Thermal versus deformation-induced relaxation in a glass-forming fluid

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Plastic yielding in glassy solids has been interpreted as a strain-biased relaxation process, or, equivalently, as a strain-induced glass transition. The similarity between the structural relaxation induced by plastic deformation and thermal equilibrium of glasses has led to the formulation of the strain-temperature superposition principle. 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. A new approach is presented that allows to study the interplay of deformation-induced and thermal relaxation. It is found that these two processes occur independently of each other over a wide range of strain rates. [DOI: 10.1063/1.1564056]

I. 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. This notion is based on the idea that structural relaxations, normally quenched below T_g, are activated by the elastic energy, much like they are activated by kinetic energy at temperatures above T_g. According to this idea, 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 liquidlike 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.[7,8,12,13] 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 a strain-temperature superposition principle.[7] It has also been realized recently that the dynamic state of amorphous systems under shear can be represented by a single fictitious temperature, obtained from fluctuations or from the Stokes–Einstein relationship.[12,14] In the case of a system deformed at a temperature below the static glass transition, this temperature is different from the thermodynamic temperature, and depends on the shear rate.[12,14] Interestingly, a wide range of different approaches to define such a fictitious temperature have been shown to yield the same value.[14]

Given the similarity of strain- or flow-induced and thermal relaxation in amorphous systems, the question arises how these two processes superimpose. This has been addressed by Malandro and Lacks,[9] who studied the relative contributions of strain- and thermally activated particle movements to the overall mean square particle displacement (and thus to the overall diffusion coefficient). Their results showed a decrease in magnitude of the shear-enhancement of the diffusion with increasing temperature and strain rate.

In this contribution, we present a different approach to this problem. We have performed deformation simulations in a glass-forming binary Lennard-Jones fluid both athermally ($T=0$), and at finite temperatures. This allows for a systematic comparison of purely deformation-induced relaxation to its purely thermal counterpart based on the functional form of suitable structural correlation functions. In addition, the relative importance of the two sources of relaxation can be quantified for deformation at finite temperatures. As discussed in detail in the remainder of this paper, it was found that the apparent structural relaxation time of a system under deformation at finite temperature can be predicted by a simple mixing rule from the static thermal relaxation time τ and the athermal relaxation strain ε_0.

II. 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 deforma-

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tion can be analyzed in an analogous way. In the extreme case of zero temperature, there is no thermal motion, and the correlation functions are constant over time as long as no deformation is applied. In order to accommodate plastic shear, however, the molecules in the glass must rearrange. This motion, as will be demonstrated in the following, leads to a decay of structural correlations which can be quantified as a function of deformation ε by the intermediate scattering function $\Phi_s(\mathbf{k},\varepsilon)$, 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[15] in order to model the glass former $Ni_{80}P_{20}$. This particular system was selected because its thermal dynamics have been studied in great detail by Kob and Andersen[16–18] and, more recently, by Sastry *et al.*[19]

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. The total potential energy of the system is given by the sum over all pair potentials

$$E_{ij}=4\varepsilon_{ij}[(\sigma_{ij}/r_{ij})^{12}-(\sigma_{ij}/r_{ij})^{6}]+c_{ij}r_{ij}^{2}+d_{ij}, \tag{1}$$

for $r_{ij}<r_c$, where r_{ij} is the distance between atoms i and j, and ε_{ij} and σ_{ij} are the energy and length parameters, respectively. The constants c_{ij} and d_{ij} are introduced to render E_{ij} continuously differentiable at the cut-off radius r_c. The values of $\varepsilon_{AA}=1.0$, $\varepsilon_{AB}=1.5$, and $\varepsilon_{BB}=0.5$ and $\sigma_{AA}=1.0$, $\sigma_{AB}=0.8$, and $\sigma_{BB}=0.88$ were used. The masses of the particles of type A and type B were $m_A=1.0$ and $m_B=0.53$, respectively. The length of the simulation box was 15. A cut-off radius $r_c=2.5$ was used in all the cases. All quantities in this contribution are expressed in terms of reduced units, i.e., length in units of σ_{AA}, energy and temperature in units of ε_{AA}, and time in units of $(m_A\sigma_{AA}^2/\varepsilon_{AA})^{1/2}$. The molecular-dynamics simulations were performed by integrating the equations of motion using the velocity form of the verlet algorithm with a time step of 0.05.

