How a supercooled liquid borrows structure from the crystal (F) (SCI)

View Online   Export Citation   CrossMark

Ulf R. Pedersen,[1] (iD) Ian Douglass,[1,2] and Peter Harrowell[2,a] (iD)

AFFILIATIONS

[1] Glass and Time, IMFUFA, Department of Science and Environment, Roskilde University,
P.O. Box 260, DK-4000 Roskilde, Denmark
[2] School of Chemistry, University of Sydney, Sydney, New South Wales 2006, Australia

[a] Author to whom correspondence should be addressed: peter.harrowell@sydney.edu.au

ABSTRACT

Using computer simulations, we establish that the structure of a supercooled binary atomic liquid mixture consists of common neighbor structures similar to those found in the equilibrium crystal phase, a Laves structure. Despite the large accumulation of the crystal-like structure, we establish that the supercooled liquid represents a true metastable liquid and that liquid can "borrow" the crystal structure without being destabilized. We consider whether this feature might be the origin of all instances of liquids with a strongly favored local structure.

Published under license by AIP Publishing. https://doi.org/10.1063/5.0033206

The notion that glasses are rigid due the aperiodic accumulation of low energy local structures has had some success. This idea is the basis of Zachariasen's model of amorphous silica based on a random network of (slightly distorted) SiO_4 tetrahedra.[1] The validity of this model of silica has been supported by experiment[2] and simulation.[3] Water also accumulates, on supercooling, local tetrahedral coordination of hydrogen about each oxygen to form the low density amorphous phase.[4] In each of these cases, the low energy structure is very similar to that found in the stable crystal phase. While crystal-like structures have also been invoked to describe supercooled atomic mixtures,[5] the majority of studies of glass-forming alloys have focused on non-crystalline local structures.[6,7] Over the years, a range of candidate structures have been proposed, starting with Franck's suggestion[8] of the regular icosahedron. The difficulty with this type of analysis is the large structural diversity typically found in atomic mixtures[9] and the associated low concentration of nominated local structures of interest. There are, however, exceptions to this scarcity of favored local structures. In 2007, Coslovich and Pastore[10] demonstrated a substantial accumulation of local icosahedral structures in a supercooled equimolar binary Lennard-Jones mixture introduced by Wahnström.[11] As a result, the Wahnström liquid has become an important exemplar of the proposition that supercooled liquids can be characterized by a favored local structure.[6,7]

In 2010, it was shown[12] that the Wahnström liquid freezes into a crystal with the $MgZn_2$ (C14) Laves structure at a composition A_2B [see Fig. 1(a)]. In this crystal, along with the related Cu_2Mg (C15) Laves structure, *every* small particle (i.e., the A particles) has an icosahedral coordination shell. In this sense, the icosahedra in this supercooled liquid can be regarded as a structure borrowed from the crystal. Since Laves structures are the most abundant crystal forms found in binary intermetallics,[13] this structural link between icosahedra in supercooled liquids and the equilibrium crystal phase is likely to be relevant to a wide range of metal alloys.

