Spatially Heterogeneous Dynamics in the Density Scaling Regime: Time and Length Scales of Molecular Dynamics near the Glass Transition

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SUPPORTING INFORMATION

S.1 Decoupling between the segmental relaxation time τ and χ_4^{max} of PVAc

The analysis of the combined power law density scaling of τ and χ_4^{max} has been also performed for a representative of polymers. We have examined eq. 1 by using earlier reported experimental data of polyvinyl acetate (PVAc) (see Materials and Methods). The power law density scaling of the segmental relaxation times τ of PVAc has been achieved (the inset in Fig. S.1(a)) with the scaling exponent $\gamma = 2.35 \pm 0.02$ found by fitting (Fig. S.1) the experimental dependences $\tau(T,\rho)$ to eq. 3. The values of χ_4^{max} have been estimated for PVAc in the way described in Materials and Methods on the additional assumption that χ_4^{max} determines the correlation volume of the average number of dynamically correlated polymer segments. By fitting $\chi_4^{max}(T,\rho)$ to eq. 4 (Fig. S.1(b)), the value of the scaling exponent $\gamma_\chi = 1.74 \pm 0.01$ has been found, and then it has been very satisfactorily applied to scale the estimated values of χ_4^{max} of PVAc (the inset in Fig. S.1(b)). The comparative analysis of the isochronal dependences of χ_4^{max} on pressure is presented in Fig. S.1(c). The pressure dependences of the values of χ_4^{max} estimated at $\tau = 100s$, 1s, and 10ms are compared with their counterparts predicted from eq. 5b with the values of its parameters found from fitting $\tau(T,\rho)$ and $\chi_4^{max}(T,\rho)$ to eq. 3 and eq. 4, respectively. The obtained decreasing pressure dependences of the estimated values of χ_4^{max} at $\tau = const$ are in accord with their predicted counterparts. A discrepancy between estimated and predicted dependences at $\tau = 100s$ at the highest pressures can be caused by a large extrapolation of the values of τ and χ_4^{max} predicted from eqs. 3 and 4 beyond the pressure range of isothermal dielectric measurements at the highest temperatures.

