Unveiling Dimensionality Dependence of Glassy Dynamics: 2D Infinite Fluctuation Eclipses Inherent Structural Relaxation

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By using large-scale molecular dynamics simulations, the dynamics of two-dimensional (2D) supercooled liquids turns out to be dependent on the system size, while the size dependence is not pronounced in three-dimensional (3D) systems. It is demonstrated that the strong system-size effect in 2D amorphous systems originates from the enhanced fluctuations at long wavelengths which are similar to those of 2D crystal phonons. This observation is further supported by the frequency dependence of the vibrational density of states, consisting of the Debye approximation in the low-wave-number limit. However, the system-size effect in the intermediate scattering function becomes negligible when the length scale is larger than the vibrational amplitude. This suggests that the finite-size effect in a 2D system is transient and also that the structural relaxation itself is not fundamentally different from that in a 3D system. In fact, the dynamic correlation lengths estimated from the bond-breakage function, which do not suffer from those enhanced fluctuations, are not size dependent in either 2D or 3D systems.

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Dimensionality plays a key role in the physics of solids and liquids—from high to low dimensions—and fluctuation shows up differently, as typically observed in phase transitions [1,2]. Indeed, two-dimensional (2D) systems often exhibit enhanced fluctuations, leading to various anomalies that are not experienced in three-dimensional (3D) systems. The melting of a 2D solid is a marked example [3–9] where the long-wavelength structural correlation is induced by thermal fluctuations that span an infinite length. For the glass transition from supercooled liquids to amorphous solids, the dimensionality dependence of the fluctuation has become an issue only recently. Gigantic fluctuation in 2D supercooled liquids has been observed that is far stronger than that in their 3D counterparts [10–12]. The aim of this Letter is to elucidate the similarity of this fluctuation to that in crystals [13], and also to investigate the heterogeneous dynamics in both 2D and 3D systems.

For a crystalline solid of monodisperse particle assemblies, the mean-squared thermal displacement (MSTD) is given by using the vibrational density of state (VDOS) \( g(\omega) \) as a function of angular frequency \( \omega \) as

\[
\langle |u|^2 \rangle = \frac{d k_B T}{m} \int g(\omega) \frac{1}{\omega^2} d\omega,
\]

where \( m \) is the particle mass, \( d \) the spatial dimension, and \((k_B T)^{-1}\) the inverse temperature. Under the Debye approximation for the VDOS of acoustic plane waves, \( g(\omega) \) becomes proportional to \( \omega^{d-1} \) [14]. It leads to divergence of the integral in 2D systems owing to the low-frequency acoustic waves, while it converges in 3D systems. As a result, the long-range translation order is prohibited in 2D systems [15,16]. Integration of Eq. (1) over \( \omega \geq 2\pi c/L \) provides us with its dependence on the linear system size \( L \) as

\[
\langle |u|^2 \rangle \sim \frac{k_B T}{2\pi} \frac{1}{\mu + 1} \ln \left( \frac{L}{\sigma_0} \right),
\]

where \( \mu \) and \( K \) are shear and bulk moduli, \( \sigma_0 \) is the particle radius, and \( c \) is the velocity of sound. Such a fluctuation is the source of the size-dependent behavior of 2D solids undergoing melting [4,6,7,9].

In amorphous solids, \( g(\omega) \) is known to behave quite differently than it does in crystals. Simulations [17–23] and experiments [24–28] indicate an abundance of acoustic excitations in amorphous solids, exhibiting the so-called boson peak. For frequencies far lower than the boson peak, the Debye model can be supposed because the microscopic details are irrelevant to long-wavelength modes [26,29]. Several attempts have been made to verify the Debye model description on a microscopic basis by using molecular simulations [21,30], but no conclusive simulation data have been provided on the asymptotic behaviors at low frequencies. Therefore, it is still an open issue as to how these low-frequency vibration modes affect the dimensionality dependence of thermal fluctuations.
In this study, we address the dimensionality dependence of the low-frequency thermal vibrations and dynamics. The 2D binary 50:50 soft-core (2D SC) [31,32] and 3D binary 80:20 Kob-Andersen-type Lennard-Jones (3D KALJ) [33] potentials are used for our simulation. The standard Newtonian dynamics simulation is performed for supercooled states. The simulation results are presented in terms of the reduced units [34]. Simulations have also been performed for 2D KALJ and 3D SC with smaller system sizes, but the results do not qualitatively differ.

