

Freezing, melting and the onset of glassiness in binary mixtures

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We clarify the relationship between freezing, melting and the onset of glassy dynamics in a prototypical glass-forming mixture model. Our starting point is a precise operational definition of the onset of glassiness, as expressed by the emergence of inflections in the time-dependent correlation functions. By scanning the temperature-composition phase diagram of the mixture, we find a disconnect between the onset of glassiness and freezing. Surprisingly, however, the onset temperature closely tracks the melting line, along which the excess entropy is approximately constant. At fixed composition, all characteristic temperatures display nonetheless similar pressure dependencies, which are very well predicted by the isomorph theory. While our results rule out a general connection between thermodynamic metastability and glassiness, they call for a reassessment of the role of crystalline precursors in glass-forming liquids.

Two-step relaxation is one of the most prominent features of liquids approaching the glass transition [1]. It manifests itself as a plateau in time-dependent correlation functions and reflects the strong separation of timescales between fast microscopic motion and a spectrum of much slower relaxation processes. In a thermal cooling process, two-step relaxation first appears around a crossover temperature T_0 , which marks the onset of slow dynamics [2] or, as we shall write in the following, “onset of glassiness” [1]. Below T_0 , the system ceases to be a normal liquid and develops the typical features of glassy dynamics, including dynamic heterogeneity and super-Arrhenius dependence of relaxation times. Predicting and explaining the origin of these features in materials as diverse as supercooled liquids [3], spin glasses [4] or type-II superconductors [5] is a key challenge in the field of disordered systems.

One important and yet often eluded question is whether the onset of glassiness is related or not to thermodynamic metastability with respect to an ordered phase. From a theoretical standpoint, a connection between the onset of glassiness and frustrated crystallization has been invoked in a phenomenological model of the glass transition [6]. In a similar vein, the so-called frustration-limited domains theory [7] attributes the onset of glassiness to an avoided crystallization, which occurs however in a curved space where geometric frustration is lifted. On the other hand, in theoretical approaches based on mean-field spin glass models or infinite-dimensional systems [8] crystallization is ruled out from the outset, and the onset of glassiness results from activated transitions between amorphous metastable states [9, 10]. Most other theories of the glass transition [3] also neglect the role of crystallization.

From an empirical point of view, it is clear that thermodynamic metastability is not a necessary condition for glassy dynamics: liquid silica, for instance, displays glassy dynamics already at the melting temperature T_m [11]. A connection between crystallization and the onset of glassiness may

nonetheless hold within subsets of liquids [12]. Previous analysis of experimental data [13] indicated a rough correlation between the melting temperature T_m and a crossover temperature T_A , akin to T_0 , at which super-Arrhenius behavior sets in [14]. Recent simulation studies of a Lennard-Jones (LJ) binary mixture even suggested an identity, $T_m \approx T_0$ [15, 16]. In multi-component systems, however, the liquid phase can be metastable with respect to a pure crystal, to coexisting liquid and crystal phases or to phase-separated crystals, and freezing and melting transitions must be clearly distinguished. These aspects have not been addressed in any detail so far. There are also indications that thermodynamic properties related to the excess entropy [17] change sharply around T_0 [15]. Our goal is to clarify these connections in a prototypical glassy binary mixture with different chemical compositions, disentangling the role of freezing and melting, and to provide the basis for a systematic analysis on a broader range of liquids.

One technical hurdle is the determination of the onset temperature T_0 , for which there is no generally agreed, operational definition. In fact, while the concept of the onset of glassiness is well-established, its practical determination has never been standardized. The appearance of super-Arrhenius dependence of the structural relaxation time τ_α can be used as a proxy for T_0 , but such a procedure is often done “by eye” or assuming a functional form for $\tau_\alpha(T)$ [7, 14, 18]. The onset of glassiness is also associated to a decrease of the inherent structure energy with decreasing temperature [2, 9], but the crossover is broad and does not provide a clear-cut definition. Alternative but more complex procedures have been proposed [19, 20]. In the following, we provide a straightforward and precise definition of the onset of glassiness in terms of the inflection points of time-dependent correlation functions. Our procedure removes the above difficulties and is generally applicable to both simulation and experimental data, as it does not require knowledge of the interaction potential.

