Role of Attractive Interactions in Structure Ordering and Dynamics of Glass-Forming Liquids

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A key question in glass physics is what the origin of slow glassy dynamics is. The liquid structure is a natural candidate; however, an apparently severe counterexample has been known. Two model glass-forming liquids, with the standard Lennard–Jones interaction potential and its Weeks–Chandler–Andersen variation without the attractive tail, exhibit very similar structures at the two-body level but drastically different dynamical behaviors in the supercooled states. Here we look at the liquid structure through a (many-body) structural order parameter Θ characterizing the packing capability of local particle arrangements. We show that the structures of these two systems seen by Θ are actually very different at a many-body level, but, quite surprisingly, the macroscopic structure (Θ)-dynamics (τ_α) relationships commonly follow a Vogel–Fulcher–Tammann-like function. Furthermore, the mutual information analysis reveals strong local structure-dynamics correlations. Therefore, we conclude that attractive interactions affect the liquid structure in a nonperturbative manner, but a general structural origin of slow dynamics holds for these systems.

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Introduction.—Crystals and gases are perfectly ordered and disordered, respectively. In contrast, the liquid state of matter is intermediate in nature with complex structures and dynamics, remaining a central research topic in condensed matter physics. Conventional wisdom from the theory of simple liquids, dated back to van der Waals, is that the short-ranged repulsive interactions play a dominant role in determining the structure of liquid states and hence the thermodynamics, with the long-ranged attraction acting as a cohesive background [1]. This idea, which was further developed by Weeks, Chandler, and Andersen, forms the basis of the successful perturbation theories of liquid states [1–3]. However, the generalization of this wisdom to viscus supercooled liquids to explain the dynamics was severely challenged in a series of works initiated by Berthier and Tarjus [4–17]. It was shown that two model glass formers, with the standard Lennard–Jones (LJ) interaction and the Weeks–Chandler–Andersen (WCA) variation without the attractive tail, exhibit almost identical structures at a two-body level but drastically different dynamics at low temperatures [4]. These results posed serious challenges to theories, e.g., the mode-coupling theory, based solely on pair density correlations [5,6], and therefore provided an excellent benchmark for reconsiderations of the basic understanding of glass-forming liquids [4–17].

Since the structure and dynamics appear to respond differently to attractive interactions in the above example, the crucial question is whether they can, in principle, decouple with each other in realistic structural glass formers. From a thermodynamic perspective, it was shown that hidden scale invariance exists in the phase diagram of the so-called Roskilde-simple liquids, i.e., "isomorph" curves along which structure and dynamics in reduced units are invariant to a good approximation [8–10,15,18]. The LJ and WCA liquids follow different isomorphs [8,9]. Therefore, their dynamic difference might be rationalized from the underlying thermodynamic difference [8,15], which in turn suggests subtle structural differences not detected by two-body correlators [12,13]. Local structure analyses using topological cluster classification [11] and Voronoi face analysis [12] indeed evidenced such differences. Therefore, the question turns to be whether a unified physical framework exists to understand the structure and dynamics and their relationship for both LJ and WCA systems.

In this Letter, we aim to address the above question quantitatively from two aspects based on a new structural order parameter Θ [19,20]. (i) Macroscopically, we identify a distinct structural difference between LJ and WCA systems but establish a common relationship between Θ and the structural relaxation time τ_α. (ii) Microscopically, we reformulate the question as "how much *information* of the dynamic heterogeneity can be *predicted* from the structure." We employ the mutual information (MI) to quantify the degree of microscopic structure-dynamics correlations [21–23]. We find that to achieve maximum MI, i.e., the best prediction of dynamics, we need to take into account structural order correlated over a length scale,

ξ, which grows with decreasing temperature. For both LJ and WCA systems, we obtain unprecedentedly high values of MI at low temperatures, suggesting that the spatially correlated structure order primarily controls dynamic heterogeneity. Our results thus establish a simple physical mechanism for the nonperturbative role of attractive interactions in glass-forming liquids from the structural perspective.

