Role of phonon softening induced by anisotropic fluctuations in the enhanced mobility at free glassy surfaces

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The surface of a glassy material exhibits enhanced mobility compared to the bulk counterpart, however the underlying mechanism for this remains elusive. Herein, we present studies of the dynamical properties of a prototypical glass-forming metallic liquid $Zr_{50}Cu_{50}$ as a function of the distance from both the free surface and pinned surface using molecular dynamics simulations. We found that the surface mobility increases gradually on approaching the free surface, with a concomitant increase of the non-Gaussianity. The phonon density of states at the free surface exhibits lower characteristic frequencies than in the bulk and pinned surface. These results suggest phonon softening caused by anisotropic fluctuations at free surfaces as an alternative physical mechanism leading to the enhanced dynamics at free glassy surfaces from the perspective of collective excitations.

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I. INTRODUCTION

The dynamical properties at the free surface of glassy materials can be significantly different from those in the bulk. For example, the surface mobility of glasses can be several orders of magnitude higher, and shows a much weaker temperature dependence than the bulk [1–10]. As a consequence, the onset of crystallization is typically from the free surface, with a distinct mechanism contrasting with what occurs in the bulk [11–13]. From a fundamental point of view, studying the near-surface mobility of glasses has the potential to provide new insights about the structural relaxation and glass transition [14,15], and from an application perspective the presence of a more mobile surface has practical implications for thin-film coatings related to lubrication, wear, and friction. The presence of the free surfaces leads to a substantial decrease of the glass transition temperature (T_g) of glass thin films [16], but on the other hand the enhanced surface mobility accelerates the sampling of lower energy configurations of the system during physical vapor deposition, creating glasses that are kinetically and thermodynamically ultrastable with increased T_g, higher density, and improved mechanical properties [17–21].

In the last few years, enhanced mobility at free surfaces has been observed in diverse glass-forming systems including metallic glasses [5,22], molecular glasses [2], polymers [3], and silicon [9]. However, a thorough understanding of the underlying mechanism is still lacking. Theorists are seeking an appropriate explanation by applying existing theories of glass transition [14] or proposing new theories that specifically address the surface phenomena [23,24]. For example, the random first order transition (RFOT) theory attributes the enhanced surface mobility to the shorter dynamical correlation length therein, while Lonard *et al.* consider the vapor-glass interface as a macroscopic dynamic heterogeneity that has an analogous enhancement found at the microscopic level in the mobile regions generated by thermal fluctuations [25]. Recent experimental studies found that the fast surface diffusion is decoupled from the film's relaxation dynamics, opening new questions on the nature of glassy surface mobility [26,27]. While it is difficult to directly investigate the microscopic dynamics of a glass surface with experiments, atomistic simulations can be an appropriate and effective tool.

In this work, we studied the surface dynamics of a model metallic glass former, $Zr_{50}Cu_{50}$, at both free surfaces and pinned surfaces using molecular dynamics (MD) simulations. The results show that, for both elements, the lateral mobility at the free surface is evidently enhanced, accompanied by a counterintuitive increase of the non-Gaussian parameter $\alpha_2(t)$. Furthermore, by computing the vibrational density of states, we found that the phonon modes at the free surface shift to lower energy compared with that of the bulk. These findings reveal a distinct dynamical mechanism associated to the enhancement of mobility at the free surface of glasses.

