover is in fact a complex combination of aging dynamics and stress induced relaxation. The aging dynamics tends to make the system stiffer (see below), so that the observed $\sigma_{\text{peak}}$ is higher than the value one would extrapolate from high shear rates.

The dependence of the stress overshoot $\sigma_{\text{peak}}$ on the imposed shear rate is often expressed with a simple formula which goes back to the Ree–Eyring’s viscosity theory,\(^{5,33}\)

$$\sigma_{\text{peak}} = \sigma_0 + k_B T / \nu^* \ln(\gamma_{\text{tot}} / \nu_0).$$  \hspace{1cm} (1)

Here, the activation volume, $\nu^*$, is interpreted as the characteristic volume of a region involved in an elementary shear motion (hopping) and $\nu_0$ is the attempt frequency of hopping. Obviously, Eq. (1) makes sense only at high enough shear rates, for in the case of $\gamma_{\text{tot}} < \nu_0$, the second term on the right-hand side of Eq. (1) becomes negative. Fitting the data of Fig. 8 to Eq. (1), we obtain $\nu^* \approx 2.3$ at $T = 0.2$ and $\nu^* = 3.0$ at $T = 0.4$. This result is comparable to the estimates of the free volume from experiments on polycarbonate, where a value of $\nu^* \approx 3.5 \text{ nm}^3$ per segment is reported.\(^{34}\)

Ho HUu and Vu-Khanh\(^{34}\) have extensively studied the effects of physical aging and strain rate on yielding kinetics of polycarbonate (PC) for temperatures ranging from $-80 ^\circ\text{C}$ to $60 ^\circ\text{C}$ [note that $T_g(\text{PC}) = 140 ^\circ\text{C}$]. In particular, they have measured the tensile stress at yield point, $\sigma^p$, as a function of strain rate, $\dot{\varepsilon}$, for various temperatures and different ages of the sample. As for the effect of temperature, they find that the slope of $\sigma^p(\ln \dot{\varepsilon})$ $\propto$ $T$, the activation volume is practically independent of $T$. Our data also show only a weak dependence of $\nu^*$ on temperature, as illustrated in the inset of Fig. 8. Note that we have also restricted the data-range to higher shear rates where Eq. (1) is expected to hold better.

The above qualitative agreement on the strain rate dependence of the stress at yield point for our molecular model glass and polycarbonate suggests that, for strains smaller than, say 10%, the relevant length scale is that of a segment. In other words, the chain connectivity has a rather subordinate effect on the stress at the yield point (in fact, the connectivity becomes important for larger strains, where the well-known strain hardening sets in).\(^{30}\)

For the same binary mixture of Lennard-Jones particles as in the present work, Rottler and Robbins\(^{35}\) studied the dependence of $\tau_{\text{dev}}$, the maximum of the deviatoric stress, on the shear rate. In contrast to our results, a crossover similar to that shown in Fig. 8 does not seem to show up. Letting differences in cutoff radius of the LJ potential and the pressure in the system apart, we first mention that the system studied by Rottler and Robbins is subjected to deformation after a waiting time of $t_w = 1000$ LJ time units. This must be compared to $t_w = 40 000$ for the data shown in Fig. 8. The relatively fast aging dynamics in the case of Ref. 35 may thus shift the mentioned crossover to higher shear rates. Indeed, Rottler and Robbins observe a change in the rate behavior of $\sigma_{\text{peak}}$, albeit at shear rates higher than $10^{-4}$ (Ref. 36) and thus close to $\gamma_{\text{tot}} = 10^{-3}$ for which the system could no longer equilibrate the stress throughout. Therefore, in Ref. 35, a clear distinction of both regimes in the behavior of $\sigma_{\text{peak}} - \gamma_{\text{tot}}$ curve is quite difficult.

As to the temperature dependence of the slope of $\gamma_{\text{tot}}$ curve observed in our simulations, $\tau_{\text{dev}} - \ln \gamma_{\text{tot}}$ curves studied in Ref. 35 are all parallel for $T \in [0.01, 0.2]$. However, for a higher temperature of $T = 0.3$, a significant change in the slope of $\tau_{\text{dev}} - \ln \gamma_{\text{tot}}$ curve is observed [see Fig. 2(b) in Ref. 35]. Note that (due to a shorter cutoff radius and a lower pressure) the glass transition temperature in the mentioned reference lies close to $T = 0.25 [0.3 \leq T_g \leq 0.35$ (Ref. 35)]. On the other hand, $T_g$ of our model is quite close to $T = 0.4$ (the mode coupling critical temperature of our model is $T_g = 0.435$. As $T_g$ usually lies about 10% below $T_C$, this gives $T_g = 0.39$). Thus, both temperatures of $T = 0.4$ in the case of our model and $T = 0.3$ in the case of Ref. 35 lie close to the glass transition point of the respective system. One could therefore ask if the change with temperature in the slope of the high $\gamma_{\text{tot}}$-branch of the data shown in Fig. 8 is a consequence of the proximity of the system to the glass transition point. In other words, if, sufficiently below $T_g$, the slope of $\sigma_{\text{peak}} - \ln(\gamma_{\text{tot}})$ is independent of temperature.

