

## Comparison between thermal and deformation-induced structural relaxation in atomic glasses

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### ABSTRACT

Plastic yielding in glassy solids has been interpreted as a strain-biased relaxation process, or, equivalently, as a strain-induced glass transition. In the present work, the atomic motions caused by athermal plastic deformation of a binary Lennard-Jones glass are compared to thermal motion in the liquid in terms of the self part of the intermediate structure factor. We find that like at finite temperature, athermal plastic deformation leads to diffusive atomic motion at all length scales beyond about one interatomic distance, effectively promoting structural relaxation. The present approach allows to study the interplay of deformation-induced and thermal relaxation. Preliminary evidence is presented that these two processes occur independently of each other over a wide range of strain rates.

### INTRODUCTION

Both glasses and crystalline solids undergo plastic yielding when subjected to sufficient deviatoric stress. Whereas the phenomenon of yielding and plastic deformation can be described quantitatively in terms of the nucleation and mobility of lattice defects in the case of crystalline materials [1], the elementary processes of deformation are still not completely understood for amorphous solids.

One possible viewpoint is that deviatoric stress causes a de-vitrification, analogous to the glass-to-liquid transition that occurs as the system is heated above its glass transition temperature  $T_g$ . According to this concept, the onset of plastic deformation would therefore be indicative of a stress- or strain-induced glass transition [2–5]. A closely related concept interprets plasticity as a stress-biased relaxation [6].

Recently, strong fundamental interest has arisen in the fluidization of amorphous systems by shear [7–10]. It has been realized that while glass-forming fluids behave liquid-like under shear, flow stops below a critical shear stress. The term “jamming” has been coined for this phenomenon [11]. The decay of structural correlations in simulations of a glass-forming system under shear at finite temperature has been studied in detail by Berthier and Barrat [7, 9, 12, 13]. Their results show that while structural relaxation is efficiently promoted by plastic deformation, the functional form of the relaxation curves remains essentially unaltered. These results have led to the formulation of the strain-temperature superposition principle [7].

This raises the question how deformation-induced and thermal relaxation processes superimpose at finite temperature. To address this problem, we have performed deformation simulations both at  $T = 0$  as well as at finite temperature. This allows for a systematic comparison of purely deformation-induced relaxation to its thermal counterpart,

and to quantify the relative importance and superposition of the two sources of relaxation for deformation at finite temperature. As discussed in detail in the remainder of this paper, it was found that deformation-induced and thermal relaxation processes are largely independent of each other, superposing in an additive manner over a wide range of strain rates.

## MODEL AND SIMULATION DETAILS

Structural relaxation in liquids is commonly characterized in terms of the decay of structural correlations as a function of time. In particular, the self part of the intermediate scattering function  $\Phi_s(\mathbf{k}, t)$  has been used for this purpose. Structural relaxation in glasses under plastic deformation can be analyzed in an analogous way. The application of plastic deformation leads to a decay of structural correlations which can be quantified as a function of deformation  $\epsilon$  by the intermediate scattering function  $\Phi_s(\mathbf{k}, \epsilon)$ , the shape of which can then be compared to its time-dependent counterparts  $\Phi_s(\mathbf{k}, t)$  obtained from the thermal liquid.

Our study has focused on a binary Lennard-Jones fluid similar to the system introduced by Stillinger and Weber [14] in order to model the glass former  $\text{Ni}_{80}\text{P}_{20}$ . This particular system was selected because its thermal dynamics have been studied in great detail by Kob and Andersen [15–17] and, more recently, by Sastry *et al.* [18].

The model used in this study consists of 3200 type A and 800 type B atoms in an orthorhombic box subject to periodic continuation conditions. Thermal equilibrations at various temperatures was carried out by using molecular dynamics simulations by integrating the equations of motion using the velocity form of the verlet algorithm with a time step of 0.05 followed by velocity rescaling. All quantities in this paper are indicated in terms of reduced units based on the mass  $m_A$ , Lennard-Jones well depth  $\epsilon_{AA}$ , and equilibrium separation  $\sigma_{AA}$  between type A particles. Plastic deformation was applied by changing the dimensions of the box by small amounts, while maintaining the fractional coordinates constant, and re-minimizing the potential energy of the system with respect to the fractional coordinates after each deformation step [19–23]. Pure shear mode of deformation was used, which conserves the volume of the simulation box. The deformation at finite temperature and strain rate was carried out by deforming the simulation cell after every time step. The affine deformation component was removed before calculating the self part of the intermediate structure factor to make sure that only the dissipative part of the particle displacement is considered [24]

