Understanding the mechanisms by which crystal nuclei form is crucial for many phenomena such as gaining control over crystallisation in glassforming materials or accurately modelling rheological behaviour of magma flows. The microscopic nature of such nuclei, however, makes their understanding extremely hard in experiments, while computer simulations have hitherto been hampered by short timescales and small system sizes. Here we use highly-efficient GPU simulation techniques to address these challenges. The larger systems we access reveal a general nucleation mechanism in mixtures. In particular, we find that the supercooled liquid of a prized atomistic model glassformer (Kob-Andersen model) is inherently unstable to crystallisation, i.e. that nucleation is unavoidable on the structural relaxation timescale, for system sizes of 10,000 particles and larger. This is due to compositional fluctuations leading to regions comprised of one species that are larger than the critical nucleus of that species, which rapidly crystallise. We argue that this mechanism provides a minimum rate of nucleation in mixtures in general, and show that the same mechanism pertains to the metallic glassformer copper-zirconium (CuZr).

I. INTRODUCTION

Crystallisation in supercooled liquids has profound implications in fields as diverse as the development of amorphous materials [1], magma flows in volcanoes [2] and aqueous solutions of ions [3]. Materials in question include metallic, inorganic and chalcogenide glassformers, where mixtures of a number of different constituents have the effect of suppressing or controlling crystallisation [4]. Alas, this tendency to crystallise places stringent limits on the size of the pieces of amorphous material that can be formed: large pieces are more likely to undergo crystal nucleation [5, 6]. This “Achilles heel” of glass formation thus limits the exploitation of metallic glasses for example, whose superior mechanical properties otherwise hold great promise [7].

It is clear that any liquid cooled below its freezing point must, for a sufficiently large system, nucleate [8, 9]. However, the practical limits of cooling rate versus system size required for vitrification are not known in general. In addition to these practical considerations, crystallisation is one solution to the Kauzmann paradox of vanishing configurational entropy upon which a number of theories of the glass transition rest [4, 10]: crystallisation avoids the need to invoke any particular theoretical description of divergent viscosity in amorphous materials [11, 12].

It is known empirically that increasing the number of constituent species and introducing a size disparity among these components, together with a negative heat of mixing, tends to suppress nucleation – this has been the guiding principle in the development of bulk metallic glasses [5]. However despite recent innovative approaches using model systems [13, 14] and novel sampling techniques [15, 16], there is still a lack of fundamental understanding of the mechanisms by which glass-forming mixtures crystallise.

Here we consider a crystallization mechanism that is always present when a glass-former is produced by mixing constituents which by themselves are poor glass-formers, as is often the case. We therefore expect this mechanism to be remarkably widespread. In particular, compositional fluctuations in the supercooled liquid lead to regions containing just a single constituent, and eventually such a region will occur that is large enough – and long-lived enough – that it will nucleate a crystal of that one species. Of course, depending on the specific mixture, there may be other, faster, nucleation mechanisms. Nucleation by compositional fluctuations nevertheless provides a lower bound for the nucleation rate in mixtures. We emphasize that compositional fluctuations occur even in the absence of any underlying demixing behaviour driven by a thermodynamic transition. In fact, the first mixture we investigate below is specifically designed not to demix, using a non-additive attractive cross interaction between the two species. Thus the compositional fluctuations we consider are distinct from enhanced crystal nucleation rates due for example to density fluctuations related to a nearby critical point [17, 18]. Clearly, our analysis falls within the concept of the Ostwald rule of stages, suitably generalised to mixtures [19]. In this context, we emphasise that the crystals formed through such compositional fluctuations will in general not be thermodynamically stable.

Having argued for compositional fluctuations as a relevant mechanism for crystal nucleation, we turn our attention to situations in which this mechanism may dominate. We begin with the Kob-Andersen (KA) binary Lennard-Jones mixture. Since its inception in 1994, this model,
we cannot infer any crystal growth within the fluctuations. 

locally favoured structure (LFS) and dark blue and light pink particles are liquid. 

FCC for A and B particles respectively; light blue and orange are HCP; purple and dark pink are bicapped antiprism liquid locally favoured structure (LFS) and dark blue and light pink particles are liquid. 

Population of local structures as a function of time reveals rapid crystallisation of FCC and HCP for $N = 10,000$. BCC is found in very small quantities and the bicapped square antiprism liquid LFS (which is incompatible with FCC and HCP) is also shown. Inset shows that at short times ($\lesssim 5\tau_α$), we cannot infer any crystal growth within the fluctuations. 

