Nucleation kinetics in a supercooled metallic glass former

F. Puosi^{*} and A. Pasturel

Univ. Grenoble Alpes, CNRS, Grenoble INP^b, SIMaP, F-38000 Grenoble, France

Abstract

We use molecular dynamics simulations to shed light on the mechanism underlying crystal nucleation in a supercooled metallic glass former characterized by a concurring crystal and amorphous local order based on icosahedral symmetry. At a crossover temperature, well below the melting point, we find that the supercooled phase exhibits glassy dynamics which includes a breakdown of the Stokes-Einstein relation and the emergence of spatially heterogeneous dynamics. In addition, we show that the origin of these phenomena can be related to a structural heterogeneity caused by the increase of icosahedral symmetry upon cooling. We also reveal that crystal nucleation occurs close to the glass transition and takes place in regions of high icosahedral symmetry, which can be interpreted by a strong reduction of the crystal-liquid interfacial energy. This scenario provides a framework for testing the estimation of the nucleation time according to the classical nucleation theory. More specifically, our findings allow to quantify how the heterogeneous character of the supercooled phase affects the predictions of this theory.

Keywords: metallic glass, supercooled liquid region, nucleation, heterogeneity, molecular dynamics

^b Institute of Engineering Univ. Grenoble Alpes

^{*} francesco.puosi@df.unipi.it; Present address: Dip. di Fisica “Enrico Fermi”, Università di Pisa, Largo B. Pontecorvo 3, I-56127 Pisa, Italy

I. INTRODUCTION

The ultimate fate of a liquid upon cooling below its equilibrium melting temperature, T_F , - whether it crystallizes or becomes a glassy state - depends on how easily the crystal can nucleate. In this supercooling regime, the characteristic of time scale for crystal nucleation, the nucleation time τ_n , is mainly described by the so-called time-temperature-transformation diagram (TTT diagram) which exhibits a “nose” shape [1]. In other words, the nucleation time displays a sharp minimum, $\tau_n(T_{nose})$ at the “nose” temperature T_{nose} , located below T_F . It is widely believed that crystallization mechanism changes from a nucleation process above T_{nose} to a growth-controlled process below [2]. The TTT diagram is also often used to discuss the glass forming ability (GFA) of a supercooled liquid. To form a glass, the liquid must be cooled from T_F to below T_{nose} in a time less than $\tau_n(T_{nose})$ [3]. This defines a critical cooling rate $R_c \sim (T_F - T_{nose})/\tau_n(T_{nose})$, above which a liquid avoids crystallization and form a metastable supercooled liquid that freezes into a non-equilibrium glassy state at T_g when structural relaxation is too long to be observable within experimental time scales.

Yet, crystallization rather than the glass transition may still occur in this deep supercooling region. Indeed, the structural relaxation time, τ_α and the nucleation time τ_n , which are well separated close to T_F (being τ_α much shorter), become comparable with decreasing temperatures below T_{nose} . Such a behavior defines a “lower metastability limit” (LML) or a “homogeneous nucleation limit” (HNL), below which the supercooled liquid ceases to be observable because it nucleates before it can equilibrate [4–6].

A reasonable description for the temperature-dependence of the structural relaxation time below T_F [7] is given by the Vogel-Fulcher-Tamman law (VFT), $\tau_\alpha(T) = \tau_0 \exp[BT_0/(T - T_0)]$ where τ_0 and B are constants and T_0 the so-called VFT temperature. B is known as the fragility index, which is negatively correlated with the fragility [8]. Namely a smaller B in the VTF law corresponds to a more fragile liquid and it is associated to a steep increase of $\tau_\alpha(T)$ with decreasing temperature.

An estimate of the nucleation time can be obtained from the classical nucleation theory (CNT) [9] which considers that the initial homogeneous disordered liquid and the final ordered crystal phases are the only key ingredients of nucleation. For homogeneous nucleation, the nucleation time is given by $\tau_n(T) = K \exp(\Delta G^*/RT)$, where R is the gas constant and ΔG^* the free energy cost of a crystal nucleus at the top of the nucleation barrier. Here K is a kinetic prefactor propor-

tional to the characteristic time of material transport controlling crystallization, namely the inverse of the liquid diffusion, D^{-1} . Tanaka [5] argued that HNL depends on how one treats the kinetic prefactor. Assuming that D^{-1} is proportional to τ_α via the Stokes-Einstein (SE) relation (here we use the structural relaxation time as a proxy for viscosity), CNT suggests that $\tau_n(T)$ is always greater than τ_α , which implies that the equilibration of the supercooled liquid is always obtained prior to nucleation or in other words the HNL does not exist. In this context, Tanaka pointed out that a liquid will exhibit a HNL if D^{-1} is strongly decoupled to τ_α in the supercooled regime and the SE relation breaks down. Cavagna *et al.* [6] obtained similar conclusions by incorporating the SE breakdown into CNT through viscoelastic effects. In contrast, Zanutto *et al* observed the occurrence of a HNL without the breakdown of SE relation [10], suggesting that the latter is not a necessary condition.

Some studies [7] attributed the breakdown of the SE relation to the emergence of dynamic heterogeneities (DHs) which provide an explicit connection between spatial fluctuations and relaxation kinetics [11]. Specifically, the breakdown has been associated to the particles in fast regions while particles in slow regimes obey the SE relation [12]. However, some other studies proposed that it is not necessary to invoke DHs to explain the breakdown of SE relation [13–15] and also evidenced that particles in both fast and slow regions can deviate from the SE relation [13, 16]. Therefore, despite intensive efforts, the physical factors that control these dynamic phenomena that characterize the deep supercooled region remain elusive. More particularly, the structural signature of the dynamical arrest at the origin of the glass transition is still under debate [17].