## RESULTS AND DISCUSSION

The self part of the intermediate structure factor  $\phi_s(k, t; \epsilon)$  was obtained from molecular dynamics simulation of the binary Lennard-Jones liquid for various temperatures as a function of time, and as a function of strain for the deformation simulations. The results are isotropically averaged, and the magnitude of the  $\mathbf{k}$  vector was chosen at  $|\mathbf{k}| = 7.251 \sigma_{AA}^{-1}$ , close to the maximum of the static structure factor. Both thermal relaxation and plastic deformation cause the structure factor to decay to zero, indicating complete structural relaxation within the time / deformation scale of the simulation. The

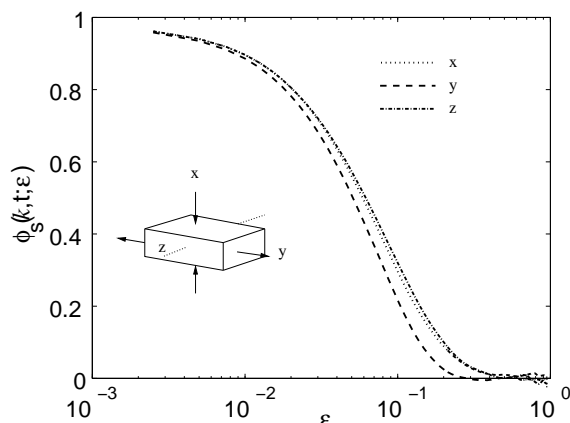


FIG. 1: Self part of the intermediate structure factor  $\Phi_s(\mathbf{k}, \epsilon)$  for various directions of  $\mathbf{k}$  at  $T=0$ . A: uniaxial deformation B: pure shear deformation

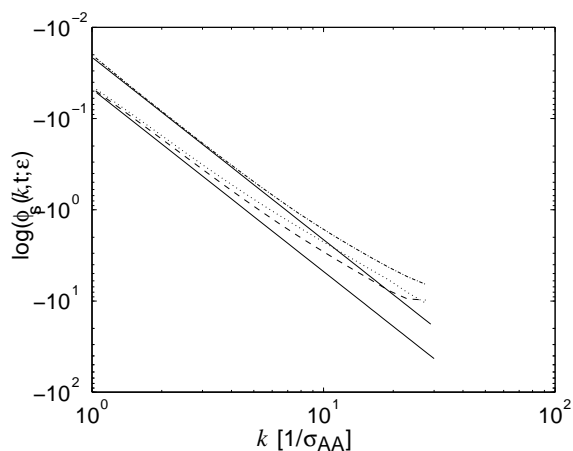
TABLE I: KWW stretching exponent values for thermal and strain-induced relaxation

condition	Structure Factor			
	$\beta_x$	$\beta_y$	$\beta_z$	$\beta_{iso}$
Pure Shear Deformation	1.02	1.23	1.03	1.15
$T=0.61$				0.89
$T=0.7$				0.91
$T=0.8$				0.92
$T=1.0$				0.96
$T=2.0$				1.02

Kohlrausch-Williams-Watts stretched exponential functions  $\exp -(t/t_0)^\beta$  or  $\exp -(\epsilon/\epsilon_0)^\beta$ , respectively, were found to provide very good fits to the simulation data. The values of the stretching exponent  $\beta$  are indicated in Table I. The thermal dynamics of the binary Lennard-Jones system have previously been studied in terms of  $\Phi_s$  by other authors [17, 18]. Our values for the stretching exponent  $\beta$  as well as the relaxation time  $t_0$ , obtained for thermal equilibration, are in quantitative agreement to those reported by Sastry *et al.* [18].

The decay of the intermediate structure factor caused by deformation is slightly faster than exponential (Table I). The correlation strain  $\epsilon_0$  was found to be about 8%, which approximately coincides with the yield strain of the system under study here [25]. Structural memory in this glassy solid is therefore lost very shortly after global plastic yielding sets in. This result is in agreement with the observation that the physical aging history in glasses is erased by deformation past the yield point [25–27].