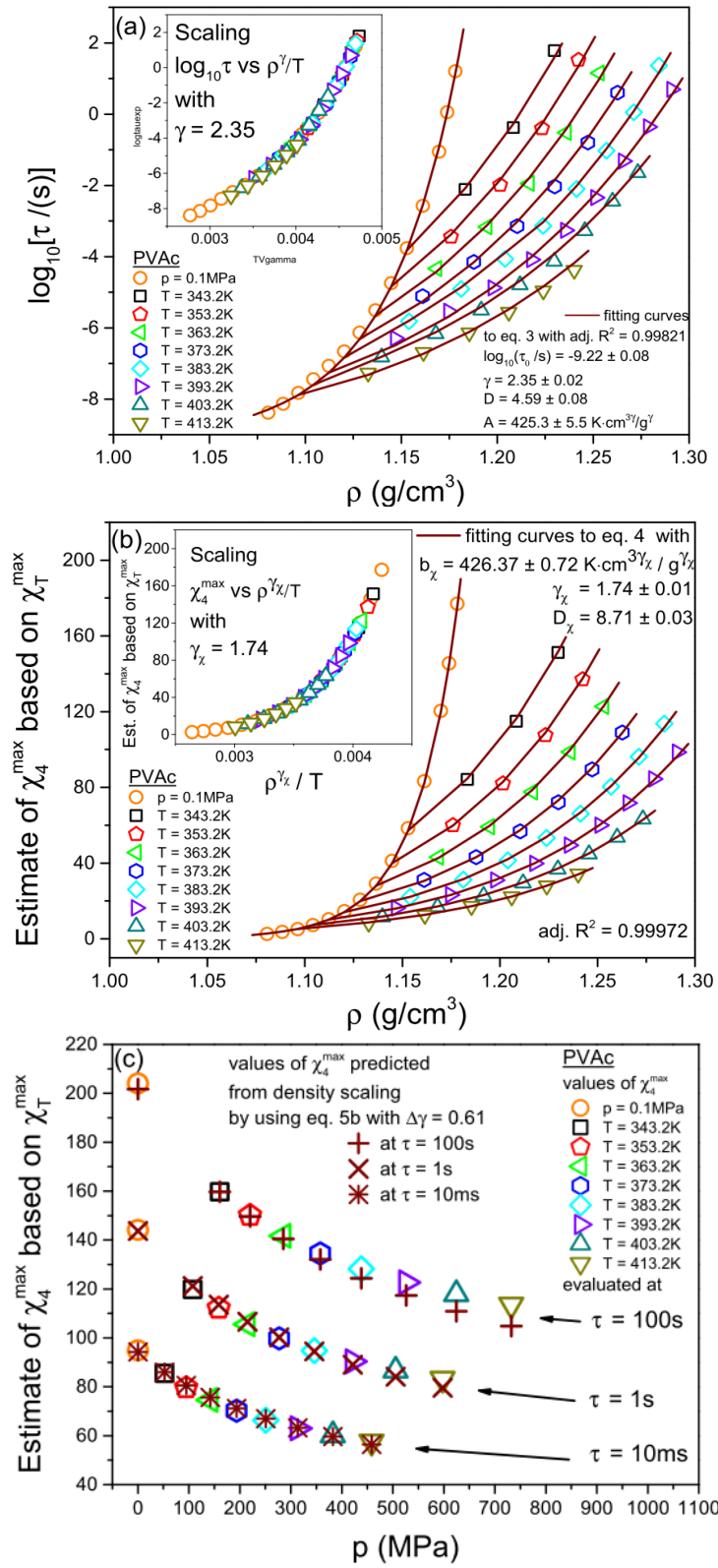Fig. S.1 The combined power law density scaling of τ and χ_4^{max} for PVAc (a) Plots of dielectric segmental relaxation times vs density. The inset in panel (a) presents the scaling $\tau\left(\rho^{\gamma}/T\right)$ with the values of γ found from the fitting shown in the panel. (b) Plots of the degree of the dynamic heterogeneity vs density evaluated at each (T,ρ) at which $\tau(T,\rho)$ is determined from experimental measurements. The inset in panel (b) presents the scaling $\chi_4^{max}\left(\rho^{\gamma_\chi}/T\right)$ with the values of γ_χ found from the fitting shown in the panels (c) Isochronal pressure dependences of the degree of the dynamic heterogeneity. Open symbols in panel (c) denote the evaluated values and the other symbols indicate values predicted from eq. 5b. The adjusted R^2 in panels (a) and (b) denotes the coefficient of determination appropriately adjusted by the degrees of freedom of the estimate of the population variance of the dependent variable and the estimate of the underlying population error variance, which is a measure of how well analyzed data are described by a tested nonlinear model. The quality of a fit is ideal if the adjusted $R^2 = 1$.

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S.2 Attempt to explain different scaling exponents for τ and $\chi_4^{\max}$ in real glass formers

The non-omissible difference between the values of the scaling exponents γ_χ and γ, which has been observed by us for real glass formers, is surprising and requires determining theoretical grounds for its explanation. We make the first attempt at elucidating this problem. Based on the fact that the established values $\gamma_\chi < \gamma$ for van der Waals liquids 1,1'-bis (p-methoxyphenyl) cyclohexane (BMPC) and *o*-terphenyl OTP as well as polymer PVAc, a reasonable scenario seems to consist in assuming that the attractive forces contribute to the dynamic heterogeneity that involves both spatial and temporal correlations in another way than these interactions affect the time scale of the structural relaxation near the glass transition. The scaling exponent γ in the power law $\tau\left(\rho^\gamma / T\right)$ is commonly related[26-33] to the exponent of the repulsive part of the short range effective intermolecular potential, $U(r) = A\left(r / \sigma\right)^{-m_{ILJ}} - B$, where B is a small constant or linear attractive background and $m_{IPL} \approx 3\gamma$. As can be seen in Fig. S.2, if we replace a small attractive background B with a small attractive term that is proportional to $\left(r / \sigma\right)^{-1}$ in the approximated Lennard-Jones potential, i.e., if we change the effective contribution of the attractive forces to the approximated potential, the value of the exponent of the repulsive IPL term, $m_{IPL} = 16$, is smaller than that ($m_{IPL} = 18$) estimated in the case of the effective potential with a constant small attractive term B.