Even more rapid crystallisation occurs when $N = 100,000$, here irreversible growth in the FCC population is found within one relaxation time. Inset: Liquid LFS and HCP populations are compared with FCC population as shown in the main figure.

based on the metallic glassformer Nickel-Phosphorous, has been a mainstay of model systems with which to tackle the glass transition [20]. Prized for its simplicity, speed of computation and its stability against crystallisation, the KA model is among the most widely used atomistic glassformers in computer simulations. It is only recently, with the advance of high performance GPU computing, that the KA model has been crystallized by direct simulation [14], where an estimate was made of the nucleation rate at a single temperature and system size. Here instead we carry out large-scale simulations and focus on the mechanism for crystallisation.

Our results reveal that nucleation in the KA model is induced by composition fluctuations as discussed above. The KA model is thus representative of systems crystallizing via this mechanism, and we expect our results to have profound consequences for the glassforming ability of mixtures, such as metallic glasses [7] and oxides [21]. We illustrate the generality of our results by presenting results for the model metallic glassformer $\text{Cu}_x\text{Zr}_{1-x}$ using a range of compositions from $x = 0.15$ to 64.5.

\section{Freezing in the Kob-Andersen Model Glassformer}

We begin the presentation of our results by studying crystallisation in the KA mixture using a global structural analysis for $\rho = 1.204$ and $T = 0.40$ in Figs. 1b and c. We use the NVT ensemble with an Nose-Hoover thermostat [22]. Figures 1b and c show, respectively, the time evolution of the population of liquid local structures (bicapped square antiprisms) and crystalline structures for system sizes of $N = 10,000$ and $N = 100,000$.

Here and henceforth we scale time by the structural relaxation time $\tau_α$. For $T = 0.40$, we have that the structural relaxation time $\tau_α = 2.91 \times 10^3$ simulation time units. A snapshot of a crystal nucleus, comprised predominantly of the majority A species, is shown in Fig. 1a. We identify particles in liquid local structures and FCC, HCP crystalline with the topological cluster classification (TCC) algorithm [23] and BCC crystalline regions with bond-orientational order (BOO) parameters [24, 25]. Our choice of order parameter is motivated by the ability of the TCC to identify the liquid local structure (and HCP and FCC), and we have in any case confirmed that our results for identification of the crystal structures are very similar between the two methods (see Methods for simulation details and order parameters).

We see from Fig. 1b that the liquid begins to freeze on a timescale of a few structural relaxation times $\tau_α$. Thus, for these parameters of $T = 0.40$ and $N = 10,000$, it is hard to regard the KA mixture as anything but a remarkably poor glassformer. We further see that the locally favoured structure (LFS) in the liquid, the bicapped square antiprism (pictured in Fig. 1b), transforms into the crystal in much the same way as in one-component hard spheres where the liquid LFS competes with the crystal symmetry [26].

Here of course we have a binary system, but the predominant crystal structures we find are FCC and hexagonal close-packed (HCP) of the large A species only, and very little mixed AB BCC. The lack of BCC is consistent with predictions that the crystal nucleation barrier is much higher relative to FCC [27] and with the equilibrium KA phase diagram [28]. For the KA model, we therefore neglect the BCC structure and focus on the HCP and FCC crystals in the following.
In Fig. 1b, we see that there seems to be very little incubation time. However, close inspection (Fig. 1b inset) reveals that for timescales of a few $\tau_\alpha$, the fluctuations in crystal population are larger than the increase, so the liquid may in fact be regarded as metastable on short timescales. In Fig. 1c, we show that upon a further increase of system size, to $N = 100,000$, this short time metastability vanishes, and the crystal nuclei grow immediately.

We now consider the formation of critical crystal nuclei and estimate their size. In Figs. 2a and b, we show the number of particles $N_{\text{stat}}$ in the largest connected region of crystal particles (HCP or FCC) for different system sizes. Here we select a run with a relatively long incubation period (Fig. 2a). We see that the crystal regions are smaller than 100 particles for around 40 $\tau_\alpha$ before growing. These data enable us to infer a critical nucleus size of approximately 50–100 particles for $T = 0.40$. Figure 2b shows the run at $N = 100,000$ where crystal growth is immediate and thus it is difficult to infer a critical nucleus size in this case.

