Nonlinear rheology of a highly supercooled liquid

R. YAMAMOTO and A. ONUKI

Department of Physics, Kyoto University, Kyoto 606-01, Japan

Abstract. – We numerically examine nonlinear rheology of a highly supercooled two-dimensional fluid in shear flow via molecular-dynamics simulation. The viscosity exhibits marked shear-thinning behavior when the shear rate $\dot{\gamma}$ exceeds the inverse of the α relaxation time τ_α. Bond breakage events among particle pairs are found to occur collectively in clusters. The characteristic size ξ of such clusters grows strongly with lowering the temperature and decreases rapidly with increasing $\dot{\gamma}$ as $\xi \sim \tau_b(\dot{\gamma})^{1/4}$. Here $1/\tau_b(\dot{\gamma})$ is the bond breakage rate tending to $1/\tau_\alpha$ for $\dot{\gamma}\tau_\alpha \ll 1$ and growing as $\dot{\gamma}$ for $\dot{\gamma}\tau_\alpha \gg 1$. The viscosity is of order $\tau_b(\dot{\gamma})$ in glassy states.

In highly supercooled fluids below the melting temperature the structural relaxations are very slow [1], [2]. The zero-shear viscosity $\eta(0)$ is expected to be proportional to a long rheological time τ_η. An experiment on polymers suggested that τ_η is on the order of the so-called α relaxation time τ_α [3]. Then we are interested in a nonlinear response regime in shear flow when the shear rate $\dot{\gamma}$ exceeds the inverse of τ_α [4]. Though experiments on glass-forming fluids in this direction have not been abundant [5]-[7], Simmons *et al.* found that the viscosity $\eta(\dot{\gamma}) = \sigma_{xy}/\dot{\gamma}$ exhibits marked shear-thinning behavior $\eta(\dot{\gamma}) \cong \eta(0)/[1+\dot{\gamma}\tau_\eta]$ in soda-lime-silica glasses in steady states under shear. After application of shear, they also observed overshoots of the shear stress before approach to steady states. However, because recent theoretical efforts have been focused on slow relaxation of time correlation functions, such nonlinear, nonequilibrium regimes have not attracted enough attention. The aim of this letter is to numerically examine nonlinear rheology in a two-dimensional model fluid mixture in supercooled amorphous states.

Our system is composed of two different atomic species, 1 and 2, with the numbers $N_1 = N_2 = 5000$, interacting via the soft-core potential $v_{\alpha\beta}(r) = \epsilon(\sigma_{\alpha\beta}/r)^{12}$ with $\sigma_{\alpha\beta} = (\sigma_\alpha + \sigma_\beta)/2$, where r is the distance between two particles and $\alpha, \beta = 1, 2$ [8]. The interaction is truncated at $r = 4.5\sigma_1$. The leapfrog algorithm is adopted to solve the differential equations with a time step of $0.005\tau_0$. The space and time are measured in units of σ_1 and $\tau_0 = (m_1\sigma_1^2/\epsilon)^{1/2}$. The average density is fixed at $n = 0.8/\sigma_1^2$. We take the size and mass ratios at $\sigma_2/\sigma_1 = 1.4$ and $m_2/m_1 = 2$. In our two-component system the difference of the particle sizes prevents crystallization at low temperatures, which will occur in one-component systems. We specify the thermodynamic
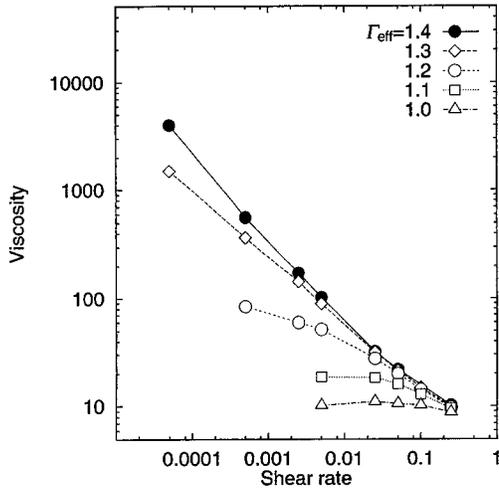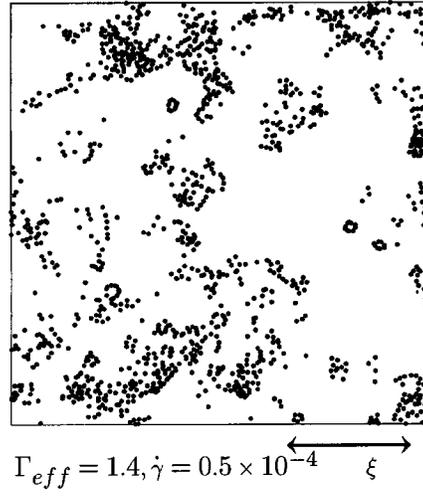
Fig. 1

