Front-mediated melting of ultrastable glasses

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Ultrastable vapor-deposited glasses display peculiar properties. In particular, upon heating they melt via a liquid front that originates at the free surface and propagates over a mesoscopic crossover length, before crossing over to bulk melting. We combine swap Monte Carlo with molecular dynamics simulations to prepare and melt amorphous films of a kinetic stability comparable to experiments. We observe both bulk and front melting, and the crossover between them. We measure the front velocity over a broad range of conditions, and a crossover length scale that grows to nearly 400 particle diameters in the regime accessible to simulations.

Amorphous films created by physical vapor deposition have the same kinetic stability as liquid-cooled glass films aged for thousands of years [1]. Such exceptional stability makes these materials promising for a wide range of applications, including drug delivery [2], protective coatings [3,4], and lithography [5]. There is therefore acute interest in better controlling the physical characteristics of these ultrastable glasses, and especially the way they lose stability [6,7]. Ordinary liquid-cooled glasses melt homogeneously from the bulk, but ultrastable films melt via a constant-velocity front initiated at the free surface, a process reminiscent of melting crystals [8]. This analogy is difficult to rationalize theoretically [9,10] because glass and liquid are not distinct thermodynamic phases. The interplay between molecular structures, film anisotropy, specificities of the nonequilibrium vapor deposition, densification, melting temperature, and kinetic stability in the melting are not well understood.

Melting fronts in vapor-deposited glasses are nevertheless robustly observed [7,11,22]. Generally, melting depends both on the initial preparation temperature of the film, Ti, and on its melting temperature, Tm. Experiments suggest that ultrastable glass films melt via a well-defined flat front that propagates from the free surface at constant velocity, v = v(Ti, Tm), a phenomenon without equivalent in conventionally prepared glasses. Quantitatively, v decreases when the glass stability (controlled by Ti) increases and increases with Tm. Two different functional forms are used to describe results: (i) an Arrhenius scaling [19,20], v = v0(Ti)eEa/Te, where Ea is an activation energy (with Boltzmann constant set to unity); and (ii) a power-law scaling

\[ v = C(T_1)\tau_0(T_m)^{-\gamma}, \]

where \(\gamma \leq 1\), and \(\tau_0(T_m)\) is the equilibrium bulk structural relaxation time at \(T_m\) [11,15,19,21]. Note that the prefactor of both forms captures the stability dependence of v encoded in Ti. In thick films, the melting front propagates over a finite distance, \(\ell_c = \ell_c(T_1, T_m)\), because deeper layers have homogeneously melted by a distinct bulk-like mechanism by the time the front reaches them. Available data suggest that \(\ell_c\) can vary from 20 to 2000 times the molecular size [15,21], smaller \(\ell_c\) being reported for less stable systems and higher \(T_m\) [12,22]. Such a large length scale characterizing the dynamics of supercooled liquids is theoretically enticing, but it is unclear what physical parameters control its behavior.

At the theoretical level, a treatment based on an extended mode-coupling theory predicts an interplay between front-mediated and bulk melting [9], with the melting front being triggered by the increased mobility of top layers. Dynamical facilitation can also be analyzed using kinetically constrained models to shed light on front melting [23,24]. A three-dimensional East model suggests that the Arrhenius scaling of the front velocity breaks down at low melting temperatures, and that Eq. (1) with \(\gamma = 0.95\) then holds for all \(T_m\) [23]. A modified East model predicts the existence of a characteristic film thickness \(\ell_c\). Similar conclusions were drawn from another constrained model, reporting \(\gamma \approx 0.83\) [24]. A two-dimensional plaquette model illustrates a nucleation and growth picture of melting for sufficiently stable glasses [10], and evinced that the large associated length scale is related to \(\ell_c\). Numerical simulations could be expected to critically assess these various proposals, but limited attempts have been made because preparing glassy films sufficiently large and stable for a melting front to develop is computationally challenging. Direct simulation of the vapor deposition process does not provide a sufficiently large gain in stability [25,26], and the resulting evidence for front melting is weak [25]. Although random pinning [27] can create fairly stable inhomogeneous two-dimensional films, a modest \(\ell_c\) growth is observed, associated with \(\gamma \approx 1\).