Next, we consider the statistics of nucleation in the KA glassformer. From the ten runs we performed for $N = 10,000$ and $T = 0.40$ (all of which crystallised), we determine the mean nucleation time from $\tau_X = \sum_{n=1}^{\infty} t_{X(i)} / n$, where $n$ is the total number of simulations, to be $\tau_X = 38.4 \pm 26.8 \alpha_\tau$ (the error is the standard deviation). Here $t_{X(i)}$ is the time when the size of the largest crystal region reaches, and does not subsequently drop below, 100 particles. At higher temperatures, the driving force for crystallisation is of course reduced, but the dynamics is much faster. We find that the system does crystallise at higher temperatures (we probed up to $T = 0.45$) but that not all the runs do so. In this case, we determine the mean nucleation time for each state point following the method of Ref. [29]. In particular, we presume that nucleation is exponentially distributed in time, such that the probability of a nucleation event happening at time $t$ is $p(t) = 1/\tau_X \exp(-t/\tau_X)$. The probability that a given run of length $\tau_{\text{run}}$ crystallises is then $\int_0^{\tau_{\text{run}}} p(t) dt = 1 - \exp(-\tau_{\text{run}}/\tau_X)$. The fraction of runs which crystallised then gives us $\tau_X$. Errors are estimated by considering the case that one more, or one fewer, simulation runs underwent crystallisation. While more sophisticated analyses have been developed, which enable accurate determination of the critical nucleus size [30], even with the considerable computational resources we have used, it has only been possible to carry out ten runs per state point. This limits the extent to which we can implement such methods.

We see from Fig. 3a that, when scaled by the relaxation time, the time to nucleate drops rapidly with temperature at $N = 10,000$ and that well before the dynamical divergence temperature predicted from a Vogel-Fulcher-Tammann fit to the temperature dependence of the relaxation time ($T_0 \approx 0.30$, see Supplementary Material), the nucleation time $\tau_X$ is expected to fall below $\tau_\alpha$ at $T \approx 0.38$. Moreover in the range $T \lesssim 0.43$, we find an exponential scaling with temperature, $\tau_X/\tau_\alpha \sim e^{AT}$ with $A \approx 97$. Of course this observation rests on only the four data points which we fit, but given the significant magnitude of the fall in $\tau_X/\tau_\alpha$ with temperature, we are confident that, were this trend to continue, the observation that for some $T > T_0$, $\tau_X < \tau_\alpha$ would hold.

When we simply plot the nucleation time in simulation time units (Fig. 3a inset), we make two observations. Firstly, the absolute nucleation time does not change hugely (around one order of magnitude) throughout the temperature range in question, while the relaxation time changes by three orders of magnitude. Secondly, there is an upturn at the lowest temperature that we consider, $T = 0.395$. The reason for the minimum in $\tau_X(T)$ presented in the inset of Fig. 3a is then competition between the decrease in the average nucleation time (for a given system size) and the increase in relaxation time upon cooling though we emphasise that this is only one data point and more statistics would be helpful to confirm this observation. In any case, this is dwarfed by the increase in relaxation time, so the scaled quantity $\tau_X/\tau_\alpha$ continues to drop. Turning to the system size dependence of nucleation in Fig. 3b we find, as expected, a system size scaling consistent with $\tau_X \sim 1/N$. Note that in Fig. 3b, we consider a single temperature, $T = 0.40$, so that $\tau_\alpha$ does not enter into the scaling.

### III. Composition Fluctuations

Next, we proceed to investigate the role of compositional fluctuations in crystallization. To quantify these, we use the order parameter illustrated in Fig. 4b. We seek to find the largest region of liquid A particles which is devoid of any B particles. We presume that such a large compositional fluctuation would be most likely to drive crystallisation.

Therefore, we use the following procedure for a given snapshot.

1. We find the A particle which is furthest from the nearest B particle.
2. We define a sphere, centred on the A particle, whose radius is its distance to the nearest B particle.
3. The number of particles in the sphere, $n_s$, is taken as the current largest compositional fluctuation.
4. We iterate to smaller AB separations and hence smaller spheres, avoiding particles already contained in a previous sphere, and updating $n_s$ if a larger region is encountered.

Since there will be small noncritical fluctuations of crystal particles in the liquid, and we are looking for the largest region of liquid A particles, we seek to avoid the effects of such A particles in crystalline environments. Therefore, we accept a maximum of 10% of the particles...
a Run with incubation period of around 40\(\tau_\alpha\) prior to growth of crystalline region \((N = 10,000)\). b Immediate crystal growth at \(N = 100,000\).

FIG. 2: Time-evolution of the largest crystalline region. All data are for temperature \(T = 0.40\) and shading is to guide the eye.