Initial structures were thermalized, departing from a fcc lattice, by the metropolis Monte Carlo method[20] at $T=5$ for 10^4 cycles. They were then equilibrated at $T=1.0$ by molecular dynamics with velocity rescaling for a total time of $t_{\mathrm{equil}}=10^3$. Subsequently, the temperature was set to the target value, and molecular dynamics was run for twice as long as necessary for the correlation functions to decay to zero. Only the second half of these runs was used for evaluation of the correlation functions reported in the following.

Plastic deformation simulations departed from the inherent structure obtained by conjugate gradient potential energy minimization[21] after the initial equilibration at $T=1.0$. Athermal 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.[22–26] This procedure essentially corresponds to coupling the system to a heat bath with infinite capacity at $T=0$. Pure shear and uniaxial modes of deformation were used, with single step deformation tensors $d\varepsilon_{xx}=-0.125\times10^{-3}$, $d\varepsilon_{yy}=0.125\times10^{-3}$, $d\varepsilon_{zz}=d\varepsilon_{xy}=d\varepsilon_{xz}=d\varepsilon_{yz}=0$, and $d\varepsilon_{xx}=-0.125\times10^{-3}$, $d\varepsilon_{yy}=d\varepsilon_{zz}=0.0625\times10^{-3}$, $d\varepsilon_{xy}=d\varepsilon_{xz}=d\varepsilon_{yz}=0$, respectively, up to a maximum deformation of $\varepsilon_{xx}=2.6$.[27] Note that the volume of the sample is conserved in these deformation modes. The potential energy of the system, the stress tensor and the coordinates of all the atoms were stored after each deformation/minimization step. The deformation at finite temperature was carried out by deforming the simulation cell by $d\boldsymbol{\varepsilon}=\dot{\boldsymbol{\varepsilon}}dt$ where $\dot{\boldsymbol{\varepsilon}}$ represents the strain rate tensor after every time step dt.

The self part of the intermediate structure factor $\Phi_s(\mathbf{k},t)$, also called the incoherent scattering function, is given as the Fourier transform of the normalized van Hove auto correlation function $G_s(\mathbf{r},t)$

$$\Phi_s(\mathbf{k},t)=\int G_s(\mathbf{r},t)e^{-i\mathbf{k}\cdot\mathbf{r}}d\mathbf{r}\Big/\int G_s(\mathbf{r},0)e^{-i\mathbf{k}\cdot\mathbf{r}}d\mathbf{r}, \tag{2}$$

where $G_s(\mathbf{r},t)d\mathbf{r}$ is proportional to the probability of observing a particle within $d\mathbf{r}$ of $\mathbf{r}$ at time t, given that it was located at the origin at time 0.[28] In the present contribution, we have calculated Φ_s as a function of time t for the thermal fluid and of deformation ε for the athermal glass. In the latter case, we have also studied the anisotropy of $\Phi_s(\mathbf{k},\varepsilon)$ along different directions in $\mathbf{k}$ space.

The motion of atoms caused by plastic shear deformation can be decomposed into two components. The first, purely caused by affine deformation of the particle positions, is not dissipative in nature and essentially corresponds merely to a change of frame of reference. In order to obtain the dissipative part of the particle displacements, which can meaningfully be compared to thermal motion in the liquid it is, therefore, necessary to remove the affine deformation contribution. This is readily achieved in the following way: The position of the ith particle at a particular stage of deformation, at strain ε, is given by

$$\mathbf{r}_i(\varepsilon)=\mathbf{H}(\varepsilon)\mathbf{s}_i(\varepsilon), \tag{3}$$

where the columns of the matrix $\mathbf{H}$ contain the basis vectors of the simulation cell and $\mathbf{s}_i$ is the fractional position vector of the ith particle. The change in the position of the particle i, between two different states of deformation ε_1 and ε_2, is given by

$$\Delta\mathbf{r}_i(\varepsilon_1,\varepsilon_2)=\mathbf{H}(\varepsilon_1)\mathbf{s}_i(\varepsilon_1)-\mathbf{H}(\varepsilon_2)\mathbf{s}_i(\varepsilon_2). \tag{4}$$

The change in the position of the particle due to affine deformation is given by

$$\Delta\mathbf{r}_i^{\mathrm{affine}}(\varepsilon_1,\varepsilon_2)=[\mathbf{H}(\varepsilon_1)-\mathbf{H}(\varepsilon_2)]\mathbf{s}_i(\varepsilon_1), \tag{5}$$

as $\mathbf{s}_i(\varepsilon_1)=\mathbf{s}_i(\varepsilon_2)$ for affine deformation. On subtracting this affine contribution from Eq. (4) we get

$$\Delta\mathbf{r}_i(\varepsilon_1,\varepsilon_2)-\Delta\mathbf{r}_i^{\mathrm{affine}}(\varepsilon_1,\varepsilon_2)=\mathbf{H}(\varepsilon_2)[\mathbf{s}_i(\varepsilon_1)-\mathbf{s}_i(\varepsilon_2)]. \tag{6}$$

This is the displacement we have used in the calculation of the deformation-dependent correlation functions.

