

Supporting Information: Construction of Quantitative Relation between Structural Relaxation and Dynamic Heterogeneity by Vibrational Dynamics in Glass-Forming Liquids and Polymers

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Molecular Dynamic Simulation

Molecular dynamic simulations are carried out for the six typical metallic glass-forming liquids by using open source code LAMMPS¹ package. Each metallic system is composed of 16000 atoms interacting by embedded-atom method (EAM) potentials. The initial configuration is equilibrated for 2 ns at $T = 2000$ K and $P = 0$ GPa with the time step of 2 fs in the isobaric-isothermal (NPT) ensemble by employing the Nose-Hoover barostat and thermostat. As for $\text{Cu}_{50}\text{Zr}_{50}$ liquids, different target pressure with $P = 0, 2, 5, 8, 10, 12, 15$ GPa is considered. Then the liquid is cooled down 300 K at a rate of 1.0 K ps^{-1} and constant pressure. The configurations collected at different temperature and a constant pressure

during quenching are subsequently further relaxed in NPT ensemble. Then the ensemble is switched to the canonical ensemble (NVT) and relaxed for 1 ns before the dynamics data is collected.

The CG bead-spring model² of a linear polymer chain is employed, which is widely used to investigate the glassy dynamics of supercooled polymer melts.^{3,4} The simulation system consists of 3200 monomers in all cases but $n=3$ where 3201 monomers are contained with the chain length from $n=2$ to 16. The nonbonded interaction of monomers is described via the truncated and shifted Lennard-Jones (LJ) potential which is given by $U_{LJ} = 4\epsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 \right] + U(r_{cut})$ where σ is the length scale, and ϵ is energy scales of the system, which controls the strength of the interaction. The reduced units are used in the simulated results. The length, energy and mass are separately in units of σ , ϵ and each bead mass m . The time and temperature are separately in units of $(m\sigma^2/\epsilon)^{1/2}$ and ϵ/k_B , where k_B is the Boltzmann constant. The constant $U(r_{cut})$ ensures a smooth transition of the full LJ potential to zero at the cutoff distance r_{cut} . The finitely extensible nonlinear elastic (FENE) potential, $U_{\text{FENE}}(r) = -\frac{1}{2}k_b R_0^2 \ln[1 - (\frac{r}{R_0})^2]$ with $k_b = 30\epsilon/\sigma^2$ and $R_0 = 1.5\sigma$, is employed to maintain the bond connectivity along neighboring beads of a chain. We consider the different nonbonded interaction potentials with $r_{cut}=1.5, 2.5$ and $\epsilon=0.85, 1.0, 1.5$ for $n = 16$ system. In order to check the effect of the chain rigidity on the relation between structural relaxation and dynamic heterogeneity, an additional angle potential, $U_B(\theta) = k_{bend}(1 + \cos\theta)$, is used to tune the chain stiffness by the values of k_{bend} and we consider the three different values of $k_{bend}=0.0, 1.0, 2.0$ for $n = 16$ system. $r_{cut}=2.5, \epsilon=1.0$ and $k_{bend}=0.0$ are used for other polymer systems with $n = 2, 3, 4, 5$. The initial particle configuration of the BS polymer melt is equilibrated for at least 100 times structural relaxation time τ_α at $T = 1$ and $P = 1$ in the NPT ensemble by utilizing Nose-Hoover barostat and thermostat. We use different target pressure with $P = 1, 5, 10$ for $n = 16$ polymer system. The last equilibrated configuration at higher temperature is use as the initial configuration, and is gradually cooled down to the next target temperature at the cooling rate of 4×10^{-6} . After sufficient long relaxation

at the target temperature and pressure, the configuration of the BS model polymer melts is further relaxed for $100\tau_\alpha$ in NVT ensemble before producing the dynamic properties. The time step is chosen as 0.005 and 0.01 at high and low temperature, respectively.

The TraPPE UA force field⁵ is adopted for the atomistic simulation of APS melt, and the more details can be found in the previous paper of our group.⁶ We use the CG APS model built by our group, where each PS monomer is mapped to a single LJ particle with force field parameters given in Ref.⁷ The CG model shows a rather excellent transferability in a very wide temperature of 100-600K. We use the naming method to specify the polymer systems, for example UAAPS10 referring to UA APS with 10 monomers per chain. UAAPS10 and UAAPS50 with the number of chain $M=125$ and 30 are considered in UA APS system. As for CG APS system, CGAPS50 and CGAPS100 are used, and the corresponding M are 240 and 100, respectively. MD simulations of UA and CG APS melts are both performed by using Gromacs⁸ package. The time step is separately set to 2 fs and 10 fs in UA and CG simulations. The initial configurations of APS system are equilibrated for at least 500ns under the NPT ensemble conditions of 1 atm and 600 K by using the Nose-Hoover thermostat and the Parrinello-Rahman barostat. Then, the equilibrated configuration at 600K is stepwise cooled down to 100K at the cooling rate of about 10^{-4}Kps^{-1} , which is long enough to ensure the equilibration of the system energy, density, chain conformations and local packing even at low temperatures.⁶ The equilibrated configurations in the NPT ensemble are used as the initial configurations to perform MD simulations in the NVT ensemble. After adequate relaxation at a temperature of interest, 5000 configurations are collected to analyze the dynamics properties of UA and CG APS.