In order to answer this question, we measured $\sigma_{\text{peak}}$ as a function of $\gamma_{\text{tot}}$ for an extremely low temperature of $T = 0.01$. Contrary to the above suggestion the slope of the $\sigma_{\text{peak}} - \ln(\gamma_{\text{tot}})$ curve at $T = 0.01$ is quite different from that corresponding to $T = 0.2$ (not shown). Thus, the slope of the $\sigma_{\text{peak}} - \ln(\gamma_{\text{tot}})$ curve seems to vary with temperature even far below $T_g$.

Recall that the impact of temperature on $\sigma_{\text{peak}}$ strongly depends on the imposed shear rate (see Fig. 8). Focusing further on the interplay between the temperature effect and that of the shear rate, we have performed, for two characteristic shear rates of $\gamma_{\text{tot}} = 10^{-3}$ and $10^{-5}$, simulations at various temperatures ranging from $T = 0.01$ to $T = 0.43$ (recall that $T_C = 0.435$). For this purpose, a large system of 64 000 particles (88 000 including the wall atoms) was prepared in exactly the same way as in the case of $T = 0.2$ (in particular, the waiting time was chosen to $t_w = 38 000$ LJ time units). As shown in Fig. 9, for the higher shear rate of $\gamma_{\text{tot}} = 10^{-3}$ and for a wide range of temperatures below $T_g$, $\sigma_{\text{peak}}$ is practically independent of $T$ thus indicating that the system response is dominated by the imposed shear motion. [Note that, the temperatures at which a dependence on $T$ shows up correspond to the proximity of $T_g$. At these (higher) temperatures, the relaxation time of the system is of the order of $10^3$ and thus comparable to the inverse of the applied shear rate. See Fig. 18 (below).]

In the case of $\gamma_{\text{tot}} = 10^{-5}$, however, a continuous variation of $\sigma_{\text{peak}}$ with temperature is observed. Even at extremely low temperatures of $T = 0.01$ and 0.05, $\sigma_{\text{peak}}$ varies significantly with $T$. This is in accordance with the idea of the concurrence between the inherent (aging) dynamics of the system and the shear induced dynamics. The lower the shear
rate, the stronger the impact of the inherent system dynamics and thus of temperature.

As an inspection of Fig. 6 reveals, the difference between the peak and the steady state stresses decreases as $\dot{\gamma}_{\text{tot}}$ is reduced thus suggesting that, in the limit of vanishing shear rate, $\sigma^{\text{peak}}$ converges towards the steady state stress (and therefore coincides with the yield stress that could be extracted from homogeneous flow experiments). Figure 10 compares these two quantities, underlining this expectation further.

It has been shown in experiments on amorphous polymers like poly(styrene) and polycarbonate$^{30,34}$ that aging strongly alters the response of the system to an applied strain. At small deformations (below, say 5%) the slope of the stress–strain curve (elastic shear modulus) increases with progressive aging. Furthermore, the maximum of the stress–strain curve, $\sigma^{\text{peak}}$, is larger for “older” systems and the subsequent decrease of the stress (“strain softening”$^{29}$) is more pronounced. Similar observations are also made in experiments on metallic glasses.$^{31}$ Interestingly, Fig. 11 shows that these features are not limited to polymers or metallic glasses but can also occur in simpler models. In Fig. 11 the stress is depicted versus applied strain (defined as $\gamma=\dot{\gamma}_{\text{tot}} t_{\text{wall}}/L_z$). Before shearing, the system is first equilibrated at a temperature of $T=0.5$. The motion of the (left) wall is then started at a time $t_{\text{w}}$ after the temperature quench. Varying $t_{\text{w}}$, we observe similar effects on the stress response as described above. It is also observed that, whereas the maximum stress $\sigma^{\text{peak}}$ increases with $t_{\text{w}}$, the elastic shear modulus (slope of the stress–strain curve) seems to saturate already for $t_{\text{w}} \approx 2000$ (this is, however, hardly distinguishable in the scale of the figure).