II. METHODS

The MD simulations were performed using LAMMPS [28] with a 1 fs integration time and covered a wide temperature range from 900 K to 1,200 K between the glass transition point $T_g = 677$ K and the melting point $T_m = 1{,}231$ K [29]. The interactions between the Zr and Cu atoms were described by a binary embedded atom method (EAM) potential [30,31]. For the bulk system, we used a cubic box with 40,000 atoms (20,000 Zr and 20,000 Cu) and periodic boundary conditions enforced in all three dimensions. We first heated up the system to 2,000 K and equilibrated it at zero external pressure, and

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then cooled it down to the subsequent target temperatures with a cooling rate of 1 K/ps. At each target temperature, we reequilibrated the system at zero external pressure to obtain the correct density. Afterwards, we reequilibrated the system in the constant temperature, constant volume (NVT) ensemble and collected the production trajectory. For the systems with free surfaces, we placed the same number of atoms in a slab with a length (along the z axis) of 40 Å. The width and the height (along the x and y axis) of the slab were set according to the density. After the system was reequilibrated in the NVT ensemble, we created two free surfaces by doubling the size of the simulation box along the z axis. For comparison, we also created another simulation system with two pinned surfaces by fixing all atoms in a 5 Å layer of the surface. We reequilibrated each system in the NVT ensemble after the surfaces were created, then we collected the production trajectory. All results presented are based on the average of the two surfaces of each slab. The statistical analysis was performed using the LIQUIDLIB package [32] developed by our group.

III. RESULTS AND DISCUSSIONS

Figure 1(a) shows the density profiles of the free and pinned surface systems for both the Zr and Cu atoms, as well as their averages. The density is calculated by slicing the system into layers 1.0 Å thick along the z axis. Periodic density variations down to $z \approx -10$ Å deep indicative of layered structure are observed for both the free and pinned surface systems. This is consistent with previous experimental observations [33–37]. In the free surface case, the two outermost layers are rich in Zr. This could be attributed to the stronger attractive interaction between Cu atoms than that between Zr atoms [30]. As the structural symmetry is broken at the free surface, imbalanced interactions are produced. Cu atoms tend to stay in the bulk and fully coordinated, leaving relatively more Zr at the free surface as a consequence.

For dynamical quantities, we sliced the system into layers 1 Å thick along the z axis. The dynamical quantities were then computed along the xy plane for each layer. An atom is assigned to a certain layer if it remains in that layer both at the initial time t_0 and the inspection time t. We computed the number of atoms that moved out of the layer at 0.1 ps, the boundary between the ballistic and diffusional motions, and found that the out-of-plane contribution to the overall mobility is negligible compared to the in-plane counterpart. Figure 1(b) shows the lateral (i.e., along the xy plane) diffusion coefficient D_{xy} as a function of the depth z to the surface. Here, D_{xy} is obtained by integrating the velocity autocorrelation function in the xy plane using the Green-Kubo relation $D = \frac{1}{d}\int_0^\infty \langle \mathbf{v}_{xy}(0)\cdot\mathbf{v}_{xy}(t)\rangle dt$ [38], where $d = 2$ in this case. One can clearly see that the diffusion of both elements increases continuously when the free surface is approached. The depth-dependent lateral diffusion coefficient D_{xy} can be described by an exponential form suggested by the RFOT [14] as well as a double exponential form suggested by the elastically cooperative nonlinear Langevin equation (ECNLE) [39–41]. However, the data quality is not sufficient to discriminate between these theories.

For comparison, we also computed the D_{xy} for the pinned surface system using the same protocol. In contrast to the free surface case, D_{xy} of the pinned surface system shows a continuous decrease [Fig. 1(b)] as the surface is approached. This observation agrees with previous studies of the structural relaxation time defined by the self intermediate scattering functions which trace the same subsets of particles at various time intervals [39,42,43]. As the ECNLE theory and simulations have shown the existence of an exponential form for $\ln[\tau(z)/\tau_\infty]$ instead of $\tau(z)$ near the pinned surface [39–41], we also presented the corresponding fits in Fig. 1(b). Note that both the free and the pinned surfaces show similar periodic density variations [Fig. 1(a)], however their dynamics are distinctly different, one accelerated and the other slowed down compared to the bulk. This observation suggests that the formation of ordered layer structure or the density is not the immediate cause of the dynamics modifications, in agreement with the previous studies [44,45]. One striking observation is that the dynamics are enhanced even in the densest layer

