Non-monotonic dynamic correlations beneath the surface of glass-forming liquids

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Collective motion over increasing length scales is a signature of the vitrification process of liquids. We demonstrate how distinct static and dynamic length scales govern the dynamics of vitrifying films. In contrast to a monotonically growing static correlation length, the dynamic correlation length that measures the extent of surface-dynamics acceleration into the bulk, displays a striking non-monotonic temperature evolution that is robust also against changes in detailed interatomic interaction. This non-monotonic change defines a cross-over temperature $T_*$ that is distinct from the critical temperature $T_c$ of mode-coupling theory (MCT). We connect this non-monotonic change to a cross-over from mean-field like liquid dynamics to glass-like dynamics that is signalled by a morphological change of cooperative rearrangement regions (CRR) of fast particles, and as the point where fast-particle motion decouples from structural relaxation. We propose a rigorous definition of this new cross-over temperature $T_*$ within a recent extension of MCT, the stochastic $\beta$-relaxation theory (SBR).

Dynamical processes in a liquid close to the glass transition become cooperative across spatial regions of increasing extent [1], and it is thus natural to seek an intrinsic correlation length whose divergence would signal the transition. But the hallmark of the glass transition is a dramatic change in the dynamics that is caused by only weak changes in the statics. Consistently, attempts at defining static correlation lengths have found only weak changes in these quantities close to the (computationally or experimentally accessible part) of the transition [1–4]. Only recently it has become clear that in certain perturbed systems, dynamic correlation lengths can be defined that display a much more interesting, non-monotonic behavior [5–7] with a peak at some cross-over temperature. Such non-monotonic variations near the glass transition have since emerged as a signature of various non-equilibrium glass-forming systems [8, 9].

The prevailing methodology to detect spatial correlations in glassy systems is suggested by the random first-order theory (RFOT) [10–12]: pinning a subset of particles in the equilibrium fluid, one examines how the configuration of the rest of particles is influenced [13–16]. While this point-to-set (PTS) protocol is designed to keep the static properties of the system in equilibrium, it represents a strong perturbation of the dynamics [17]: The freezing of some particles can be viewed as imposing a zero-temperature region and hence a strong temperature gradient, yet the associated linear-response regime shrinks to zero at the glass transition [18]. We propose the study of glassy films as a new method to detect such dynamic correlation lengths by measuring how far the statics and dynamics into the bulk liquid affected by the accelerated mobility on the surface.

We show here that the dynamics in equilibrated films is similarly governed by a non-monotonically dynamical correlation length. This opens an interesting link between the study of such films and our fundamental understanding of the glass transition in the bulk, in analogy to the situation that the diverging width of a gas–liquid interface at its critical point is governed by the same diverging correlation length in the bulk [19]. Furthermore the free-surface dynamics is an important factor in the preparation of glassy films [20–22], and more specifically ultra-stable glasses [23–27] and nanostructured materials [28] that are produced by depositing atoms layer-by-layer on an amorphous substrate.

We demonstrate that a specific cross-over temperature $T_*$ governs both the point of maximal dynamical correlations in the film geometry, and the point where cooperative rearrangement regions (CRR) of fast particles in the bulk undergo a shape transition. This cross-over point $T_*$ is significantly above the critical temperature $T_c$ of the mode-coupling theory (MCT). We rationalize this new cross-over point in the context of a recent extension of MCT, the stochastic $\beta$-relaxation theory (SBR), as the point where the effect of long-range fluctuations in the dynamical order parameter of the theory is most pronounced in decoupling fast-particle dynamics from bulk relaxation.

We study two exemplary glass formers by molecular dynamics (MD) simulations: the Kob-Andersen Lennard-Jones binary mixture (LJBM) [29] showing weak surface layering, and a model of the molten CuZr alloy with embedded-atom method (EAM) many-body interactions [30] showing strong layering. Simulations (using the LAMMPS package [31]) start in the bulk liquid at high temperature ($T = 0.6$ for LJBM; $T = 2000$ K for CuZr) and zero pressure. A liquid-vacuum interface was created by an instantaneous increase of the box length along the $z$-axis [see the illustration in Fig. 1(a)]. Af-