Metallic Glass-Forming Liquids

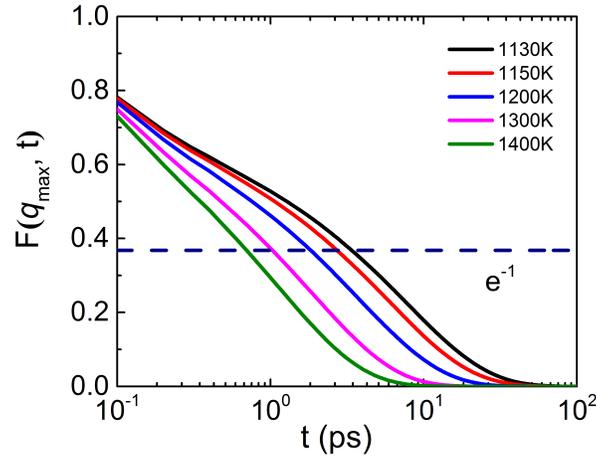


Figure S1: The incoherent intermediate scattering function $F_s(q_{max}, t)$ of $\text{Cu}_{50}\text{Zr}_{50}$ at several typical temperature. The structural relaxation time τ_α is defined by $F_s(q_{max}, \tau_\alpha) = e^{-1}$ as shown by the horizontal dashed line.

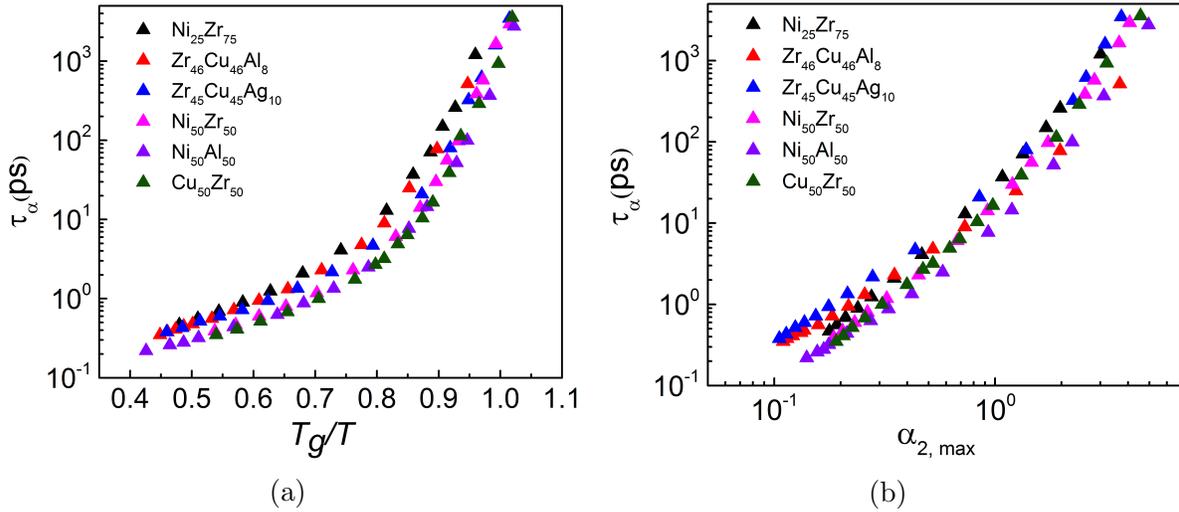


Figure S2: (a) Angell plots of the structural relaxation time τ_α versus T_g/T , where T_g is defined by $\tau_\alpha(T_g) = 10^4\text{ps}$ as the same with Ref.,⁹ (b) variation of τ_α with $\alpha_{2,\text{max}}$.

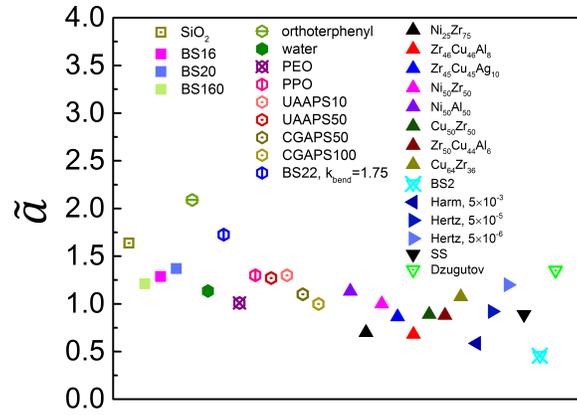


Figure S3: The values of \tilde{a} obtained by fitting in various types of glass-forming liquids.