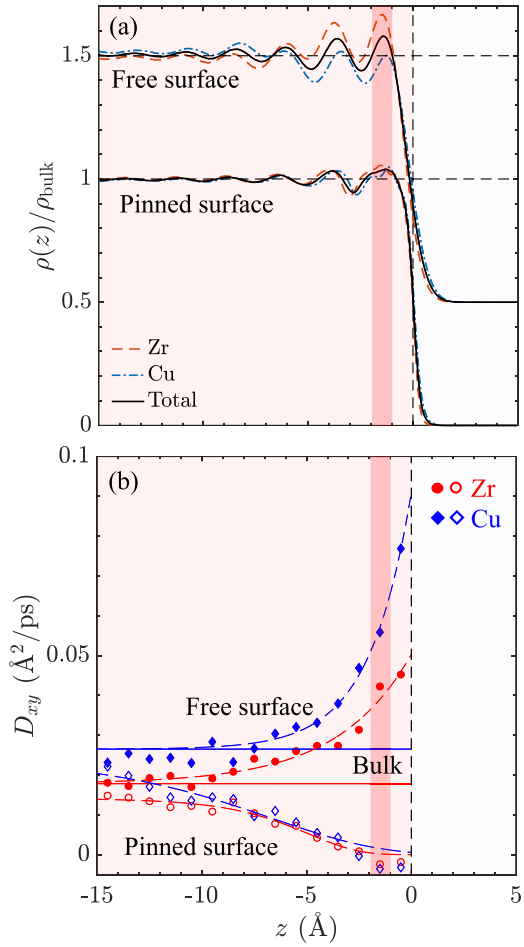

FIG. 1. (a) The normalized density profiles of the free and pinned surface systems at 900 K. The pink region represents the metallic liquids. The surface is located at $z = 0$. The density of the free surface system was shifted by 0.5 for clarity. The black solid lines are the average densities. (b) The lateral diffusion coefficient (along the xy plane) as a function of depth from the free (solid symbols) and pinned (open symbols) surfaces at 900 K. The two horizontal solid lines represent 2/3 of the diffusion coefficients of Cu (blue) and Zr (red) in the bulk metallic glass. The dashed lines are the RFOT fits near the free surface, and the ECNLE fits near the pinned surface.

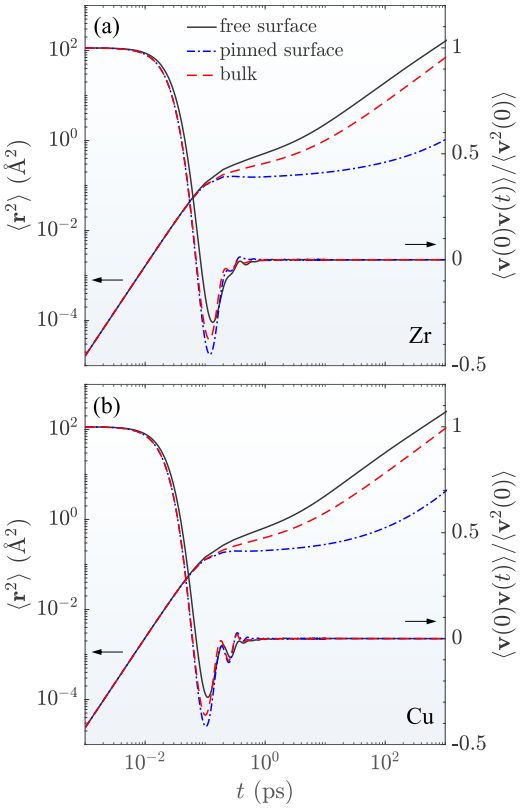

FIG. 2. The mean squared displacement (left axis) and normalized velocity autocorrelation function (right axis) for (a) Zr and (b) Cu at 900 K at the free surface, the pinned surface, and in the bulk.