In this work, we study the composition dependence of the onset of glassiness in the Kob-Andersen (KA) mixture [21], which is an LJ mixture of two types of particles, A and B . The concentration of B particles is x , with $x = 0.2$ corresponding to

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the canonical KA mixture. We performed molecular dynamics simulations for a KA mixture composed of $N = 500$ particles using the atooms simulation framework [22], both along constant pressure and constant density paths. As a cross-check, we did additional simulations for a larger system size ($N = 8000$) using RUMD [23]. All quantities are expressed in standard LJ units. More details are given in the Supplementary Material (SM) [24].

We compute the self intermediate scattering function $F_s(k, t)$ for the A -particles (the results for the B -particles are qualitatively similar [24]). We focus on wavenumbers k around the first peak of the structure factor $S_{AA}(k)$. The calculation of the time derivative $F'_s(k, t)$ requires some care as it can be affected by statistical noise: to cope with this, we first compute $dF_s(k, t)/d\log t = tF'_s(k, t)$ by central differences, then fit it to a 4th order polynomial in $\log t$, restricting the time range such that F_s is between 0.05 and 0.98, and extract its critical points. Small changes to the fit range do not change our conclusions. The onset is defined by the emergence of two minima in $tF'_s(k, t)$. The height δ of the smallest barrier separating the two minima of tF'_s provides a precise, observable-dependent order parameter for the onset of glassiness: δ becomes finite below T_0 . Although T_0 depends in principle on the chosen observable, we found that its dependence on wavenumber, chemical species and correlation function is weak, see below. Therefore, as a crossover, the onset of glassiness remains well-defined.

Our procedure is illustrated in Fig. 1 for the canonical concentration $x = 0.2$ at pressure $P = 10.19$ and wavenumber $k = 7.2$. We start by equilibrating the system at high temperature, in the liquid phase, and decrease the temperature at fixed pressure until $\delta > 0$. Once T_0 has been bracketed, we perform additional simulations to refine its determination. Panel (a) displays $F_s(k, t)$ around T_0 . The definition of the onset can be grasped from panels (b) and (c): below T_0 , the time derivative $tF'_s(k, t)$ displays one local maximum, corresponding to the sought-for inflection of $F_s(k, t)$. The polynomial fit, indicated by solid lines, is fairly robust and works well even with noisy data [24]. Small oscillations in $tF'_s(k, t)$ at short times, unrelated to the onset of glassiness [24, 25], are visible with high-quality statistics, but they do not affect the calculation of δ . To locate T_0 precisely, we fit $\delta(T)$ to a linear function that vanishes at T_0 . A simpler bisection procedure, which avoids any fitting, provides consistent results [24]. Finally, we show in panel (d) the activation energy $E(T) = T \log(\tau_\alpha/\tau_\infty)$ [7] associated to the structural relaxation time $\tau_\alpha(T)$, at which $F_s(k, \tau_\alpha) = 1/e$. The microscopic time τ_∞ is obtained by fitting the high-temperature data to an Arrhenius equation. As expected, the onset of two-step relaxation is accompanied by the appearance of super-Arrhenius temperature dependence at T_A . We find that T_A is slightly higher than T_0 and is sensitive to the range of the Arrhenius fit, which holds anyway only approximately at high temperature [26].