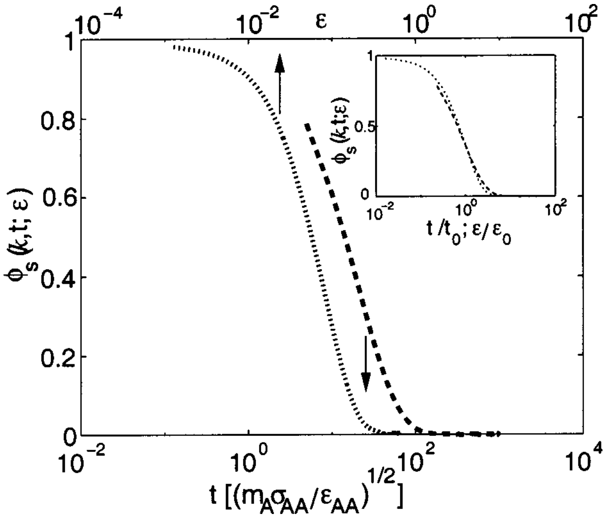

FIG. 1. Self part of the intermediate structure factor $\Phi_s(|\mathbf{k}|,t;\varepsilon)$ for temperature equilibration at $T=1.0$ (dashed line) and pure shear deformation at $T=0$ (dotted line) vs t. $|\mathbf{k}|=7.251$. A master curve representation of the same data is shown in the inset.

III. RESULTS AND DISCUSSION

Figure 1 shows the time dependence of the self part of the intermediate structure factor $\phi_s(k,t;\varepsilon)$ obtained from molecular-dynamics simulation of the binary Lennard-Jones liquid at $T=1.0$, and as a function of strain for the athermal 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 Kohlrausch–Williams–Watts stretched exponential functions $\exp-(t/t_0)^\beta$ or $\exp-(\varepsilon/\varepsilon_0)^\beta$, respectively, were found to provide very good fits to the simulation data. The values of the stretching exponent β are indicated in Table I. Even though similar studies have been carried out for deforming a glassy system at finite temperature,[8,29] the self part of the intermediate structure factor for athermal deformation of glasses has not been reported. In the absence of deformation the thermal dynamics of the binary Lennard-Jones system have previously been studied in terms of Φ_s by other authors.[16,19] Our values for the stretching exponent β as well as the relaxation time t_0, obtained for thermal equilibration, are in quantitative agreement to those reported by Sastry *et al.*[19] As is well known, the stretching exponent obtained from Φ_s tends to unity at high temperatures $T>1$, whereas slowed dynamics lead to lower values of β in the deeply supercooled regime $T_g<T<1$.

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

Condition	Structure factor			
	β_x	β_y	β_z	β_{iso}
Pure shear deformation	1.02	1.23	1.03	1.15
Uniaxial deformation	0.94	1.14	1.15	1.07
$T=0.61$ (no deformation)				0.89
$T=0.7$ (no deformation)				0.91
$T=0.8$ (no deformation)				0.92
$T=1.0$ (no deformation)				0.96
$T=2.0$ (no deformation)				1.02