On the other hand, at large deformations, the stress response does not show any systematic dependence on the age of the system thus indicating a recovery of the time translation invariance: steady shear “stops aging.”$^{35}$ In fact, it is well known that the shear motion promotes structural relaxation and sets an upper bound ($\sim 1/\dot{\gamma}_{\text{tot}}$) to the corresponding time scale. Once the steady shear state is reached (which is the case at deformations comparable to unity), no dependence on the system age is expected. Results shown in Fig. 11 are also in qualitative agreement with data reported in Ref. 28, where the system response to a homogeneous shear was studied via Monte Carlo simulations of a binary Lennard-Jones mixture (very similar to the present model). Note that, in Ref. 28, only the contribution to the system

![FIG. 9. The maximum of the stress–strain curves, $\sigma^{\text{peak}}$, vs temperature for two characteristic shear rates of $\dot{\gamma}_{\text{tot}}=10^{-3}$ (shear dominated response) and $\dot{\gamma}_{\text{tot}}=10^{-5}$ (low shear rate regime) (see also Fig. 8). While at the higher shear rate temperature has a rather weak effect on the stress response, $\sigma^{\text{peak}}$ continuously decreases with increasing $T$ in the case of $\dot{\gamma}_{\text{tot}}=10^{-5}$.](image)

![FIG. 10. The maximum of the stress–strain curves as shown in Fig. 6, $\sigma^{\text{peak}}$, and the steady state stress vs strain rate for a temperature of $T=0.2$. For $\sigma^{\text{peak}}$, we average the results for both system sizes shown in Fig. 8.](image)

![FIG. 11. Aging effects on the stress response to an applied strain. $\sigma(\gamma)$ is shown for a strain rate of $\dot{\gamma}_{\text{tot}}=10^{-3}$ at $t_{\text{w}}=20$, $2 \times 10^3$, $4.18 \times 10^3$, and $3.99 \times 10^3$ LJ time units. At small deformations, the stress increases faster with progressive aging. The maximum observed stress, $\sigma^{\text{peak}}$, is reached at smaller strains and is higher for “older” samples. At large deformations, however, the stress converges towards the same average value regardless of the age of the system. This is a signature of the recovery of time translation invariance, or, equivalently, the erasure of the memory effects due to shear induced structural relaxation. The inset shows the variation of the maximum stress with the waiting time. Note that, here, $t_{\text{w}}$ is varied by more than 4 orders of magnitude, i.e., from $t_{\text{w}}=20$ to $t_{\text{w}}=3.99 \times 10^5$. The solid line is a guide for the eye. The data correspond to a system size of $L_x=L_y=L_z=5$ (a sole run). For the largest waiting time $t_{\text{w}}=3.99 \times 10^5$ (and $10^6$ MD steps), however, average over 10 independent runs of a smaller system size is used ($L_x=L_y=L_z=10$). Note that already at this (smaller) system size, the size effects are practically negligible (see also Fig. 8).](image)
response of the so-called inherent structure (configurations corresponding to the minima of the energy landscape) has been considered and the effect of aging is investigated by applying different cooling rates (not by “quenching and waiting” as is the case in our work). Despite these differences in details, results reported in Ref. 28 and our observations are qualitatively similar. More quantitative data on the effect of physical aging on the system at the yield point is shown in the inset of Fig. 11. Here, \(\sigma_{\text{peak}}\) is depicted as a function of the waiting time, where \(t_w\) is varied by more than four decades. A logarithmic dependence of \(\sigma_{\text{peak}}\) on \(t_w\) is clearly seen for waiting times larger than a few hundred LJ time units thus covering about three decades in \(t_w\). Such an increase in \(\sigma_{\text{peak}}\) is consistent with the qualitative idea that the system visits deeper energy minima as aging time increases. A stronger stress is therefore necessary to overcome the energy barriers towards steady flow. It is interesting to note that such a \(t_w\) dependence of the stress overshoot is also observed in the SGR model.\(^1\)

As indicated above, simultaneous consideration of Figs. 8 and 11 indicates a rather complex behavior of \(\sigma_{\text{peak}}\) as a function of \(t_w\) and \(\gamma_{\text{tot}}\). Considering the similarity in dependence for large \(\gamma_{\text{tot}}\) or large \(t_w\), it is tempting to suggest a rewriting of Eq. (1) in the form \(\sigma_{\text{peak}} = \sigma_0 + k_B T / v^* \ln(\gamma_{\text{tot}}t_w)\). This modified version of Eq. (1) does, however, not describe our data consistently. At \(T = 0.2\), for example, the \(\sigma_{\text{peak}}/T\) versus \(\ln(\gamma_{\text{tot}}t_w)\) curve exhibits different slopes for the data obtained by varying the imposed shear rate (Fig. 8) as compared to the simulation results where \(t_w\) is the adjustable parameter (corresponding to the data shown in the inset of Fig. 11).