It should be stressed that both the small effective contributions of attractive interactions to the effective intermolecular potential should not weaken the tendency to the density scaling related to the repulsive part of the approximate potential, because they result in almost the same approximations in the short-range limit. However, they imply in general different values m_{IPL} of the exponent of the repulsive IPL term, and consequently the scaling exponents predicted by $m_{IPL} / 3$ are also different. In this way, one can rationalize the discrepancy, $\gamma_\chi < \gamma$, obtained for real glass formers, making the assumption that the effective short-range intermolecular potential valid for the characteristic correlation volume is more affected by the attractive forces than that

proper for the characteristic time scale. Then, m_{IPL} is expected to be smaller for χ_4^{max} than that for τ, and consequently $\gamma_\chi < \gamma$.
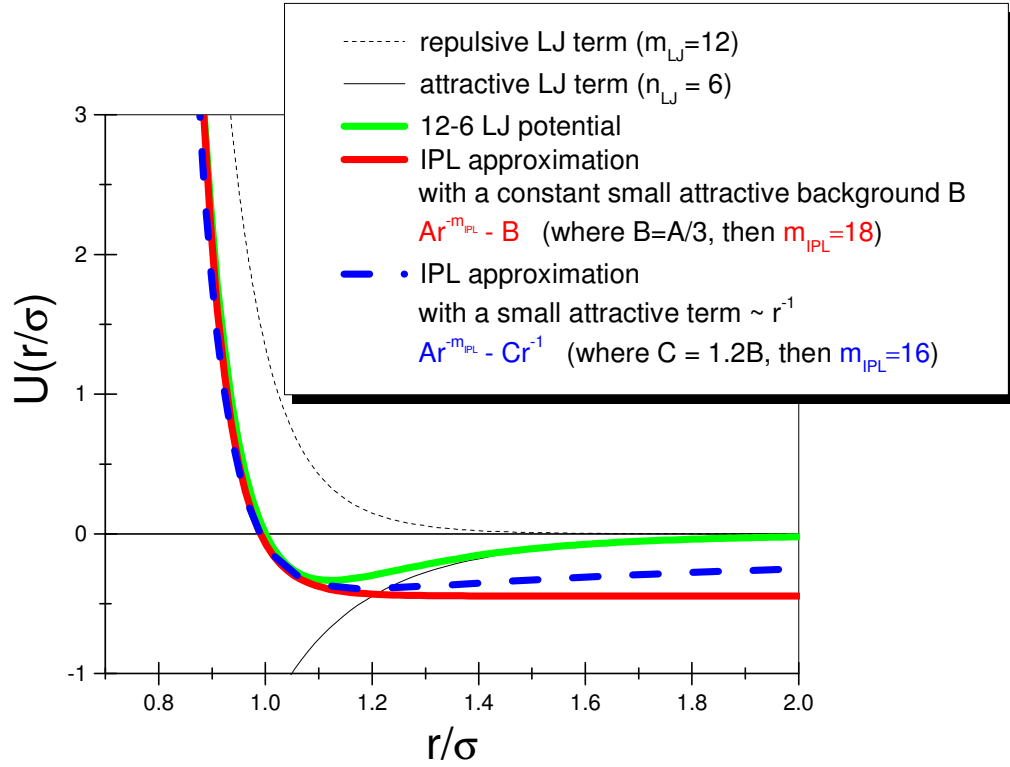