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ter re-equilibration, the membranes were cooled down to subsequently lower target temperatures in the canonical ensemble (NVT); data was collected in the microcanonical ensemble (NVE) over 16 realizations per state point. To check that finite-size effects are irrelevant, we compare simulations of two system sizes: small systems (S) with \( L_x = L_y \approx 13 \sigma, L_z \approx 31 \sigma \) and at least \( N = 5000 \) particles; and large systems (L) with \( L_x \approx 40 \sigma \) and at least \( N = 7000 \) particles (where \( \sigma \) is a typical atomic size, \( \sigma \approx 2.7 \) Å for CuZr; precise information is given as Supplemental Information [32]). Our simulations are in equilibrium in the sense that all particles are at the same temperature, and no external field is required to maintain the state, once prepared, in the microcanonical ensemble.

The spatially resolved dynamics can be assessed through the overlap correlation function suggested by the PTS method [11]: the simulation box is discretized into small cubic units of size \( \delta \) (about \( 0.52 \sigma \approx 1.4 \) Å for CuZr and \( 0.6 \sigma \) for the LJBM), and the overlap of configurations a time \( t \) apart is calculated as:

\[
q_c(z,t) = \langle \sum_i n_i(t) n_i(0) \delta(z_i - z) \rangle / \langle \sum_i n_i(0) \delta(z_i - z) \rangle,
\]

where \( n_i = 1 \) if box \( i \) at distance \( z_i \) from the surface is occupied by an atom and \( n_i = 0 \) otherwise, and \( \langle \cdot \rangle \) denotes an average over the simulation ensemble.

The functions \( q_c(z,t) \) follow a standard two-step relaxation pattern of dynamical correlation functions near the glass transition [Fig. 1(c)]: a short-time relaxation to an intermediate-time plateau is followed by stretched-exponential structural relaxation from the plateau. At long times, \( q_c(z,t) \) decays to a non-zero \( z \)-dependent constant \( q_c(z,\infty) \) that represents frozen-in density fluctuations: the introduction of a free surface induces a static density profile \( \rho(z) \) [Fig. 1(b)], and we find \( q_c(z,\infty) \propto \rho(z) \) [Fig. 1(d)]. This is the expected behavior for a stationary ergodic system, and it marks an important difference of our system to previous PTS analyses where a non-trivial long-time limit of \( q_c(z,t) \) signalled a frozen-in nonergodic component of the dynamics. The static overlap evolves smoothly with decreasing temperature, and it decays exponentially towards the bulk density; thus, a static correlation length \( \xi_{\text{stat}} \) can be extracted from fits of the form \( q_c(z,\infty) \propto \rho(z) = A(z) \exp(-z/\xi_{\text{stat}}) + \rho(\infty) \), where \( \rho(\infty) \) is the density of the bulk liquid. We use the function \( A(z) = A_0 \sin(2\pi(z-z_0)/d_p) \) to capture the pronounced surface-induced layering effects seen for CuZr. They are in agreement with experiments on metallic [33] and nonmetallic liquids [34, 35], and grand-canonical MD simulations of liquid films [36]. The LJBM does not show pronounced layering [37], so that there \( A(z) = A_0 \) is used. In both cases, the static length scale \( \xi_{\text{stat}} \) increases monotonically and mildly across the temperature range that we investigate (open symbols in Fig. 2). This monotonic increase with decreasing temperature is consistent with the prediction of RFOT and with other computer simulation results [1, 3, 13].

To obtain the dynamical correlation length, we parametrize the long-time decay of the overlap correlation function by stretched-exponential functions,

\[
q_c(z,t) = q_0(z) \exp[-(t/\tau_{\text{ov}}(z))]^{\beta(z)} + q_c(z,\infty),
\]

where \( \tau_{\text{ov}}(z) \) is a \( z \)-dependent relaxation time. Similar fits have been performed for the collective and self-intermediate scattering function (SISF), and we only discuss the features that are robustly displayed by all relaxation times, taking that of the SISF as a proxy \( \tau(z) \); see Fig. 1(d) and Supplemental Material [32].