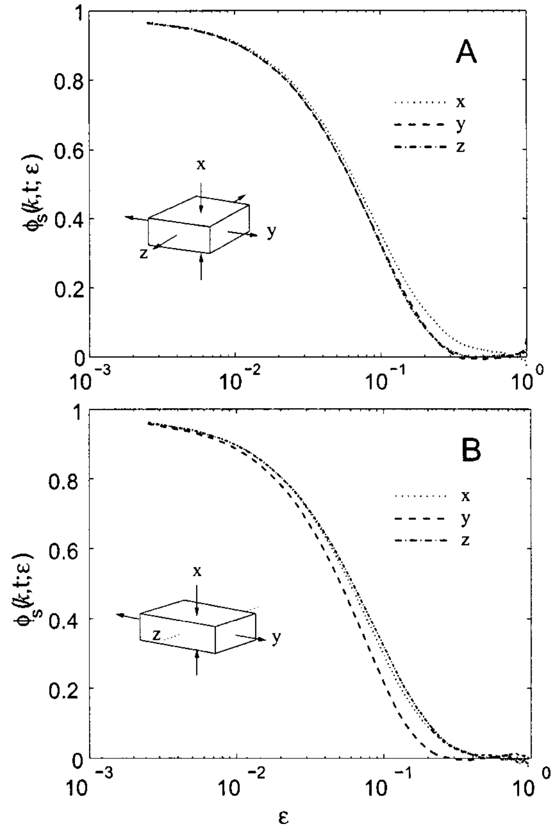

FIG. 2. Self part of the intermediate structure factor $\Phi_s(|\mathbf{k}|,\varepsilon)$ for various directions of $\mathbf{k}$ at $T=0$. A: uniaxial deformation; B: pure shear deformation.

The decay of the intermediate structure factor caused by deformation is slightly faster than exponential (Table I). The correlation strain ε_0 was found to be about 8%, which approximately coincides with the yield strain of the system under study here.[30] 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.[30–32] It also fits very well with a recent experimental study by Zhou *et al.*, which has shown the diffusion of diluents in glassy polymers to be greatly enhanced by plastic flow.[33]

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 $\Phi_s(\mathbf{k},\varepsilon)$ for various directions of $\mathbf{k}$ is shown in Fig. 2. 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 $\Phi_s(k,t;\varepsilon)$. On the other hand, the stretching exponent β does display some dependence on direction (cf. Table I).

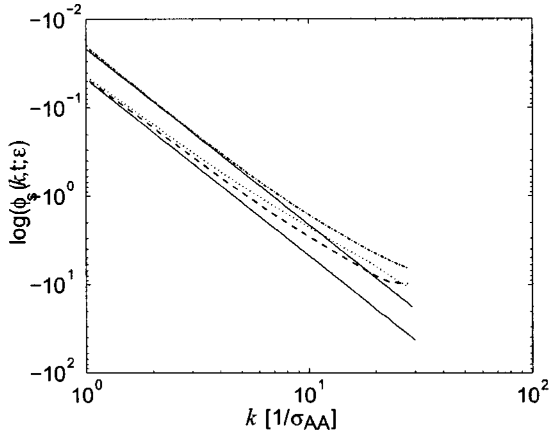

FIG. 3. $\log(\Phi_s(|\mathbf{k}|,t_0;\varepsilon_0)$ vs $\mathbf{k}$ for temperature equilibration at $T=0.61$ (dotted line) and at $T=1.0$ (dashed line) and pure shear deformation at $T=0$ (dot-dashed line). t_0 and ε_0 are the correlation time and strain, respectively. Straight lines with a slope of -2 have been included for comparison.

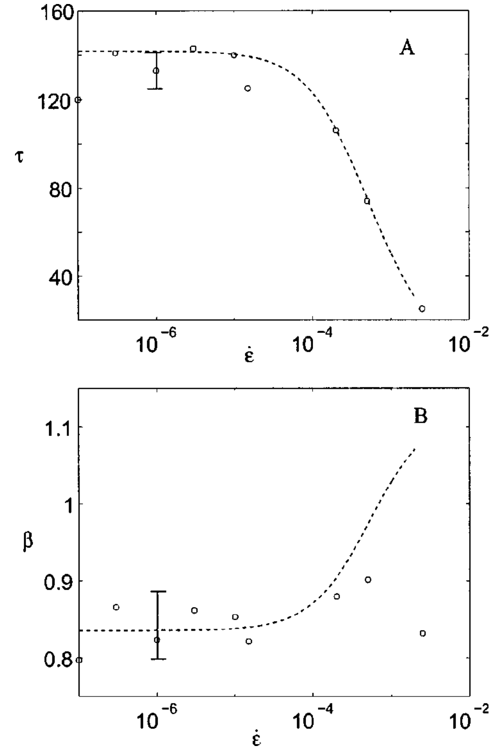

FIG. 4. The relaxation time τ (A) and the stretched exponential β (B) values obtained from the self part of the intermediate structure factor $\Phi_s(|\mathbf{k}|,t)$ for pure shear deformation at $T=0.61$ as a function of the strain rate. The dashed lines indicate the reference curves obtained by curve fitting the product equation (7) obtained for various strain rates.