First, we study the mean-square displacements (MSD) of 2D SC and 3D KALJ. Between the short-time ballistic and long-time diffusive regimes, there exists a plateau in each MSD, and its height can be estimated directly as its magnitude \( \langle |\Delta r(t_p)|^2 \rangle \) at the plateau time \( t = t_p \). In Fig. 1, the MSDs \( \langle |\Delta r(t)|^2 \rangle = \langle 1/N \sum_j |\Delta r_j(t)|^2 \rangle \) are plotted for (a) 2D SC and (b) 3D KALJ, with \( \Delta r_j(t) = r_j(t) - r_j(0) \) being the particle displacement. For particle numbers \( N = 250, 1000, 4000, \) and \( 16 000 \) in 2D SC, the plateaus are distinctly observed, as indicated by the horizontal lines in (a). The plateau is a bit raised for \( N = 64 000 \), exhibiting a crossover to the long-time diffusive regime. Finally, the plateau disappears for \( N = 256 000 \). Cage-relative MSDs (CR-MSD) \( \langle |\Delta r_{\text{CR}}(t)|^2 \rangle \) [35–37] are also plotted for 2D SC with \( N \leq 64 000 \). CR-MSD is defined as the averaged mean square of the displacement \( \Delta r_{j,\text{CR}}(t) \) that is relative to the center of mass of neighboring particles [34]. The collapsed data of CR-MSD exhibit an absence of finite-size effect in CR-MSD. In 3D KALJ in (b), the MSDs exhibit virtually no size dependence for \( N \geq 2500 \).

This size dependence in the MSDs is attributed to the long-wavelength acoustic sound modes, represented in the VDOS at low frequencies comparable to \( \omega \sim 2\pi c/L \)—the limiting behavior in the limit of \( \omega \to 0 \) matters. Although the VDOS is usually estimated by the normal mode analysis, it becomes more difficult as the system size becomes larger because the eigenvector calculation of the \( dN \times dN \) Hessian matrix is required. As an alternative, the VDOS is obtained by directly calculating the velocity correlation function as \( g(\omega) = 2(\pi dN k_B T)^{-1} \int dt e^{i\omega t} \sum_j [m_j v_j(0) \cdot v_j(t)] \) [20], with \( m_j \) and \( v_j(t) \) representing the mass and the velocity of particle \( j \). The time development of the thermal vibration has been simulated at low temperatures, \( T = 0.01 \) for 2D SC and \( 0.008 \) for 3D KALJ. The initial particle configurations are prepared by the steepest descent method, in order to begin the simulation from the local potential minimum. We find that these temperatures are low enough that the obtained VDOS provides a faithful description of the normal modes. The collapsed data of CR-MSD also indicate the absence of finite-size effect in CR-MSD. In 3D KALJ in (b), the MSDs exhibit virtually no size dependence for \( N \geq 2500 \).