Fig. S.2. Illustration of the Lennard-Jones potential and its short range effective approximations

The suggested different sensitivities of τ and χ_4^{max} to intermolecular interactions seem to be reasonable, because the two point correlation function, which enables to determine the structural relaxation time τ, and the four point correlation function, the maximal value of which, χ_4^{max}, is analyzed in isochronal conditions, can be characterized by effectively different correlation ranges in case of real glass formers. It means that the four point correlation function can probe intermolecular interactions over a distance larger than that probed by the two point correlation function, whereas this distance is usually the same in the case of the four and two point correlation functions calculated from simulation data, because it is determined by the cutoff of the interactions assumed to perform the simulations.

S.3 Relation between τ and χ_4^{max} in the KABLJ model

After analyzing the relation between τ and χ_4^{max} for real glass formers, the next intriguing question arises as to whether the proposed formalism is valid for the simple models of supercooled liquids, which are widely exploited to investigate heterogeneous molecular dynamics by using direct measures of the dynamic heterogeneity that are naturally available in simulation studies, but are almost not applied to studies based on experimental data due to already mentioned large difficulties in measuring the four-point dynamic susceptibility. To answer the question we analyze our simulation data for the Kob-Andersen binary Lennard-Jones (KABLJ) model in the *NVT* ensemble.

It is already known that the structural relaxation times of the KABLJ liquid do not obey the power law density scaling in the exact sense,[30] but one can find an effective value of the scaling exponent γ that enables the scaling in terms of the function $\tau(\rho^\gamma/T)$ to a good approximation at least in limited ranges of T and ρ, which are, however, quite wide.[35] By using the Avramov scaling model (eq. 3), we find here (Fig. S.3(a)) the value $\gamma=4.59\pm0.05$ for the KABLJ system of 8000 particles, which enables us to scale τ in LJ units vs ρ^γ/T to a good approximation. However, an attempt at applying the function (eq. 4) previously used to scale the degree of the dynamic heterogeneity of real glass formers to determine a corresponding value γ_χ has ended with an insufficiently satisfactory fit of the dependence $\chi_4^{max}(T,\rho)$. The result of the preliminary test can be understood in the context of earlier reports,[14-17] according to which one can rather expect as already mentioned that $\ln\tau = f(\ln\xi_4^{max})$ for simple binary fluid models and kinetically constrained models. In fact, a high quality of the fit has been found (Fig. S.3(b)) for the *T-ρ* dependence of χ_4^{max} by means of the following scaling function,

$$\chi_4^{max} = (\chi_4^{max})_0 \exp\left[\left(A_\chi \rho^{\gamma_\chi}/T\right)^{D_\chi}\right], \qquad (S.1)$$

which morphologically corresponds to the Avramov scaling equation for the structural relaxation n time (eq. 3), but it has in general different parameters. Consequently, for the KABLJ model and other simple binary fluid models, and presumably for kinetically constrained models, eq. (1) can be interpreted as $\tau = g\left(\rho^{\Delta\gamma} f(\ln\chi_4^{max})\right)$ if the power law density scaling is valid at least to a good

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approximation. By analogy, $\tau = g\left(\Re(\rho)f(\ln \chi_4^{max})\right)$ with $\Re(\rho) = \Im_\tau(\rho)/\Im_\chi(\rho)$, is a version of

eq. 2 for simple models based on the Lennard-Jones potential and presumably for kinetically

constrained models, which is the generalization about eq. 1 not limited to a single power law

density scaling. Invoking the Avramov scaling model for τ and χ_4^{max}, eqs. 3 and S.1, we can

express eq. 1 for the KABLJ model as follows

$$\tau = \tau_0 \exp\left[\left(\rho^{\Delta\gamma}\left(\ln\left(\chi_4^{max}/(\chi_4^{max})_0\right)\right)^{1/D_\chi} A/A_\chi\right)^D\right]. \tag{S.2a}$$

Then,

$$\chi_4^{max} = (\chi_4^{max})_0 \exp\left[\left(\rho^{-\Delta\gamma}\left(\ln(\tau/\tau_0)\right)^{1/D} A_\chi/A\right)^{D_\chi}\right]. \tag{S.2b}$$

The above equations are postulated to be valid for the KABLJ model instead of eqs. 5a and

5b, which have been successfully verified by experimental data for BMPC and OTP.