Methods.—We perform molecular dynamics simulations of the simplest model glass former consisting of polydisperse particles in two dimensions (2D) for which the structural order parameter Θ is well defined [19,24]. The interaction potential between particles i and j is $V(r_{ij}) = 4\epsilon[(\sigma_{ij}/r_{ij})^{12} - (\sigma_{ij}/r_{ij})^{6}] + f(r_{ij})$, when $r_{ij}/\sigma_{ij} < R_c$ and zero otherwise, where r_{ij} is the particle separation, σ_{ij} is the sum of the particle radii, and $f(r_{ij})$ guarantees the continuity of both potential and force at $r_{ij} = R_c\sigma_{ij}$ [25]. Here $R_c = 2^{1/6}$ and 2.5 correspond to WCA and LJ systems, respectively. The particle size follows the Gaussian distribution with polydispersity $\Delta(=\sqrt{\langle\sigma^2\rangle - \langle\sigma\rangle^2}/\langle\sigma\rangle) = 13\%$. All particles have the same mass m. Length, energy, time, and temperature are in units of the averaged diameter $\langle\sigma\rangle$, ϵ, $\sqrt{m\langle\sigma\rangle^2/\epsilon}$, and ϵ/k_{B}, where k_{B} is the Boltzmann constant. We set the number density $\rho = 0.89$ for both systems, corresponding to typical moderate pressure condensed matter states. Our results do not sensitively depend on these choices. Systems with $N = 4096$ particles are simulated in square boxes in the NVT ensemble with periodic boundary conditions.

The structural order parameter Θ is constructed to characterize the local packing capability in an order agnostic manner [19]. Figure 1(a) illustrates a typical local particle configuration. Each pair $\langle ij\rangle$ of the nearby neighbors, together with the central particle o, constitutes a basic structural unit in 2D, i.e., a triangle [26]. The corresponding reference configuration with these three particles in perfect relative distances is shown in Fig. 1(b). For finite range repulsive interactions, such perfect relative distances are set by particle radius [19]. Here we generalize the definition to LJ systems by using the repulsive core to define the effective radius. The imperfectness of the original triangle configuration is measured as the deviation of the central angle $\theta_{ij}^{(1)}$ from its reference $\theta_{ij}^{(2)}$. The structural order parameter for particle o is then defined as $\Theta_o = \sum_{\langle ij\rangle} |\theta_{ij}^{(1)} - \theta_{ij}^{(2)}|/N_o$, where N_o is the number of pairs of neighbors next to each other and the summation runs over all the pairs. Larger Θ indicates greater deviation from perfect arrangements, hence more disordered. Different from Ref. [19], here the structural order is measured in instantaneous liquid states rather than the inherent states, which is crucial to establish the quantitative relationships in this work.

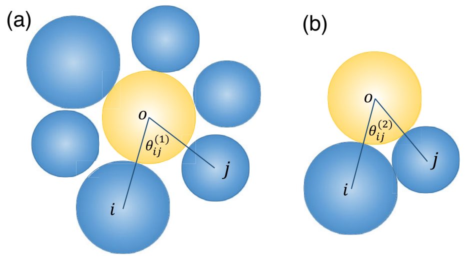

FIG. 1. Definition of the structural order parameter. (a) A typical local configuration with a central particle, o, and its six neighbors. Two neighbors indicated as i and j have a central angle $\theta_{ij}^{(1)}$. (b) The reference configuration with the three indicated particles in perfect relative distances with each other, with a central angle $\theta_{ij}^{(2)}$. See text for the expression of order parameter Θ.

To avoid the influence of long-wavelength Mermin–Wagner fluctuations, the dynamics in 2D is characterized using relative positions $\underline{\mathbf{r}}_j(t) = \mathbf{r}_j(t) - \sum_k \mathbf{r}_k(t)/n_j$, where the summation runs over all nearest neighbors of particle j [27–30]. Self-intermediate scattering function $F_s(k,t) = \langle\sum_j \exp\left(i\mathbf{k}\cdot[\underline{\mathbf{r}}_j(t) - \underline{\mathbf{r}}_j(0)]\right)/N\rangle$ is measured with $k = |\mathbf{k}|$ set to the first peak of the static structure factor. Accordingly, the structure relaxation time τ_α is defined from $F_s(k,\tau_\alpha) = e^{-1}$.

