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Stress Fluctuations in Glass-Forming Systems: Elastic Response and Long-Range Correlations

*Liudmyla Klochko, Jörg Baschnagel, Joachim Wittmer, Alexander Semenov**

Institut Charles Sadron, Université de Strasbourg, CNRS UPR22, 67034
Strasbourg, France

Summary: The dynamics of two model glass-formers (3D oligomer melt and 2D polydisperse colloidal system) are analyzed using MD simulations. It is found that the standard deviation of the shear modulus shows a striking peak near the glass transition T_g , which is explained with a quantitative theory. The simulation data well below T_g suggest that static multi-point correlations of local stress are long-range. The obtained correlation functions of time-dependent and wavevector-resolved stress for the 2D system are in excellent agreement with the developed theory indicating that the frozen-in stress inhomogeneities in the glassy state are correlated according to a power law.

Keywords: viscoelasticity; vitrification; polydispersity; colloids; correlations

Introduction

Some liquids (in particular, polymer melts) can be easily supercooled avoiding crystallization (even if the crystal state is favorable thermodynamically). Such supercooled liquids show dramatic slowdown of their dynamics (reflected in a strong increase of the α -relaxation time τ_α) as temperature T is cooled towards the vitrification point T_g where the system becomes kinetically arrested and forms an amorphous solid. Below T_g the relaxation time τ_α exceeds the time-scale t_{lab} accessible experimentally (or in a computer simulation). The glass transition region around T_g is characterized by a number of anomalies including a jump of the heat capacity, or an emergence of elasticity (of a finite quasi-static shear modulus μ) in a nearly discontinuous manner. However, this solidification is not accompanied by a significant change of the liquid structure which remains disordered. In particular, the static structure factor $S(q)$ changes very little near T_g .^[1, 2]

This common view implies that structural correlations in glass-forming systems must remain short-range near and below T_g . There is however a growing opinion that (at least for fragile glass-formers) the glassy structure is characterized by some (perhaps hidden and subtle) long-range correlations that are not visible in $S(q)$. Indeed, this idea is supported by the mosaic or random first order transition (RFOT) theories^[3, 4], by the concept of frustration-limited domains^[5, 6] and other approaches.^[3, 7, 8] In the present paper we show that investigations of stress fluctuations provide a powerful tool to study both the emergence of shear rigidity μ at the glass transition and the

long-range structural correlations in supercooled liquids.^[9, 10] We study two distinct glass-forming systems both theoretically and using MD simulations: The first system is a 3-dimensional (3D) melt of M oligomer chains, each of 4 beads.^[10, 11] The beads interact pairwise with a Lennard-Jones potential

$$u_{LJ}(r) = 4 (r^{-12} - r^{-6})$$

(r is the distance between two particles) which was truncated at $r_{cut} = 2.3$ and shifted so that $u_{LJ}(r) = 0$ for $r \geq r_{cut}$. The bond potential is harmonic, $u_b(r) = 0.5k_{bond}(r - l_{bond})^2$ with $k_{bond} = 1110$ and $l_{bond} = 0.967$ chosen to avoid chain crossings. The second system is a 2-dimensional (2D) polydisperse mixture of spherical LJ particles. Each pair of particles (of sizes d_i and d_j) interact with energy $u_{LJ}(r/d_{ij})$, where $d_{ij} = (d_i + d_j)/2$.

Simulation details

The 3D system consists of $M = 3072$ or $M = 768$ 4-mers. It was kept at pressure $P = 0$. It was equilibrated at different temperatures T by several relaxation stages as described in refs.^[11, 12]. An ensemble of $m = 100$ independent configurations was produced. The stress tensor was recorded at regular time points t_i :

$$t_i = i\delta t, i = 0, 1, \dots, \Delta t/\delta t \quad (1)$$

with the step $\delta t = 0.05\text{LJ}$ over the whole sampling time of $\Delta t = 10^5\text{LJ}$ (the time is measured using the LJ time unit ^[10]). The 2D system ^[13, 14] involves $N = 10^4$ particles. The particle size d_i , $i = 1..N$, is uniformly distributed between 0.8 and 1.2. The system was kept at constant external pressure $P = 2$ (in LJ units). It was equilibrated using the particle swap technique.^[15] Periodic boundary conditions are always applied.