It is interesting that the scaling $\chi_4^{max}\left(\rho^{\gamma_\chi}/T\right)$ for the KABLJ system examined in LJ

units is achieved in terms of eq. S.1 with the value $\gamma_\chi = 4.70 \pm 0.02$, which is slightly greater

than γ. Thus, in contrast to the tested real glass formers, $\Delta\gamma \gtrsim 0$, which causes that χ_4^{max}

slightly increases with density (or pressure) at $\tau = const$ (see squares in Fig. S.3(c)). This

behavior resembles an isochronal increase in the fragility parameter

$m_p = \partial \log_{10}(\tau)/\partial(T_g/T)\big|_p$ with density reported by Sastry[59] for the KABLJ model of 256

particles, which does not also match the usually decreasing[26-28] dependence of m_p on pressure

established from experimental data at the glass transition temperature T_g defined at $\tau = const$,

e.g., $\tau = 100 s$. It should be emphasized that the suggested formalism that links the density

scaling and the dynamic heterogeneity predicts an opposite effect of changes in temperature

and density on the dynamic heterogeneity in the case of the negative value of $\Delta\gamma$ determined

for the tested KABLJ liquid than that found for real glass formers. Very recently, we have

evaluated[12,13] that the isochoric changes of T more strongly exert on the dynamic

heterogeneity than the isothermal changes of ρ if we transform a real glass former from a state

(T,ρ) characterized by a structural relaxation time to another state at a different τ. A thorough

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inspection of the degrees of the dynamic heterogeneity $\chi_4^{\max}$ of the KABLJ liquid in isothermal and isochoric conditions as functions of the structural relaxation times τ confirms (the left panel of Fig. S.3(d)) the predicted opposite behavior of the dynamic heterogeneity in this model on varying ρ and T.

However, the theory of isomorphs[44] recently formulated for viscous liquids clarifies that a hidden scale invariance[33,34] in such liquids can be revealed if the already mentioned reduced units are applied. Therefore, we investigate the molecular dynamics of the KABLJ liquid and its scaling properties also by using the reduced units (see Materials and Methods). As a result (Fig. S.3(e)), we find a slightly better scaling $\tilde{\tau}\left(\rho^{\gamma}/T\right)$ in the reduced units than $\tau\left(\rho^{\gamma}/T\right)$, especially in the short-time limit, which is in accord with previously reported results[34,35] for the KABLJ system of 1000 particles. What is more, the value of γ obtained from fitting $\tilde{\tau}$ to the Avramov scaling model matches the value γ_{χ} that enables us to scale $\chi_4^{\max}$ vs $\rho^{\gamma_{\chi}}/T$ in terms of eq. S.1. This finding expected within the theory of isomorphs[44] and also established[36] for the KABLJ system of 1000 particles in a narrower density range is meaningful. Since $\Delta\gamma = 0$, eq. 1 represents a single variable function of $\chi_4^{\max}$ (see Fig. S.3(f)), and consequently an isochronal state is also characterized by a constant value of $\chi_4^{\max}$, which is independent of thermodynamic conditions and only depends on the structural relaxation time, e.g.,

$$\chi_4^{\max} = (\chi_4^{\max})_0 \exp\left[\left(\left(\ln(\tilde{\tau}/\tilde{\tau}_0)\right)^{1/\tilde{D}} A_{\chi}/A\right)^{D_{\chi}}\right], \qquad (S.3)$$