For metallic liquids, it was conjectured that local configurations with a high degree of five-fold symmetry (FFS) or local icosahedral symmetry may explain the stability of supercooled states against crystallization [18]. Recently, the degree of local FFS was shown to be a structural indicator to interpret the temperature-dependence of dynamic properties during supercooling in metallic melts [19]. The increase in FFS-based motifs in the supercooling regime has been also used to present the glass transition as a frustration against crystallization. A popular scenario is based on geometrical frustration associated with the fact that FFS-based motifs would form on cooling a continuous ordered phase if the space is curved [20]. In the Euclidian space, that growth is frustrated, giving rise to the formation of limited domains only. An alternative scenario is proposed [21], based on frustration effects of non-extendable FFS- based motifs on crystal-like ordering, which prevent crystallization and favor glass formation. In both approaches, FFS-based motifs act as inhibitors of crystallization.

Yet, an open question is to investigate the physical factors that control the interplay between crystallization and glass formation when FFS-based motifs can be also regarded as structural motifs linked to a crystalline ground state. To address this question, we focus on the Cu-Zr system since it is known to exhibit a good glass-forming ability over a wide composition range [22] but also to crystallize in an ordered phase at the specific composition Cu_5Zr , characterized by a remarkable fraction of local icosahedral symmetry. In this work, we use large-scale molecular dynamics simulations for the Cu_5Zr metallic liquid to investigate the role of icosahedral symmetry in the interplay between crystallization and glass formation in its deep supercooling regime.

We find that crystal nucleation can be identified from the determination of the TTT diagram with a “nose” temperature located in the deep supercooling region, just above the glass transition temperature. Dynamics slowdown in this region is associated with the presence of DHs and the breakdown of the SE relation which occur at a crossover temperature located well above the “nose” temperature. By exploring the evolution of local ordering during cooling we show that this crossover temperature corresponds to the increase of local icosahedral symmetry in slow regions of DHs. We also evidence that local icosahedral symmetry develops during crystallization. All these results allow to propose a scenario in which slow regions of DHs act as crystal nucleation precursors. Finally these findings are used to test the validity and the predictive power of CNT.

II. COMPUTATIONAL DETAILS

We consider a model for the Cu_5Zr alloy with atoms interacting via an embedded-atom model (EAM) potential [23]. Molecular Dynamics (MD) simulations are carried out using LAMMPS molecular dynamics software [24]. The system consists of a total number of 23328 atoms, 19440 Cu and 3888 Zr atoms, contained in a box with periodic boundary conditions in three dimensions. The initial configurations are equilibrated at 2000 K for 5 ns followed by rapid quenching (10^{11} K/s) to 500 K in NPT ensemble. During quenching, the cell size is adjusted to give zero pressure and configurations at different temperatures are collected. More specifically, dynamic and structural properties are computed from 1500 K to 825 K, in a range where liquid equilibrium is established on time scale much shorter than the nucleation time. This prevents any interference of nucleation events on the accurate determination of liquid properties.

For dynamic properties, we focus on self-diffusion, structural relaxation and the emergence of DHs. Self-diffusion coefficients are evaluated from the mean-square displacement of each

component i ($i = \text{Cu or Zr}$):

$$R_i^2(t) = \frac{1}{N_i} \sum_{k=1}^{N_i} \langle [\mathbf{r}_k(t + t_0) - \mathbf{r}_k(t_0)]^2 \rangle \quad (1)$$

where $\mathbf{r}_k$ represents the position of atom k of specie i at time t . The angular brackets represent the average over time origins t_0 . The self-diffusion coefficient D_i is then determined from the long time limit of $R_i^2(t)$, namely $D_i = \lim_{t \rightarrow \infty} R_i^2(t)/6t$

Structural relaxation times are obtained by the self-intermediate scattering function which is defined for each component by:

$$F_{s,i}(q, t) = \frac{1}{N_i} \left\langle \sum_{k=1}^{N_i} \exp[i\mathbf{q} \cdot (\mathbf{r}_k(t + t_0) - \mathbf{r}_k(t_0))] \right\rangle \quad (2)$$

The structural relaxation time of component i , τ_α^i , is defined as the time needed for the corresponding self-intermediate scattering function $F_{s,i}(q, t)$ to be equal to $1/e$ at a wave vector $q = q_{max}$, corresponding to the main peak in the static structure factor [25].

To quantify the emergence of DHs, we consider the non-Gaussian parameter (NGP) [26] defined by:

$$\alpha_2(t) = 3R^4(t)/5 [R^2(t)]^2 - 1 \quad (3)$$

where $R^2(t)$ and $R^4(t) = N_i^{-1} \sum_{k=1}^{N_i} \langle [\mathbf{r}_k(t + t_0) - \mathbf{r}_k(t_0)]^4 \rangle$ are respectively the mean-square and mean-quadruple displacements of one component. $\alpha_2(t)$ exhibits a peak at a characteristic time scale t^* , signaling that the degree of DHs is maximum at t^* . We indicate as α_2^{max} the maximum value of $\alpha_2(t)$.

To investigate DHs more in details, we resort to the method introduced by Widmer-Cooper and Harrowell [27] based on the so-called isoconfigurational (IC) ensemble. Here 100 NVT trajectories are simulated starting from the same initial configuration but with different initial velocities, drawn randomly from a Maxwell-Boltzmann distribution. Typically, each simulation lasts for a time at least of the order of the structural relaxation time to allow DHs to evolve. Atomic mobility is evaluated via the IC averaged mean square displacement:

$$\langle \Delta r_{j,\alpha}^2(t) \rangle_{ic} = \langle |\mathbf{r}_{j,\alpha}(\Delta t) - \mathbf{r}_{j,\alpha}(0)|^2 \rangle \quad (4)$$

where $\mathbf{r}_{j,\alpha}(0)$ and $\mathbf{r}_{j,\alpha}(\Delta t)$ are the positions of the j th atoms at the beginning and after a time Δt in the α th trajectory and the average $\langle \dots \rangle_{ic}$ is taken over all the IC trajectories.