The Bead-Spring Model Polymer Melts

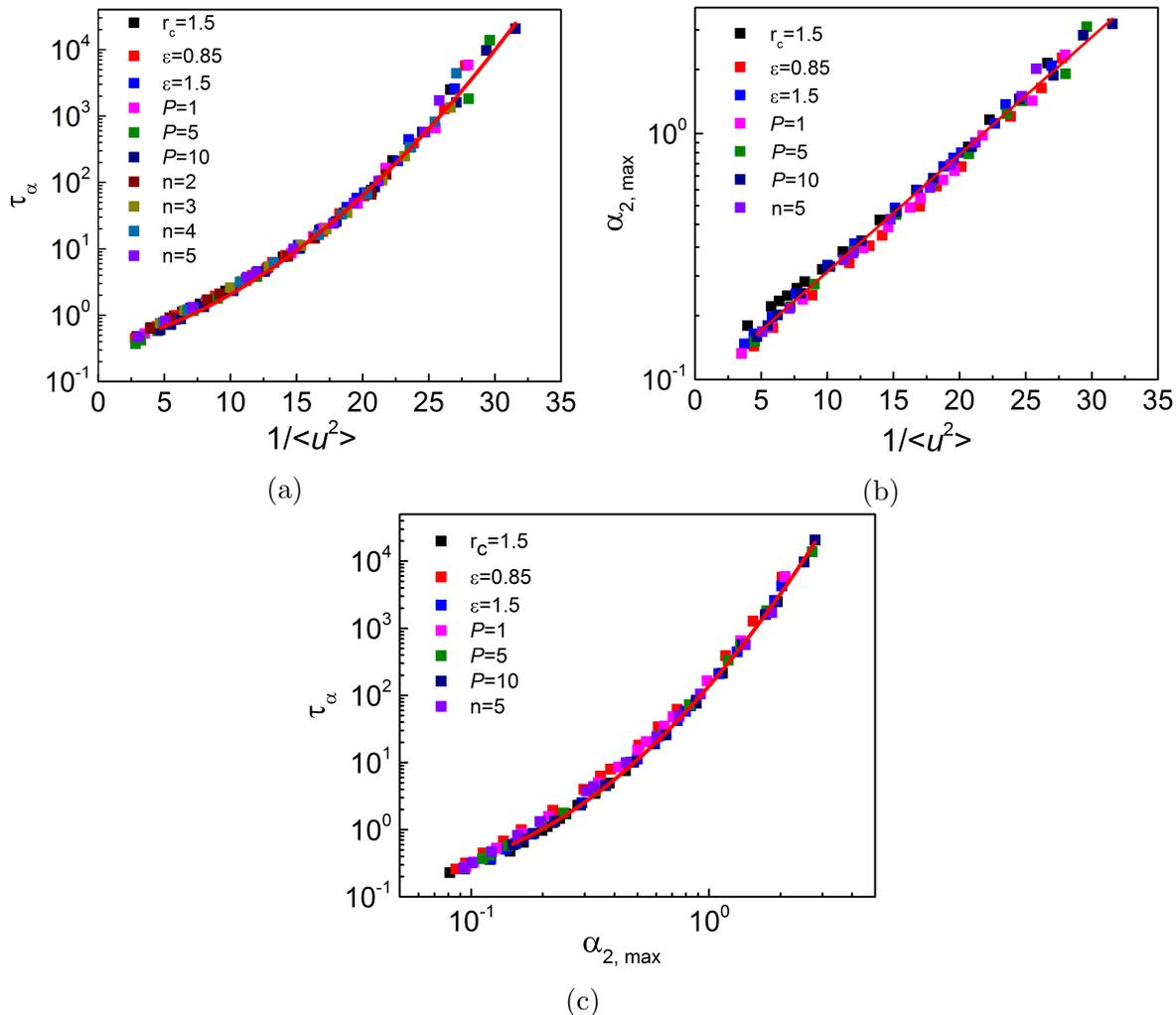


Figure S4: (a) Structural relaxation time τ_α versus the DW factor $\langle u^2 \rangle$, (b) the correlation between $\alpha_{2, \max}$ and $\langle u^2 \rangle$, and (c) the variation of τ_α with $\alpha_{2, \max}$ for the BS model polymer melts with different nonbonded interaction potential, chain length and pressure.

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