When we observe a crystal-like structure in a supercooled liquid, is the observed structure an intrinsic feature of the liquid or is it a result of an instability of the liquid, possibly arrested, with respect to crystallization? Moore and Molinero[14] reported that a model of water based on the modified silicon potential exhibited an instability to crystallization at a temperature close to that associated with the onset of local ordering. No such instability has been observed in more complex models of water.[15] Fitzner *et al.*[16] have, however, reported the presence of sixfold rings of hydrogen bonded molecules (a vestige of the equilibrium crystal phase) in supercooled water that are associated with preferred sites of crystal nucleation. The goal of this paper is (i) to establish the degree to which the local structure of the supercooled Wahnström liquid shares the common neighbor organization found in the crystal and (ii) to determine
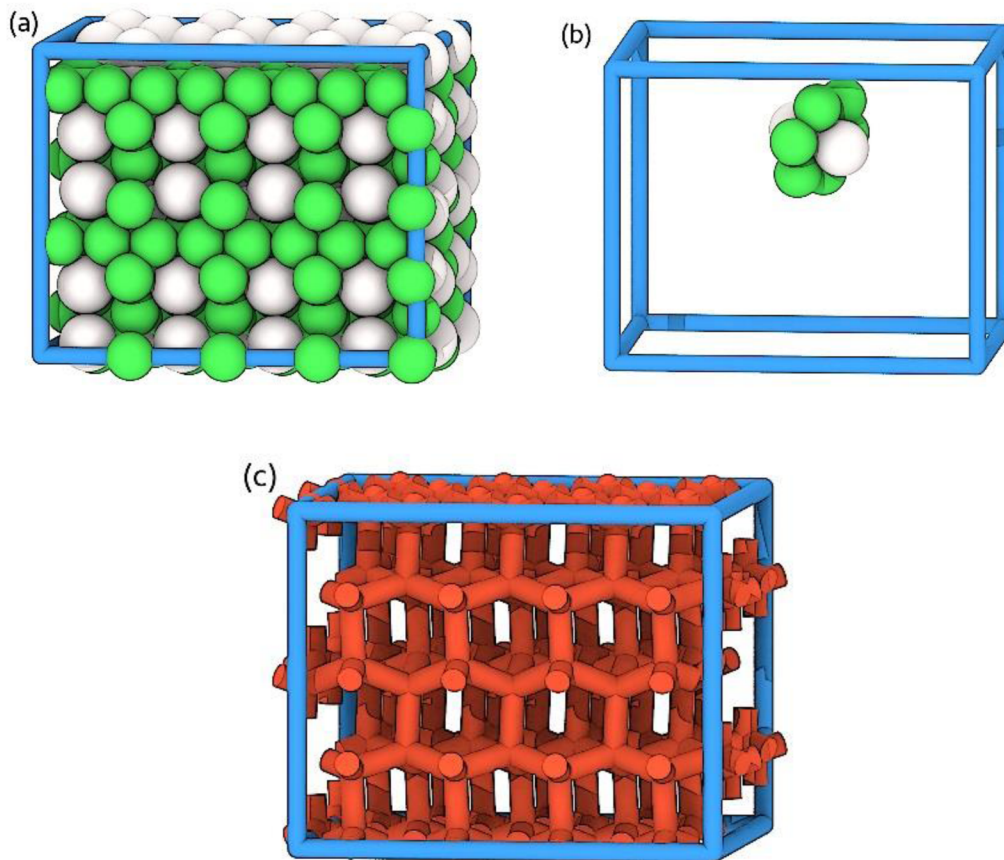
FIG. 1. (a) Illustration of the MgZn$_2$ crystal structure with A and B particles shown in green and gray, respectively. (b) A single pair of B particles with their six common A neighbors from the crystal corresponding to a Frank–Kasper (FK) bond. (c) The MgZn$_2$ crystal depicted as a tetrahedral network of FK bonds.

whether this structure is an intrinsic feature of the metastable liquid or the result of an incipient instability of the liquid with respect to crystallization.

The Wahnström mixture[11] consists of particles interacting via Lennard-Jones potentials $\phi_{ij}(r) = 4\varepsilon_{ij}[(\sigma_{ij}/r)^{12} - (\sigma_{ij}/r)^6]$ with the following interaction parameters: $\sigma_{AA} = \sigma_{AB}/1.1 = \sigma_{BB}/1.2$ and $\varepsilon_{AA} = \varepsilon_{AB} = \varepsilon_{BB}$. The particle masses are related via $2m_A = m_B$. As we are interested in exploring the possible instability of the liquid with respect to growth of the A$_2$B crystal, we have chosen to study the liquid not at the equimolar concentration usually used in this model but at the A$_2$B concentration, congruent with that of the crystal. All calculations have been carried out at a fixed reduced density of 0.874. At this density, the freezing point lies in the range $0.94 \leq T_f \leq 1.1$. Molecular dynamics (MD) simulations have been carried out at fixed NVT using RUMD[17] with N = 576 (unless otherwise indicated) using the Nose–Hoover thermostat.[18]