Results

Viscoelastic properties of a liquid can be characterized by the shear relaxation modulus $G(t)$ which is a central rheological function of a material. $G(t)$ is closely related to the dynamical moduli $G'(\omega)$, $G''(\omega)$, where t is time and ω , the angular frequency. To obtain $G(t)$ for both systems we benefit from its relation to the temporal correlation functions of mechanical stress:

$$C(t) = \frac{V}{T} \langle \sigma(t+t')\sigma(t') \rangle$$

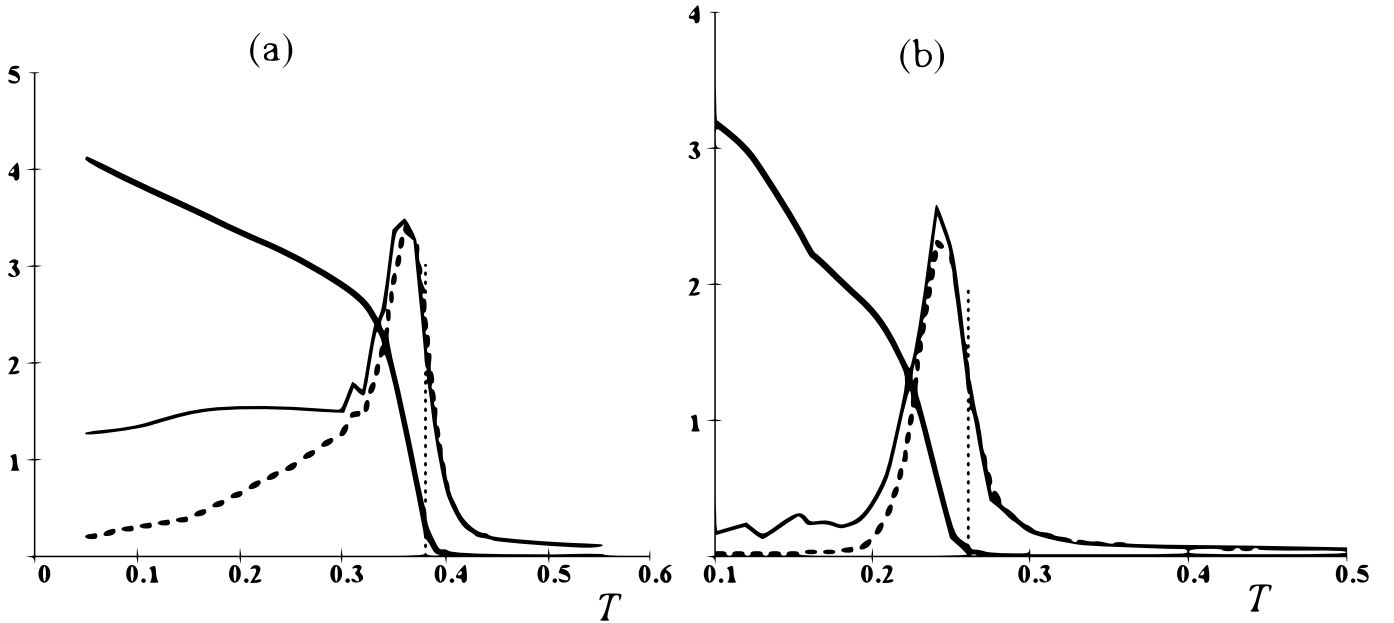


FIG. 1: (a) Temperature dependence of the quasi-equilibrium shear modulus μ (thick solid line shows $\mu/4$), its standard deviation $\delta\mu$ (thin solid line), and $\delta\mu_F^{(G)}$, the theoretical Gaussian approximation of $\delta\mu_F \approx \delta\mu$ (dashed curve) for the 3D 4-mer system with 12288 beads, with dilatometric $T_g = 0.38$. (b) Similar dependencies of $\mu/8$, $\delta\mu$ and $\delta\mu_F^{(G)}$ for the 2D polydisperse LJ system of $N = 10^4$ particles, $T_g = 0.26$. In both cases the sampling time is $\Delta t = 10^5 \text{LJ}$. The dotted vertical lines indicate T_g .

where V is the system volume, $\sigma(t) = \sigma_{xy}(t)$ is the shear stress (xy component) averaged over the whole system, and the brackets $\langle \dots \rangle$ mean averaging over the equilibrium ensemble which is equivalent to averaging over the time t' (below T_g we consider a quasi-equilibrium ensemble corresponding to a particular glassy state, i.e., a metabasin in the configurational space).