Here, we build on a recent advance in sampling methods for glass-forming liquids [28,29] to create three-dimensional films of exceptional thickness, homogeneity and kinetic stability for a model glass former. The wide
range of kinetic stabilities and the well-controlled geometry and film preparation allow us to observe and quantitatively characterize the emergence of front-mediated melting and its competition with the bulk process. We resolve the applicability of Eq. (1), and provide a robust estimate of the characteristic length scale \( \ell_c \). Our results show that kinetic stability and melting temperature are the key control parameters in the front-melting process of stable glasses, and that very large \( \ell_c \) emerge naturally in the non-equilibrium melting of ultrastable glasses, even when starting from equilibrium isotropic films.

We consider a glass-former composed of size polydisperse Lennard-Jones particles with pair interaction \( V_{nm}(r) = \epsilon \left[ \frac{4}{\sigma_{nm}/\sigma} - 1 \right] \) where each particle \( n \) has a diameter \( \sigma_n \) randomly chosen from the distribution \( P(\sigma) = A/\sigma^3 \), with \( \sigma \in [0.73, 1.62] \) and normalization constant \( A \). We choose a nonadditive mixing rule, \( \sigma_{nm} = \frac{1}{2}(\sigma_n + \sigma_m)(1 - \Delta/|\sigma_n - \sigma_m|) \) with \( \Delta = 0.2 \), in order to suppress fractionation and ordering at low pressure, \( P \), and temperature, \( T \). The unit of energy is set to \( \epsilon \), the unit of length is the average particle diameter, \( \sigma_0 \), and, because all particles have the same mass \( m \), the unit of time is \( \sqrt{\sigma_0^3 m/\epsilon} \). To characterize bulk systems, we first thermalize configurations with \( N = 2000 \) particles from constant \( NPT \) swap Monte Carlo simulations at \( P = 0 \) [29]. Dynamical properties are then determined using standard molecular dynamics simulations with the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) [30]. We measure the time decay of the self-intermediate scattering function \( F_s(q,t) = N^{-1} \langle \sum \delta_0 e^{-i2\pi q z} \rangle \), where \( q = 7.1 \) maximizes the static structure factor, and define the structural relaxation time, \( \tau_\alpha \), as \( F_s(q,\tau_\alpha) = e^{-1} \).

In Fig. 1 we use \( \tau_\alpha(T) \) to determine the onset temperature by observing departure from high-temperature Arrhenius scaling, \( \tau_\alpha \propto e^{E_m/T} \) below \( T_m \approx 0.12 \), with \( E_m = 0.57 \). The experimental glass temperature \( T_g \) is not directly accessible in simulations, but can be reliably estimated by measuring dynamics over the accessible numerical window and fitting \( \tau_\alpha \) to various functional forms [29]. Previous work has shown that the parabolic fit \( \tau_\alpha = \tau_\alpha(T_m) e^{E_m/(T_m - T)} \) yields an accurate extrapolation of \( \tau_\alpha \) towards experimental timescales to obtain \( T_g \) as \( \tau_\alpha(T_m) = 10^{12} \tau_\alpha(T_m) \). We find \( T_g = 0.063 \), which sets a reference scale for film stability.

To prepare films, we first run bulk simulations of systems using various thermal protocols at initial temperatures \( T_i \) [31]. These configurations are true equilibrium states for \( T_i \geq 0.65 \), but only well-aged glasses for \( T_i = 0.04 \) where complete thermalization cannot be ensured. Films are then obtained by removing the periodic boundary condition in the \( z \) direction, immobilizing a bottom layer of thickness 5 to create a substrate, and leaving the top layer free. The resulting films have a height of about 42 and the periodic box side in the orthogonal directions is about 40. After being rapidly heated from \( T_i \) to \( T_m \) at a rate of \( 2 \cdot 10^{-4} \), the films are finally held at \( T_m \), with a Nosé-Hoover thermostat to study their melting.

The snapshots in Fig. 2(a,d,g) illustrate three melting regimes: (a) pure surface-initiated melting with a flat front that propagates over the entire film; (d) front-mediated melting competing with bulk melting; (g) pure bulk melting with no apparent front. The numerical observation of these three regimes for films thicker than 40 particles is our central achievement.

To quantify these observations, we identify melted regions using a spatially-resolved overlap function:
increases linearly with the distance from the film surface, see, e.g., Fig. 2(c). Deviations from a linear $z$ dependence only appear when $\tau_m$ reaches $\tau_o(T_m)$. Remarkably, the slope is independent of $\tau_w$ and thus provides a robust estimate of the front velocity $v$. In practice, the front velocity is obtained by fitting $\tau_m = \tau_w - z/v$, while making sure that the result is also consistent with the waiting time needed to fully melt the system.