The MgZn$_2$ crystal [see Fig. 1(a)] can be represented in terms of "bonds" between neighboring pairs of B particles, where each bond consists of six common A neighbors to the two "connected" B particles, as shown in Fig. 1(b). (Two particles are identified as neighbors if their separation is less that the first minimum of the

species-appropriate pair distribution function.) We have previously called these common neighbor configurations Frank–Kasper (FK) bonds.[12] The MgZn$_2$ crystal can be represented by a hexagonal diamond network of FK bonds in which each B particle occupies a fourfold vertex [see Fig. 1(c)] and every A particle is at the center of an icosahedron that consists of six A and six B particles. This is a hierarchical structure with well-defined short-range order (the icosahedral coordination) and intermediate range order (the FK bonds). The intermediate structure can be resolved using two distinct order parameters: the first order parameter, a measure of crystallinity X ($=N_{4FK}/N_B$), where N_{4FK} is the number of B particles participating in 4 FK bonds, and the second order parameter, the mole fraction of FK bonds n ($=N_{FK}/N_B$), where N_{FK} is the number of FK bonds. These two-order parameter descriptions encompass the possibility that the liquid could accumulate FK bonds *without* accumulating the fourfold vertices characteristic of the crystal. A liquid might, in this way, "borrow" stable FK bond structures from the crystal while eschewing crystallinity itself.

To understand the stability of the liquid as a function of the density of FK bonds, we need to be able to control the latter quantity. In the metastable liquid, this is complicated by the background

crystallization rate. A biased Monte Carlo (BMC) algorithm allows us to control the value of n in the liquid at a temperature high enough that the intrinsic nucleation kinetics cannot interfere. The biased Monte Carlo (BMC) calculations are performed with a harmonic weighting for a target value of $n = n_o$[19] at temperatures in the range $0.6 \leq T \leq 0.8$. (Note that the actual mean value n of the FK bonds achieved by the BMC is typically less than the target n_o and we shall refer to the actual value of n throughout this paper.) These calculations were carried out at the A_2B composition with $N = 576$ and at a fixed density of 0.874. The BMC method will allow us to determine the degree to which the liquid can accumulate FK bonds before being forced into crystallinity.

We shall work with the reduced structural landscape spanned by the space of (n, X) depicted in Fig. 2. This plane includes regions that are impossible to achieve. It is not possible to have more fourfold FK sites than there are FK bonds to make them. It is equally impossible to avoid fourfold sites once the FK bond concentration is high enough. These inaccessible regions of the (n, X) plane are indicated in Fig. 2 by shading. The red curve represents the relationship between n and X, $X = \left(\frac{n}{2}\right)^4$, corresponding to the case where the bonds are distributed randomly with no preference to aggregate into fourfold crystal vertices. The straight line (green) represents the other limit, i.e., the case where the *only* FK bonds present are those taking part in crystal vertices. The percolation line (dashed) represents an interpolation of the random bond percolation on the diamond lattice[20] (at $n = 0.86$) and the site percolation on the same lattice (at $n = 0.78$).[21] The values of n and X from the BMC calculations are plotted in Fig. 2. We find that the simulation structures lie quite close to the line predicted assuming a random distribution of FK bonds; one in which the crystalline organization in the form of the 4FK sites occurs only as required by random aggregation. We shall refer to this observed liquid structure as a *quasi-random* distribution of FK bonds. The quasi-random structure of bonds includes an accompanying concentration of icosahedral coordination shells about the small particles. As previous studies[10] have
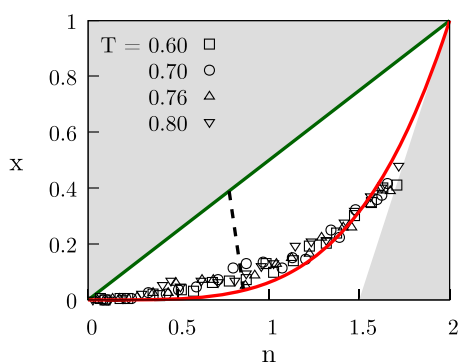