In the relative enhancement of the mobility \( \mu(z) = 1/\tau(z) \), given by \( \tau(\infty)/\tau(z) - 1 \), there emerge two spatial regimes at low temperature [Fig. 1(e,f)]: close to the surface \( (z \lesssim 2\sigma) \), an initial exponential decay is identified, whose typical length scale depends only weakly on temperature. This regime corresponds to distances where the static density profile has not yet saturated to its bulk value. An intermediate \( z \)-range with a much slower decay opens at lower temperatures \( (T \lesssim 1000 \text{K for CuZr, } T \lesssim 0.45 \text{ for LJ}) \). This intermediate regime expands as \( T \) is lowered. Here, \( \rho(z) \approx \rho(\infty) \), and thus this is the regime where an intrinsic dynamical correlation length \( \xi_{\text{dyn}} \) can be extracted from the exponential decay of \( \mu(z) \), viz.

\[
\mu(z) = C \exp[-z/\xi_{\text{dyn}}] + \mu(\infty).
\]

One already anticipates from Fig. 1(e-f) that this dynamical correlation length shows a non-monotonic temperature dependence: curves for intermediate temperature (around \( T = 810 \text{K in the CuZr liquid, and around } T = 0.4 \text{ in the LJ binary mixture} \) extend further into the bulk than those both at higher and at lower temperatures.

The resulting dynamical correlation lengths \( \xi_{\text{dyn}} \) display clear maxima at a temperature \( \Gamma^* \) (Fig. 2). Both above and below \( \Gamma^* \), the dynamic and static (symbols with dashed lines in Fig. 2) correlation lengths become similar. In particular, below \( \Gamma^* \), \( \xi_{\text{dyn}} \) decreases towards the smaller static one, \( \xi_{\text{stat}} \), again. This is not a finite-size effect: only around the maximum in \( \xi_{\text{dyn}} \), some slight effects of system size (in line with those expected from conventional four-point correlations in supercooled liquids [38–40]) are seen that disappear both at higher and at lower temperatures, and thus give additional evidence that the dynamical correlation length peaks at \( \Gamma^* \). In both the CuZr and the LJBM system, we note that the peak observed in \( \xi_{\text{dyn}} \) over \( \xi_{\text{stat}} \) is at least a factor of 2. It is hence a robust phenomenon across systems with different microscopic interactions and surface features.

We now demonstrate the intimate link of the maximum in the dynamic correlation length near the surface with a cross-over point that governs the bulk dynamics. Such a link is remarkable, because the point of maximal correlation length, \( T_\star \), is clearly above the \( T_c \) of MCT, to which candidates of structural changes impacting the relevant dynamical regime have so far been linked. One example is a change in morphology of the CRR as suggested by RFOT [41].

We identify CRR as nearest-neighbor clusters of fast particles in simulations of the bulk systems. Following
FIG. 1. Characterization of dynamic properties near the surface. (a) Illustrative snapshot of the simulation setup (CuZr system, colors indicating atomic species). (b) Static density profiles $\rho(z)$ as a function of distance $z$ from the surface along the normal into the bulk, for the CuZr liquid and the Lennard-Jones binary mixture (LJBM) (in units of the average atomic radius $\sigma$, shifted vertically in steps of $0.4/\sigma^2$ for clarity). Solid lines are fits to extract the static correlation length. (c) Static and dynamic parameters characterizing the overlap correlation function (CuZr; $T=850$ K). The normalized static overlap $q_c(z,\infty)/q_c(\infty,\infty)$ (crosses) follows the normalized density profile $\rho(z)/\rho(\infty)$ (line). The normalized change in the relaxation time $\tau(\infty)/\tau(z)$ (squares) is shown in comparison to the corresponding quantity obtained from the $z$-resolved SISF (circles). (e) and (f): Position-dependent relative mobility enhancement $\tau(\infty)/\tau(z)−1$ (from the layer-resolved SISF) for CuZr and the LJBM.