As for the effect of the temperature on the (transient) stress response, it is generally known that, due to faster structural relaxation at higher \(T\), the shear stress decreases at higher temperatures. This is verified in Fig. 12 where stress–strain curves are shown at \(T = 0.2, 0.4, 0.43,\) and \(0.5\) for a strain rate of \(\dot{\gamma}_{\text{tot}} = 10^{-3}\). Similar to the effect of a decreasing shear rate, both the maximum and the steady state values of the stress decrease with increasing temperature. Furthermore, at small strains, the slope of stress–strain curves (elastic shear modulus) decreases with increasing temperature (see the inset) thus indicating a softening of the system structure at higher \(T\) (compare to Fig. 6). Note, however, that these changes are much more pronounced in a narrow temperature interval around \(T_c\). Results here correspond to averages over ten independent runs. The system size was \(L_x = L_y = 10\) and \(L_z = 40\). The inset shows a magnification of the small strain region of the same data.

\[\frac{d\gamma_{\text{tot}}}{dt} = 10^{-3}\]

\[\begin{array}{c|c|c|c|c|c|c|c|c}
0 & 0.1 & 0.2 & 0.3 & 0.4 & 0.5 & 0.6 & 0.7 & 0.8 & 0.9 & 1
\hline
0 & 0 & 0.2 & 0.4 & 0.6 & 0.8 & 1 & 0.8 & 0.6 & 0.4 & 0.2
\end{array}\]

\[T = 0.5, 0.43, 0.4, 0.2\]

\[\text{strain}\]

\[\text{shear stress}\]

\[\sigma(\gamma)\] is shown for a strain rate of \(\dot{\gamma}_{\text{tot}} = 10^{-3}\) at \(T = 0.2, 0.4, 0.43,\) and \(0.5\) (note that the mode coupling critical temperature of the system is \(T_c = 0.435\)). For temperatures below \(T_c\) the system was first aged during \(t_w = 4 \times 10^4\) LJ time units before the beginning of the measurement. Similar to the effect of a decreasing shear rate, both the maximum and the steady state values of the stress decrease with increasing temperature. Furthermore, at small strains, the slope of stress–strain curves (elastic shear modulus) decreases with increasing temperature (see the inset) thus indicating a softening of the system structure at higher \(T\) (compare to Fig. 6).

FIG. 12. Effect of temperature on the stress response to an applied strain. \(\sigma(\gamma)\) is shown for a strain rate of \(\dot{\gamma}_{\text{tot}} = 10^{-3}\) at \(T = 0.2, 0.4, 0.43,\) and \(0.5\) (note that the mode coupling critical temperature of the system is \(T_c = 0.435\)). For temperatures below \(T_c\) the system was first aged during \(t_w = 4 \times 10^4\) LJ time units before the beginning of the measurement. Similar to the effect of a decreasing shear rate, both the maximum and the steady state values of the stress decrease with increasing temperature. Furthermore, at small strains, the slope of stress–strain curves (elastic shear modulus) decreases with increasing temperature (see the inset) thus indicating a softening of the system structure at higher \(T\) (compare to Fig. 6). Note, however, that these changes are much more pronounced in a narrow temperature interval around \(T_c\). Results here correspond to averages over ten independent runs. The system size was \(L_x = L_y = 10\) and \(L_z = 40\). The inset shows a magnification of the small strain region of the same data.

IV. RESULTS AT IMPOSED STRESS

In this section we study the response of the system to imposed shear stress. The system is prepared at a temperature of \(T = 0.2\) (far below the mode coupling critical temperature of the system, \(T_c = 0.435\)) in a similar way as described in previous sections so that, at the beginning of the measurement, the structural relaxation times of the system are much larger than the time scale of the simulation. Starting with \(\sigma(t = 0) = 0\), we gradually increase the external stress (i.e., the force acting on the atoms of the left wall) and record quantities of interest, such as the internal energy, the stress across the system, the center of mass velocity of the walls and of the fluid, etc.

It is generally accepted that imposing an external stress leads to a shift in the density of states towards higher energy configurations. For the binary Lennard-Jones model of the present work, Fig. 13 shows the potential energy per particle, \(e_{\text{pot}}\), as measured in simulations where the imposed stress is periodically varied in the range \(\sigma \in [-0.8, 0.8]\) (see the zigzag line in Fig. 13). Similar stress ramps were also used by He and Robbins\(^{26}\) in order to determine the static friction between two solid bodies mediated by a layer of adsorbed molecules.

Note that the maxima and minima of the potential energy correspond to \(|\sigma| = 0.8\) and \(\sigma = 0\) respectively. Starting at a minimum of \(e_{\text{pot}}\) (\(\sigma = 0\)), the potential energy fluctuates for a while around this minimum before increasing sharply towards a maximal value. This corresponds to a branch where \(|\sigma|\) increases from 0 to 0.8. The descent from this maximum towards the subsequent minimum (\(|\sigma|\) decreases from 0.8 to 0) is, however, more gradual and indicates a dependence of \(e_{\text{pot}}\) on the stress history. Finally, we also observe that, at
FIG. 13. Effect of the rate of stress increase on potential energy per particle. 