Close inspection of results from pure shear and uniaxial deformation simulations reveals that β values above unity are obtained in directions of extensional strain, whereas all other directions exhibit exponential relaxation. It is conceivable that this effect is an artifact caused by the strict isochoric conditions under which the simulations were carried out. To good precision, the decay curve $\phi_s(k,\varepsilon)$ can be superimposed onto the high temperature thermal relaxation curve $\phi_s(k,t)$ by suitable scaling of the horizontal axis, as shown in the inset of Fig. 1. Plastic deformation with a constant strain rate $\dot{\varepsilon}$, therefore, seems to produce structural relaxation dynamics similar to the high temperature liquid.[7,8,29] This result reinforces the shear-temperature superposition concept in glassy systems introduced by Barrat and Berthier[7] and also supports the suggestion by Liu and Nagel regarding the equivalence of shear and temperature as control parameters in jammed systems.[11] Whereas the thermal glass transition takes the glassy solid to a supercooled liquid, in which structural relaxation follows a stretched exponential, athermal plastic yielding seems to circumvent the slowed dynamics characteristic of the supercooled regime, and directly brings about exponential relaxation reminiscent of the high-temperature fluid. This finding contrasts with the effective temperature calculated by Berthier and Barrat for shearing a binary Lennard-Jones system at finite temperature, which lies in the supercooled regime.[8]

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 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. Figure 3 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 cagelike motion over short length scales.[34]

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 both thermal and deformation induced relaxation, the next logical step is to study the interplay between the two. 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,[8,29] 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 contributions of the deformation induced relaxation and thermal relaxation when these two processes occur simultaneously.

The system was deformed isothermally at $T=0.61$ at various strain rates, and the self part of the intermediate structure factor $\Phi_s(k,t)$ was obtained from these runs. Again, the data are very well represented by stretched exponential functions, with the relaxation times τ and stretching exponents β shown in Fig. 4. At low strain rates, the relaxation time is independent of $\dot{\varepsilon}$, and corresponds to the static value for this temperature. Above $\dot{\varepsilon}\approx 10^{-5}$, a steep drop in τ is observed. This behavior is related to the phenomenon of shear thinning, which has been reported earlier.[7,29] By contrast, the observed β values are independent of the strain rate over the entire range investigated within the precision of the available data.

When thermal and deformation-induced relaxation processes occur simultaneously, it seems intuitively clear that their relative importance should depend on the strain rate. One expects that under conditions where $\varepsilon_0/\dot{\varepsilon}\gg\tau_0$ (where ε_0 represents the athermal relaxation strain and τ_0 the static thermal relaxation time), the apparent relaxation time should be entirely dominated by the deformation-induced processes. Conversely, at very low strain rates, thermal relaxation should be essentially complete before ε_0 is reached, and the apparent relaxation time is expected to be close to τ_0, independently of $\dot{\varepsilon}$. The relaxation times presented in Fig. 4 do follow this general scheme.

It is important to note that the above argument is based on the assumption that deformation-induced and thermal relaxation processes occur independently of each other, or at least nearly so. Our simulation data makes it possible to test this assumption quantitatively. If the two relaxation processes act independently, the total self part of the structure factor $\Phi_s(k,t)$ at finite temperature and strain rate should simply be product of the Φ_s obtained by athermal deformation and static thermal relaxation

$$\Phi_s(\mathbf{k},t)=\Phi_s^{T=0.61}(\mathbf{k},t)\Phi_s^{\varepsilon}(\mathbf{k},\dot{\varepsilon}t). \tag{7}$$

To a good numerical precision, the structure functions obtained from this product can again be represented by stretched exponentials. The resulting τ and β values are indicated as dashed lines in Fig. 4. To the available precision, the relaxation times are predicted by Eq. (7) over the entire range of strain rates. On the other hand, the stretching exponent β is predicted to raise to the athermal value of $\beta\approx 1.1$ at very high strain rates, whereas the simulations yield a value of $\beta=0.83\pm 0.4$, independent of $\dot{\varepsilon}$. This is in accord with earlier results from nonequilibrium molecular-dynamics simulations by Berthier and Barrat,[12] which also yielded a strain-rate independent stretching exponent. The same authors also reported that the stretching exponent goes to unity at temperatures below the static glass transition. More detailed simulations with the current approach in order to investigate this temperature dependence are currently underway in our laboratory and will be reported at a later occasion.

IV. 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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