For structural properties, we compute the orientational order parameter, following the prescription proposed by Steinhardt *et al.* [28]. First, we define the set of neighbors of the atom j as all the atoms k within a cutoff distance r_c given by the first minimum in the radial distribution function. The corresponding vectors joining neighbors, $\mathbf{r}_{jk}$, are called bonds. The orientation of the vector $\mathbf{r}_{jk}$ determines the polar and azimuthal angle $\theta(\mathbf{r}_{jk})$ and $\phi(\mathbf{r}_{jk})$. The structure around the particle j is characterized by the $2l + 1$ quantities:

$$q_{l,m}(j) = \frac{1}{N_b(j)} \sum_{k=1}^{N_b(j)} Y_{l,m}(\theta(\mathbf{r}_{jk}), \phi(\mathbf{r}_{jk})) \quad (5)$$

where $Y_{l,m}$ are spherical harmonics and $N_b(j)$ is the number of bonds of particle j . The bond orientational order (BOO) parameters are defined by the rotationally invariant combinations:

$$q_l(j) = \left[\frac{4\pi}{2l+1} \sum_{m=-l}^l |q_{l,m}(j)|^2 \right]^{1/2} \quad (6)$$

Following previous works [29, 30], we focus on q_l with $l = 6$, which is known to be very sensitive to any kind of crystallization.

III. RESULTS

A. Time-temperature-transformation (TTT) diagram

To quantify the crystal nucleation kinetics, we monitor the evolution of the potential energy of distinct configurations during the isothermal annealing at different temperatures, ranging from 1000 K to 800 K. This range of temperatures is well below the experimental melting temperature, i.e. $T_F = 1300$ K, and then corresponds to supercooled conditions. Fig. 1(a) shows the time dependence of the potential energy of one representative sample between 860 K and 800 K. For each temperature, the crystal nucleation is detected by a significant drop in the potential energy with annealing time. Interestingly, the onset time of potential energy drops exhibits the typical shape of the TTT diagram with minimum nucleation time around 837 K. In the inset of Fig. 1(a), we show the mean nucleation time given by the average over at least six independent realizations. **Note that simulation cells are large enough to observe more than one nucleation event.** Uncertainties are computed as the standard deviation of the mean. We can estimate $T_{nose} \approx 830$ K. Then, above T_{nose} , we note that the potential energy displays a nearly constant variation before

FIG. 1. Panel a): time evolution of the potential energy of a sample along isotherms at selected temperatures. Open triangles mark the nucleation times, defined as the onset time of potential energy drops. Inset: temperature dependence of the mean nucleation time τ_n as obtained by the average over at least six independent sample. Panel b): corresponding time dependence of the inherent structure energy. Dashed line indicates the energy of the Cu_5Zr crystal.

dropping abruptly at a time which defines the nucleation time as the latest time at which the liquid contains no crystalline nuclei. Below T_{nose} , the potential energy starts to decrease slowly during isothermal annealing, which indicates that nucleation will be concomitant to transient aging induced by the cooling process at low temperatures. Yet, we can still detect the nucleation time from a well-pronounced drop of the potential energy. In addition, we show in Fig. 1(b) the evolution of the inherent structure energy E_{IS} , i.e., the mean energy of the local minima in the potential energy explored by the system [31]. For $T > T_{nose}$, E_{IS} of the supercooled liquid drops to a value similar to that of the Cu_5Zr crystal, which is a first indication of the Cu_5Zr crystallization. For $T < T_{nose}$ the difference between E_{IS} of the supercooled liquid and that of Cu_5Zr remains significant even at the end of our annealing process, which may indicate a sluggish crystal growth [32]. Indeed, the comparison with the energy of the glassy state, $E_{IS} \approx 3.82$ eV/atom, estimated after cooling the liquid to 500 K, confirms that a fraction of non-crystallized phase still exists and becomes more and more important with decreasing temperature. Another indication of such dynamic slowing down is the proximity of the glass transition, since its estimation from the inherent structure energy during the cooling process yields $T_g \sim 750$ K.

B. Dynamic properties in the supercooled region

To analyze more in details dynamic properties of the Cu_5Zr liquid in its supercooled regime, we first evaluate the temperature dependence of the structural relaxation time of each component, τ_α^i . Here, the supercooled state means a stationary metastable state whose evolution starts from an initial random configuration and is monitored for a time interval during which no crystal nucleation occurs. At high temperatures, τ_α^i changes almost linearly with $1/T$ as shown in Fig. 2(a), indicating an Arrhenius behavior. At lower temperatures, τ_α^i increases drastically and deviates from the linear behavior below a crossover temperature, $T_S \sim 1100$ K (for each component), located well below T_F . Fig. 2(a) indicates that the VFT law gives a good representation of the calculated structural relaxation times in the investigated temperature range. More specifically, we mention that fitted values, $B = 1.33(1)$ and $T_0 = 700(2)$ K, do not depend on the component (the reported uncertainties account for the small differences of the fitting parameters for Cu and Zr data). The small value of B points to the fragile character of the Cu_5Zr alloy. A rapid comparison of the temperature dependence of τ_α^i with that of τ_n (see Fig. 1(a)) shows that above T_{nose} , τ_n remains greater than τ_α^i by at least three orders of magnitude, indicating that the liquid equilibrium is well

established prior to crystal nucleation. This comparison within the framework of CNT will be discussed more in details below.

FIG. 2. Panels a) and b): Arrhenius plot of the structural relaxation time τ_{α}^i (panel (a)) and self-diffusion coefficient D_i (panel (b)) of Cu and Zr atoms. Inset of panel b): temperature dependence of the ratio between Cu and Zr diffusivity. Panel c): Arrhenius plot of the viscosity. Full lines in a) are fitted with the Arrhenius law $\tau_{\alpha}^i = A_i \exp(E_i/T)$. Dashed lines in b) and c) are fitted with the Vogel-Fulcher-Tammann (VFT) laws $X = A \exp(BT_0/(T - T_0))$ where $X = \tau_{\alpha}^i, \eta$. Panel d): temperature dependence of the Debye-Waller factor $\langle u^2 \rangle$ of Cu and Zr atoms. The dashed lines correspond to the linear fits in the low temperature range.