To establish the microscopic correlation between structure and dynamics, we use the isoconfigurational ensemble [31,32], within which the part of dynamic heterogeneity related to the structure is reinforced, whereas fluctuations with a purely dynamical origin are averaged out. Up to 200 independent trajectories starting from each initial configuration are simulated. Accordingly, we define $F_s^j(k,t) = \langle\exp\left(i\mathbf{k}\cdot[\mathbf{r}_j(t) - \mathbf{r}_j(0)]\right)\rangle_{\mathrm{iso}}$ for each particle j, with $\langle\cdot\rangle_{\mathrm{iso}}$ indicating the isoconfigurational average. We deduce microscopic τ_α from $F_s^j(k,\tau_\alpha^j) = e^{-1}$, which is expected to be a better measurement of the *propensity* of particle relaxations compared to mean squared displacements [19]. Structural order is characterized for the initial configurations. Spatial coarse graining is used to describe the structural order at a given length scale [19]. Mutual information between two quantities x and y is defined as $\mathrm{MI}(x,y) = \int\int p_j(x,y)\log_2[p_j(x,y)/p(x)p(y)]dxdy$, where $p_j(x,y)$ is the joint probability distribution function of x and y and $p(x)$ is the probability distribution functions of x [21]. MI is an information theoretic quantity based on Shannon entropy [21], which provides a sensible measurement of the structure-dynamics correlations [22,23]. Within this Letter, $\log_{10}(\tau_\alpha)$ instead of its original value is used in the calculation of MI, although the notion of "τ_α" is used for simplicity.

Macroscopic structure and dynamics.—The temperature dependence of τ_α shown in Fig. 2(a) indicates that, with decreasing temperature, the dynamics of LJ systems becomes much slower than WCA systems. Meanwhile, the temperature dependence of Θ shown in Fig. 2(b) reveals a clear difference between the two systems. In particular, the smaller values of Θ in LJ systems indicate better

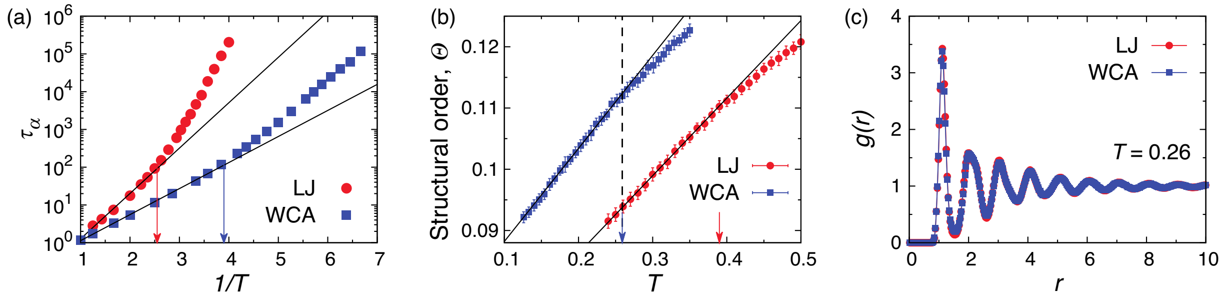

FIG. 2. Macroscopic structure and dynamics in LJ and WCA systems. (a) Temperature dependence of τ_α. High-temperature data, above the onset temperature T_{on} indicated by arrows, are fitted by the Arrhenius law $\tau_\alpha \sim \exp(\Delta E/T)$ (solid lines). (b) Temperature dependence of the structural order, Θ, which shows clear differences between the two systems. Error bars indicate standard derivations. Solids lines are linear fittings to data below T_{on}: $\Theta - \Theta_0 = \kappa(T - T_0)$. See text for the meaning of parameters. T_{on} from panel (a) are indicated by arrows. The vertical dashed line indicates $T = 0.26$ chosen for calculating the pair correlation function $g(r)$, as shown in (c).