FIG. 3. The fraction $f_{icos} = N_{icos}/N_A$ of icosahedral coordination shells as a function of the fraction $n = N_{FK}/N_B$ of FK bonds in the A_2B mixture. The data come from weighted simulations of a high temperature (T = 0.9) liquid where no sign of crystallinity (i.e., fourfold FK sites) is observed.

analyzed the amorphous structures in terms of local icosahedral coordination, rather than FK bonds, it is useful to establish the correlation between the two quantities. In Fig. 3, we plot the fraction f_{icos} (=N_{icos}/N_A) of A particles in icosahedral environments as a function of the FK bond density. The data come from weighted simulations of a high temperature (T = 0.9) liquid where no sign of crystallinity (i.e., fourfold FK sites) was observed. The observed increase in the fraction of icosahedra due to the increase in the FK bond count at a fixed high temperature corresponds to ~0.5 of the A particles involved in FK bonds being in icosahedral environments. We conclude that the presence of FK bonds induces icosahedral ordering, but with a degree of correlation of roughly two icosahedra per FK bond in the quasi-random distribution, well below the value of six icosahedra per FK bond found in the ordered $MgZn_2$ crystal.

What is the energetics of this quasi-random assembly of FK bonds? In Fig. 4, we have calculated the potential energy per particle of the liquid, generated via the BMC method, as a function of

FIG. 2. Plot of X, the crystalline order parameter, against n, the fraction of FK bonds, obtained from the biased MC calculations of the A_2B mixture at the different temperatures shown. At the density of 0.874, the freezing point lies in the range $0.94 \leq T \leq 1.1$.[10] The predictions for the randomly distributed bonds and for the case where bonds occur only in the crystal are shown as a red curve and a green line, respectively. The estimated percolation transition is shown as a dashed line and shaded areas indicate unphysical parts of the (n, X) plane (see the text).
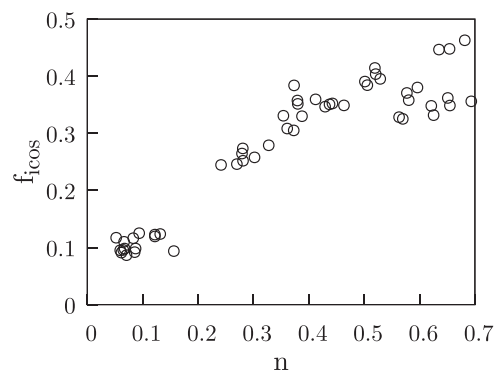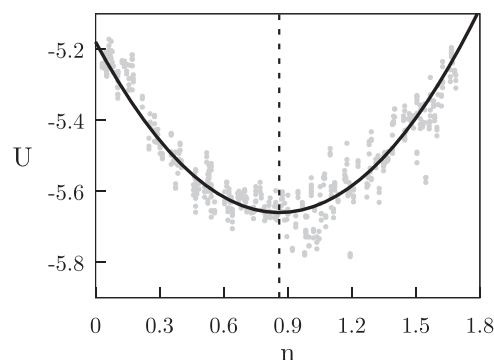

FIG. 4. The energy per particle, U, of configurations with different values of n. All calculations were carried out at T = 1.0. The vertical dashed line indicates the random bond percolation value of n = 0.86.[20] The curve corresponds to a quadratic fit $U - U_o = c(n - 0.86)^2$, where $U_o = -5.66$ and c = 0.65.

n, the density of FK bonds. We find a clear potential energy minimum at $n \sim 0.9$. This corresponds closely to the value $n = 0.86$ for bond percolation on a diamond lattice, suggesting that the FK bonds added beyond the random percolation point introduce strain into the liquid structure. The increase in U for $n > 0.9$ via the continuation of the quasi-random distribution of FK bonds means that this structural option is no longer favored on cooling. The fact that we generate these high energy states using BMC suggests that the algorithm only samples a restricted portion of configurations space, most probably due to the applied bias weighing against reorganizations that proceed via intermediates with low n. Any path to lower energy states must, therefore, involve deviations from the quasi-random structure, deviations characterized by an increase in the crystalline order parameter X. The value of n at percolation, therefore, represents an upper bound on the value at which this deviation will occur.