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FIG. 1. Solid lines indicate the MSD \( \langle |\Delta r(t)|^2 \rangle \) of (a) 2D SC at \( T = 0.64 \) and (b) 3D KALJ at \( T = 0.47 \) for various system sizes. In the insets, the respective plateau regions (indicated by red boxes) are magnified. In (a), the height of the plateaus are indicated by the horizontal dotted lines, and the curved dotted lines indicate the CR-MSD \( \langle |\Delta r_{\text{CR}}(t)|^2 \rangle \) for various system sizes \( N \leq 64 000 \) with the corresponding colors.
of crystalline solids [14], the VDOS can be explicitly estimated to be \( g_D(\omega) = \omega n / (2\pi n c_L^2) \), where \( n = N/L^d \) and \( c_L^2 = (c^2 + c_T^2) / 2 \), with \( c_L \) and \( c_T \) being the longitudinal and transverse sound velocities, respectively. The VDOS asymptotically approaches \( g_D(\omega) \), assuming up to 1.4 times larger values in the present frequency region. The sound velocities are estimated by dynamic structure factors (DSFs) \( S_{L,T}(k,\omega) = 2\tilde{m}(2\pi N k_B T)^{-1} \int dt e^{i\omega t} \langle j_{L,T}(k,0) \cdot j_{L,T}(k,t) \rangle \), with \( j_{L,T}(k,\omega) \) representing the longitudinal and transverse current velocities [23,38] and \( \tilde{m} \) the average particle mass. The wave numbers \( k = |k| \) at the peak values of the DSFs satisfy the linear dispersion relations \( \omega = c_{L,T} k \), as seen for \( S_T(k,\omega) \) of 2D SC in Fig. 2(b).

The linear fit provides the estimate values of sound velocities as \( c_L = 11.9 \) and \( c_T = 4.7 \) and 3.8 for 2D SC and 3D KALJ, respectively.

If the half of the MSD plateau height \( \langle |\Delta r(t_P)|^2 \rangle \) arises as a superposition of harmonic vibration modes, it is equal to the squared thermal amplitude \( A_p^2 = 2\langle |u|^2 \rangle \). Therefore, the half of the plateau height is a value that can be directly compared with the MSTD \( \langle |u|^2 \rangle \) estimated either from the VDOS data using Eq. (1) or from the Debye approximation in Eq. (2). For both Eq. (1) and Eq. (2), the integration is cut off at \( \omega_{\text{min}} = 2\pi c_T / L \), so that the MSTD can be estimated as a function of the box length \( L \). For the direct integration of \( g(\omega) \) in Fig. 2(a), the size dependence is mainly due to a small number of available low-frequency modes (\( \omega \lesssim 1 \)). On that account, the integration is performed for \( L < 148\sigma_{11} \), with \( \sigma_{11} \) being the radius of the 1st component particles, and all of the particle masses are replaced by its average \( \tilde{m} \). For Eq. (2), the shear and bulk moduli of 2D SC are \( \mu = \rho c_L^2 = 26.6 \) and \( K = \rho c_T^2 - \mu = 142.1 \), with \( \rho = \tilde{m}n \) being the mass density. In the given Fig. 2(c), half of the MSD plateau height (the open circles) is considerably larger than the estimations. In order to remove contributions from the local center-of-mass fluctuations, CR-MSTD at the same time \( t_P \), \( \langle |\Delta r_{CR}(t_P)|^2 \rangle \), is further subtracted from the plateau height \( \langle |\Delta r(t)|^2 \rangle \). We find that the value agrees with the estimates made using VDOS where the sole effect of long-wavelength motion is taken into account after subtraction. This observation further attributes the cause of 2D systems size dependence to the Debye asymptote in \( g(\omega) \).

Also, in 3D systems, the VDOS is expected to exhibit Debye asymptote behavior at low frequencies. This is shown for 3D KALJ with \( N = 102400000 \) in Fig. 2(d), and it is also shown over a wider range of \( \omega \) for \( N = 1600000 \) in its inset. The VDOS asymptotically approaches \( g_D(\omega) = \omega^2 / (2\pi^2 n c_M^2) \), which is given by the Debye approximation with \( c_M^2 = (c_L^3 + 2c_T^3) / 3 \). The low-frequency modes have small influences on the integration of Eq. (1) because \( g_D(\omega) \sim \omega^3 \) rapidly goes to zero in the \( \omega \rightarrow 0 \) limit. This fact fits together with the lack of finite-size effects in MSTD in 3D KALJ. The VDOS still exhibits the values that are 1.6 to 2.6 times larger values in the range 0.25 \( \leq \omega \leq 1 \). It remains an open question whether or not the VDOS further approaches the Debye asymptote at lower frequencies. It is notable that a previous experiment also shows a few times larger VDOS than the Debye asymptote [26].