$\Gamma_{eff} = 1.4, \dot{\gamma} = 0.5 \times 10^{-4}$ ξ

Fig. 2

Fig. 1. – The viscosity $\eta(\dot{\gamma})$ vs. the shear rate $\dot{\gamma}$ at various Γ_{eff} in dimensionless units.

Fig. 2. – A snapshot of the broken bonds at $\Gamma_{\text{eff}} = 1.4$ and $\dot{\gamma} = 0.5 \times 10^{-4}$. The time interval is $0.05\tau_{\text{b}}$, so 5% of the initial bonds are broken here. The arrows indicate ξ. The horizontal axis is in the flow direction, while the vertical axis is in the velocity gradient direction.

states using the coupling parameter $\Gamma_{\text{eff}} = n(\epsilon/k_{\text{B}}T)^{1/6} \sum_{\alpha,\beta} x_\alpha x_\beta (\sigma_\alpha + \sigma_\beta)^2/4$ [8], [9], where x_1 and x_2 are the compositions of the two components and are $1/2$ in our case. Data are taken at $\Gamma_{\text{eff}} = 1.0$, 1.1, 1.2, 1.3, and 1.4. The temperature is 2.54, 1.43, 0.850, 0.526, and 0.337, respectively, in units of ϵ/k_{B}. The pressure is 32.8, 27.0, 23.6, 21.63, and 20.5, respectively, in units of ϵ/σ_1^2.

We have detected no enhancement of the composition fluctuations, which are the fluctuations of the difference $n_1 - n_2$ between the two densities, n_1 and n_2, at any wave numbers, so the system is effectively one-component. The system is also confirmed to be highly incompressible in the sense that the combination $\sigma_1^2 n_1 + \sigma_2^2 n_2$, which may be regarded as the volume fraction of particles, exhibits very small fluctuations at long wavelengths ($q \ll 2\pi/\sigma_1$). The system is quiescent for $t < 0$ and is sheared for $t > 0$. To this end, we add the average velocity $\dot{\gamma}y$ to the velocities of all the particles in the x direction at $t = 0$ and afterwards maintain the shear flow by using the Lee-Edwards boundary condition [10], [11]. Then steady states are realized after a transient time. In our case shear flow serves to destroy glassy structures and produces no long-range structure. The temperature is kept at a constant value using the Gaussian constraint thermostat [10], [11]. (No difference was detected in our case between the profile-based and profile-unbased thermostats [11].)

In fig. 1 we display the shear-dependent viscosity $\eta(\dot{\gamma})$ in units of m_1/τ_0 vs. $\dot{\gamma}$ in units of $1/\tau_0$ in steady states for 5 values of Γ_{eff}. Its behavior is very similar to those in the experiments, though our system is two-dimensional. The viscosity is much enhanced at low temperatures and at low shear rates, but it tends to be independent of the temperature at very high shear rates. Remarkably, glassy states exhibit large non-Newtonian behavior even when $\dot{\gamma}$ is much smaller than the microscopic frequency $1/\tau_0$ in contrast to usual liquid states [12].

We follow bond breakage processes as in our previous work on unsheared supercooled fluids [13]. That is, for each atomic configuration given at time t_0, a pair of atoms i and j is
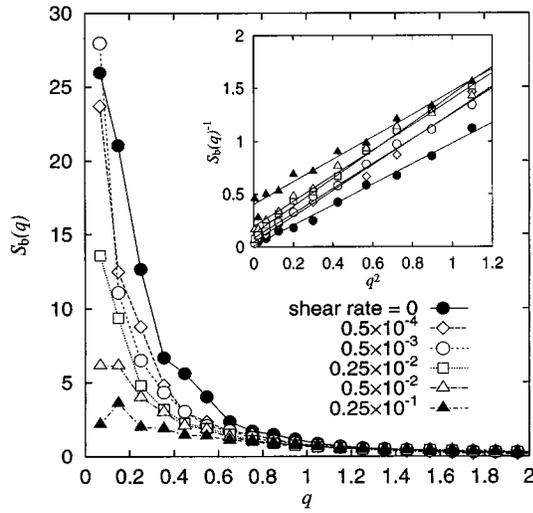
Fig. 3. – $S_b(q)$ of the broken bond density at $\Gamma_{\text{eff}} = 1.4$ for various $\dot{\gamma}$. The insert shows $1/S_b(q)$ *vs.* q^2, from which ξ^{-2} is determined.