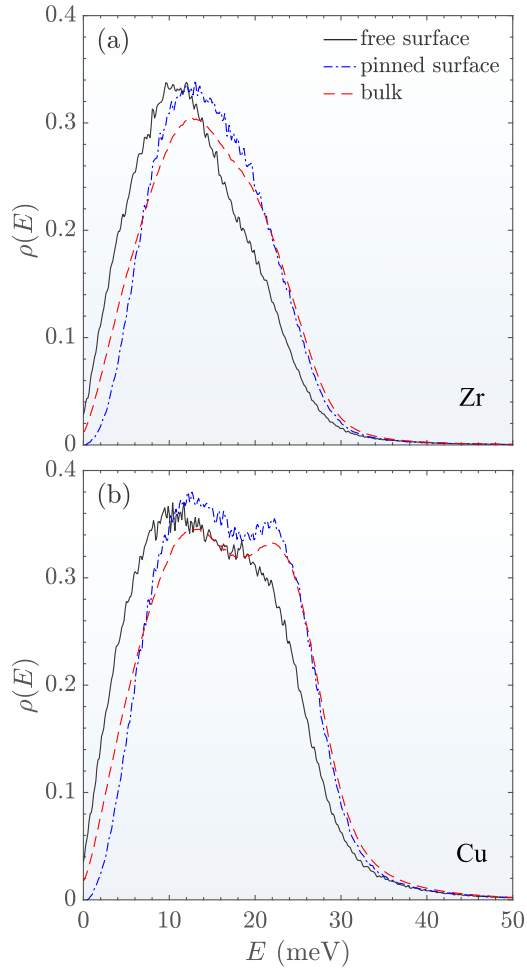

FIG. 3. The density of states (DOS) at the free surface, the pinned surface, and in the bulk for (a) Zr and (b) Cu at 900 K.

between 1 and 2 Å from the free surface (the dark pink stripe shown in Fig. 1).

To further inspect the dynamical process, we plotted the lateral mean squared displacement (MSD) and velocity autocorrelation function (VACF) at 900 K in Fig. 2 for the free and pinned surface systems in this $-2 < z < -1$ Å layer as well as the bulk. The densities of the two surface systems in this layer are higher than that of the bulk, so free volume is the not reason of the enhanced dynamics. The dynamical behavior of Zr [Fig. 2(a)] and Cu [Fig. 2(b)] are similar. In the diffusive regime at $t > 1$ ps, the enhanced mobility of the free surface system is evident with larger MSD than the bulk. In contrast, the pinned surface system shows suppressed mobility with much smaller MSD. Within the ballistic regime $t < 0.1$ ps, the MSD shows no obvious difference among all three systems, all following $\langle \mathbf{r}^2 \rangle \propto t^2$. However, the VACF up to 1 ps exhibits clearly different behaviors. The VACF of the free surface system decays slower than that of the pinned surface system and the bulk. This suggests a much weaker "cage" effect in the free surface system despite its higher density. In that sense, these results are in agreement with the observation by Sun *et al.* that the Debye-Waller factor shows a remarkable reduction at the free surface [46].

To quantify the short time collective dynamics, we computed the density of states (DOS) by Fourier transforming the VACF (shown in Fig. 3). In the bulk, the DOS of Cu exhibits two maxima at approximately 13 and 22 meV, indicating the existence of two phonon-like excitation modes. The DOS of Zr shows a similar distribution, except that the population of the high energy mode with a longitudinal nature [47] is weaker and shows up as a shoulder. In contrast, in the free surface system, the high energy mode is significantly reduced, and the low energy mode is shifted to even lower energy. Similar behavior has been observed recently at the free surface of silica glasses [48], pointing toward a universal character. Therefore, from the perspective of collective excitations, the surface of glass exhibits more liquid like behavior than the bulk because the phonons are significantly softened.