Next we report the temperature dependence of calculated self-diffusion coefficients, D_i , for each component. From Fig. 2(b), we see that their inverse temperature dependence displays an

Arrhenius-type behavior only at high temperatures while we detect a sharp deviation from the Arrhenius fit below the crossover temperature $T_S \sim 1100$ K. Interestingly, the $D_{\text{Cu}}/D_{\text{Zr}}$ ratio shown in the inset of Fig. 2(b) points out the decoupling of component diffusion below T_S .

Then, we consider viscous and vibrational dynamics. In Fig. 2(c) the temperature dependence of the viscosity η is shown. In agreement with previous observations for relaxation, VFT law provides a good description of viscosity data below T_S . Note that the fitted parameters B and T_0 are similar to those extracted from the fit of structural relaxation times. Vibrational dynamics is described by the Debye-Waller (DW) factor u^2 corresponding to the mean square vibrational amplitude of atoms. Here, we define $u_i^2 = R_i^2(t = 1 \text{ ps})$; this definition ensures that, at sufficiently low temperature, u_i^2 corresponds to the plateau value of the mean square displacement, denoting particle caging [33]. Figure 2(d) displays the evolution of u_i^2 as a function of temperature for both components. We observe that the extrapolated u_i^2 seem to vanish at the VFT temperature $T_0 \approx 700$ K. In addition significant deviations of the DW factor from the low temperature linear behavior become apparent below T_S .

Using the determination of self-diffusion coefficients and structural relaxation times, we can test the validity of the SE relation. It is well admitted that D_i/T and τ_α^i follow the SE relation, $D_i/T \propto 1/\tau_\alpha^i$ at high temperatures. Fig. 3(a)-(b) shows that D_i/T as a function of τ_α^i obeys the SE relation above T_S for both components. Below T_S , we observe a deviation from the SE relation and D_i/T and τ_α^i follow a fractional SE relation, i.e. $D_i/T \propto (\tau_\alpha^i)^{-\kappa}$ with $\kappa = 0.65$ and 0.70 respectively for Cu and Zr. Such a result confirms that relaxation and dynamics are significantly changed as T_S is traversed.

To go further in the analysis of dynamic properties in the supercooled region, we examine the emergence of DHs. The latter can be revealed from the non-Gaussian parameter by following the evolution of its maximum value $\alpha_{2,max}$ as a function of temperature. Namely, dramatic increase of $\alpha_{2,max}$ above a value of 0.2 indicates the rapid growing of DHs. The change of $\alpha_{2,max}$ with temperature can be illustrated more clearly by its first derivative against temperature, $d\alpha_{2,max}/dT$. In Fig. 4(a)-(b) we display $\alpha_{2,max}$ and $d\alpha_{2,max}/dT$ for each component. For both Cu and Zr, our findings evidence an onset of DHs at the crossover temperature T_S , below which they grow with an increasing rate.

Thus, we can consider that T_S corresponds to a strong evolution in dynamic properties of the Cu_5Zr liquid through the decoupling of diffusion, the Arrhenius-to-non-Arrhenius transition of structural relaxation time, the presence of fractional SE relation and the emergence of DHs. To

FIG. 3. Ratio D/T as a function of τ_α for Cu (panel (a)) and Zr (panel (b)) atoms. The dashed and full lines correspond to the SE relation $D_i/T \sim (\tau_\alpha^i)^{-1}$ and fractional SE relation $D_i/T \propto (\tau_\alpha^i)^{-\kappa}$ respectively.

reveal the underlying structural signature of dynamic crossover and to explore its relationship with crystal nucleation, we now investigate the structure of the Cu_5Zr liquid during quenching and isothermal annealing.

FIG. 4. Panel a): temperature dependence of the maximum value of the NGP, $\alpha_{2,max}$, for Cu and Zr atoms. Panel b): corresponding temperature derivative $d\alpha_{2,max}/dT$ as a function of temperature. The shaded region marks the onset temperature T_S , denoting the appearance of DHs.

C. Structural signatures of dynamic crossover phenomena and crystal nucleation

Here atomic structures in the Cu_5Zr liquid are characterized by the BOO parameter q_6 which can be also used to identify solid-like particles in liquids [34]. Fig. 5(a)-(b) shows the temperature dependence of the BOO parameter for each component. For the most abundant Cu component (see Fig. 5(a)) the BOO parameter at high temperatures is broadly distributed and quite similar to that of an equilibrated liquid in the Lennard-Jones system [34]. However, at low temperatures,

FIG. 5. Panel a): distribution of the local orientational order parameter q_6 of Cu atoms for selected temperature values. Vertical dashed line corresponds to the q_6 value of Cu atoms with icosahedral symmetry in Cu_5Zr crystal. Inset: temperature dependence of the fraction of Cu atoms with icosahedral local orientational order, i.e. with a q_6 in the shaded region of the main panel. Vertical line marks the onset temperature T_S . Panel b): Corresponding q_6 distribution of Zr atoms. Vertical dashed line marks the q_6 value of Zr atoms in Cu_5Zr crystal.

a second peak appears at a q_6 value ≈ 0.62 . This tendency becomes more pronounced at deeper supercooling and quite remarkably, the steep increase of this Cu fraction occurs at the crossover temperature T_S as shown in the inset of Fig. 5(a). Another interesting feature is that this q_6 value is close to that obtained in a perfectly icosahedral configuration, namely $q_6 = 0.66$. In addition, we emphasize that 80% of Cu atoms in the Cu_5Zr crystal have an icosahedral environment and thus are characterized by $q_6 = 0.66$ [35]. In Fig. 5(b) the BOO parameter of Zr component is

narrowly distributed around a peak value $q_6 \sim 0.17$ and does not present any significant change as a function of temperature. We note also that this q_6 value is close to that of Zr atoms in the Cu_5Zr crystal, namely $q_6 \sim 0.14$.