To find out how the (n, X) order actually accumulates, we have carried two sets of MD calculations. In set I, a liquid was instantly quenched to the final temperature T and then annealed for a time of $10^2 \tau_s(T)$ [where $\tau_s(T)$ is the structural relaxation time at T]. In set II, the annealing time was fixed, for all values of T, at $\sim 3 \times 10^7 \tau$, a value greater than $10^2 \tau_s(T)$ for $T > 0.63$. The results for the potential energy U and the fraction of FK bonds n vs T for the two sets of simulations are plotted in Figs. 5(a) and 5(b), respectively. For set I, we see no sign of crystallization. The potential energy U decreases linearly with T, dropping well below the minimum value found from
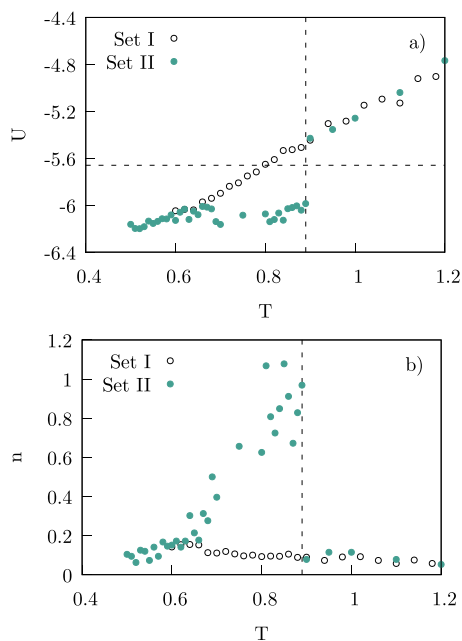

FIG. 6. The (n, X) structure landscape including the results for the MD simulations of set I and set II (see the text). Also plotted are the results of the BMC calculations, the percolation line, and the two limits as presented in Fig. 2.

the BMC calculations. As shown in Fig. 5(b), the accumulation of FK bonds in set I as it reaches the glass state does not exceed a value $n = 0.2$. For set II, we observe a step discontinuity in U and n at $T = 0.89$, which we attribute to crystallization. Increasing the system size by an order of magnitude increases the crystallization point to $T = 0.92$, but does not otherwise change the form of the data (supplementary material). As we quench to temperatures below this freezing point, we observe that the value of n decreases, indicating a decrease in the degree of crystallization, either through the decrease in crystallite size or through the trapping of an increasing degree of disorder within crystallites. This decrease in FK bonds continues until n coincides with that of the glasses generated by set I runs. Despite the decrease in FK bonds, the energy U shows little variation for set II quenches below the freezing point.

Our findings, presented graphically in Fig. 6, are summarized as follows: (1) Under the restricted sampling of the BMC algorithm, we have established the existence of a *possible* liquid structure comprised of a quasi-random network of FK bonds with an energy minimum associated with the bond percolation point. (2) The arrested disordered structure, as generated by set I quench, consists of a quasi-random arrangement of FK bonds, but one with a maximum FK bond density of only $n = 0.2$ (or $f_{icos} \sim 0.25$–0.3). This value is well short of the percolation value, as indicated in Fig. 2, leaving us to conclude that percolation plays no role in capping the accumulation of FK bonds in the metastable liquid. (3) The crystallization of the liquid is discontinuous and associated with substantial increases in n (also X). The structure clearly deviates from the quasi-random model. The abrupt and large increase in n associated with crystallization is quite distinct from the constrained accumulation of FK bonds (bounded by the value $n = 0.2$) that we associate with the supercooled liquid state and the glass that it becomes at low T. This is clear evidence that the FK bonds found in the arrested state correspond to the intrinsic structure of the metastable liquid and are not associated with any instability with respect to crystallization.