which straightforwardly results from eq. S.2b if $\Delta\gamma = 0$ and the reduced units are used. Equation S.3 is exploited to generate points at $\tilde{\tau} = const$ (circles in Fig. S.3(c)). Moreover, in this case, the transition from one isochronal state to another one at different $\tilde{\tau}$ should be independent of the thermodynamic path toured between these two dynamic states. In the right panel of Fig. S.3(d), one can see that the isochoric and isothermal paths indeed superimpose. It means that the isochoric changes of T and the isothermal changes of ρ equivalently affect the dynamic heterogeneity in the KABLJ model examined in the reduced units.
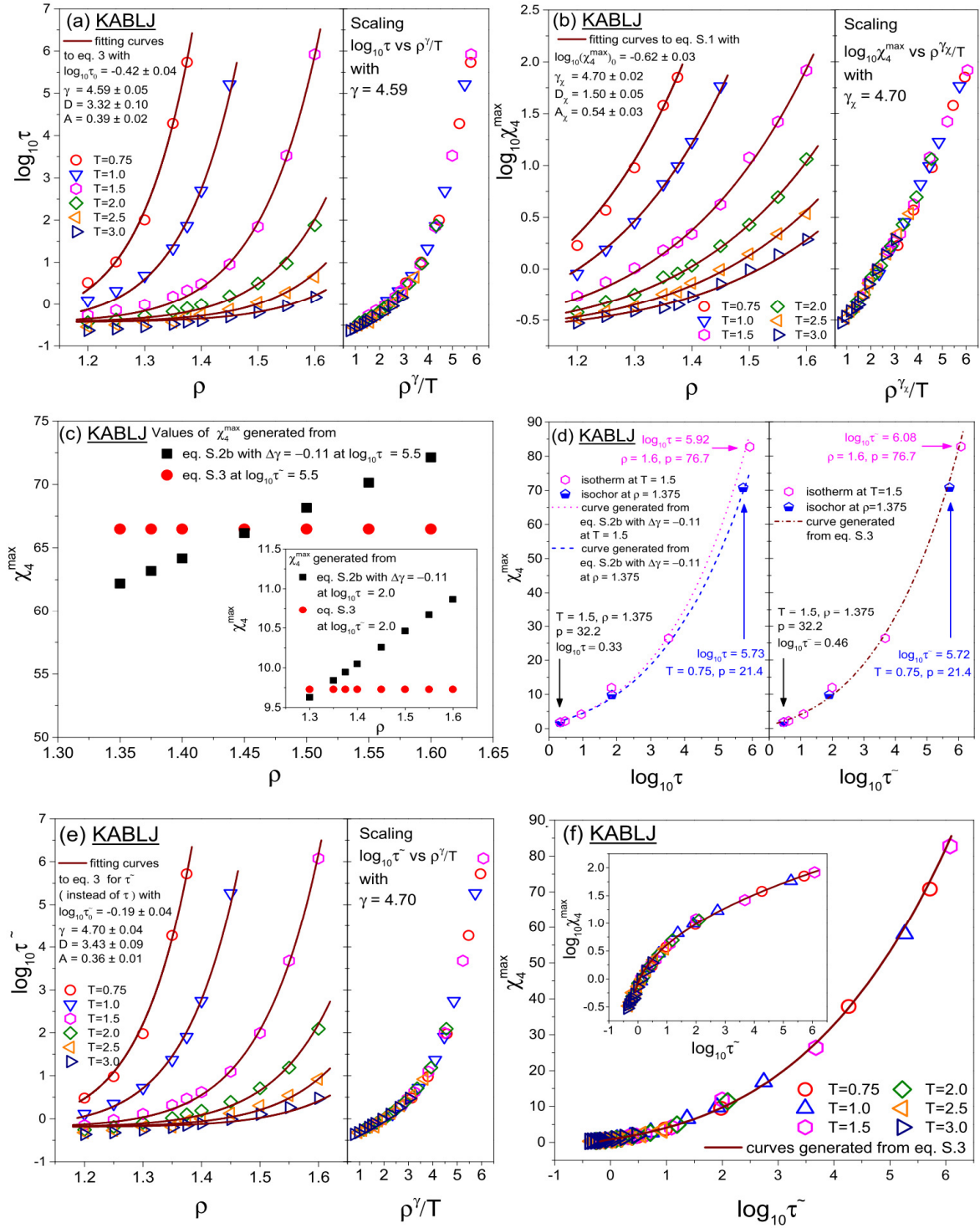
Fig. S.3. The combined power law density scaling of τ and χ_4^{max} for the KABLJ model with 8000 particles. (a) Plot of the structural relaxation time in LJ units vs the particle number density in the left panel and the scaling $\tau\left(\rho^{\gamma}/T\right)$ in the right panel with the value of γ found from the fitting shown in the left panel. (b) Plot of the degree of the dynamic heterogeneity vs the particle number density in the left panel and the scaling $\chi_4^{max}\left(\rho^{\gamma_\chi}/T\right)$ in the right panel with the values of γ_χ found from the fitting shown in the left panel. (c) Isochronal density dependences of the degree of the dynamic heterogeneity at long and (presented in the inset) short time scales expressed in LJ units (τ) and the reduced units ($\tilde{\tau}$). (d) Isothermal and isochoric changes of the degree of the dynamic heterogeneity between two dynamic states characterized by $\log_{10}\tau \approx 0.3$ and $\log_{10}\tau \approx 5.9$ vs structural relaxation times expressed in LJ units (the left panel) and the reduced units (the right panel). (e) Plot of the structural relaxation time in the reduced units vs the particle number density in the left panel and the scaling $\tilde{\tau}\left(\rho^{\gamma}/T\right)$ in the right panel with the value of γ found from the fitting shown in the left panel. (f) Plot of the degree of the dynamic heterogeneity vs the structural relaxation time in the reduced units. Its double logarithmic representation is shown in the inset.