In the sphere to be in a crystalline environment. The time evolution of the largest compositional fluctuation in each snapshot, \(n_s\), is shown in Fig. 4c. We only sample where the system has yet to crystallise, under our criterion of a nucleus size of less than 100 particles. Simply because the system has not yet crystallised does not mean that its properties are stationary, as shown in Figs. 1 and 2. However, it is still instructive to apply the same metric for the larger systems as for the smaller systems (whose properties are stationary for timescales beyond the structural relaxation time), and this we do, with the caveat that the distributions are sampled from a non-stationary system.

In Fig. 4a, we see that for the KA system at \(T = 0.40\) and \(N = 5000, 10,000\) and 100,000, the distribution of largest compositional fluctuations \(n_s\) of liquid A particles has a significant dependence on the system size \(N\). Two effects are apparent. Firstly, the typical size of compositional fluctuations increases with \(N\). Second, the distribution has a “fat tail” indicating more fluctuations of larger \(n_s\) than a symmetric distribution such as a Gaussian would predict. We note 50–100 particles was a rough estimate of the critical nucleus size and that fluctuations comparable to this are seen in the tails of the distributions.

IV. STATISTICS OF COMPOSITIONAL FLUCTUATIONS

What can we say about the origin of the distribution of the largest compositional fluctuations in Fig. 4a? Let us suppose that the distribution of all fluctuations of A particles is exponential \(P(n_A) \propto \exp(-n_A\lambda)\) where \(n_A\) is the number of A particles around a given A particle that are closer than the nearest B particle calculated for every A particle. Here \(\lambda\) is the decay constant. The extreme values of such a distribution, i.e., those fluctuations large enough to initiate nucleation, should then follow a Gumbel distribution given by \(P[z(n_s)] \propto e^{-(z+e^{-z})}\) in which...
FIG. 4: Compositional fluctuations of majority A-particles. a Distributions of largest compositional fluctuations of A-particles $n_a$ for several system sizes $N$ at $T = 0.40$. Each system size is fitted with a Gumbel distribution (see text). b Schematic indicating the order parameter $n_s$ for compositional fluctuations. Central pink particle is the A particle under consideration and dark pink particle the nearest B particle. Blue particles are A particles lying within the sphere as shown. The compositional fluctuation shown has 15 A particles. c Time-evolution of largest compositional fluctuations $n_s$ in the liquid. d Scaling of the median $\langle n_s \rangle$ calculated from fitted Gumbel distributions with system size; lines are fits (see text). Shown is data for the KA mixture at various compositions along with Cu$_{64.5}$Zr$_{35.5}$ metallic glassformers (see Methods section for details). Circles are constant pressure data ($P = 0$) and squares are constant density data ($\rho = 1.204$). For the KA mixtures, constant pressure data is taken in the NVT ensemble fixing the mean pressure at $(P) = 0$ and $T = 0.80$ and constant density data is taken at $T = 0.40$. Cu$_{64.5}$Zr$_{35.5}$ is simulated in the NPT ensemble at $T = 1270 K$ and $P = 1500 K$ and $P = 0$. e Distribution for all compositional fluctuations for several system sizes (4:1 KA mixture) at $T = 0.40$. The distribution is independent of system size above $n_A > 25$. Dashed line denotes exponential decay with decay constant $\lambda = 0.22$ (see text).

This is wildly in excess of the nucleation time in the one-component system at these temperatures which is $\tau_N \approx 41$ for a system size of $N = 13,500$ [32]. Thus, since the lifetime of the compositional fluctuations must be on the order of $\tau_n$ at least and we do not see any signs of phase separation, i.e. other mechanisms of crystallisation (see Fig. 4c and composition-composition correlation functions in the SM), we conclude that the compositional fluctuations we identify lead to crystallisation.