structural ordering [11–13]. Therefore, the van der Waals picture actually breaks down for both structure and dynamics [3]. We observe a linear temperature dependence of Θ for both systems in the supercooled regime (below the onset temperature T_{on}): $\Theta - \Theta_0 = \kappa(T - T_0)$, where T_0 is the hypothetical ideal glass transition temperature from the Vogel–Fulcher–Tammann (VFT) fitting of $\tau_\alpha = \tau_0 \exp[DT_0/(T - T_0)]$ with D being the fragility index, Θ_0 is the structural order at T_0, and κ is a fitting parameter. This indicates a general mechanism of structural ordering regardless of the attractive tail.

In comparison, Fig. 2(c) shows the pair correlation function $g(r)$ calculated around T_{on} of the WCA system [vertical dashed line in Fig. 2(b)], unveiling minor structural differences between the two systems at a two-body level. We note that a close inspection indeed detects small differences in $g(r)$ [15,33,34], which derive from the projection of many-body information to the two-body level [1]. However, in principle, we can never recover many-body correlations solely from the two-body information [35], and a many-body approach is intrinsically necessary to capture the important many-body correlations in a controlled manner.

We further seek a direct quantitative relation between Θ and τ_α. Figure 3 shows τ_α as a function of $1/(\Theta - \Theta_0)$, and a VFT-like scaling relation is identified in the supercooled regime:

$$\tau_\alpha = \tau_0 \exp\left[D_2\Theta_0/(\Theta - \Theta_0)\right], \qquad (1)$$

where τ_0 and D_2 are fitting parameters. The scaling collapse shown in the inset of Fig. 3 further confirms this relationship. It tells us that the steep increase of τ_α is controlled by the structure ordering when approaching the hypothetical ideal glass transition point. Therefore, both structure and dynamics are affected by the attractive interactions in a nonperturbative manner; nevertheless, the relationship between them, i.e., Eq. (1), remains invariant. Further analyses in systems with hard-spherelike interactions in 3D (using the structural order parameter Ω defined in the same spirit as Θ [19]) are suggestive of its generality. We hence speculate that in addition to the "isomorph" of Roskilde-simple liquids [8,10,18], additional generality may exist in glass-forming liquids, which is rooted in the subtle structure ordering at a many-body level [36–38].

Microscopic structure and dynamics.—A caution from the literature is that a macroscopic correlation between structure and dynamics does not necessarily indicate a microscopic correlation [39,40]. Therefore, we investigate the microscopic structure and dynamics for further insights in LJ and WCA systems. The self-intermediate scattering functions $F_s(k,t)$ of individual particles, together with the global average, are shown in Fig. 4(a) for the LJ system. Accordingly, the spatial distribution of microscopic τ_α is visualized in Fig. 4(b), showing significant spatial heterogeneity [41,42]. The spatial distribution of Θ for the initial state of the isoconfigurational ensemble is plotted in

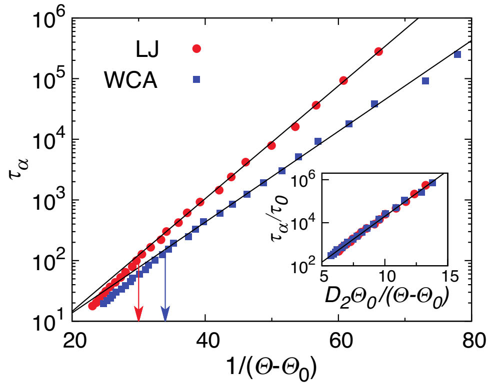

FIG. 3. Macroscopic relationship between structural order and dynamics. Structure relaxation time τ_α is plotted as a function of $1/(\Theta - \Theta_0)$. Solid lines are fittings to data below T_{on} (indicated by arrows) according to the VFT-like relation Eq. (1). Inset: Scaling collapse of τ_α/τ_0 as a function of rescaled structural order $D_2\Theta_0/(\Theta - \Theta_0)$ below T_{on}.