[42, 43], fast particles are defined as those that during the time interval corresponding to the average structural relaxation time, have moved significantly farther than what is expected from the average mean-squared displacement. Clusters are defined by fast particles closer than the first minimum position in the pair distribution function. To quantify the shape and in particular the anisotropy of these clusters, we consider the ratio of their correlation length to the expected spherical size: In analogy to percolation theory [44], the average cluster correlation length is given by

$$\xi_a^2 = \sum_s R_{g,s}^2 s^2 P(s)/\sum_s s^2 P(s),$$

where the sums run over the individual clusters of size $s$, $P(s)$ is the probability of finding a cluster of size $s$, and $R_{g,s}$ is the radius of gyration of the cluster of size $s$, defined by $R_{g,s}^2 = \frac{1}{2\pi^2} \left( \sum_{i,j \in s} (\vec{r}_i - \vec{r}_j)^2 \right)$, where the sum runs over all particles $i, j$ that are part of the cluster, and
The evolution is non-monotonic around a peak temperature $T^\ast$, the temperature is lowered, the clusters increase in size, and the average cluster size. The ratio, $\xi_{cl}/R_s$, can then be used as a simple proxy to measure the anisotropy of the fast-particle regions.

The aspect ratio of clusters, $\xi_{cl}/R_s$, exhibits a striking non-monotonic behaviour with temperature change [Fig. 3(a)], with a maximum at the same temperature $T^\ast > T_c$ where also the dynamical correlations near a free surface show a maximum. Thus we argue that $\xi_{cl}$ is intimately related to the shape transition of CRR in the bulk.

Typical shapes found for the fast-particle clusters in the bulk are also shown to demonstrate the shape transition [Fig. 3(b–d)] at high temperatures, clusters are like motion of atoms is well known in supercooled liquids [42, 43, 45, 46], this is the first report for the shape of CRR transiting back to the compact geometry at low temperatures in atomic glass formers.

The emergence of large CRR signals heterogeneities in the dynamics that inter alia lead to a breakdown of the Stokes–Einstein (SE) relation [39, 47–49]: the fast-particle dominated diffusivity decouples from the bulk relaxation that is governed by the slow particles [50, 51]. While far above $T_c$, a SE relation for the diffusion coefficient of a tracer particle, $D/T \sim \eta^{-1}$ holds well, far below $T_c$ a fractional SE relation emerges, $D/T \sim \eta^{-x}$ with some exponent $x < 1$ (Fig. 4). The maximum anisotropy of CRR at $T^\ast$ suggests that there, the coupling of fast-particle motion to the bulk dynamics changes, and that this can be connected to the breakdown of the SE relation [3].

Crucially, this allows to provide a clear first-principles definition of $T^\ast$. We do so by recalling a recent extension of the asymptotic laws of MCT, the stochastic $\beta$-relaxation theory (SBR) [52–54]. It rationalizes the crossover from regular to fractional SE relations as arising from long-wave length fluctuations in the local dynamical order parameter [55]: above $T_c$, the average dynamics is mean-field liquid-like, and the SE relation results from the realization $(1/\mu) \sim 1/(\mu)$. Below $T_c$, the relaxation dynamics is dominated by rare fluctuations of liquid regions inside a glass-like matrix, and the tail of the order-parameter distribution gives rise to a fractional SE relation, since $(1/\mu) \not\sim 1/(\mu)$. SBR describes our data well (solid line in Fig. 4).

Within SBR, we can rigorously identify the point of maximal dynamical correlation, $T^\ast$, as the point where the decoupling of fast-particle dominated motion (diffu-
FIG. 4. Stokes–Einstein plot of diffusivity \( D \) versus viscosity \( \eta \) (in LJBM units) for the bulk liquids, compared with the theoretical prediction from stochastic \( \beta \)-relaxation theory (SBR) (solid line, using the MCT exponent parameter \( \lambda = 0.75 \)). To make data collapse in different systems, \( D/T \) and \( \eta \) are scaled to \( D^*/T^* \) and \( \eta^* \) in CuZr. Dotted lines are the SBR asymptotes for high and low temperatures, i.e., a regular Stokes–Einstein law, \( D^*/T^* \sim \eta^{-1} \), and a fractional law \( D^*/T^* \sim \eta^{-0.558} \). Red circles mark the MCT-\( T_c \), and \( T_\ast \) predicted from SBR; arrows indicate the approximate maximum positions \( T_\ast \) inferred from \( \xi_{\text{dyn}} \) for the two simulated systems. We determine \( T_\ast \) within SBR from the point of maximum slope in the SE crossover curve \( d \log(D^*/T^*)/d \log(\eta^*) \) as shown in the inset.

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