In summary, the structure of the arrested amorphous state of the A_2B Wahnström mixture after the $10^2 \tau_s$ annealing time (i.e., set I calculations) consists of a significant fraction of common neighbor structures borrowed from the crystal phase. The value of n appears

FIG. 5. (a) The average potential energy per particle U as a function of T. The results of MD simulations for sets I and II (see text) are shown. A horizontal dashed line is included to indicate the value of the potential energy at the minimum in Fig. 4, and a vertical dashed line indicates the crystallization temperature $T = 0.89$. (b) The average value of the mole fraction of FK bonds n as a function of T with data from MD simulations for sets I and II.
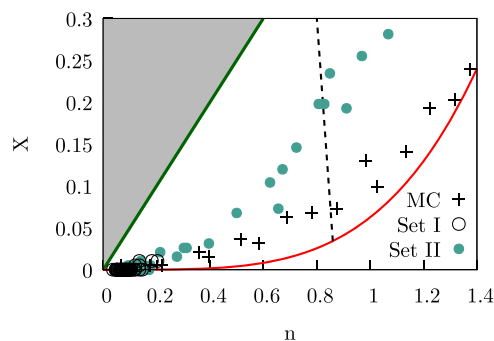
to be capped so that it does not increase continuously to the point of destabilizing the liquid. Having dismissed the bond percolation as the origin of this cap, we conclude that the most likely constraint is the slowing kinetics associated with the quasi-random ordering. The convergence of the low T structures from set I and set II runs supports this kinetic explanation. Derlet and Maaß[22] have reported that, in the extended 80 μs molecular dynamics simulations, the supercooled Wahnström model formed a nano-structured composite of the A_2B Laves crystal and B-particle rich glass. Our observation of a discontinuous ordering to some partially crystalline state is consistent with this recent report.

The network liquids such as silica and water have long represented the best known examples where the crystal-like structure is observed in the liquid. The objective of this paper is to understand how the analogous process is manifest in dense packed liquids. The "borrowing" of the crystal structure by the liquid that we observe in the Wahnström mixture is not a universal feature of alloys, with many liquid alloys failing to exhibit any sign of local crystal-like features.[6,7] As an example of this, the Kob-Andersen mixture,[23] another binary Lennard-Jones mixture studied in the context of glass formation, exhibits favored local structures quite distinct from those that appear in the crystal.[24] What is special about the model mixture studied here is its crystal structure. The Laves forming alloys are characterized by a low energy short range order (the icosahedra) that can readily organize into an intermediate range structure (the FK bond). This kind of hierarchical ordering lends itself to the stable incorporation of the crystal-like structure in the liquid. It is likely that this structural borrowing may be a generic feature of liquid mixtures that freeze into a Laves phase or, possibly, for which the Laves phase is a metastable polymorph. This proposition is consistent with the experimental of the coincidence of the glass forming ability and the stability of a Laves phases in a range of Fe-based alloys.[25] It would be interesting to test the generality of the connection, proposed here, between Laves crystals and the stability of supercooled alloys. An open question is whether this "borrowing" of structure might be a general feature whenever the equilibrium crystal has a large unit cell. In establishing how fragments of complex crystal structures can play an important role in the structure of the supercooled liquid, this work points to a potentially useful new approach to identifying classes of amorphous materials assembled from well-characterized local configurations.

See the supplementary material for additional data related to the influence of the system size on the plots presented in Figs. 5(a) and 5(b).

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

REFERENCES

[1] W. H. Zachariasen, "The atomic arrangement in glass," J. Am. Chem. Soc. **54**, 3841 (1932).

[2] A. C. Wright and M. F. Thorpe, "Eighty years of random networks," Phys. Status Solidi B **250**, 931 (2013).

[3] K. Vollmayer, W. Kob, and K. Binder, "Cooling-rate effects in amorphous silica: A computer-simulation study," Phys. Rev. B **54**, 15808 (1996).

[4] J. R. Errington and P. G. Debenedetti, "Relationship between structural order and the anomalies of liquid water," Nature **409**, 318 (2001).