We now turn to the relation between the onset of glassiness and crystallization. In Ref. 16, Pedersen *et al.* studied the phase diagram of the KA mixture and measured the freezing (or “liquidus”) line, below which the liquid crystallizes at least

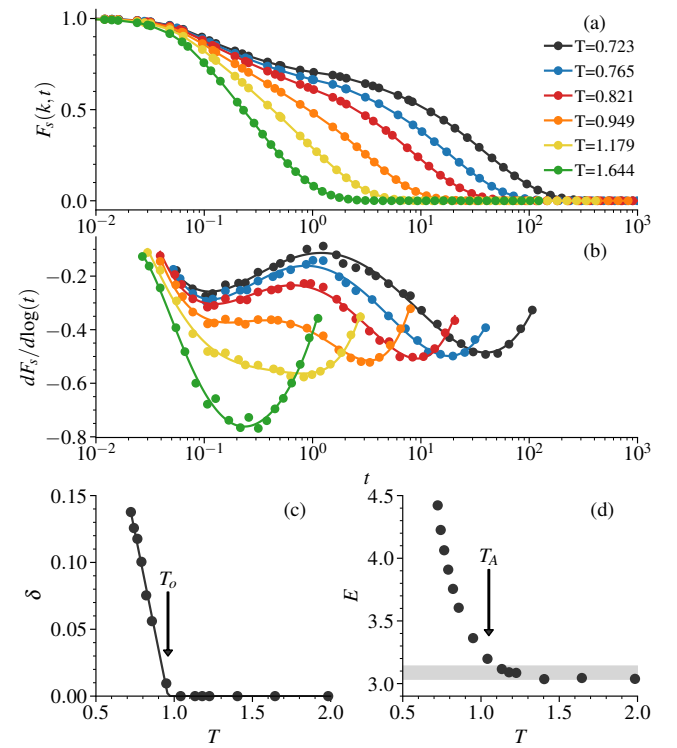


FIG. 1. Protocol to define the onset temperature, illustrated along the isobar $P = 10.19$ for $x = 0.2$: (a) $F_s(k, t)$ of A -particles ($k = 7.2$) for temperatures around T_0 ; (b) $tF'_s(k, t)$ for the same temperatures as in (a), the solid lines are 4th order polynomial fits; (c) order parameter $\delta(T)$ obtained from $tF'_s(k, t)$, the solid line is a linear fit vanishing at T_0 ; (d) activation energy $E(T)$. In (c) and (d), the arrows mark T_0 and T_A , respectively. In (d), the shaded area indicates the estimated range of validity of the high-temperature Arrhenius fit.

partially [27]. The stable crystalline phases for $x \rightarrow 0$ and $x \rightarrow 0.5$ are fcc and CsCl, respectively. At the fcc-CsCl eutectic composition $x = 0.25$, however, the stable crystalline phase has a PuBr_3 symmetry [16] and coexists with the liquid in a narrow range of compositions. As shown in the SM [24], this implies the presence of two very close eutectic points. We reproduce these results for $P = 10.19$ as thick solid lines in Fig. 2. From the location of the eutectic points and using the Gibbs phase rule [24, 28], we infer the melting (or “solidus”) lines of the underlying phase-separated crystals: above these lines, the ordered phases melt at least partially. The phase diagram at low temperature is instead unknown. We superpose on the phase diagram the onset temperatures obtained from the protocol described above. The shaded area indicates the range of onsets corresponding to the first peak of $S_{AA}(k)$, i.e., from $k = 5$ to 10 [24], while the filled points are for $k = 7.2$. It is clear that T_0 does not track the freezing temperature T_f : while the latter displays the typical V-shape of eutectic mixtures, T_0 does not show any systematic variation with x . Similar results are observed for the B -particles and when using correlation functions probing collective dynamics [24]. The corresponding onset temperatures lie within the