Now that the source of the 2D anomaly has been revealed, we address the resultant dimensionality dependence of the manner of structural relaxation, not only by investigating the density correlation but also by looking into the dynamic heterogeneity (DH) [31,32,39–44]. In the literature, DH is considered to be one of the fingerprints of vitrification, and its cause is attributed to consecutive intermittent jump motions of particles escaping out of cages [45–49]. To begin with, the system-size dependence of the self-part of the intermediate scattering function \( F_s(k,t) = \langle \{\mathbf{r}_j(t) - \mathbf{r}_j(0)\} \cdot \mathbf{k} \rangle / (N/2\pi) \) is shown for 2D SC in Fig. 3. In addition to the standard wave number \( k = 2\pi/\sigma_{11} \), three smaller wave numbers are considered. \( F_s(k,t) \) relaxes faster with larger system sizes for \( k = 2\pi/\sigma_{11} \), consistent with a previous result for 2D KALJ [11]. For a smaller \( k \), the relaxation becomes independent of the system size. Therefore, the particle motion on a length scale a few times larger than \( \sigma_{11} \) does not depend on the system size, while motion on the particle-size scale depends [note that \( A_p = \sqrt{2\langle |u|^2 \rangle} \) amounts to about 0.3\( \sigma_{11} \) in Fig. 2(c)]. The finite-size effect is observed merely as a transient effect taking place at short time and length scales induced by vibrations. It is backed by the periodic transient peaks due to the sound waves traversing over the system for small values of \( \lambda \). In 3D systems, \( F_s(k,t) \) (not shown) is independent of the system size, even for \( k = 2\pi/\sigma_{11} \).

DH is investigated in terms of the following variables that characterize the dynamics [34]. One is the four-point correlation function [42–44,50,51] that characterizes...
The configuration overlap by the overlap function using \( W_j(t) = \Theta(a - |\Delta r_j(t)|) \) using the Heaviside step function \( \Theta \). The overlap function assumes a value of unity if the particles move over a distance longer than \( a \) and zero otherwise. The threshold distance \( a \) is set to \( 0.3\sigma_{11} \), in accord with the standard choice. The other bond-breakage number \( Z_j(t) \), which addresses the correlation time and length caused by the change in the local particle connectivity \[53\]. \( Z_j(t) \) starts from \( 0 \) at the initial time \( t = 0 \) and increases one by one as \( t \) proceeds, as a pair of bonded particles get separated from each other. The DH can then be probed through these functions’ respective dynamic susceptibilities \( \chi_4(t) \) and \( \chi_B(t) \), and also the corresponding structure factors \( S_4(k,t) \) and \( S_B(k,t_B) \) at the respective peak times \( t_4 \) and \( t_B \) of the susceptibilities, which describe the wave-number dependence of the heterogeneous motions. From both the structure factors, the respective dynamic correlation lengths \( \xi_4 \) and \( \xi_B \) can be estimated by fitting with the generalized Ornstein-Zernike (OZ) function \[54\].

[FIG. 4](#) (a),(b) Size dependence of \( \chi_4(t) \) and \( S_4(k,t_4) \) and \( S_B(k,t_B) \) for 2D SC at \( T = 0.64 \). The open arrows in (a) indicate the peaks originating in the transverse sound modes, and the filled arrows \( (N \leq 64\,000) \) indicate \( t_4 \). The dotted lines in (b) represent the generalized OZ fit for each. (c),(d) Relaxation and correlation times \( (\tau_{\alpha}, t_4, t_B) \) and correlation lengths \( (\xi_4, \xi_B) \) of 2D SC, with \( t_4 \) of \( N = 256\,000 \) conjectured by the extrapolation. (e) Size dependence of \( S_4(k,t_4) \) and \( S_B(k,t_B) \) of 3D KALJ at \( T = 0.47 \). The dotted lines represent the generalized OZ fits for \( N = 10\,240\,000 \). (f) Temperature dependence of \( \xi_4 \) and \( \xi_B \) is plotted for a 3D KALJ with \( N = 1\,280\,000 \).