considered to be bonded if

$$r_{ij}(t_0) = |\mathbf{r}_i(t_0) - \mathbf{r}_j(t_0)| \leq 1.1\sigma_{\alpha\beta}, \tag{1}$$

where i and j belong to the species α and β, respectively, and $\sigma_{\alpha\beta} = \frac{1}{2}(\sigma_\alpha + \sigma_\beta)$. We have confirmed that all the pair distribution functions $g_{\alpha\beta}(r)$ have a sharp peak at $r \cong \sigma_{\alpha\beta}$. Therefore, the bonds thus defined have lengths close to $\sigma_{\alpha\beta}$ and the polygons composed of the bonds are mostly triangles [13]. We stress that our bond definition is insensitive to the factor in front of $\sigma_{\alpha\beta}$ as long as it is slightly larger than 1. After a lapse of time t a pair is regarded to have been broken if

$$r_{ij}(t_0 + t) > 1.6\sigma_{\alpha\beta}. \tag{2}$$

This definition of bond breakage is also insensitive to the factor in front of $\sigma_{\alpha\beta}$ as long as it is considerably larger than 1 and smaller than 2. We define a bond breakage time $\tau_b(\dot{\gamma})$ at various Γ_{eff} and $\dot{\gamma}$ such that 5% of the initially bonded pairs are broken in a time interval of $0.05\tau_b(\dot{\gamma})$. Our simulations can well be fitted to

$$1/\tau_b(\dot{\gamma}) \cong 1/\tau_b(0) + 0.57\dot{\gamma}. \tag{3}$$

The $\tau_b(0)$ is the thermal bond life time on the order of the α relaxation time τ_α growing strongly with increasing Γ_{eff} [13]. It may be roughly fitted to $\tau_b(0) \propto T^{-4}$ as well as to $\log \tau_b(0) \propto 1/T$ from our data. The second term of (3) is obviously the bond breakage rate induced by shear.

Figure 2 shows a snapshot of broken bonds at $\Gamma_{\text{eff}} = 1.4$ and $\dot{\gamma} = 0.5 \times 10^{-4}$ in a time interval $[t_0, t_0 + 0.05\tau_b(\dot{\gamma})]$. Here depicted are the center positions $\mathbf{R}_{ij} = \frac{1}{2}(\mathbf{r}_i(t_0) + \mathbf{r}_j(t_0))$ at the initial time t_0 of the broken pairs and the two terms on the right-hand side of (3) are of the same order.

Remarkably we can see that the broken bonds form *clusters* whose sizes grow with increasing Γ_{eff} and decrease with increasing $\dot{\gamma}$. They may be regarded as *cooperatively rearranging regions* [14] determined by Γ_{eff} and $\dot{\gamma}$. No appreciable heterogeneities can be detected from
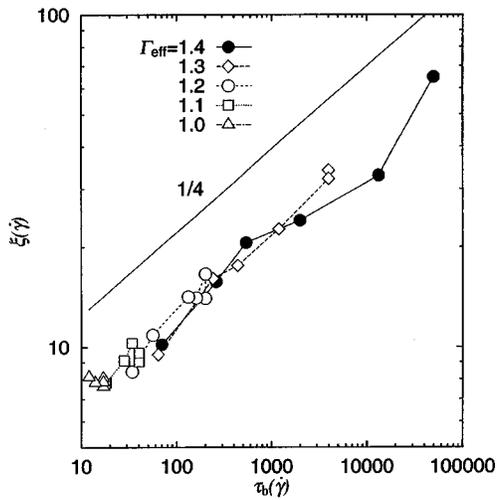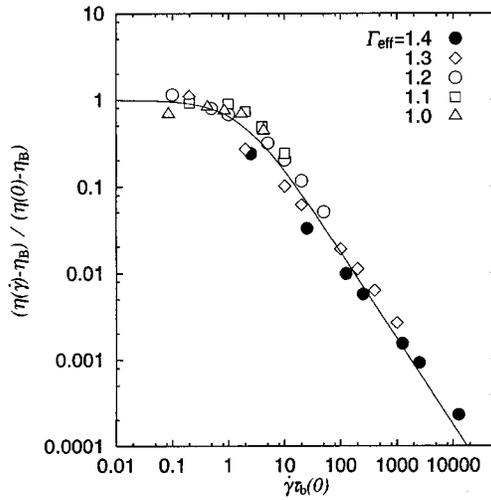
Fig. 4   Fig. 5