$$\epsilon_{pot}$$ is measured during cyclic variations of the imposed stress as sketched by the zig-zag line (note that $$\sigma$$ varies in the range $$[-0.8 \text{ to } 0.8]$$). The horizontal axis counts the number of cycles. Two rates of stress variation are shown here, $$\dot{\sigma}=2 \times 10^{-4}$$ (circles) and $$10^{-5}$$ (diamonds). As expected, $$\epsilon_{pot}$$ follows oscillations of the imposed stress. The higher the magnitude of the applied stress, the higher the potential energy per particle (note that the minima of $$\epsilon_{pot}$$ correspond to zero stresses). On the other hand, for the higher stress variation rate of $$\dot{\sigma}=2 \times 10^{-4}$$, $$\epsilon_{pot}$$ is permanently higher than its value at the very beginning of the stress cycles. The situation is different in the case of $$\dot{\sigma}=10^{-5}$$. Here, as the stress passes through zero, $$\epsilon_{pot}$$ takes again values identical to those in the absence of the stress. We thus consider this lower stress variation rate as quasistatic. The vertical dashed lines mark simultaneously the maxima of $$\epsilon_{pot}$$ and $$|\sigma|$$. They serve to better recognize the asymmetry of $$\epsilon_{pot}$$ on both sides of the stress maximum and recall the presence of a hysteresis effect.

As to the effect of $$\dot{\sigma}$$, when $$|\sigma|$$ is increased faster, a given wall velocity is reached at a higher $$|\sigma|$$. This may be rationalized by noting that, at a higher stress increase rate, the system has less time to develop a response corresponding to the actual (instantaneous) value of the stress. Therefore, the mobility increase corresponding to an increase of the stress is retarded and is observed later, i.e., at a higher stress.

Results presented above and in previous works show that our model system shares many features of the so-called soft glassy materials. In particular, the existence of a yield stress is suggested in Fig. 14. Figure 15 underlines the existence of a static yield stress still further. Here, the dramatic change in the wall velocity at a threshold stress is emphasized using a logarithmic scale for the horizontal axis. In a narrow stress range around $$\sigma=0.6$$, the wall velocity and thus the overall shear rate increases approximately by three orders of magnitude (see also Fig. 1). Besides the hysteresis already discussed above, an investigation of the decreasing branch on the stress–wall velocity curve in Fig. 15 reveals that, as $$\sigma$$ falls below a certain value, the wall velocity becomes even negative (see the inset). This clearly illustrates the presence of attractive forces which, now, are stronger than the imposed stress and thus capable of reducing the amount of strain. Indeed, an inspection of the center-of-mass position of the wall and of the fluid shows that both these quantities exhibit a maximum at the place where the velocity passes through zero (as the stress is further reduced, $$X_{cm}$$ decreases in accordance with the observation of a negative velocity). Very similar observations are also reported on the experimental side.
V. MEASUREMENT OF THE YIELD STRESS

As discussed in Sec. I, there seems to be a close connection between the existence of a yield stress and the observation of the shear banding phenomenon in many soft glassy materials. In particular, it is commonly expected that, in a state where the yield stress vanishes (at high temperatures, for example) the shear bands should also disappear, i.e., the whole system should flow. In addition to this experimental aspect, a study of the yield stress is also motivated from the theoretical point of view. For example, the so-called soft glassy rheology model (SGR) of Sollich (an extension of the trap model taking into account yielding effects due to an external flow) predicts a linear onset of the dynamic yield stress as the glass transition is approached, \( \sigma(\gamma_{\text{rel}}=0) \sim 1 - x \). Here, \( x \) is a noise temperature, \( x=1 \) corresponds to the glass transition (or "jamming") temperature, and \( x<1 \) characterizes the glassy or "jammed" phase. On the other hand, numerical studies of a \( p \)-spin mean field Hamiltonian predict that the dynamic yield stress vanishes at all temperatures.

There has recently been a more microscopic approach based on an extension to a nonequilibrium situation of the mode coupling theory of the glass transition (MCT). An analysis of schematic models within this approach shows a rather discontinuous change in the dynamic yield stress at the mode coupling critical temperature, \( T_c \).

The reader may have noticed that the above mentioned theories make predictions on the dynamic yield stress [defined as \( \sigma(\gamma_{\text{rel}}=0) \)]. Our interpretation of the shear banding, however, makes use of the idea of resistance to an applied stress which is related to the presence of a static yield stress. Similar to the difference between the dynamic and static friction, the static and dynamic yield stresses are not necessarily identical. Indeed, for our model glass, we find that \( \sigma_y > \sigma(\gamma_{\text{rel}}=0) \) (see Fig. 2). Therefore, a measurement of the static yield stress gives at least an upper bound for the dynamic counterpart. As we will see below, the static yield stress decreases rather sharply as the mode coupling critical temperature of the model (\( T_c = 0.435 \)) is approached. Unfortunately, when measuring \( \sigma_y \) at temperatures close to \( T_c \), one is faced with the problem that the time scale imposed by the external force (which if of order of the inverse stress variation rate, i.e., \( \tau_{\text{rel}} = \sigma/\dot{\gamma} \) and that of the (inherent) structural relaxation, \( \tau_{\text{rel}} \), are not well separated. In particular, the condition \( \tau_{\text{rel}} \ll \tau_{\text{rel}} \) is not valid at temperatures close to \( T_c \). Therefore, as will be discussed below in more details, a conclusive statement on the interesting limit of \( \sigma_y(T \to T_c) \) can still not be made.