By contrast, Fig. 2(e) does not show such a simple spatial dependence across the film. For instance, the decay of $F_m(z; t, \tau_w = 0)$ at $z = 13-17$ is essentially constant. The resulting profile is not perfectly linear, see, e.g., Fig. 2(f), but the decay times do decrease farther from the substrate, and hence it remains possible to extract a front velocity for that intermediate case. This juxtaposition of behaviors is consistent with the emergence of a competing melting mechanism in the bulk.

In the opposite limit shown in Fig. 2(h), the top layer of the film melts rapidly and then, after a short time, the rest of the film essentially melts at once. Accordingly, the $z$ dependence of $\tau_m(z, \tau_w)$ in Fig. 2(i) confirms that the decay time is constant throughout the film. Melting is then a purely bulk process. Remarkably, the melting time here is only 30% shorter than for $T_i = 0.04$ and $T_m = 0.12$, for which a melting front exists. Hence, films with comparable melting times need not melt in the same way, suggesting a delicate competition between the two melting mechanisms. Deducing the dominant mechanism requires resolution of the microscopic dynamics.

Evidence of front melting was obtained over a broad
range of \((T_i, T_m)\). For a given \(T_i\), a crossover from heterogeneous to homogeneous melting occurs as \(T_m\) increases, over a range \(\Delta T_m \approx 0.005\). Systems in this crossover region exhibit a melting front, but this front only relaxes a finite fraction of the film. It is however difficult to directly characterize \(\ell_c\), because the front is no longer sharply defined when the bulk process takes over.

The evolution of \(v(T_i, T_m)\) is reported in Fig. 3. If the melting temperature is large enough, \(T_m > 0.095\), an Arrhenius description with \(E_a = 2.0 \pm 0.1\) captures our data well for all \(T_i\) (Fig. 3(a)). This activation energy is about four times higher than that inferred from the temperature dependence of the relaxation time above \(T_m\), which suggests that the energy barriers overcome during melting are different from those of the bulk relaxation process at the same temperature. In addition, as found in experiments the kinetic stability of the glass only enters as a prefactor to the Arrhenius scaling, with more stable systems exhibiting slower front propagation. The Arrhenius scaling breaks down for \(T_m < 0.095\) for all \(T_i\). Following experimental observations, we then fit \(v\) to Eq. (1) and find \(\gamma \approx 1\) (Fig. 3(b)), which is compatible with the only available numerical data \(\tau_m\). The accessible range of \(v\) is however too small to fully validate the power-law scaling and obtain an accurate estimate of \(\gamma\). These results nonetheless indicate that the front velocity is controlled by the supercooled liquid dynamics for \(T \lesssim 0.95\). Here again, the glass stability only enters as a prefactor.

Whereas more stable glasses entirely melt with a moving front, the snapshots in Fig. 2 (d.g) reveal that large melted domains can appear ahead of the front. This directly shows that even without a free surface, a bulk process eventually melts the films in a finite time, \(\tau_m\). The length scale \(\ell_c\) that characterizes the crossover between front propagation and bulk melting is then given by \(\ell_c = v \tau_m\). In order to estimate \(\ell_c\) we independently determine \(\tau_m\) using bulk simulations, and combine the results with the above measurements of \(v\).

In Fig. 4 we report that \(\ell_c\) grows both upon increasing glass stability (lower \(T_i\)) and upon lowering \(T_m\). While the kinetics of both front-mediated and bulk melting slow down with decreasing \(T_m\) and \(T_i\), the fact that \(\ell_c\) grows indicates that bulk melting is more strongly suppressed than front melting. In bulk melting, regions of liquid form and grow within the glass, meaning that \(\tau_m\) is determined by a non-trivial combination of the two timescales associated with the formation and the growth of these regions. Too little is known about how \(T_i\) and \(T_m\) affect these two timescales individually to untangle their influence. The interpretation of \(\ell_c\) as the spatial separation between nucleation sites for bulk melting has not directly been confirmed.