Before we explore the compositional fluctuations for other systems, we provide some considerations as to the crystallisation mechanism. One alternative possibility is enhancement of nucleation related to density fluctuations. Now the liquid-gas binodal has been measured as lying at a temperature not much less than $T \approx 0.40$ to which we simulate [33]. It is conceivable that some density fluctuations related to the proximity of liquid-gas phase separation might act to enhance nucleation, as is known for protein-like systems [17, 18]. However the system is not in or near the two-phase region: the density of $\rho = 1.204$ we consider is much higher than the critical isochore (around 0.3). In the SM we investigate but see little evidence for density fluctuations [33]. In any case, any such nucleation enhancement would still need to invoke a mechanism for A-B demixing, which is absent. Indeed to observe demixing in similar binary systems, one needs to weaken the interaction between the species so that it is again non-additive but weaker than the additive case, i.e. a positive enthalpy of mixing [34]. In fact, we see very little evidence for A–B demixing (see SM). In short, we provide evidence that the compositional fluctuations we identify here are unrelated to the density fluctuations known to enhance nucleation in (ef-
We also consider the consequences of our choice of an instantaneous quench protocol (see Methods). In Supplementary Fig. S3, we see that the median of the largest region of liquid A particles, \(\langle n_a(T) \rangle\), shows very little dependence upon temperature. Thus, as the system samples from a nearly temperature independent distribution and due to the long mean nucleation time for \(T > 0.40\) (more than 100\(\tau_a\)), we argue that our quenching protocol does not affect our conclusions to any significant extent. The independence with respect to temperature is intriguing: we interpret this in the context that the structure of the liquid is dominated by the hard core [35], in which case a weak temperature dependence is expected.

## V. DEPENDENCE OF FLUCTUATIONS ON SYSTEM COMPOSITION

We now consider other compositions of the KA mixture. The temperature independence of the compositional fluctuations suggests that the scaling leading to large compositional fluctuations may be identified at high temperature where timescales are amenable to computer simulation, without recourse to simulations of the deeply supercooled liquid. This suggests that it may be possible to use our approach to predict the glassforming ability of mixtures in the liquid state.

Usually, as above, the 4:1 KA mixture is simulated, but upon changing the composition to be more equimolar, we expect smaller regions of pure A particles. We focus on the 2:1 KA mixture at zero pressure and at the higher temperature of \(T = 0.80\), where the relaxation times for 4:1 and 2:1 KA are comparable [36]. We also considered the 3:1 composition, which turns out to lie close to the 2:1 system. In Fig. 4d we see that at zero pressure and \(T = 0.80\), the 4:1 mixture has a value of \(\langle n_s \rangle\) very similar to that at which we see crystallisation (\(T = 0.40\)). We infer that the change in pressure also has little effect on the compositional fluctuations, which is reasonable as they are largely random, according to the exponential distribution (Fig. 4e).

As expected, the 2:1 KA mixture in Fig. 4d has very much smaller values of \(\langle n_s \rangle\), as its composition is closer to equimolar. To predict where crystallisation might occur we fit each composition to a logarithmic increase as indicated by the dashed lines in Fig. 4d. From this we find that the 2:1 KA system reaches the value of \(\langle n_s(N) \rangle = 31\) (corresponding to the 4:1 system with \(N \approx 10,000\)) at a system size of \(N = 1.2 \times 10^3\). Thus we expect that, for the mechanism of crystallisation we consider here, the 2:1 composition should be a very much better glassformer than the usual 4:1 system. We confirm this by very lengthy simulations of the 2:1 (and 3:1) KA systems at comparable supercoolings (i.e. \(T = 0.40\) for KA 4:1) and \(N = 10,000, 100,000\) and \(1,000,000\) where no crystallisation was observed. We simulated around 9 billion time steps for \(N = 10,000\) and 100,000 and 2 billion time steps for \(N = 1,000,000\).

Note that we are only considering the crystallisation mechanism based on compositional fluctuations. While we expect the mechanism to be present in all mixtures, crystallisation may be dominated by other, faster, mechanisms. For example the 1:1 KA mixture forms a mixed BCC crystal quite rapidly [37].

## VI. CRYSTALLISATION IN COPPER-ZIRCONIUM

To address whether the mechanism described above pertains to other systems, we consider the metallic glassformer copper-zirconium. Here we use Embedded Atom Model (EAM) simulations (see Methods for more details). In Fig. 5a, we show that, like the KA mixture, the extreme values of the composition fluctuations in CuZr also follow a Gumbel distribution. To determine the magnitude of the composition fluctuations in the liquid, we use the higher temperatures of \(T = 1500\text{K}\) or \(T = 1270\text{K}\) respectively, so that we can run the simulations quickly. Here we use the NPT ensemble with a Nose-Hoover thermostat [22], see Methods for further details.

The system size dependence of \(\langle n_s(N) \rangle\), where we consider fluctuations of the majority species is shown in Fig. 4d. Again we see the logarithmic scaling, moreover compositions such as Cu64.5Zr35.5 exhibit weaker fluctuations compared to the KA model. Following our analysis of the 2:1 KA mixture, here we estimate that the system may be susceptible to crystallisation at a system size of \(N = 3.5 \times 10^{16}\) (when \(n_s \approx 31\)). However, upon changing to the more asymmetric compositions Cu25Zr75 and Cu15Zr85, we see a marked increase in the fluctuations.