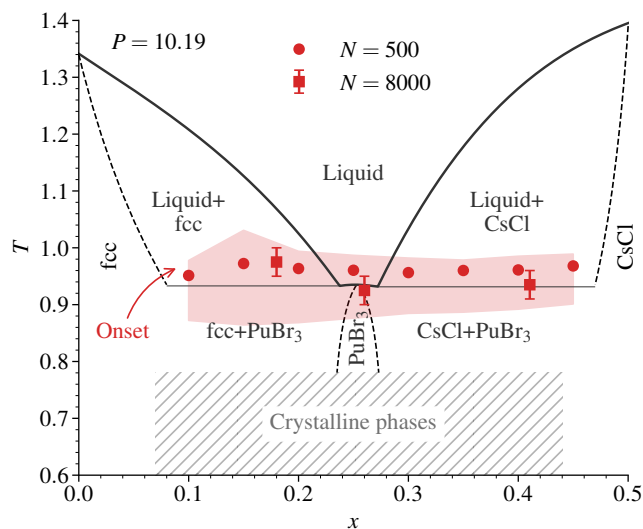


FIG. 2. Onset temperatures T_0 for $N = 500$ (circles) and $N = 8000$ (squares) as a function of x at $P = 10.19$. The shaded area indicates the range of T_0 obtained for values of k in the interval $[5, 10]$. The lines are the phase boundaries inferred from Ref. 16. The thick and thin solid lines indicate the freezing and melting lines, respectively. The dashed lines are sketches of the stability limits of the solid solutions.

shaded area indicated in Fig. 2.

The qualitatively different trends of T_f and T_0 demonstrate that the onset of glassiness and freezing are disconnected: the liquid can be thermodynamically metastable without displaying glassy dynamics. Surprisingly, however, the onset of glassiness closely follows the melting line, which runs horizontally in the phase diagram. At this stage, we emphasize that the correspondence of T_0 with the melting of the underlying stable crystals could be coincidental. Proving a causal connection would require a direct determination of the crystalline precursors in the metastable liquid – we will come back to this point in the closing paragraphs.

The results shown in Fig. 2 also allow us to dissipate a possible source of confusion. Analyzing data at $x = 0.2$, Pedersen *et al.* [16] found an “identity between onset and melting temperatures”, with the former defined as the appearance of super-Arrhenius behavior [18]. We note, however, that the word melting was used in Ref. 16 to indicate freezing. As we can see from Fig. 2, $T_m \approx T_f \approx T_0$ around the eutectic compositions, but deviations are found for other values of x . An approximate identity between T_0 and T_m holds in the KA mixture, but for a different reason from the one implied by Ref. 16. The absence of a direct connection between T_f and T_0 may be partly inferred from the trends of the iso-diffusivity lines shown in Ref. 16, which only show a weak, monotonic dependence on x . We obtained indeed similar results for the relaxation time itself [24]. However, transport coefficients *per se* do not provide direct information about the shape of time-dependent correlation functions.

Even though the freezing line does not track the onset of glassiness in the T - x diagram, T_f and T_0 scale similarly as a

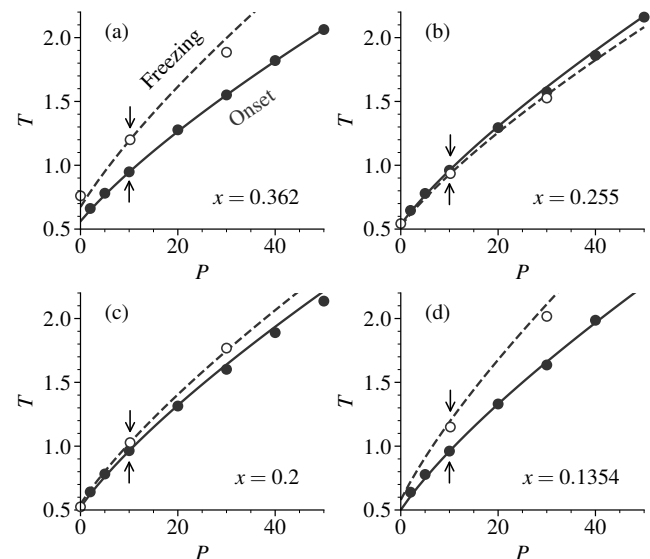


FIG. 3. Pressure dependence of the freezing temperature T_f (open circles) and of the onset temperature T_0 (filled circles) for (a) $x = 0.362$, (b) $x = 0.255$, (c) $x = 0.2$ and (d) $x = 0.1354$. The theoretical predictions of the isomorph theory for T_f and T_0 are shown as dashed and solid lines, respectively. The arrows mark the reference states used for the predictions.