The generalized relation coming from the fluctuation-dissipation theorem (FDT) [10, 12] reads:

$$G(t) = \mu_A + C(t) - C(0)$$

where μ_A is the affine shear modulus providing the instantaneous stress response to a small affine deformation of the system (μ_A was calculated as described before [10]). Using the above relation, $G(t)$ was obtained in the range $0 \leq t \leq 10^5$, and then the quasi-equilibrium shear modulus μ was calculated as a time-average of $G(t)$: [10, 12]

$$\mu = \langle G(t_i - t_j) \rangle = \mu_A - \mu_F$$

where $\langle \dots \rangle$ here mean simple arithmetic average over i and j (cf. eq. 1), and $\mu_F = (V/T) \langle (\sigma(t) - \bar{\sigma})^2 \rangle$ is the fluctuation modulus. [10, 12] The modulus μ defined above is close to $G(t)$ for $t \sim \Delta t$ both

above and below T_g .

The obtained T -dependencies of $\mu = \mu(T)$ are shown in Fig. 1 (thick solid curves); the dotted vertical lines in Fig. 1 indicate T_g in energy units. It is clear that μ is very small at high T , but starts to grow sharply right below T_g . The standard deviation $\delta\mu$ of the modulus (across the ensemble of m independent configurations) is also shown in Fig. 1 (thin curves). The peak of $\delta\mu$ near T_g obtained for both systems can be explained by the rigorous theory based on the assumption that the stress fluctuations are Gaussian.^[10] The theoretical results are shown as dashed curves in Fig. 1. While the agreement is good around T_g and above it, it is obvious that well below T_g the simulated $\delta\mu$ is much higher than the theoretically predicted $\delta\mu_F^{(G)}$. This discrepancy indicates that stress fluctuations must be strongly non-Gaussian at low T 's. Recalling that the Gaussian character of random variables averaged over a large system volume V naturally comes from their short-range correlations, the latter result also means that correlations of stress fluctuations must become long-range well below T_g . This conclusion is also supported by the revealed system size dependence of the non-Gaussian part ($\delta\mu_F^{(nG)}$) of $\delta\mu_F$: our data show that at low temperatures $\delta\mu_F^{(nG)}$ decreases with V slower than $1/V$ suggesting that the 4-point correlations of local shear stress decay with distance r slower than $1/r^D$, where $D = 3$ is the space dimension.^[10]

To study the stress correlation range for the 2D system more directly we analyzed the correlation function of the stress tensor $\sigma_{\alpha\beta}$ at different wave-vectors \underline{q} (in addition to the space-averaged stress corresponding to $\underline{q} = 0$). For each \underline{q} we define the natural coordinate system with axis 1 along the wave-vector and axis 2 perpendicular to it. The generalized correlation functions are then defined as

$$C_{\alpha\beta\gamma\delta}(\underline{q}, t) = \frac{V}{T} \langle \sigma_{\alpha\beta}(\underline{q}, t + t') \sigma_{\gamma\delta}^*(\underline{q}, t') \rangle$$

where $\alpha, \beta, \gamma, \delta = 1$ or 2 . The simulation results for $C_2(t) = C_{2222}(q, t)$ are shown in Fig. 2 for $q = 2\pi/L$ ($L \approx 100$ is the system box size) at $T = 0.3$ and $T = 0.24$ (above and below $T_g \approx 0.26$). The theoretical results obtained using the FDT relations derived before^[9] are shown in Fig. 2 as well. An excellent quantitative agreement (with no adjustable parameters) is evident. A similar agreement was also observed for other components of the correlation tensor $C_{\alpha\beta\gamma\delta}$, other T 's and other wave-vectors.

It is instructive to coarse-grain the time-dependence of $C_{\alpha\beta\gamma\delta}$ to remove the short-time oscillations with the period $\sim 2\pi/(qc_L) \sim 10$ LJ, where c_L is the longitudinal sound velocity. Such smoothed correlation functions $C_{2\sim}(t)$ (with the coarsening time-scale $t_c \sim 4\pi/(qc_L) \sim 20$ LJ) are also shown