To compare these observations with experiments, we consider toluene films, for which no molecular order develops during vapor deposition. Inhomogeneities would additionally influence both \(v\) and \(\ell_c\), as shown for indomethacin. For toluene, we take \(\sigma_0 \approx 0.6\text{nm}\). Ráfols-Ribé et al. report stability-dependent \(\ell_c\) in the range 50-200nm, and Bhattacharya et al. find \(\ell_c \approx 250\text{nm}\). The largest length scale we measure for \(T_i = 0.095\) gives \(\ell_c = 375 \pm 20\text{nm}\), which compares favorably with the measurements made using nanocalorimetry for samples vapor deposited around \(T_m \approx 0.095\). We rewrite \(\ell_c = v \tau_m = \ell_o S\), which is the product of a length \(\ell_o = v \tau_o\) and the stability ratio \(S = \tau_m/\tau_o\). We compiled experimental and numerical data from \(T_m\) to \(T_i\), and found that \(\ell_o\) is a microscopic length with weak temperature dependence (it is controlled by the small exponent \(1 - \gamma\)). As a result, the crossover length \(\ell_c\) is mainly controlled by the stability.
ratio. Since $S$ may increase up to $10^5$ \cite{31,32}, the observation of very large $\ell_c$ therefore directly reflects kinetic ultrastability \cite{22}.

Recent algorithmic progress \cite{29} allowed us to create films that are sufficiently large and stable to observe front-mediated and bulk melting, and the competition between them. We have thus replicated, with atomic resolution, a salient experimental feature of vapor-deposited glasses \cite{6,7}. Because our samples were prepared from solution, a salient experimental feature of vapor-deposited glasses is the anisotropic nature of the glass, and it can occur also in conventional glasses for well chosen melting temperatures. We have further characterized the maximum film thickness that melts via a surface-initiated front before bulk melting becomes competitive. An increase in $\ell_c$ is directly linked to the growing kinetic stability of ultrastable glasses. To better understand this competition, simulations of extremely large ultrastable glasses in the bulk are required. Directly observing the largest length scales reported here would require simulating glasses with at least $10^7$ particles, which represents an impressive, but conceivable, challenge for future numerical studies.

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Supplemental Material for “Front-mediated melting of ultrastable glasses”

THERMAL PROTOCOLS

To make sure that the film preparation does not affect our conclusions, we followed three different protocols.

1. We ran constant $P = 0$ bulk swap Monte Carlo simulations under periodic boundary conditions at $T_i = 0.065, 0.0675, 0.07, 0.0725,$ and $0.075,$ until the mean-squared displacement, $\langle \delta r^2(t) \rangle = \sum_n |r_n(t) - r_n(0)|^2,$ is larger than $10 \sigma_0,$ making sure that the energy, pressure, and volume have steadied. For $T_i = 0.04,$ clean equilibration could not be attained, but we aged the structure for the same amount of swap Monte Carlo steps, i.e., $3 \times 10^6,$ that it took systems at $T_i = 0.065$ to equilibrate. To initialize the film we first replicated the system three times in the $x$ and $y$ directions and four times in the $z$ direction. We then tethered a $0.065 \times 10^6$ wide region at the bottom of the film within which each particle is tethered with a harmonic potential $U = 0.5k (|r - r_0|^2$ where $k = 100$ and $r_0$ is the initial position of that particle. Finally, periodic boundary conditions were removed in the $z$ direction and a reflecting wall was introduced at $z = 80.$ The first set of films was melted from these configurations.

2. We ran the replicated system for an additional $100,000$ swap Monte Carlo steps to relax most of the periodic structure associated with the replication. The rest of the procedure was identical as above.

3. We equilibrated a system with $N = 72,000$ at $P = 0$ using a constant $NPT$ swap Monte Carlo algorithm. Because these simulations are very time consuming – equilibration at $T = 0.065$ took three months – we did not age a system at $T = 0.04$ with this scheme. These films were also slightly narrower than those prepared by the other two approaches, but the rest of the protocol was otherwise identical as above.

To melt the films temperature was ramped up from $T_i$ to $T_m$ at a constant rate of $2 \times 10^{-4}.$ The systems were then simulated until $\delta \rho_n(t) = \sqrt{|x_n(t) - x_n(0)|^2 + |y_n(t) - y_n(0)|^2} > 1.6$ for 90% or more of the particles for $T_m > 0.09.$ For the most stable samples, however, we could not meet this criterion for $T_m < 0.09$ using available computational resources. For these films at least 25% of the film was melted, which sufficed to measure the front velocity.

![Figure 5](image_url)

**FIG. 5:** (a) Pair correlation function and (b) the static structure factor for $T_i = 0.075, 0.0725, 0.07, 0.0675, 0.065$ and 0.04 from bulk simulations.