Given these larger fluctuations, the logarithmic scaling in Fig. 4d would indicate that the metallic glassformer should crystallise for those more asymmetric compositions on simulation timescales already around \(N \approx 10,000\), assuming similar behavior to KA. To investigate crystallisation, we run simulations at lower temperatures for two compositions, Cu25Zr75 and Cu15Zr85. Here the system was first equilibrated at \(T = 2000\text{K}\) or \(1500\text{K}\) depending on the composition and then rapidly cooled to the temperature of interest. For Cu25Zr75 and Cu15Zr85, and the temperatures at which we see crystallisation \(T = 900\text{K}\) and \(1100\text{K}\), the cooling rates are \(\Delta T/\Delta t = 3.0 \times 10^5\) and \(2.0 \times 10^5\) K/ps, respectively.

We find that CuZr indeed crystallises with representative runs freezing after 930\(\tau_a\) and 95\(\tau_a\) for Cu25Zr75 and Cu15Zr85 respectively. Here we consider the BCC crystal, as the FCC and HCP are found only in trace quantities. In the snapshot in Fig. 5b, we find that the nucleus for Cu25Zr75 is dominated by the majority species Zr, in a manner similar to that in Fig. 1a, although the growth is...
FIG. 5: Crystal nucleation in CuZr. a Compositional fluctuations of majority Zr atoms in Cu$_{25}$Zr$_{75}$ at $T = 1500\text{K}$. Lines are fits to a Gumbel distribution. b Nucleus in the early stage for Cu$_{25}$Zr$_{75}$ at $T = 900\text{K}$. Large grey particles are Zr (BCC), large pink are Cu (BCC), smaller grey and pink are liquid Zr and Cu respectively. Black are Zr in a local FCC environment as determined with bond-orientational order parameter [24]. We see that the nucleus is dominated by Zr.

more rapid in the case of this binary metallic glassformer (See SM). Note that this higher rate of growth contrasts with slow growth previously observed in CuZr with respect to other metallic glassformers, for a binary crystal [38].

We thus infer that the mechanism for nucleation, at least for these compositions is the same as that for crystallisation in KA. Again, like KA, other mechanisms are also possible in which the crystal may be mixed [39, 40]. However we argue that we have presented a general crystallisation mechanism in mixtures, which occurs in the absence of faster, specific, crystallisation pathways.

VII. OUTLOOK

Before concluding, we consider the consequences for the long-term stability of supercooled mixtures. We have shown that crystal nuclei are expected in mixtures in general. But by how much should they grow? By considering the KA mixture, the growth of FCC nuclei of A particles will deplete the remaining liquid of A particles. This depletion will tend to slow and may even arrest the growth of the one-component A crystals. In the case of the KA system, we note that if the liquid approaches a 1:1 composition then crystallisation, not of the one-component FCC, but of the 1:1 composition BCC crystal may be expected. We noted in the introduction that the Ostwald rule of stages, generalised to mixtures, would provide pathways by which the nuclei may grow [19].

Given the small dimensions of the nuclei we find, and despite the developments we present here, our simulations are still small compared to experimental system sizes, and thus it seems reasonable to suppose that the final material may be comprised of nano-crystals. Nanocrystals are known to have important consequences for the mechanical properties of glassforming materials [41]. While this behaviour has been seen in experiments [42], our work suggests that such nanocrystals may be rather prevalent in metallic glasses. Because identifying tiny crystalline regions is hard with x-ray scattering, requiring techniques such as fluctuation TEM or 3D atom probe tomography [42], it is possible that such nanocrystals may go undetected. The detection of such nanocrystals, for example with techniques such as nanobeam electron diffraction [43], or fluctuation electron microscopy [44] is an exciting avenue for future research.
VIII. DISCUSSION AND CONCLUSIONS

We have demonstrated a general mechanism of crystallisation in multicomponent systems. Our large scale simulations of the widely used Kob-Anderson model supercooled liquid reveal that it has a fatal flaw as a glassformer which is general to mixtures. Local compositional fluctuations lead to regions populated only by one species. These regions can be larger than the critical crystal nucleus size of the one-component system under similar conditions. Nucleation in these regions is fast on the timescale of this deeply supercooled liquid, apparently requiring little re-arrangement of the particles, as is known to be the case for hard spheres at deep supercooling [45, 46]. Our findings are important as the results we reveal here pose a fundamental challenge for the development of glassforming materials: mixtures whose components crystallise easily are themselves inherently unstable to crystallisation and thus ultimately compromised as glassformers. Our findings rationalise the empirical rule of thumb that increasing the number of components tends to increase glassforming ability, as the chances that a critical nucleus of one particular species are formed are reduced in that case.