From these findings, we can conclude that the steep increase of the BOO parameter of Cu atoms around $q_6 \sim 0.62$ at T_S can be considered as a signature of the underlying link between dynamic crossover and local structural ordering. To deeply explore this coupling, we present in Fig. 6 the BOO distribution at a temperature close to T_{nose} , for only Cu atoms with the lowest and highest mobility in DHs i.e. the 5% of atoms with the lowest and highest values of the dynamic propensity as defined by Eq. (5). The mobile fraction has a broad q_6 distribution, similar to the global distribution shown in Fig. 5(a) except the icosahedral peak at $q_6 \sim 0.62$. On the opposite, the distribution of the sluggish fraction is different from the global one and presents a bimodal character: the icosahedral peak is enhanced with respect to the global one at the expenses of the broad peak whose width decreases notably. Then, from Fig. 6, we clearly establish that Cu atoms with icosahedral symmetry are located in the domains of low propensity, namely the slow fraction of DHs.

FIG. 6. For isothermal annealing at $T = 837$ K, distribution of q_6 restricted to slow and fast Cu atoms in DHs, compared to the distribution for all Cu atoms (bold line).

To investigate the role of the BOO parameter in nucleation process, we examine its temporal evolution during isothermal annealing. Figure 7(a) shows the mean BOO parameter $\overline{q_6}$ of Cu atoms for the six temperatures investigated. We find that for all the temperatures $\overline{q_6}$ exhibits a

FIG. 7. Panel a): time evolution of the mean BOO parameter $\overline{q_6}$ of Cu atoms along isotherms at selected temperatures. Open triangles mark the nucleation times, defined as the onset time of potential energy drops and shown in Fig. 1. Panels c)-d): for representative temperature values, we show that the nucleation time identifies a change in the time evolution of q_6 .

change in its temporal evolution, which is more pronounced at high temperatures (above T_{nose}) than at low ones (below T_{nose}), as seen in Fig. 7(b)-(d). We also emphasize that the onset of this change is well signaled by the nucleation time as defined from the energy drops shown in Figure 1. This confirms that the weak changes seen for the low-T annealing isotherms can be ascribed to nucleation occurring in the system.

Previous observations indicate that the nucleation process can be related to the time evolution of the BOO parameter. To go further, we inspect the time dependence of the q_6 distribution along

the isotherm at a temperature close to T_{nose} . In Fig. 8(a) we observe an increase of the icosahedral peak at a time which corresponds to the onset of nucleation, namely $t = 160$ ns. Note that this increase is even more rapid at later times, as evidenced in Fig. 8(b) which shows that the associated fraction of Cu atoms double during crystallization process. Such a behavior can be related to the growth of the Cu_5Zr crystal which gives a positive feedback for the increase of icosahedral symmetry through its 80% of Cu atoms with icosahedral environment. Further two additional peaks develop at small q_6 values. The peak at $q_6 \sim 0.2$ can be referred to the other 20% Cu atoms of Cu_5Zr crystal, which are characterized by $q_6 \sim 0.192$. The other peak at $q_6 \sim 0.3$ is less obvious to interpret. It could be related to the presence of defects in the crystallized structure, as already observed for other metallic systems [36].

To identify more carefully solid clusters associated with the crystal nucleation, namely pre-nuclei and nuclei, we use the BOO parameter q_6 as initially proposed by Frenkel et al. [34]. Note that in our system, the complex structure of the Cu_5Zr crystal makes the identification of crystal nuclei a critical task, to a greater extent than in systems nucleating into simple structures. In particular, we must discriminate between atoms with icosahedral environment belonging or not to crystal nuclei. For this reason, we adopt the following criteria. We identify a Cu atom as “solid-like” if i) it is characterized by a q_6 parameter close to 0.62, ii) it has more than four of its Cu neighbors with the same condition on q_6 , and iii) its displacement on a time scale typical of diffusion motion is smaller than a threshold, fixed to the half of the mean inter-particle distance. This latter condition corresponds to an atom unable to diffuse, performing a rattling motion around its mean position. The solid cluster is defined by adding to each of these “solid-like” Cu atoms their first neighbors. Then we apply a cluster analysis to measure its size. In Fig. 8(c)-(d), we present the time dependence of such solid clusters, N_{sc} , and the size of the largest one, N_1 , during the isothermal annealing at $T \sim T_{nose}$. First, at the early stages of the annealing, we observe fluctuations in the nucleation process with the presence of few solid clusters which repeatedly rise, grow and dissolve as they do not reach the critical nucleus size. At $t \approx 160$ ns, we find that the largest cluster overcomes the critical size, estimated at 1 – 2 nm, to grow rapidly at later times. We note that this determination of the nucleation time is coherent with that given by the drop of the potential energy (see Fig. 1).

Figures 9 and 10 illustrate the nucleation process and the growth of nuclei at two different temperatures, $T = 860$ K (Fig.9) and $T = 800$ K (Fig.10), above T_{nose} and below T_{nose} respectively. We note that the nucleation and the growth processes are considerably different. More specifically,

FIG. 8. Evolution of structural indicators along the isotherm at $T = 837$ K. Panel a): evolution of the q_6 distribution for Cu atoms. Panel b): corresponding time dependence of the fraction of Cu atoms with icosahedral local orientational order. Panel c): time dependence of the number of solid clusters N_{sc} . Panel d): population of the largest cluster N_1 . The inset is a magnification at the onset of crystal nucleation. Vertical lines in c) and d) mark the nucleation time τ_n .

at $T = 860$ K at the onset of nucleation a single nucleus is detected, which at later times grows rapidly. In contrast, for $T = 800$ K we report a larger number of nuclei and a slower growth rate. We argue that the number of nuclei and their surface fraction affect also the growth process: the more the crystal nuclei are formed, the slower the systems crystallize. Indeed, such a behavior is in line with our findings in Fig. 7(b)-(d): at low temperatures $\overline{q_6}$ displays a change in its time evolution less pronounced than at high temperatures. It can be also related to experimental findings [2] which evidence a change in the crystallization mechanism from a nucleation process above T_{nose} to a growth-controlled process below. However, we emphasize that the understanding of the

FIG. 9. Crystal nuclei for selected configurations along an isotherm at $T = 860$ K, above T_{nose} . Atoms are colored according to a cluster analysis: in the specific case only one cluster is detected.

crystallization process in this deep supercooled system requires a more detailed analysis which is beyond the scope of this work.