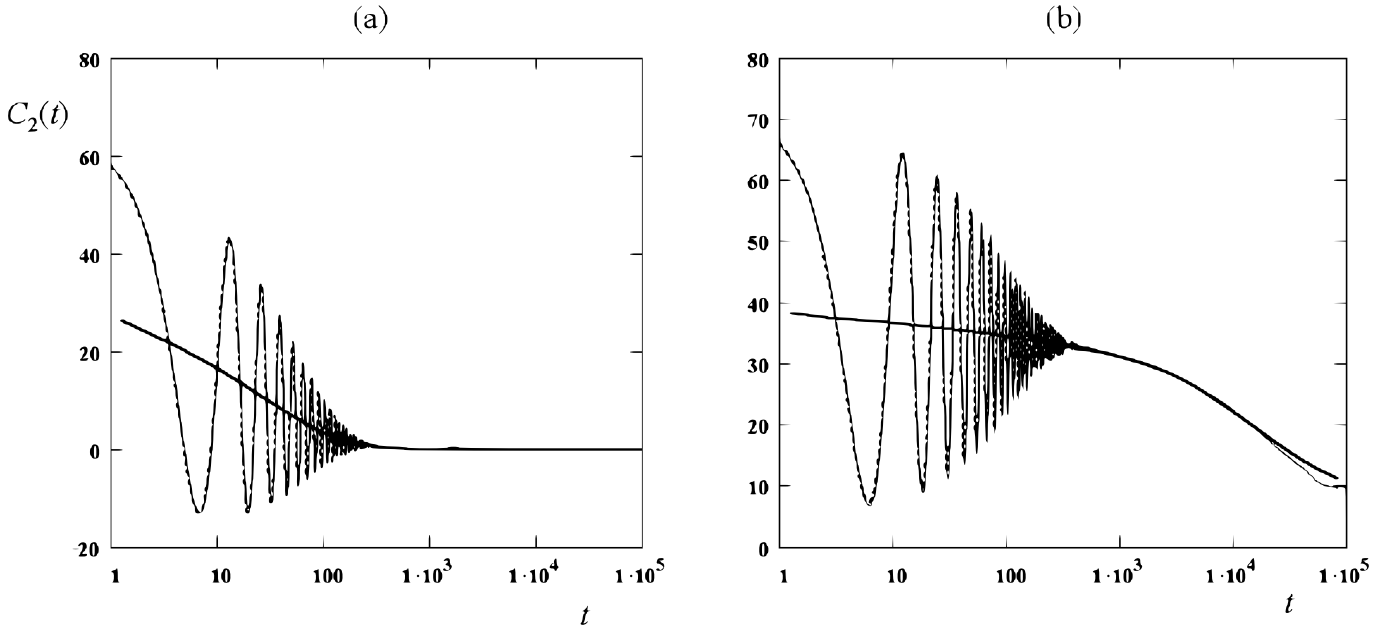


FIG. 2: (a) Time-dependence of the stress correlation function $C_2(t)$ at wave-vector $q = 2\pi/L$ for the 2D polydisperse LJ system at $T = 0.3$ (above T_g): direct simulation data (thin solid curve), theoretical predictions (thick dashed curve). Note that the two curves superimpose almost exactly. Thick solid curve corresponds to the smoothed correlation function $C_{2\sim}(t)$ with no oscillations; t is time in LJ units, $0 < t < 10^5$. (b) Similar data for $T = 0.24$ (below T_g).

in Fig. 2. The ensemble of simulation data supports the theoretical prediction^[9] that the only correlation function surviving coarse-graining at $t \gtrsim t_c$ is C_{2222} . The smoothed version of this function, $C_{2\sim}(t)$, just weakly depends on q for $q \ll q_{peak} \sim 5$ (more precisely, it is independent of q with accuracy $\sim 5\%$ for $q \lesssim 1$). This leads to the following distance dependence of the time-smoothed correlation function of the local shear stress $\sigma_{xy}(\underline{r}, t)$:

$$\langle \sigma_{xy}(\underline{r} + \underline{r}', t + t') \sigma_{xy}(\underline{r}', t') \rangle \simeq \frac{T}{\pi} C_{2\sim}(t) \left(\frac{1}{r^2} - \frac{8x^2y^2}{r^6} \right)$$

where $\underline{r} = (x, y)$. The above equation is valid for $t \gg t_c$ and $d \ll r \ll L$. It means that the stress correlations decay as $1/r^2$ in agreement with the previous simulation results^[16] and theoretical predictions^[9].

Conclusions

For the 3D oligomer system we demonstrated that the quasi-equilibrium shear modulus μ shows an anomalously strong dispersion near the dilatometric glass transition temperature T_g ^[10, 12] and that the system size dependence of this dispersion is indicative of the long-range 4-point static stress-correlations below T_g (showing a slow power-law decay, possibly with an infinite correlation

length).^[10] The MD results for tensorial stress correlations in the 2D polydisperse system we studied show an excellent quantitative agreement with the theory that we developed before^[9] both above and below T_g . These new data also indicate that below T_g the time-smoothed local stresses exhibit long-range spatial correlations decaying as $1/r^2$ with distance r . In other words, the inherent structures of this system are characterized by pronounced correlations of the anisotropic stress^[9] with almost infinite range, in agreement with the behavior reported for 2D and 3D Kob-Andersen (binary LJ) models.^[16, 17]

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