SYSTEM STRUCTURE

We noticed no statistically significant nor systematic differences in the melting of film prepared with any of the three procedures. In addition, to ensure that the average structure is the same for each of our films, we calculated the pair correlation function $g(r) = N^{-1} \sum_{m \neq n} \delta(r - |r_n - r_m|)$ and the static structure factor $S(q) = N^{-1} \sum_{n,m} e^{iq(r_n - r_m)}$ of bulk systems (Fig. 5). These pair correlation functions closely match those calculated at the center of the films. For $0.065 \leq T_i \leq 0.075$ there is almost no change in the average structure. For the aging glass at $T_i = 0.04$ the first peak of both $g(r)$ and $S(q)$ is slightly shifted and increased. Most importantly, none of the structures exhibit any sign of fractionation or crystallization.
The pressure tensor $P$ is given by $(P_x + P_y)/2$. When the film is 50% melted (blue); (iii) when the film is 90% melted (black). The shaded green region for $z < 0$ denotes the substrate position.

**CROSSOVER LENGTH CALCULATION**

To study the crossover length scale $\ell_c$, the melting time of a bulk sample prepared at $T_i$ and melted at $T_m$ is computed in systems with periodic boundary conditions. The choice of melting protocol is a subtle but important question. Although the pressure within the bulk of the film is initially zero, and the pressure in the bulk of the film after it is melted is also zero, the pressure during its melting is both non-zero and non-uniform.

To examine the pressure in the film during melting, we calculated the diagonal components of the pressure tensor,

$$P_\alpha(z) = \sum_{n=1}^{N} u_\alpha n u_\alpha n \delta(z - z_n) + \frac{1}{4} \sum_{n=1}^{N} \sum_{m \neq n=1}^{N} r^\alpha nm r^\alpha nm F_{nm} \delta(z - z_n) + \frac{1}{4} \sum_{n=1}^{N} \sum_{m \neq n=1}^{N} r^\alpha nm r^\alpha nm F_{nm} \delta(z - z_m).$$ (2)

where $u_\alpha n$ is the velocity of particle $n$ in direction $\alpha$, $r^\alpha nm$ is the $\alpha$ component of $r_n - r_m$ and $F_{nm}$ is the magnitude of the force on particle $n$ due to particle $m$. By symmetry, $P_x(z) = P_y(z)$, but $P_z(z)$ may differ. In equilibrium, in the center of the film, $P_z(z) = P_y(z) = P_z(z) = 0$. Because the surface is under tension, $P_z(z) = P_y(z) \neq P_z(z)$ at the surface of the film. We show the diagonal components of the pressure tensor $(P_x + P_y)/2$ (circles) and $P_z$ (squares) for $T_i = 0.065$ and $T_m = 0.1$ in Fig. 6 at three different melting stages: (i) when the film has just started melting (red); (ii) when the film is 50% melted (blue), and (iii) when the film is 90% melted (black). Note that $P_z = 0$ throughout the melting process but that $P_x$ and $P_y$ only vanish once that portion of the film has melted.

**FIG. 6:** The $z$ dependence of the diagonal components of the pressure tensor $P_x$ (squares) and $(P_x + P_y)/2$ (circles) for $T_i = 0.065$ and $T_m = 0.1$ is shown at three different melting stages: (i) when the film has just started melting (red); (ii) when the film is 50% melted (blue); (iii) when the film is 90% melted (black). The shaded green region for $z < 0$ denotes the substrate position.

It is impossible to run bulk equilibrium simulations under periodic boundary conditions and specify a similar pressure profile. To melt our bulk simulations we instead perform constant pressure simulations that correspond to the pressure within the bulk of the film at the start of melting. This choice provides an overestimate of the bulk melting time $\tau_m^{\text{bulk}}$ because the particles in the film have additional mobility perpendicular to the substrate. We correct for this systematic bias by comparing the melting time for films that only partially melt via a front and the melting time for our bulk simulations at finite pressure $\tau_m^p$. Because we know the front velocity $v$ in these films and we can estimate $\ell_c$ from how much of the film has melted via a front, we can estimate $\tau_m^{\text{bulk}} = \ell_c/v$. We find that $\tau_m^p$ is around 25% too large, so we correct the bulk melting time as $\tau_m^{\text{bulk}} = 0.75\tau_m^p$ in our calculation of the melting length scale.