Preliminary results on the static yield stress have been recently obtained within the driven mean field \( p \)-spin models. Using the fact that the free energy barriers are finite at finite system size, the model has been investigated by Monte Carlo simulations in the case of \( p = 3 \) for a finite number of spins, thus allowing the thermal activations to play a role which they could not play in the case of an infinite system size. Results of these simulations support the existence of a critical driving force below which the system is trapped "solid" and above which it is not "liquid". Results based on this new approach on the temperature dependence of the yield stress and, in particular, on its behavior close to \( T_c \) are, however, lacking at the moment.

Here, we adopt a method very close to a determination of the (static) yield stress in experiments, i.e., we use the definition of \( \sigma_y \) as the smallest stress at which a flow in the system is observed. As we are interested in a study of the temperature dependence of \( \sigma_y \) and, in particular, in \( \sigma_y(T) \) close to the mode coupling critical temperature, we have varied the temperature in the range of \( T \in [0.1, 0.44] \) (recall that \( T_c = 0.435 \)). For each temperature, \( \sigma \) was increased stepwise by an amount of \( d\sigma = 0.02 \) once in each 1000 LJ time units during which the velocity profile corresponding to the imposed stress is measured. Among other quantities, we also monitor the motion of the center of mass of the wall and also of the fluid itself. Note that the overall stress increase rate in these simulations is \( \dot{\gamma} = 2 \times 10^{-5} \), and thus corresponds to a quasistatic variation of the stress (see the discussion in Figs. 13 and 14). For each temperature, the simulation was performed using ten independent initial configurations.

Recall that there is always an elastic contribution to the system response to an applied stress. The corresponding center of mass velocity can simply be estimated as \( \dot{V}_{\text{cm}} = \sigma/G \). This contribution is negligible at lower \( T \) for two reasons: (i) due to the high stiffness of the system (large \( G \)), \( V_{\text{cm}} \) is relatively small and (ii) the onset of the shear motion is quite sharp at low \( T \) thus leading to much higher velocities (compared to \( V_{\text{cm}} \)) as soon as the applied stress exceeds \( \sigma_y \). In contrast, close to \( T_c \), the shear modulus is quite small (see, for example, the slope of the stress–strain curve at \( T = 0.43 \) in Fig. 12) thus leading to a larger \( V_{\text{cm}} \). Furthermore, there is no sharp variation in \( V_{\text{cm}} \) as a function of applied stress. For a measurement of \( \sigma_y \) close to \( T_c \), it is therefore important to correct for the elastic contribution to the system response. For this purpose, we have determined the \( T \)-dependence of the shear modulus. The center of mass velocity of the fluid
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shear stress. The imposed stress is shown on the vertical axis while the

distributed to the center of mass velocity cm is approximately of the order of 10

1

as

FIG. 16. Effect of temperature on the response of the system to imposed shear stress. The imposed stress is shown on the vertical axis while the center of mass velocity of the fluid (inner part of the system) is depicted as the horizontal axis. Each curve corresponds to an average over ten independent runs. The stress was increased stepwise by an amount of dσ = 0.02 once in each dt = 1000 LJ time units (σ ~ 2 × 10^-3). Note that the contribution of the elastic deformation to the center of mass velocity [Vcm = L, σ/(2G)], has already been subtracted from the data. Note also that the statistical uncertainty of Vcm is of the order of 10^-4. The vertical dashed lines show the limits of the Vcm-range used in the fit to σ = σy + aVcm.

has then been corrected subtracting, for each temperature, the

Vcm = dσ/(2G), has already been subtracted from the data. Note also that the statistical uncertainty of Vcm is of the order of 10^-4. The vertical dashed lines show the limits of the Vcm-range used in the fit to σ = σy + aVcm.

FIG. 17. The effect of the temperature on the static yield stress, σy. The solid line shows σy obtained from fits to σy = σy + aVcm (a and σy are fit parameters) using the fit range Vcm = [0.0003, 0.005] (see Fig. 16). The symbols correspond to σy defined as the smallest stress for which (and for all subsequent higher stresses) the wall velocity exceeds a certain minimum value, Vcm min. Three choices of Vcm min are compared: 10^-4 (circles), 10^-3 (diamonds), and 10^-2 (triangles). While σy is relatively insensitive to a choice of Vcm min at low temperatures, it is not the case for temperatures close to Tw, where it continuously decreases as the Vcm min is reduced. The vertical arrow marks the mode coupling critical temperature Tw = 0.435. For clarity, error bars are shown for the case of Vcm min = 10^-3 only.