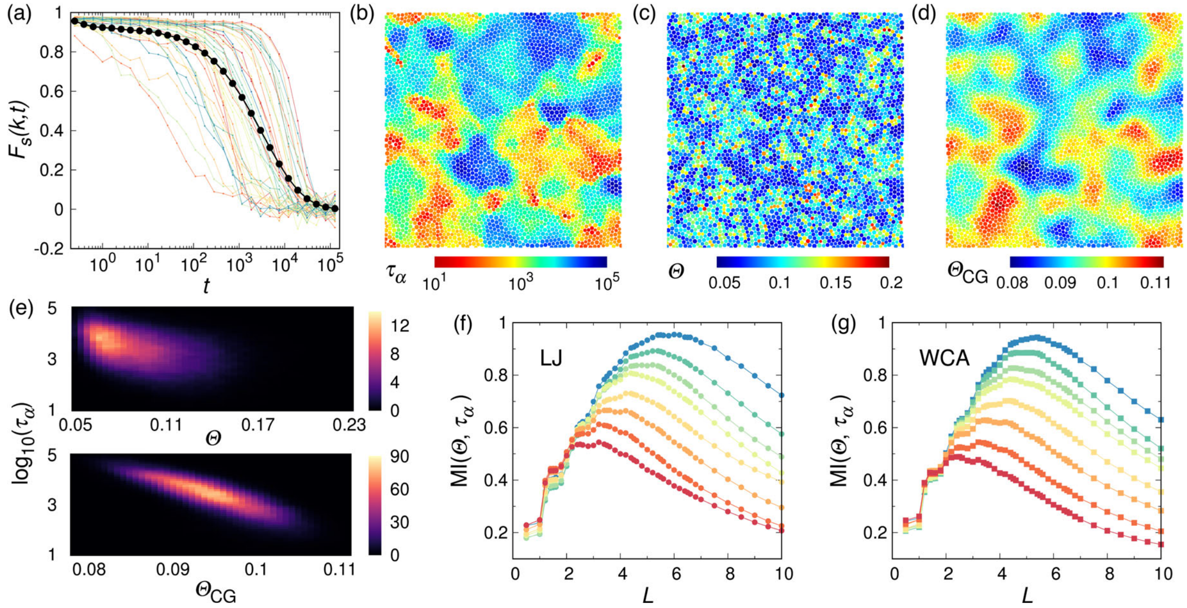

FIG. 4. Microscopic correlation between structural order and dynamics. (a) Self-intermediate scattering function $F_s(k,t)$ of each particle (background) and the whole system (black circles) for LJ system at $T = 0.305$. (b)–(d) Spatial distribution of microscopic τ_α, bare structural order, Θ, and its coarse graining with $L = 5.5$, Θ_{CG}, respectively. Note that red color indicates faster dynamics or less ordered structures. (e) Joint probability distribution of microscopic relaxation time $\log_{10}(\tau_\alpha)$ and bare structural order Θ (top), as well as that coarse grained with $L = 5.5$, Θ_{CG} (bottom). (f),(g) MI between microscopic τ_α and Θ as a function of coarse graining length L for LJ and WCA systems, respectively. $L = 0.5$ means without coarse graining. Temperature decreases from red to blue, corresponding to a range of macroscopic $\tau_\alpha \sim 3$ to 10 000.

Fig. 4(c), which, however, shows only a weak correlation to microscopic τ_α. This is because, according to the nonlocal scenario of structure-dynamics correlations [19], the cooperative α relaxation is not controlled by the local structure but rather the structural order over its static correlation length. We therefore plot the spatial distribution of Θ after coarse graining in Fig. 4(d), which indeed exhibits a remarkable similarity compared to microscopic τ_α in Fig. 4(b).