The features of the DOS of the pinned surface system are largely the same as the bulk, with one peculiar exception at the low energy end ($E < 5$ meV). The population of these low energy modes shows a remarkable decrease. This is in sharp contrast to the case of free surfaces, where these low energy modes are enhanced. In other words, the low energy collective excitations are prone to the presence of walls or surfaces. The correlation between this phonon behavior with the lateral diffusions [Fig. 1(b)] suggest that the enhanced dynamics at the free surface could come from phonon softening,

whereas the suppressed dynamics at the pinned surface is due to phonon hardening. Our observation is consistent with the ECNLE theory by Schweizer *et al.* [23], which attributed the higher mobility at the free surface to a softer confinement potential. Computational evidence of the relation between altered diffusion and vibration of confined supercooled liquids at surfaces has also been provided by Vogel *et al.* [40,41]. Additionally, Sun *et al.* proposed that the Debye-Waller factor as the origin of the enhanced dynamics at the free surface [46]. Herein, by comparing the free surface and pinned surface, we move further to suggest that softening of the phonon modes is the underling physical mechanism. This picture is favored by the previous observation of Ding *et al.* in a similar metallic glass that the atoms participating preferentially in soft vibrational modes have the highest propensity to undergo rearrangements [49].

Lastly, to further investigate the origin of the phonon softening, we study the non-Gaussian behavior of free surface system. The non-Gaussian parameter $\alpha_2(t)$ describes the degree of the deviation of the dynamics from a Gaussian behavior [50,51]. The maximum of $\alpha_2(t)$, α_2^*, directly reflects the degree of non-Gaussianity of the system's dynamics. In two dimensions (2D), the non-Gaussian parameter is defined as $\alpha_2(t) = \frac{\langle \Delta \mathbf{r}^4 \rangle}{2\langle \Delta \mathbf{r}^2 \rangle^2}$ [52]. Figure 4(a) shows $\alpha_2(t)$ as a function of time t at 900 K for different distances z from the surface. The inset shows their maxima α_2^* as a function of the depth z. From the bulk to the free surface, α_2^* decreases slightly for $z < -5$ Å, and surprisingly increases rapidly on approaching the surface from $z > -5$ Å. In other words, the non-Gaussianity is enhanced close to the free surface. Furthermore, the characteristic relaxation time defined at α_2^* is shifted towards a shorter timescale on approaching the free surface, in agreement with the observed enhanced dynamics at the free surface [Fig. 1(b)].

Figures 4(b) and 4(c) present the α_2^* of Zr and Cu, respectively, as a function of z and temperature T, from which we can clearly identify the existence of a surface layer with much larger value of α_2^* than the bulk across the investigated temperature range from 1200 to 900 K. As the temperature is decreased, the depth of this layer with enhanced non-Gaussianity increases from ∼3 Å (about one atomic layer) at 1200 K to ∼5 Å (about two atomic layers) at 900 K, and α_2^* also increases.

It is generally accepted that the dynamics in supercooled liquids and glasses is heterogeneous, with individual relaxing units in the system having site-specific relaxation times [53]. This so-called dynamic heterogeneity is oftentimes quantified by the four-point correlation functions $\chi_4(t)$ [54–56], but sometimes can also be quantified by the non-Gaussian parameter [51,57–68]. This is because both quantities are enhanced simultaneously in supercooled liquids and glasses [60–62,69,70]. However, an enhanced non-Gaussianity does not necessarily imply more heterogenous dynamics. Actually, non-Gaussianity has also been associated with heterogenous fluctuations [71], intermittency or temporal heterogeneity [72], spatial anisotropy [72], and anharmonicity [73]. As shown in Fig. 4, the liquid dynamics are more non-Gaussian close to the free surface, nonetheless the dynamics are enhanced. Therefore, we attribute this observed