We find a scaling with system size which, once parameterised, may be used to predict the largest system which is stable against crystallisation, and therefore the largest pieces of amorphous material which can be prepared from a given mixture. That the compositional fluctuations are rather random and insensitive to temperature, suggests that simulations in the liquid at higher temperature where the dynamics are much faster may be used to predict the system size at which crystallisation may be expected. We have demonstrated this principle using the 2:1 (and 3:1) KA mixtures and have predicted that both can reach system sizes, for comparable simulation times and supercoolings, very much larger than the usual 4:1 mixture before crystallisation occurs. These compositions may thus be used when a better glassformer is needed in simulations than the standard 4:1 model.

The binary model we use demonstrates the use of a mixture to suppress crystallisation, as is typically employed in metallic and inorganic glassformers and is encountered in vitreous magmas. Although prevalent and accessible to computer simulation for the model systems we consider, we expect the same mechanism will operate for more general binary mixtures, and indeed for multicomponent systems frequently employed in the quest for ever-better glassforming alloys [7]. We demonstrate this by considering the well-studied CuZr metallic glassformer, which exhibits the same behaviour. Experimental evidence in support of the mechanism we find has been seen in some metallic glasses [42] and we suggest that the presence of such nanocrystals as we identify here would be worth investigating further in metallic glasses.

Crystallisation via compositional fluctuations thus forms a lower bound to nucleation: other mechanisms involving more complex crystal structures may prove faster, as indeed seems to be the case for some models [39, 47] and for certain compositions of the Kob-Anderson [37] and CuZr [39] models considered here. Nevertheless we have shown that liquids which rely on mixing for their stability against crystallisation are fundamentally compromised and provide a principle by which their glassforming ability may be optimised.

In addition to the number of components, crystallisation may be suppressed in alloys by the use of systems with a negative heat of mixing. Here, the Kob-Anderson mixture is engineered in that way, precisely to inhibit crystallisation. However, our analysis in section IV suggests that such negative heat of mixing has little impact: the Gumbel distribution assumes that the two species are randomly distributed in space, so given its success in describing the statistics we infer that our analysis is robust to the case where there is a negative heat of mixing. Noting that small size disparities will permit rapid crystallisation, and that for certain size ratios, binary crystals form an addition route to crystallisation as noted in section VII [13, 40], we expect that increasing the size ratio will inhibit crystallisation. We leave the prospect of a detailed analysis of the role of size disparity for the future.

In addition to the metallic glasses we consider here, an intriguing case is aqueous solutions. Here crystallisation of water occurs through segregation to ion-rich and ion-poor regions, the latter being where the ice nucleates, which appears similar to that we observe here, for the A particles [3]. However, the various anomalies in the thermodynamic behaviour of water, not least increasing fluctuations, which may be related to an (avoided) liquid-liquid transition [48, 49], mean that further study of that system would be needed to ascertain whether the mechanism we have identified here dominates water crystallisation in some aqueous solutions.

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Roskilde University.

Methods

Simulation and model details. — We simulate the KA binary mixture in the NVT ensemble (Nose-Hoover thermostat [22]) at $p = 1.204$ using the Roskilde University Molecular Dynamics (RUMD) package [50] optimized for highly-efficient GPU simulations; the longest simulations took more than 100 days. The interatomic interactions of the 4:1 binary mixture is defined by $v_{ij}(r) = \epsilon_{\alpha\beta}[\left(\frac{r}{\sigma}\right)^{12} - \left(\frac{r}{\sigma}\right)^{6}]$ with parameters $\sigma_{AB} = 0.80$, $\sigma_{BB} = 0.88$ and $\epsilon_{AB} = 1.50$, $\epsilon_{BB} = 0.50$ ($\alpha, \beta = A, B$). The pair potential is cut-and-shifted at $r_c = 2.5\sigma_{\alpha\beta}$. We employ a unit system in which $\epsilon_{BB} = 1$, $\sigma_{BB} = 1$, and $m_A = m_B = 1$. We study system sizes $N = 125, 250, 500, 1000, 2000, 4000, 5000, 7000, 10,000, 20,000, 30,000, 50,000, 80,000, 100,000$ and 200,000 at $T = 0.40$. Several different temperatures $T = 0.395, 0.40, 0.415, 0.43, 0.45$ are studied at $N = 10,000$. The protocol for studying crystallisation in the KA mixture is identical for all temperatures and system sizes studied. We equilibrate at $T = 2.00$ and then perform an instantaneous quench to low temperatures simulating between 9 and 36 billion time steps after the quench ($\Delta t = 0.0025$). The cooling rates are $\Delta T/\Delta t = 642, 640, 634, 628$, and 620 in reduced units. For each temperature and system size we perform 10 independent quenches. Additionally, 4:1, 3:1 and 2:1 KA mixtures were also simulated in the NVT ensemble at a mean pressure $\langle P \rangle = 0$ and $T = 0.80$ with $N = 1000, 5000$, and 10,000 at which the relaxation times of the systems are similar.