IV. DISCUSSION

We have demonstrated that the supercooled Cu_5Zr liquid displays local icosahedral ordering which develops in slow regions of DHs upon cooling. Local icosahedral order was also found to induce the nucleation process of the crystalline phase during isothermal annealing in the deeply supercooled region where DHs exist. An intuitive conclusion is that the nucleation process starts in slow regions of DHs. To firmly establish this connection, we compare at $T \sim T_{nose}$ the spatial distribution of slow regions and crystal-like ones at different times, spanning from the pre-nucleation

FIG. 10. Crystal nuclei for selected configurations along an isotherm at $T = 800$ K, below T_{nose} . Atoms are colored according to a cluster analysis: distinct colors for atoms belonging to different clusters.

regime (50ns and 80ns) where no or few sub-critical nuclei exist to the first stages of crystallization (160ns and 200ns). First, Fig. 11 displays the slow regions defined by the 5% slowest atoms in DHs; we can see that the slowest atoms are not randomly distributed and tend to aggregate to form large regions. Next, during the isothermal annealing, we observe a clear correlation between slow regions of DHs and regions where the crystal nucleation is starting, namely the occurrence of sub-critical and stable crystal nuclei. Thus this correlation suggests that the physical mechanism behind the nucleation process of Cu_5Zr in the supercooled regime is a matching of the bond orientational symmetry between slow regions of DHs and the crystal phase. The relevance of this scenario of symmetry-matching induced preferential nucleation in slow regions of DHs is supported by the fact that more than 100 nucleation events observed in this study all occur selectively

in slow regions. A similar link between crystal nucleation kinetics and DHs in a supercooled liquid was reported by Gupta *et al.* [37], who showed that below a given crossover temperature the sizes of critical nuclei and the nucleation rate are controlled by the size of cooperatively rearranging regions (CRRs), i.e., the size scale of relaxation in a dynamically heterogeneous liquid.

FIG. 11. Correlation between crystal nuclei (colored particles) and the slow regions of dynamical heterogeneities (transparent particles) for selected configurations along an isotherm at $T = 837$ K, close to T_{nose} .

Within CNT, this influence of preexisting order on the nucleation of the crystal phase in liquid can be understood in terms of the interfacial energy, γ , between the liquid and solid phases: the reduction of the interfacial energy significantly reduces the free-energy barrier for crystal nucleation. Assuming that the entropic contribution to γ is dominant [38, 39], we can express the interfacial

energy as $\gamma = \alpha \Delta S_F / (N_A V_M^2)^{1/3}$ where α is a temperature-independent quantity that provides a measure of the configurational entropy of the interface and ΔS_F the entropy of fusion. V_M denotes the molar volume and N_A Avogadro number. Experimental and theoretical estimates of α show a systematic dependence on the topological structure of the solid phase [40]. As a matter of fact, α decreases as the degree of tetrahedral and icosahedral order in the solid phase increases. For instance, for the polytetrahedral phases $\alpha \sim 0.4$, significantly smaller than those found for simple crystal with cubic or hexagonal structures, namely $\alpha^{fcc/hpc} \sim 0.85$ and $\alpha^{bcc} \sim 0.70$ [40]. Note that such a behavior is also consistent with experimental studies in supercooled metallic systems [41, 42], which is another strong evidence of the importance of tetrahedral and icosahedral order in these systems.

To have a more quantitative understanding, we can evaluate the free-energy barrier ΔG^* for the formation of a nucleus of critical size. According to nucleation theory, $\Delta G^* = 16\pi\gamma^3/3\Delta G_V^2$ with $\Delta G_V = G_L - G_S$, the difference of Gibbs free energy per unit volume of liquid (G_L) and solid (G_S) phases. The previous expression is derived assuming that critical nuclei have spherical shapes. This first approximation seems reasonable for the present case, if looking to Fig. 11 where crystal nuclei appear as rather compact objects. For metallic systems, the driving force for nucleation ΔG_V can be approximated by $\Delta G_V = \Delta S_F \Delta T V_M^{-1}$ with $\Delta T = T_F - T$ [43]. With the previous approximation for the interfacial energy, we find that ΔG^* obeys a temperature dependence based on CNT of the type $\Delta G^* = \mathcal{C}T^3/\Delta T^2$ with $\mathcal{C} = \frac{16\pi}{3N_A}\alpha^3\Delta S_F$. The entropy of fusion ΔS_F is determined to be $12.82 \text{ J mol}^{-1} \text{ K}^{-1}$ at $T_F = 1290 \text{ K}$ [44].