[5] H. Tanaka, "Bond orientational order in liquids: Towards a unified description of water-like anomalies, liquid-liquid transition, glass transition, and crystallization," Eur. Phys. J. E **35**, 113 (2012).

[6] Y. Q. Cheng and E. Ma, "Atomic-level structure and structure-property relationship in metallic glasses," Prog. Mater. Sci. **56**, 379–473 (2011).

[7] C. P. Royall and S. R. Williams, "The role of local structure in dynamical arrest," Phys. Rep. **560**, 1–75 (2015).

[8] F. C. Frank, "Supercooling of liquids," Proc. R. Soc. London, Ser. A **215**, 43 (1952).

[9] D. Wei, J. Yang, M.-Q. Jiang, L.-H. Dai, Y.-J. Wang, J. C. Dyre, I. Douglass, and P. Harrowell, "Assessing the utility of structure in amorphous materials," J. Chem. Phys. **150**, 114502 (2019).

[10] D. Coslovich and G. Pastore, "Understanding fragility in supercooled Lennard-Jones mixtures. I. Locally preferred structures," J. Chem. Phys. **127**, 124504 (2007).

[11] G. Wahnström, "Molecular-dynamics study of a supercooled 2-component Lennard-Jones system," Phys. Rev. A **44**, 3752 (1991).

[12] U. R. Pedersen, T. B. Schroder, J. C. Dyre, and P. Harrowell, "Geometry of slow structural fluctuations in a supercooled binary alloy," Phys. Rev. Lett. **104**, 105701 (2010).

[13] D. L. Thoma, "Intermetallics: Laves phases," in *Encyclopedia of Materials Science and Technology* (Elsevier, 2001), pp. 4205–4213.

[14] E. B. Moore and V. Molinero, "Structural transformation in supercooled water controls the crystallization rate of ice," Nature **479**, 506 (2011).

[15] J. C. Palmer, F. Martelli, Y. Liu, R. Car, A. Z. Panagiotopoulos, and P. G. Debenedetti, "Metastable liquid-liquid transition in a molecular model of water," Nature **510**, 385–388 (2014).

[16] M. Fitzner, G. C. Sosso, S. J. Cox, and A. Michaelides, "Ice is born in low-mobility regions of supercooled liquid water," Proc. Natl. Acad. Sci. U. S. A. **116**, 2009 (2019).

[17] N. Bailey *et al.*, "RUMD: A general purpose molecular dynamics package optimized to utilize GPU hardware down to a few thousand particles," SciPost Phys. **3**, 038 (2017).

[18] W. G. Hoover, "Canonical dynamics: Equilibrium phase-space distributions," Phys. Rev. A **31**, 1695–1697 (1985).

[19] D. Frenkel and B. Smit, *Understanding Molecular Simulation: From Algorithms to Applications* (Academic Press, 2001).

[20] D. S. Gaunt and M. F. Sykes, "Series study of random percolation in three dimensions," J. Phys. A: Math. Gen. **16**, 783 (1983).

[21] P. N. Suding and R. M. Ziff, "Site percolation threshold for Archimedean lattices," Phys. Rev. E **60**, 275–283 (1999).

[22] P. M. Derlet and R. Maaß, "Emergent structural length scales in a model binary glass-The micro-second molecular dynamics regime," J. Alloys Compd. **821**, 153209 (2020).

[23] W. Kob and H. C. Andersen, "Testing mode-coupling theory for a supercooled binary Lennard-Jones mixture I—The van Hove correlation function," Phys. Rev. B **51**, 4626–4641 (1995).

[24] P. Crowther, F. Turci, and C. P. Royall, "The nature of geometric frustration in the Kob-Andersen mixture," J. Chem. Phys. **143**, 044503 (2015).

[25] S. Gosh, J. Basu, D. Ramachandran, E. Mohandas, and M. Vijayalakshmi, "A unified approach to phase and microstructural stability for Fe-ETM alloys through Miedema's model," Intermetallics **23**, 148–157 (2012).