Simulations of Cu$_2$Zr$_{1-x}$ mixtures were performed in the NPT ensemble using a Nose-Hoover thermostat and barostat with the LAMMPS package [22, 51] and compositions of $x = 15, 20, 25, 35.5$, and 64.5%. The Embedded Atom Model (EAM) method of Finnis-Sinclair was applied [52] simulating at a pressure $P = 0$ ($\Delta t = 0.002$ ps). Three system sizes were simulated $N = 1000, 5000$, and 10,000 at high temperatures for composition statistics and nucleation was studied for $N = 10,000$.

Relaxation Time Determination. — For the KA model, we determine the relaxation time of the liquid $\tau_\alpha$ from the self-part of the intermediate scattering function $F_s(q,t) \equiv \langle \exp[iq\Delta r] \rangle$ of the $A$-particles using the criterion $F_{A\alpha}(q,\tau_\alpha) = 0.2$; the length of the wave vector is $q = 7.25$. A system size of $N = 1000$ is used for these simulations to suppress nucleation but has a minor effect on $\tau_\alpha$. In the case where we cannot measure $\tau_\alpha$ directly in simulations due to extremely long simulation timescales we extrapolate using a VFT fit (see SM for more details). For Cu$_2$Zr$_{1-x}$ we obtained the intermediate scattering function from the Zr atoms and used a wave vector with $q \approx 26$ nm$^{-1}$.

Identifying Local Structure. — To detect the FCC and HCP crystals, and bicapped square antiprisms liquid locally favoured structure, we use the topological cluster classification (TCC), employed previously to identify local structures in the KA mixture [23]. That is to say, we carry out a standard Voronoi decomposition and seek structures topologically identical to geometric motifs of particular interest.

For the BCC crystal, we employ a bond-orientational order (BOO) parameter analysis [24]. For each particle $i$ we define complex order parameters $q_{lm}^i \equiv 1/n_q \sum_{j=1}^{n_q} Y_{lm}(\theta_{ij}, \phi_{ij})$, where $Y_{lm}$ is the spherical harmonic function with degree $l$ and order $m$, $\theta$ and $\phi$ are the spherical coordinates for the vector $r_{ij} \equiv r_i - r_j$, and $n_q$ is the number of neighbours defined from the 12 nearest neighbors. We use the complex order parameters to differentiate between solid and liquid particles using the criteria that for at least 7 nearest-neighbor bonds the scalar product $q_i^l \cdot q_i^l / \|q_i^l\| \|q_i^l\|$ should be greater than 0.70 to be classified as a solid particle. $q_i^l$ is a $(2l + 1)$-dimensional complex vector. The identity of each solid particle is then determined [53] using the third-order invariant order parameters

$$ W_i^l \equiv \sum_{m_1,m_2,m_3=0}^{l} \begin{pmatrix} l & l & l \\ m_1 & m_2 & m_3 \end{pmatrix} Q_{lm_1}^{m_1} Q_{lm_2}^{m_2} Q_{lm_3}^{m_3} / |Q_i^l|^3, $$

where the term in the parentheses is the Wigner $3-j$ symbol and $Q_{lm}^{m} \equiv 1/(n_q + 1) \sum_{j=1}^{n_q} q_{lm}^j$ is the average bond-orientational order parameter [25]. BCC particles are identified as all solid particles having $W_i^l > 0$. We checked that the TCC and BOO methods for the detection of FCC and HCP gave similar results.

[3] Bullock, G. & Molinero, V. Low-density liquid water is the mother of ice: on the relation between mesostructure, thermodynamics and ice crystallization in solutions.