In CNT, the so-called nose temperature is a result of the competition between thermodynamic and kinetic effects, respectively the increase of the driving force for crystallization and the decrease of mobility upon cooling. Thus we can express the temperature dependence of the nucleation time as

$$\tau_n^{CNT}(T) = K' D^{-1}(T) \exp\left(\frac{\mathcal{C}'T^2}{\Delta T^2}\right) \quad (7)$$

taking into account approximations used to determine ΔG^* and $\mathcal{C}'$ given by $\mathcal{C}/k_B$ with k_B the Boltzmann's constant. K' depends only weakly on temperature if compared to the exponential term and $D^{-1}(T)$. The temperature dependence of $D^{-1}(T)$ is extracted from MD simulations via the fractional SE relation, which links $D(T)$ with $\tau_\alpha(T)$ (see Fig. 3), and assuming a VFT-type dependence on the temperature for τ_α (see Fig. 2). Accordingly, Eq. 7 becomes:

$$\tau_n^{CNT}(T) = \frac{K''}{T} \exp\left(\kappa \frac{BT_0}{T - T_0} + \frac{\mathcal{C}'T^2}{\Delta T^2}\right) \quad (8)$$

First, to compare the temperature dependence of $\tau_n^{CNT}(T)$ with that given by MD simulations, we choose K'' to obtain $\tau_n^{CNT} = \tau_n$ at $T = 837$ K. Further, taking into account the high degree of local icosahedral ordering in the Cu_5Zr crystal, we choose the α value to be 0.4 in agreement with previous estimations [40]. Note that a change of ± 0.1 does not modify our conclusions. The result of this comparison is shown in Fig. 12 (dash-dotted line) and evidences that the functional form of CNT satisfactory describes the MD- based nucleation times at different temperatures. In Fig. 12, we also compare the temperature dependence of $\tau_n^{CNT}(T)$ to that of $\tau_\alpha(T)$. Below $T = 837$ K, we see that the gap between τ_n^{CNT} and $\tau_\alpha(T)$ is closing rapidly, suggesting that the supercooled liquid reaches a HNL in the vicinity of 770 K, which is only 20 K higher than T_g . We stress that the temperature extrapolation of τ_n^{CNT} , which is necessary to obtain this conclusion, is only about 40 K.

Interestingly, we can quantify the role played by the SE breakdown in the occurrence of HNL as discussed by Tanaka [5]. To do so, we also estimate the temperature dependence of the nucleation time using the data for $D(T)$ related to $\tau_\alpha(T)$ via the SE relation (dashed line in Fig. 3). Within this assumption, Eq. 8 is modified as:

$$\tau_n^{CNT/SE}(T) = \frac{K''}{T} \exp\left(\frac{BT_0}{T - T_0} + \frac{C'T^2}{\Delta T^2}\right) \quad (9)$$

We see in Fig. 12 that below $T = 800$ K, $\tau_n^{CNT/SE}(T)$ is as much as an order of magnitude larger than τ_n^{CNT} and that $\tau_n^{CNT/SE}$ and τ_α are more widely separated and converging less rapidly than τ_n^{CNT} and τ_α . Then, this result suggests that if the SE relation were obeyed, HNL would be shifted to lower T , in agreement with Tanaka's conclusions obtained for a strong metallic glass former.

Next, we seek to determine the nucleation time in CNT from the steady-state nucleation rate described in the conventional form [45–47] by:

$$I_{ss} = N_0 \sqrt{\frac{\sigma}{k_B T}} \frac{D(T)}{a} \exp\left(-\frac{\Delta G^*}{k_B T}\right) \quad (10)$$

where N_0 is the number of potential nucleation sites and a the typical interatomic spacing obtained from the number density. The nucleation time is then given by $\tau_n^{CNT} = (I_{ss} V_{sys})^{-1}$ with V_{sys} the system volume [48]. With the previous assumptions, the steady-state nucleation rate is:

$$I_{ss} = N_0 \sqrt{\frac{\alpha \Delta S_F}{R}} \frac{D(T)}{a^2} \exp\left(-\frac{C'T^2}{\Delta T^2}\right) \quad (11)$$

For homogeneous nucleation, each atom in the liquid acts as a potential nucleation site and $N_0 = N_A/V_M$. Such an assumption yields a value of $\tau_n^{CNT} \sim 50$ ps at $T = 837$ K, which is 5 orders of

FIG. 12. Temperature dependence, in Arrhenius form, of the nucleation time τ_n and structural relaxation time τ_α of Cu atoms. Solid line is the Vogel-Fulcher-Tammann (VFT) fit of relaxation data. Dash-dotted and dashed lines correspond to Eq. 7 and Eq. 8 respectively, i.e., the predictions of the nucleation time according to CNT. The shaded regions marks the onset temperature T_S and the nose temperature T_{nose} (with their uncertainty).

magnitude smaller than that determined from MD simulations. Note that at this temperature, the estimation of $D(T)$ using or not the fractional SE equation cannot explain such a difference. We emphasize that this value is smaller than that of the relaxation time, giving an unphysical behavior of HNL which would be shifter to higher temperatures with respect to MD simulations.

An alternative approach is to consider that DHs induce a heterogeneous character in the nucleation process. Indeed, we have revealed that the supercooled Cu_5Zr liquid is not spatially homogeneous, but intrinsically has static structural heterogeneity. More specifically, crystal nucleation is not promoted in the whole volume of the supercooled phase but only in slow regions of DHs and for Cu atoms with the BOO parameter $q_6 \sim 0.62$. From an estimation based on the

different MD runs, we find that at $T = 837$ K, 5% of particles present in slow regions of DHs can act as a nucleation site. Therefore, the volume fraction of liquid where nucleation process can proceed is drastically reduced and taking into account this effect gives a much higher value for the nucleation time, ~ 20 ns, as compared to the homogeneous approximation, and not too far from the MD-based value. Note that a similar approach was used in an experimental study of the nucleation rates of several silicate systems [49].

V. CONCLUSIONS

In summary, we investigated the role of dynamic heterogeneities in the nucleation kinetics of the supercooled metallic Cu_5Zr liquid using MD simulations.

- We find that the cross-over temperature T_S which marks the onset of DHs and the breakdown of SE relation is located well above the supercooled region where crystal nucleation events are observed. Moreover, at T_S we observe the development of local icosahedral symmetry which has a connection to the equilibrium crystal structure.

- Well below T_S , we find that the underlying nucleation mechanism is clearly not homogeneous since a clear correlation is established between the slow regions of DHs and crystal-like ones. The sequence of crystallization can be then described as follows: (i) inhomogeneous supercooled liquid (ii) slow regions of DHs with a high degree of local icosahedral symmetry acting as nucleation precursors (iii) final crystallization.