As a first attempt to determine the yield stress, we apply linear fits to the data shown in Fig. 16. As shown in the same figure, the chosen fit range roughly corresponds to the plateau region at low temperatures. For T \( \leq 0.35 \), we thus expect the fit result not to be significantly different from the “real” value of σy. However, as an investigation of the high-T behavior of Vcm in Fig. 16 suggests, this method is not expected to give accurate results for σy at high temperatures (T \( \geq 0.38 \), say).

A slightly different approach in determining σy is to find the smallest stress for which the center of mass velocity exceeds a certain, small value, Vcm min. Here, we further require that Vcm must remain larger than Vcm min for all subsequent stresses. This last condition serves to reduce errors due to fluctuations of Vcm. In applying this definition, we use the result of each independent run on Vcm separately and thus obtain, for each Vcm min, a set of yield stress values. This allows an estimate of the statistical error. Figure 17 compares the yield stress obtained via the linear fit to Vcm with results of the second approach for Vcm min = 10^-4, 10^-3, and 10^-2. Not unexpectedly, it is seen from Fig. 17 that the quality of results on σy strongly depends on temperature. At temperature far enough from Tw, say, for T < 0.35, σy is rather insensitive to a change of Vcm min (differences caused by various choices of Vcm min are of order of the statistical error). At higher temperatures, however, the variation of σy with the choice of Vcm min is remarkable. At T = 0.43 it varies between 0.14, 0.22, and 0.33 for Vcm min = 10^-4, 10^-3, and 10^-2. Therefore, result on σy at temperatures close to Tw should be considered as rough estimates only.

Moreover, for a temperature of T = 0.2, we have also studied the effect of the waiting time on σy with the main result that, for waiting times of \( t_w \geq 4 \times 10^4 \), aging effects on σy are negligible at the studied temperature.19

The origin of the difficulty in estimating the static yield stress of the system at temperatures close to Tw, can be understood by comparing the time scales relevant to the problem. First, there is a time scale related to the imposed stress Tw = σ/\( \dot{\sigma} \). The second relevant time scale is that of the structural relaxation, Tw rel. The static yield stress is well defined in the limit of a quasistatic variation of stress, i.e., \( \dot{\sigma} \rightarrow 0 \) while at the same time keeping Tw rel ≫ Tw. Using \( \dot{\sigma} = 0.5 \) and \( \dot{\sigma} = 2 \times 10^{-5} \) (note that this value of \( \dot{\sigma} \) was used at all temperatures in order to determine the yield stress) we obtain Tw = 2 × 10^4. We are therefore led to verify if the condition Tw rel ≫ Tw = 2 × 10^4 is satisfied at all temperatures. For this purpose, we define Tw rel as the time needed by the mean square displacement of a tagged particle to reach the particle size. Figure 18 shows the mean square displacement of the unsheared system for T \( \in [0.1, 0.44] \) (recall that Tw = 0.435). For all these temperatures, the waiting time between the temperature quench (from an initial temperature of T = 0.5 to the actual temperature) and the beginning of the measurement was Tw = 1.8 × 10^4. At low temperatures, the MSD practically remains on a plateau for the whole duration.
of the simulation indicating that $\tau_{\text{relax}}$ is much larger than the simulated time of $2 \times 10^3$ LJ time units. At higher temperatures ($T \approx 0.41$), however, after a long plateau, the MSD eventually enters the diffusive regime and reaches a value comparable to unity within the simulated time window. Obviously, the condition $\tau_{\text{relax}} \gg t_w$ is violated at these temperatures. Hence at least for a waiting time of $t_w = 4 \times 10^4$ and for the choice of $\dot{\gamma} = 2 \times 10^{-5}$, the computed static yield stress is not well defined close to $T_c$.

VI. CONCLUSION

Results on the yield behavior of a model glass (a 80:20 binary Lennard-Jones mixture), studied by means of molecular dynamics simulations, have been reported. One of the major motivations of the present work is the observation of shear localization (below the glass transition temperature and at low shear rates) in the present model and the suggestion of a link between this phenomenon and the existence of a static yield stress (under applied stress, the system does not flow until the stress exceeds a threshold value). A particular emphasis thus lies on the yield stress and its dependence on temperature.

First, the system stress–strain curve under startup of steady shear has been studied. The effect of physical aging (characterized by the waiting time, $t_w$), shear rate ($\dot{\gamma}_{\text{tot}}$), and temperature on the stress–strain relation has been investigated. Regardless of these parameters, all observed stress–strain curves first exhibit an elastic regime at small shear deformations ($\gamma \approx 0.02$). The stress then increases up to a maximum, $\sigma_{\text{peak}}$, before decreasing towards the steady state stress at large deformations. The steady state stress (corresponding to large deformations) shows a dependence on temperature and on the applied shear rate, but is independent of the system history, indicating a recovery of the time transla-
tion invariance due to shear induced structural relaxation.\(^5\) In contrast, the stress overshoot $\sigma_{\text{peak}}$ (the first maximum of the stress–strain curves, sometimes described as a dynamical yield stress) depends both on the imposed shear rate and on the waiting time (physical aging). It is observed that, at relatively high shear rates or for large waiting times, the maximum stress increases with $\ln(\dot{\gamma}_{\text{tot}})$ or with $\ln(t_w)$, respectively. These observations are consistent with experiments on amorphous polymers\(^{30,34}\) and on metallic glasses,\(^{31,32}\) and also correspond to the behavior predicted using the soft glassy rheology model.\(^1\)