Fig. 4. – Universal relation independent of Γ_{eff} between the correlation length $\xi(\dot{\gamma})$ and the bond breakage time $\tau_{\text{b}}(\dot{\gamma})$. The data points at the largest $\tau_{\text{b}}(\dot{\gamma})$ for each Γ_{eff} are those at zero shear already given in ref. [13]. The line of the slope 1/4 is a viewing guide.

Fig. 5. – Universal relation between the ratio $(\eta(\dot{\gamma}) - \eta_{\text{B}})/(\eta(0) - \eta_{\text{B}})$ and $\dot{\gamma}\tau_{\text{b}}(0)$.

snapshots of the density, composition, and stress tensor [13]. As shown in fig. 3, by averaging 4-20 snapshots, we have calculated the structure factor $S_{\text{b}}(q)$ of the broken bond density defined by

$$S_{\text{b}}(q) = N_{\text{b}}^{-1} \left\langle \left| \sum \exp[i\mathbf{q} \cdot \mathbf{R}_{ij}] \right|^2 \right\rangle. \tag{4}$$

Here the summation is over the broken pairs and N_{b} is the total number of the broken bonds. The anisotropy of the structure factor is not large and the angular average over the direction of the wave vector is taken in fig. 3. By fitting $S_{\text{b}}(q)$ to the Ornstein-Zernike form $S_{\text{b}}(q) = S_{\text{b}}(0)/[1 + \xi^2 q^2]$, we can determine the characteristic length ξ of the clusters. As shown in fig. 4, we have found that $\xi(\dot{\gamma})$ is uniquely determined by $\tau_{\text{b}}(\dot{\gamma})$ only as

$$\xi(\dot{\gamma}) \sim \tau_{\text{b}}(\dot{\gamma})^{1/4} \tag{5}$$

for any Γ_{eff} and $\dot{\gamma}$ used in our simulations. This relation suggests that the steady states may be characterized by a single parameter, $\tau_{\text{b}}(\dot{\gamma})$ or $\xi(\dot{\gamma})$, and that each steady state in the non-Newtonian regime may be mapped onto a quiescent state at a higher temperature with the same $\tau_{\text{b}}(\dot{\gamma})$ (or $\xi(\dot{\gamma})$). Here we conjecture that the α relaxation in shear is characterized solely by the shear-dependent bond breakage time $\tau_{\text{b}}(\dot{\gamma})$. To check this point experiments of dielectric relaxations in shear flow would be very informative.

We have further examined the relation between $\eta(\dot{\gamma})$ displayed in fig. 1 and $\tau_{\text{b}}(\dot{\gamma})$ given in (3). In agreement with Simmons et $al.$ [5], [6] our simulations yield a simple rheological relation

$$\eta(\dot{\gamma}) \cong 0.34\tau_{\text{b}}(\dot{\gamma}) + \eta_{\text{B}} \cong 0.34\tau_{\text{b}}(0)/[1 + 0.57\dot{\gamma}\tau_{\text{b}}(0)] + \eta_{\text{B}}, \tag{6}$$

where $\eta_{\text{B}} \cong 6.25$ is independent of Γ_{eff} and $\dot{\gamma}$. Figure 5 demonstrates that the ratio $(\eta(\dot{\gamma}) -$

$\eta_B)/(\eta(0) - \eta_B)$ can well be fitted to the universal curve of $1/(1 + 0.57x)$ with $x = \dot{\gamma}\tau_b(0)$ independently of Γ_{eff}. For $\dot{\gamma}\tau_b(0) \gg 1$ we obtain the temperature-independent behavior $\eta(\dot{\gamma}) \cong 0.59/\dot{\gamma} + \eta_B$, which is evident in fig. 1. When $1/\tau_b(0) \ll \dot{\gamma} \ll 0.1$, the shear stress is simply given by 0.59 (in units of $m_1/\tau_0^2 = \epsilon/\sigma_1^2$). Namely, the shear stress tends to a *limiting stress* while $\eta(\dot{\gamma}) \gg \eta_B$.