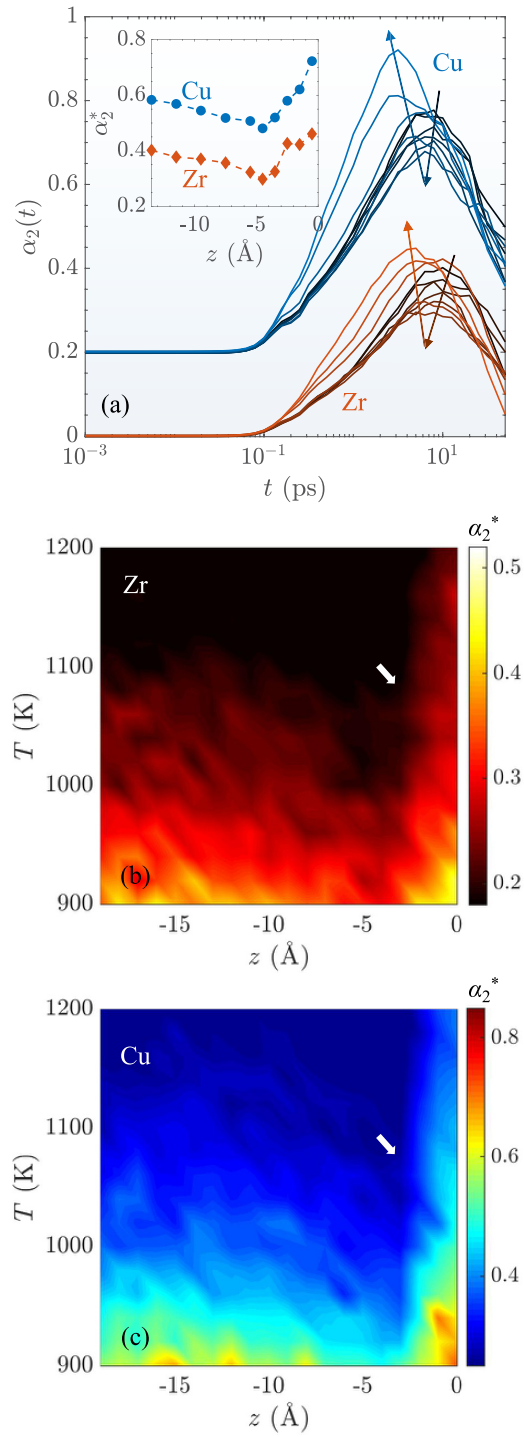

FIG. 4. (a) The non-Gaussian parameter $\alpha_2(t)$ at various distances z from the free surface at 900 K. The $\alpha_2(t)$ of Cu is shifted by 0.2 for clarity. The colored arrows indicate the distance from the bulk to the surface. The inset shows the maxima of the non-Gaussian parameter α_2^* as a function of the depth z. (b) and (c) show the α_2^* as functions of the depth z and temperature T for Zr and Cu, respectively. A surface layer with large non-Gaussianity is evident in all temperatures.

enhanced non-Gaussianity to the anisotropic fluctuations at the free surface, which is a special kind of spatially heterogenous fluctuation at surfaces [71]. Likewise, the phonon

softening at the free surface also comes from the anisotropic fluctuations. On the other hand, the small number of atoms in each layer do not allow us to compute $\chi_4(t)$ reliably. The rough $\chi_4(t)$ calculation seems to suggest a decreasing trend of the dynamic heterogeneity on approaching the free surface, however a definite conclusion on the behavior of dynamic heterogeneity cannot be drawn.

IV. CONCLUSIONS

In conclusion, by comparing with the bulk and pinned surface systems we found that, at the free surface of disordered $Zr_{50}Cu_{50}$, the atomic mobility is faster, the low energy collective excitations modes (DOS) are enhanced, and the dynamics are more non-Gaussian. Indeed, the softened phonon modes can facilitate the structural rearrangements of the liquids and glasses and thus contribute to an enhanced dynamics at free surfaces. This picture suggests phonon softening caused by anisotropic fluctuations at surfaces, evidenced by the enhanced non-Gaussian behavior, as an alternative physical mechanism leading to the enhanced dynamics at free glassy surfaces from the perspective of collective excitations.

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