For shear rates below a certain, cross over shear rate, $\dot{\gamma}_{\text{co}}$, however, a decrease in the slope of $\sigma_{\text{peak}} - \gamma_{\text{tot}}$ curve is seen. A comparison with the steady state shear stress suggests that $\sigma_{\text{peak}}$ saturates at the steady state stress level as the imposed shear rate approaches zero. Moreover, an analysis of the mean square displacements of the unsheared system reveals that the cross over shear rate, $\dot{\gamma}_{\text{co}}$, is very close to $1/t_{\text{co}}$, where $t_{\text{co}}$ marks the time for which the mean square displacement gradually departs from the plateau-regime (see Fig. 5). We therefore associate this crossover with the beginning of the cage relaxation, which leads to the possibility of small (compared to the size of a particle) rearrangements thus allowing at least a partial release of the stress. $\dot{\gamma}_{\text{co}}$ is also comparable to the inverse of the waiting time: for $\dot{\gamma}_{\text{tot}} < \dot{\gamma}_{\text{co}}$, the response of the system is directly influenced by the aging dynamics.

In order to build a closer connection between our studies and typical rheological experiments, stress ramp simulations are performed and the system response is analyzed for various stress increase rates. In agreement with experiments on complex systems like pastes, dense colloidal suspensions and foams,\(^{14}\) hysteresis loops in the system response are observed. These loops become wider as $\dot{\gamma}$ increases. An analysis of the potential energy per particle for different $\dot{\gamma}$ nicely shows that high energy configurations are favored by the faster stress variations. This also yields an estimate of quasi-static stress application. We find that, for our model, $\dot{\gamma} = 2 \times 10^{-5}$ (LJ units) is slow enough so that simulations with this stress variation rate can be used in order to obtain a reliable estimate of the static yield stress.

Finally, the static yield stress, $\sigma_y$, is determined and its reliability is discussed. Our numerical results confirm the observation of Ref. 17, that the static yield stress is higher than the low shear rate limit $\sigma_y(\dot{\gamma}_{\text{tot}}=0)$ observed in steady shear experiments. The system can therefore produce shear bands for stresses in the range $\{\sigma_y(\dot{\gamma}_{\text{tot}}=0), \sigma_f\}$.

At temperatures far below the mode coupling critical temperature of the model ($T_c = 0.435$), a slight increase of $\sigma_y$ with further cooling is observed. At temperatures close to $T_c$, however, the static yield stress strongly decreases as $T$ is increased towards $T_c$. As to the reliability of the data, relatively accurate estimate of $\sigma_y$ is obtained at low temperatures (for $T \leq 0.35$). Results on the yield stress at temperatures close to $T_c$, however, are very sensitive to the applied criterion. An investigation of the dynamics of the unperturbed system reveals that, for $T$ close to $T_c$, the structural relaxation times are far from being large compared to the time scale imposed by the external force (the inverse of the stress
increase rate, $\dot{\sigma}/\sigma$). Therefore, for the simulated waiting time of $4 \times 10^4$, the static yield stress is no longer well defined at these high temperatures. This underlines the fact that a clear separation of time scales between the externally imposed and intrinsic time scales is necessary in order to properly define a static yield stress.

It must, however, be emphasized that, even though an increase of $\sigma$ apparently leads to a validity of $\tau_{\text{relax}} \gg \tau_{\text{w}}$, this would violate the condition of a quasistatic variation of the stress. A more physical way to improve the accuracy of results on $\sigma_{\text{Y}}$ is to increase the waiting time, in order to allow $\tau_{\text{relax}}$ to grow beyond $\tau_{\text{w}}$. Noting that, at higher temperatures (but still below $T_s$), $\tau_{\text{relax}}$ increases less strongly with $\tau_{\text{w}}$ (interrupted aging), the limit of large $\tau_{\text{relax}}$ becomes progressively more time consuming in terms of computation time.

Our numerical study shows that a very simple model, studied numerically on relatively short time scales, can exhibit most of the complex rheological behavior of soft glassy systems, but also of “hard” (metallic) glasses (it is interesting in this respect to note that the simulated system was originally intended to mimic a NiPd metallic glass). This suggests that these features are generic to most glassy systems, although in practice the values of the parameters may considerably vary from system to system.

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11 See, however, D. J. Lacks, Phys. Rev. Lett. 87, 225502 (2001), for an investigation of shear thinning in terms of potential energy landscape.