Such an enhancement of structure-dynamics correlations by the spatial coarse graining procedure is further illustrated by the joint probability distribution function of microscopic τ_α and local Θ, as well as its coarse graining, Θ_{CG} [see Fig. 4(e)]. It is initially very broad but shrinks significantly into a narrow band after coarse graining, indicating a strong structure-dynamics correlation via a nonlocal mechanism [19]. Quantitatively, we explore "how much *information* of the dynamic heterogeneity can be *predicted* from the structure" by systematically calculating $\mathrm{MI}(\Theta, \tau_\alpha)$ as a function of the coarse graining length L for a wide range of temperatures. As shown in Figs. 4(f) and 4(g), $\mathrm{MI}(\Theta, \tau_\alpha)$ exhibits a peak at certain L, which grows with decreasing temperature. The maximum value of $\mathrm{MI}(\Theta, \tau_\alpha)$ also grows and reaches unprecedentedly high values at low temperatures [22,23]. The same features are observed for both LJ and WCA systems, suggesting a general mechanism of structure-dynamics correlations, consistent with the macroscopic results (see Fig. 3). We stress that the coarse graining is a purely static operation, and therefore, the intriguing behavior of $\mathrm{MI}(\Theta, \tau_\alpha)$ contains two important implications. (i) The structural order develops upon cooling while accompanying the growth of its correlation length. (ii) The spatially correlated structural order directly controls the cooperative α relaxation in a nonlocal manner.

Discussions.—The thermodynamics of a glass-forming liquid is, in principle, determined by free energy, with both energy and entropy contributions. For hard-spherelike systems, entropy dominates, which is controlled by the structure [19,20]. However, our results suggest that LJ systems in typical condensed phase states are also "hard spherelike," with the same behaviors of structure ordering and structure-dynamics relationships as WCA systems. This appears counterintuitive, considering that the attractive tail of LJ potential affects both structure and dynamics in a nonperturbative manner. To resolve the mystery, we check how the potential energy correlates with microscopic dynamics (kinetic energy is expected to be spatially uniform and therefore neglected). The local potential energy of particle i is calculated as $E_i = \sum_j V(r_{ij})$, with the summation going over all interacting neighbors. Figure 5 shows $\mathrm{MI}(E, \tau_\alpha)$ as a function of the coarse graining length L for LJ and WCA systems. Overall, $\mathrm{MI}(E, \tau_\alpha)$ is in the order of 0.01 and does not show obvious dependence on T and L, indicating marginal information of microscopic dynamics from the local potential energy even after coarse graining.

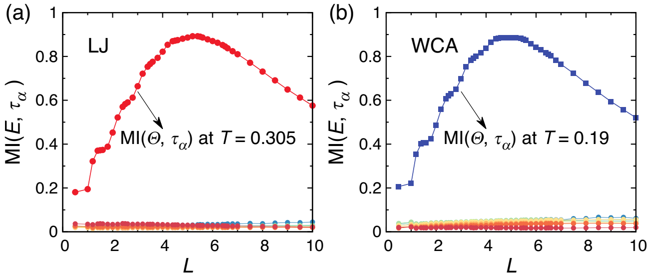

FIG. 5. Mutual information between microscopic τ_α and local potential energy E as a function of coarse graining length L for (a) LJ and (b) WCA systems. Symbols are the same as Figs. 4(f) and 4(g). MI(Θ, τ_α) at temperature of macroscopic $\tau_\alpha \sim 3000$ is plotted as a comparison.

Therefore, we may conclude that potential energy affects dynamics indirectly only through its influence on the structural ordering at a many-body level. This result thus unveils a compelling mechanism for the interplay between energy and entropy.

Concluding remarks and prospects.—In this Letter, we propose a novel structural approach for the nonperturbative role of attractive interactions through careful studies of two simple glass formers interacting with LJ and WCA potentials. We show that both structure and dynamics are affected by the attractive interactions in a nonperturbative manner, but the general relation between them remains valid and invariant both macroscopically and microscopically. Our study is not exhaustive, e.g., we have not considered different models with different ranges of attractions or with nonadditive interactions, and therefore, the generality of our findings should be checked through more extensive investigations. Nevertheless, our results exemplify the fundamental role of structure ordering in supercooled liquids when approaching the glass transition. If the general relevance of this physical picture is confirmed, because of its simplicity, it may provide a basic framework for future theoretical developments of the long-standing glass transition problem.

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