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List of equations
(referred in the SI according to their numbering in the main text)

$$\tau = g\left(\rho^{\Delta\gamma} f(\chi_4^{\max})\right) \text{ with } \Delta\gamma = \gamma - \gamma_\chi \qquad (1)$$

$$\tau = g\left(\Re(\rho) f(\chi_4^{\max})\right) \text{ with } \Re(\rho) = \Im_\tau(\rho)/\Im_\chi(\rho) \qquad (2)$$

$$\tau = \tau_0 \exp\left[\left(A\rho^\gamma / T\right)^D\right] \qquad (3)$$

$$\chi_4^{\max} = (\chi_4^{\max})_0 \left(A_\chi \rho^{\gamma_\chi} / T\right)^{D_\chi} \qquad (4)$$

$$\tau = \tau_0 \exp\left[\left(\rho^{\Delta\gamma}\left(\chi_4^{\max} /(\chi_4^{\max})_0\right)^{1/D_\chi} A / A_\chi\right)^D\right] \qquad (5a)$$

$$\chi_4^{\max} = (\chi_4^{\max})_0 \left(\rho^{-\Delta\gamma}\left(\ln(\tau/\tau_0)\right)^{1/D} A_\chi / A\right)^{D_\chi} \qquad (5b)$$

References
(cited in the SI according to their numbering in the main text)

(12) Grzybowski, A.; Kolodziejczyk, K.; Koperwas, K.; Grzybowska, K.; Paluch, M. Effects of lowering temperature and raising pressure on the spatially heterogeneous dynamics of glass-forming van der Waals liquids. *Phys. Rev. B* **2012**, *85*, 220201(R)-1 - 220201(R)-5.

(13) Koperwas, K.; Grzybowski, A.; Grzybowska, K.; Wojnarowska, Z.; Sokolov, A. P.; Paluch, M. Effect of Temperature and Density Fluctuations on the Spatially Heterogeneous Dynamics of Glass-Forming Van der Waals Liquids under High Pressure, Phys. Rev. Lett. **2013**, *111*, 125701-1 - 125701-5.

(14) Hohenberg, P. C.; Halperin, B. I. Theory of dynamic critical phenomena, Rev. Mod. Phys. **1977**, *49*, 435-479.