function of pressure. This is shown in Fig. 3 for selected compositions. We used a constant wavenumber $k = 7.2$ for the calculation of the onset temperature, independent of composition and pressure. Interestingly, it is possible to accurately predict the pressure dependence of both quantities using the isomorph theory [29]. By assuming they both follow an isomorph, we predict $T_f(P)$ and $T_0(P)$ at any fixed x from the sole knowledge of thermodynamic properties at $T_f(P_0 = 10.19)$ and $T_0(P_0 = 10.0)$, respectively. See Refs. [16, 30, 31] and the SM for more details. The agreement is excellent for T_0 , while some discrepancies are seen for T_f at $x = 0.362$, see also Ref. 16. This is consistent with the observation that the freezing line is an isomorph only approximately [32].

Our results indicate that changes of the onset temperature are closely connected to those of the excess entropy S_{ex} , which is defined as the difference between the total entropy and its ideal gas contribution [17, 33] and is constant along an isomorph. Previous works have also connected T_0 to a change in the n -body contributions to the excess entropy per particle $s_{ex} = S_{ex}/N$. More precisely, the residual many-body entropy is defined as $\Delta s = s_{ex} - s_2$, where s_2 is the two-body approximation to s_{ex} [34]. It was found that Δs changes sign, in the KA mixture, at a temperature slightly lower than T_0 [33]. Note that $\Delta s = 0$ has also been proposed as an empirical criterion for freezing in one-component liquids [35, 36].

To perform a stringent test of these ideas, we compute s_{ex} and s_2 over a range of compositions. We carry out thermodynamic integration from a low-density, high-temperature state ($\rho = 10^{-4}$, $T = 5$), where we assume that the system behaves like an ideal gas [33]. To determine s_{ex} along the isobar

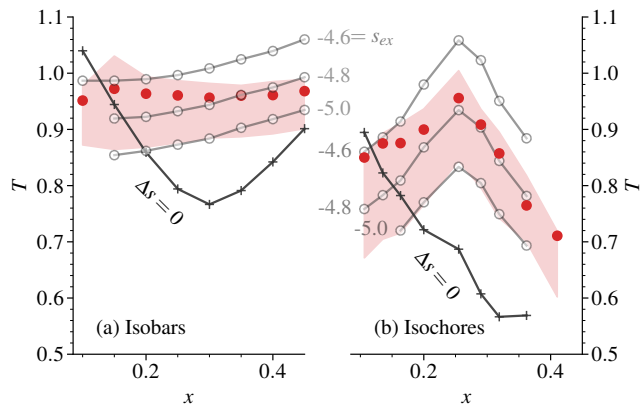


FIG. 4. Excess entropy measures in the T - x diagram along (a) isobars at $P = 10.19$ and (b) isochores at densities corresponding to freezing, $\rho(T = T_f, P = 10.19, x)$. The temperatures at which $s_{ex} = \text{const}$ and $\Delta s = 0$ are indicated as open empty circles and crosses, respectively. The onset temperatures are shown as in Fig. 2.

$P = 10.19$, we first follow an isotherm at $T = 5$ up to density $\rho(T = 5, P = 10.19)$ and then proceed with batches of small isothermal and isochoric paths, keeping the system along the selected isobar [24]. We also compute s_{ex} along isochores for each composition, fixing the density at $\rho(T = T_f, P = 10.19)$. Our results for s_{ex} agree within error bars with those of Bell *et al.* [17].