The mapping relation between sheared states and quiescent states is still a hypothesis and should be further checked in future work. At present we have confirmed that the structure factors $S_{\alpha\beta}(q)$ $(\alpha, \beta = 1, 2)$ of the density fluctuations are not much different from those in quiescent states even for non-Newtonian shear $\dot{\gamma}\tau_\alpha > 1$ as long as $\dot{\gamma}\tau_0 \ll 1$. Our system is so dense such that the soft-core potential energy changes drastically even for slight changes of the distance of neighboring particle pairs. Therefore, the pressure is produced mostly from the potential part and is $20\epsilon/\sigma_1^2$ at $\Gamma_{eff} = 1.4$ or at $k_B T/\epsilon = 0.337$. It is then natural that even slight anisotropic changes of the pair correlation functions $g_{\alpha\beta}(r)$ near the first peak $(\sim \sigma_{\alpha\beta})$ gives rise to a shear stress on the order of a few percents of the pressure in our system. On the other hand, in many fluid systems such as near-critical fluids or polymer solutions the structure factor $S(\mathbf{q})$ of the composition can be strongly anisotropic at long wavelengths when $\dot{\gamma}$ exceeds a small underlying relaxation rate [4].

We have also examined the transient behavior of the shear stress as a function of time after application of shear to find stress overshoots in glassy states in accord with the experiments. This aspect will be discussed in a forthcoming paper.

We propose more rheological experiments in glassy states of various glass-forming fluids. In particular, experiments in glassy states of colloidal mixtures seem to be promising, in which glassy structures may be disrupted even by gentle shaking. It is also known that shear flow can induce phase separation in asymmetric viscoelastic mixtures due to stress-diffusion coupling [4]. Such shear-induced effects can generally be expected near glass transition, though our system of the soft-core interaction exhibits no tendency of phase separation for the parameters chosen.

In summary, from MD simulations on a 2D soft-core mixture, we have examined nonlinear rheology in glassy states. The bond breakage time $\tau_b(\dot{\gamma})$ given in (3) is related to the correlation length ξ as (5), where ξ is obtained from the kinetic heterogeneities in the bond breakage process. The universal relations among ξ, $\tau_b(\dot{\gamma})$, $\dot{\gamma}$, and the excess viscosity $\eta(\dot{\gamma}) - \eta_B$ are simplest among those consistent with the experiments [5]-[7].

$$***$$

REFERENCES

[1] JÄCKLE J., *Rep. Prog. Phys.*, **49** (1986) 171.
[2] EDIGER M. D., ANGELL C. A. and NAGEL S. R., *J. Phys. Chem.*, **100** (1996) 13200.
[3] RICHTER D., FRICK R. and FARAGO B., *Phys. Rev. Lett.*, **61** (1988) 2465.
[4] ONUKI A., *J. Phys. C*, **9** (1997) 6119.
[5] SIMMONS J. H., MOHR R. K. and MONTROSE C. J., *J. Appl. Phys.*, **53** (1982) 4075.
[6] SIMMONS J. H., OCHOA R., SIMMONS K. D. and MILLS J. J., *J. Non-Cryst. Solids*, **105** (1988) 313.
[7] YUE Y. and BRÜCKNER R., *J. Non-Cryst. Solids*, **180** (1994) 66.
[8] MURANAKA T. and HIWATARI Y., *Phys. Rev. E*, **51** (1995) R2735.

[9]   BERNU B., HIWATARI Y. and HANSEN J. P., *J. Phys. C*, **18** (1985) L371.

[10] ALLEN M. P. and TILDESLEY D. J., *Computer Simulation of Liquids* (Clarendon, Oxford) 1987.

[11] EVANS D. J. and MORRISS G. P., *Statistical Mechanics of Nonequilibrium Liquids* (Academic, New York) 1990.

[12] HANLEY H. J. M., EVANS D. J. and HESS S., *J. Chem. Phys.*, **78** (1983) 1440.

[13] YAMAMOTO R. and ONUKI A., *J. Phys. Soc. Jpn.*, **66** (1997) 2545.

[14] ADAM G. and GIBBS J. H., *J. Chem. Phys.*, **43** (1965) 139.