(15) Toninelli, C.; Biroli, G.; Fisher, D. S. Spatial structures and dynamics of kinetically constrained models of glasses. *Phys. Rev. Lett.* **2004**, *92*, 185504-1 - 185504-4.

(16) Ritort, F.; Sollich, P. Glassy dynamics of kinetically constrained models. *Adv. Phys.* **2003**, *52*, 219-342.

(17) Bouchaud, J.-P.; Biroli, G. On the Adam-Gibbs-Kirkpatrick-Thirumalai-Wolynes scenario for the viscosity increase in glasses, *J. Chem. Phys.* **2004**, *121*, 7347-7354.

(26) Floudas, G.; Paluch, M.; Grzybowski, A.; Ngai, K. *Molecular Dynamics of Glass-Forming Systems: Effects of Pressure*; Series: Advances in Dielectrics; Kremer, F., Series Ed.; Springer-Verlag: Berlin, Heidelberg, 2011; Chapter 2.

(27) Roland, C. M.; Hensel-Bielowka, S.; Paluch, M.; Casalini, R. Supercooled dynamics of glass-forming liquids and polymers under hydrostatic pressure. *Rep. Prog. Phys.* **2005**, *68*, 1405 - 1478.

(28) Alba-Simionesco, C.; Tarjus, G. Temperature versus density effects in glassforming liquids and polymers: A scaling hypothesis and its consequences. *J. Non-Cryst. Solids* **2006**, *352*, 4888-4894.

(29) Pedersen, U. R.; Bailey, N. P.; Schrøder, T. B.; Dyre, J. C. Strong pressure-energy correlations in van der Waals liquids. *Phys. Rev. Lett.* **2008**, *100*, 015701-1 - 015701-4.

(30) Bailey, N. P.; Pedersen, U. R.; Gnan, N.; Schrøder, T. B.; Dyre, J. C. Pressure-energy correlations in liquids. I. Results from computer simulations. *J. Chem. Phys.* **2008**, *129*, 184507-1 - 184507-13.

(31) Coslovich, D.; Roland, C. M. Thermodynamic scaling of diffusion in supercooled Lennard-Jones liquids. *J. Phys. Chem. B* **2008**, *112,* 1329-1332.

(32) Coslovich, D.; Roland, C. M. Pressure-energy correlations and thermodynamic scaling in viscous Lennard-Jones liquids. *J. Chem. Phys.* **2009**, *130*, 014508-1 - 014508-5.

(33) Schrøder, T. B.; Pedersen, U. R.; Bailey, N. P.; Toxvaerd, S.; Dyre, J. C. Hidden scale invariance in molecular van der Waals liquids: A simulation study. *Phys. Rev. E* **2009**, *80*, 041502-1 - 041502-6.

(34) Pedersen, U. R.; Schrøder, T. B.; Dyre, J. C. Repulsive reference potential reproducing the dynamics of a liquid with attractions. *Phys. Rev. Lett.* **2010**, *105*, 157801-1 - 157801-4.

(35) Grzybowski, A.; Koperwas, K.; Paluch, M. Scaling of volumetric data in model systems based on the Lennard-Jones potential. *Phys. Rev. E* **2012**, *86*, 031501-1 - 031501-9.

(36) Coslovich, D.; Roland, C. M. Density scaling in viscous liquids: From relaxation times to four-point susceptibilities. *J. Chem. Phys.* **2009**, *131*, 151103-1 - 151103-4.

(44) Gnan, N.; Schrøder, T. B.; Pedersen, U. R.; Bailey, N. P.; Dyre, J. C. Pressure-energy correlations in liquids. IV. "Isomorphs" in liquid phase diagrams. *J. Chem. Phys.* **2009**, *131*, 234504-1 - 234504-18.

(59) Sastry, S. The relationship between fragility, configurational entropy and the potential energy landscape of glass-forming liquids. *Nature* **2001**, *409*, 164-167.