Whereas thermal structural relaxation in the liquid state is isotropic by definition, some degree of anisotropy is to be expected in the case of plastic shear deformation. The self part of the intermediate structure factor  $\Phi_s(\mathbf{k}, \epsilon)$  for various directions of  $\mathbf{k}$  is shown in Fig. 1. The anisotropy is small, as indicated by only slight differences in the decay curves, and the correlation strain is independent of the direction of  $\mathbf{k}$ . This justifies discussion on the basis of the isotropic average  $\Phi_s(k, t; \epsilon)$ . On the other hand, the stretching exponent  $\beta$  does display some dependence on direction (cf. Table I). Close inspection of results from pure shear deformation simulations reveals that  $\beta$  values slightly above unity are obtained in directions of extensional strain, whereas all other directions exhibit exponential relaxation. By comparing the  $\beta$  values obtained for both thermal and plastic relaxation, it can be concluded that plastic deformation with a constant strain rate  $\dot{\epsilon}$  produces structural relaxation dynamics similar to the high temperature liquid. This result confirms even at zero temperature the de-vitrification hypothesis, as well as the shear-temperature concept proposed by Barrat and Berthier [7]. It is also in accord with the equivalence of temperature and shear as control parameters for jamming in granular systems [11]. Whereas the thermal glass transition takes the glassy solid to a supercooled liquid, in which



**FIG. 2:**  $\log(\Phi_s(|\mathbf{k}|, t_0; \epsilon_0))$  versus  $\mathbf{k}$  for temperature equilibration at  $T=0.61$  (dotted line) and at  $T=1.0$  (dashed line) and pure shear deformation at  $T=0$  (dashed-dotted line).  $t_0$  and  $\epsilon_0$  are the correlation time and strain, respectively. Straight lines with a slope of  $-2$  have been included for comparison.

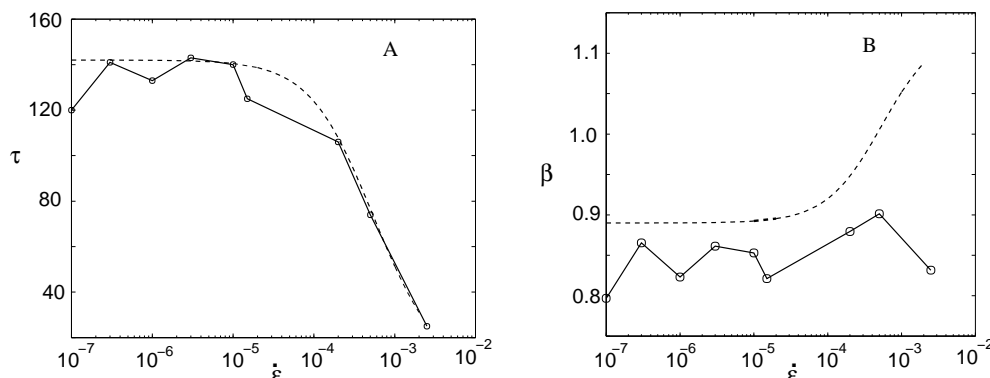
the structural relaxation follows a stretched exponential, plastic yielding seems to circumvent the slowed dynamics of the supercooled regime, and directly brings about exponential relaxation reminiscent of the high-temperature fluid. Recently it was reported that continuous shear in a system very similar to the one under study here leads to a stretching exponent close to 1 at temperatures below the static glass transition [12]. Our results are in agreement with this finding.

In addition to the time dependence of the intermediate structure factor, the  $k$  dependence also carries interesting information. In the case of a purely diffusive process, where each particle performs a perfect random walk, a Gaussian dependence  $\Phi_s(k, t) = \exp -Dtk^2$  would be expected. In this limit, a plot of  $\log \log \Phi_s$  versus  $\log k$  at a fixed time  $t$  yields a straight line with a slope of  $-2$ . Fig. 2 presents the simulation data in this form, with  $k$  in units of  $1/\sigma_{AA}$ . In the range  $1 < k < 2$ , the thermal relaxation curves exhibit a slightly smaller slope, which is caused by the influence of the energy landscape. Deviations from a straight line are visible above about  $k > 2$  for a temperature of  $T = 1.0$ , whereas they set in at a somewhat smaller  $k$  at lower temperature. These deviations are indicative of ballistic and cage-like motion over short length scales [28].

Again, the curve obtained from plastic deformation very closely resembles the thermal relaxation data at high temperature. A straight line with the appropriate slope of  $-2$  is observed at  $k$  values up to about 5. This indicates that apart from the mass transport due to the affine part of the particle displacement, plastic deformation induces diffusive motion of the particles in an atomic glass at length scales above about one half of a particle diameter.