The results are summarized in Fig. 4. As shown in Fig. 4(a), \( \chi_4(t) \) exhibits peaks for large system sizes where \( N \geq 64\,000 \) at \( t = (n + \frac{1}{2})L/c_T(n = 0, 1, 2, \cdots) \) (the open arrows) owing to the transverse sound waves traversing the whole periodic system. Although the transient peaks encompass the whole time region, \( S_4(k,t) \) is estimated at \( t = t_4 \), which maximizes the heterogeneity of the configuration overlap. We conjecture that the overall peak position can be identified for \( N \leq 64\,000 \), as indicated by the filled arrows. Figure 4(b) shows both of the structure factors for 2D SC as functions of wave number \( k \). While \( S_4(k,t_4) \) exhibits strong divergence with \( N \) at a small \( k \), \( S_B(k,t_B) \) exhibits no size dependence. For 2D SC, Figs. 4(c) and 4(d) show that the \( \alpha \)-relaxation time \( \tau_\alpha \), and four-point time and length \( t_4 \) and \( \xi_4 \) exhibit strong size dependence owing to the vibration motion. By contrast, \( t_B \) and \( \xi_B \) exhibit no size dependence. For 3D KALJ, \( t_4 \) and \( t_B \) exhibit no size dependence for \( N \geq 2500 \). The structure factors \( S_4(k,t_4) \) and \( S_B(k,t_B) \) in Fig. 4(e) show that there are no finite-size effects in the dynamics. For the entire range of temperatures under investigation, the two dynamic correlation lengths \( \xi_4 \) and \( \xi_B \) exhibit a perfect coincidence, as shown in Fig. 4(f).

For 2D systems, these two correlation functions treat different aspects of dynamic fluctuation. As described previously, the thermal amplitude \( A_p \) reaches a magnitude of \( 0.3\sigma_{11} \)—or even exceeds this value as the system becomes larger. Most of the traditional correlation functions for glassy dynamics, including the standard MSD, self part of the intermediate scattering functions, and four-point functions, are under the influence of such vibration motion. For a 2D system with small system sizes, the thermal fluctuation is weak enough that it does not mask the intermittent jump motion of individual particles (giving rise to particle displacement with a magnitude on the order of \( \sigma_{11} \)) \[10\]. The jump motion is further eclipsed by the vibrations with larger amplitudes as the system size becomes larger, so the dual nature of the dynamics becomes indistinguishable. By contrast, the bond-breakage function is trivially free from coherent motion including long-wavelength vibrations because the broken-bond number assumes finite values only when particle rearrangement takes place. Therefore, the bond-breakage function takes over this role as a structural relaxation indicator. In line with this depiction, the lack of size dependence of bond-breakage correlations ensures the existence of rearranging dynamics even in a large 2D system. It is worth mentioning that such a dual nature of DH in a 2D system is also confirmed by the use of another dynamic correlation function based on a cage-relative variable \[34\].

In conclusion, 2D supercooled liquids exhibit a strong thermal vibrational fluctuation whose amplitude grows infinitely in the limit of \( N \to \infty \). Our observations establish that the infinite fluctuation is due to a mechanism similar to that in 2D crystalline solids, i.e., enhancement of low-frequency sound waves. In addition, the influence of
such fluctuation on the dynamic time and length is clarified. The standard correlation functions fail to characterize the original structural glassy relaxation, which can be retrieved by quantifying the change in the relative particle positions. The bond-breakage correlation function successfully undertakes this role, and its correlation function exhibits no system-size dependence. Therefore, the correlation length $\xi_B$ is expected to represent the underlying length inherent to the dynamics. It leads us to come to the second conclusion that the modality of the glassy structural relaxation is similar between the 2D and 3D systems after separating out the 2D-specific thermal vibration. The infinitely growing fluctuation could still affect the fundamental nature of a 2D glass transition, but this is left for future investigation.

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[34] See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevLett.117.245701 for the following details: an explanation of the models, definitions of the dynamic correlation functions, and discussions on the DH based on cage-relative quantities.