Excess entropy data are shown in Fig. 4. Interestingly, the lines of constant s_{ex} display the same qualitative behavior as the onset of glassiness: they vary weakly with x at constant pressure and are non-monotonic along isochoric paths, with a maximum around the eutectic compositions. We also found that the reduced structural relaxation times for different x collapse on a master curve when shown as a function of the excess entropy [24], in line with the concept of quasi-universality put forth by Bell *et al.* [17]. The value of s_{ex} at T_o lies between -4.7 and -4.9 . Combining these observations with those inferred from Fig. 2, we conclude that melting occurs in this same range of excess entropies and could be a quasi-universal property in the sense of Ref. 17.

From Fig. 4 we also see that the locus of points where $\Delta s = 0$ has a non-monotonic behavior, with a minimum around the eutectic compositions. This trend is thus qualitatively similar to the one of the freezing line, cf. Fig. 2, but Δs vanishes at a temperature lower than T_f by 10–50% depending on composition. It is also clear that $\Delta s = 0$ does not provide a sound criterion for the onset of glassiness, which occurs instead around the same temperature irrespective of x . Similar discrepancies are observed on paths at constant density, see panel (b): the non-monotonic behavior of T_o is well reproduced by the lines of constant s_{ex} , while those at which $\Delta s = 0$ display a qualitatively different trend. Therefore, the splitting of s_{ex} into two-body and many-body contributions does not bear any clear connection with the onset of glassiness in the KA mixture.

One conclusion to be drawn from our work is the lack of a

general connection between thermodynamic metastability and the onset of glassiness. Not only a liquid can be highly viscous without being metastable, as is the case for silica: the large gap between T_f and T_o seen in Fig. 2 shows that a liquid can be metastable without displaying yet any glassy feature. Key to this observation is the distinction between freezing and melting, which was not duly taken into account in previous computational studies of the KA mixture. The second main result is that the onset of glassiness occurs close to the solidus line, which marks the melting of the underlying crystalline phases. The generality of this connection can now be tested straightforwardly for computational models whose phase diagram is known [37–39]. We did preliminary calculations for the Wahnström LJ mixture, whose phase diagram has been determined recently [40], and we found very similar results to those presented therein: T_o and T_m are very close to each other. Our method to determine T_o can in principle be adapted to the analysis of dynamic susceptibilities relevant to experiments [41], where precise measurements of the onset temperature are rare, see Ref. 42 for an exception.

The apparent correspondence between T_m and T_o motivates a critical reassessment of the role of locally favored structures in glass-forming liquids [43–45]. It has been argued that the competition between crystalline precursors, corresponding to different crystalline phases, can contribute to stabilize the metastable liquid [38]. In this respect, it would be interesting to identify precursors of the PuBr₃ phase in the KA mixture, as this is the stable phase close to the eutectic compositions. This crystalline phase contains bicapped trigonal prisms, akin to some of the locally favored structures of the model at the canonical composition [46], and has been so far overlooked in crystallization studies of the KA model [47–49]. We emphasize that the connection between melting and the onset of glassiness could be specific to liquids that “borrow” their local structure from the underlying stable crystal [50]. Structural analyses across the melting line will provide a crucial test of the role of crystalline precursors.

Predicting when liquids first start to show glassy behavior is a well-defined open problem, and currently a challenge for the theories of the glass transition that rely on structure or thermodynamics. Our work lays down the basis to address this problem quantitatively and short-lists some of the proposed solutions, starting from entropy-based approaches. Among the outstanding approaches, we expect mode-coupling theory [51, 52] and its extensions [53, 54] to provide at least qualitatively correct predictions. Another promising approach to predict the onset of glassiness from first principles builds on the relationship between the caging dynamics and the local curvature of the potential energy surface, see Refs. 55 and 56 for recent work in this direction.

SUPPLEMENTARY MATERIAL

The supplementary material includes additional details on methods and analysis, as well as tabulated results.

AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author contributions

Daniele Coslovich: Writing - review & editing (equal).
Leonardo Galliano: Writing - review & editing (equal).
Lorenzo Costigliola: Writing - review & editing (equal).

DATA AVAILABILITY

The data and workflow necessary to reproduce the findings of this study will be available after publication of the paper in the Zenodo data repository [57].

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