Having studied separately the thermal and deformation induced relaxation, the next logical step is to study the interplay between these two modes of relaxation. This can be achieved by carrying out the deformation of the sample at a finite temperature ( $T=0.61$ ) and by analyzing the self part of the intermediate structure factor resulting from this study. Even though the intermediate structure factor for deformation at finite temperature has been studied previously [8, 9], the present approach benefits from the fact that we have studied deformation at zero temperature and at finite temperature. This gives us the opportunity to analyze the deformation induced relaxation and thermal relaxation separately and also to study and compare the relaxation when these two processes occur simultaneously.

The system was deformed at finite temperature ( $T=0.61$ ) with varying strain rates. This was done by deforming the simulation cell at a given strain rate after every MD time step.



**FIG. 3:** The relaxation time  $\tau$  (A) and the stretched exponential  $\beta$  (B) values obtained from the self part of the intermediate structure factor  $\Phi_s(|\mathbf{k}|, t)$  for pure shear deformation at  $T=0.61$  as a function of the strain rate. The dashed lines indicate the reference curves obtained by curve fitting the product equation(1) obtained for various strain rates.

The self part of the intermediate structure factor obtained from these runs  $\Phi_s(t)$  was curve fitted and the relaxation times  $\tau$  and the stretched exponential  $\beta$  values were obtained for various strain rates. Fig. 3 shows the variation of the  $\tau$  and  $\beta$  thus obtained as a function of strain rate. If the thermal relaxation and the relaxation induced by plastic deformation are independent of each other, the combined relaxation behavior can be predicted by the product expression of thermal equilibration at  $T=0.61$  and plastic deformation at  $T=0$  (1).

$$\Phi_s^0(\mathbf{k}, t) = \Phi_s^{T=0.61}(\mathbf{k}, t) \Phi_s^\varepsilon(\mathbf{k}, \dot{\varepsilon} \cdot t) \quad (1)$$

The product equation thus obtained for various strain rates was curve fitted and the values for  $\tau$  and  $\beta$  obtained are shown as the reference curves (dashed lines) in Fig. 3. The  $\tau$  values obtained for deforming the system at a finite temperature ( $T=0.61$ ) follows the reference curve closely apart from some numerical scatter occurring at low strain rates. Any significant deviation from the reference curve would have indicated that these two modes of relaxation are not independent of each other. But the absence of any such deviation shows that these two modes of relaxation are independent of each other. Fig. 3(b) shows the variation of  $\beta$  with strain rate. At low strain rates, the product equation (1) predicts that the relaxation will be dominated by the temperature component and at high strain rates, the system will gradually approach purely strain-induced relaxation behavior. While this is reflected in the relaxation times  $\tau$ , the  $\beta$  values obtained from deforming the system at finite temperature do not follow this predicted behavior. Even at high strain rates, the  $\beta$  values obtained are close to that of a thermal liquid (at  $T=0.61$ ). We therefore conclude that, for the temperature studied, the overall relaxation behavior can be predicted to follow a stretched exponential, with an apparent relaxation time that can be calculated from the purely thermal and purely strain induced relaxation times, and a stretching exponent characteristic of thermal relaxation at the same temperature. As far as the stretching exponent is concerned, this is in accord with recent results reported by Berthier and Barrat [13]. The same authors have also shown that the relaxation behavior is different at temperatures below the static glass transition, where a stretching exponent close to 1 was observed. More detailed simulations in order to further verify this behavior at various temperatures are currently underway in our group, and will be reported at a later occasion.

## CONCLUSION

In summary, systematic comparison of the dynamics caused by thermal relaxation in an atomic liquid and by athermal plastic deformation of the corresponding glass has shown striking similarity between the two processes. Plastic deformation, while proceeding by localized elementary relaxation events, globally produces diffusive motion, and complete structural relaxation is achieved shortly after the yield point. This result supports the concept of a strain-induced glass transition or stress-biased relaxation [6] as the fundamental mechanism of plasticity in amorphous solids. The availability of relaxation data at zero temperature allows to study the relative importance of thermal and strain induced relaxation during deformation at finite temperature. At  $T = 0.61$ , our results show that the two types of processes contribute to the total relaxation in an additive manner, and the apparent relaxation time can be predicted from the two contributions. The stretching exponent, however, remains at the same value irrespective of the strain rate.

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