- In the framework of CNT, we determine that the occurrence of HNL at T close to T_g is directly related to the decoupling of diffusion from the structural relaxation time. We also propose simple arguments based on DHs to restore the predictive character of CNT for crystal nucleation in deep supercooled liquids.

ACKNOWLEDGEMENTS

The authors acknowledge the financial support from the Centre of Excellence of Multifunctional Architected Materials “CEMAM” No ANR-10-LABX-44-01 funded by the “Investments for the Future” Program. This work was granted access to the HPC resources of IDRIS under the allocation 2017-A0020910083 made by GENCI. Some of the computations presented in this paper were performed using the Froggy platform of the CIMENT infrastructure (<https://ciment.ujf->

grenoble.fr), which is supported by the Rhône-Alpes region and the Equip@Meso project (reference ANR-10-EQPX-29-01) of the programme Investissements d’Avenir supervised by the Agence Nationale pour la Recherche.

- [1] J. Fisher, J. Hollomon, and D. Turnbull, *J. Appl. Phys* **19**, 775 (1948).
- [2] J. Schroers, Y. Wu, R. Busch, and W. Johnson, *Acta Mater.* **49**, 2773 (2001).
- [3] W. L. Johnson, J. H. Na, and M. D. Demetriou, *Nat. Commun.* **7**, 10313 EP (2016).
- [4] W. Kauzmann, *Chem. Rev.* **43**, 219 (1948).
- [5] H. Tanaka, *Phys. Rev. E* **68**, 011505 (2003).
- [6] A. Cavagna, A. Attanasi, and J. Lorenzana, *Phys. Rev. Lett.* **95**, 115702 (2005).
- [7] L. Berthier and G. Biroli, *Rev. Mod. Phys.* **83**, 587 (2011).
- [8] C. A. Angell, K. L. Ngai, G. B. McKenna, P. F. McMillan, and S.W.Martin, *J. Appl. Phys.* **88**, 3113 (2000).
- [9] D. Turnbull, *Contemp. Phys.* **10**, 473 (1969).
- [10] E. D. Zanotto and D. R. Cassar, *J. Chem. Phys.* **149**, 024503 (2018).
- [11] M. D. Ediger and P. Harrowell, *J. Chem. Phys.* **137**, 080901 (2012).
- [12] S. K. Kumar, G. Szamel, and J. F. Douglas, *J. Chem. Phys.* **124**, 214501 (2006).
- [13] S. R. Becker, P. H. Poole, and F. W. Starr, *Phys. Rev. Lett.* **97**, 055901 (2006).
- [14] K. L. Ngai, *J. Phys. Chem. B* **103**, 10684 (1999).
- [15] N. Jakse and A. Pasturel, *Phys. Rev. B* **94**, 224201 (2016).
- [16] M. G. Mazza, N. Giovambattista, F. W. Starr, and H. E. Stanley, *Phys. Rev. Lett.* **96**, 057803 (2006).
- [17] J. Ding and E. Ma, *npj Comput. Mater.* **3** (2017).
- [18] F. C. Frank, *Proc. R. Soc. London* **215**, 43 (1952).
- [19] Y. C. Hu, F. X. Li, M. Z. Li, H. Y. Bai, and W. H. Wang, *Nat. Commun.* **6**, 8310 EP (2015).
- [20] G. Tarjus, S. A. Kivelson, Z. Nussinov, and P. Viot, *J. Phys.: Condens. Matter* **17**, R1143 (2005).
- [21] H. Tanaka, *Eur. Phys. J. E* **35**, 113 (2012).
- [22] Y. Cheng and E. Ma, *Progress in Materials Science* **56**, 379 (2011).
- [23] M. Mendelev, M. Kramer, R. Ott, D. Sordélet, D. Yagodin, and P. Popel, *Philos. Mag.* **89**, 967 (2009).
- [24] S. Plimpton, *J. Comput. Phys.* **117**, 1 (1995).

- [25] K. Binder and W. Kob, *Glassy materials and disordered solids: an introduction to their statistical mechanics* (World Scientific, Singapore, 2005).
- [26] W. Kob and H. C. Andersen, Phys. Rev. E **51**, 4626 (1995).
- [27] A. Widmer-Cooper and P. Harrowell, Phys. Rev. Lett. **96**, 185701(4) (2006).
- [28] P. J. Steinhardt, D. R. Nelson, and M. Ronchetti, Phys. Rev. B **28**, 784 (1983).
- [29] H. Tanaka, T. Kawasaki, H. Shintani, and K. Watanabe, Nature Materials **9**, 324 EP (2010).
- [30] M. Leocmach and H. Tanaka, Nature Communications **3**, 974 EP (2012).
- [31] F. H. Stillinger and T. A. Weber, Phys. Rev. A **25**, 978 (1982).
- [32] J. Orava and A. L. Greer, J. Chem. Phys. **140**, 214504 (2014).
- [33] F. Puosi, N. Jakse, and A. Pasturel, J. Phys.: Condens. Matter **30**, 145701 (2018).
- [34] P. R. ten Wolde, M. J. Ruiz-Montero, and D. Frenkel, The Journal of Chemical Physics **104**, 9932 (1996).
- [35] Cu₅Zr crystal has a cubic Be₅Au-type crystal structure (space group $F - 43m$). In the 24- atoms unit cell, 16 Cu atoms (Cu2) occupy equivalent sites with an icosahedral environment while the 4 other Cu (Cu1) and the 4 Zr atoms occupy sites with a similar complex atomic environment consisting of a 16-vertex Frank-Kasper polyhedron.
- [36] E. V. Levchenko, A. V. Evteev, I. V. Belova, and G. E. Murch, Acta Mater. **59**, 6412 (2011).
- [37] P. K. Gupta, D. R. Cassar, and E. D. Zanotto, J. Chem. Phys. **145**, 211920 (2016).
- [38] F. Spaepen, Acta Metall. **23**, 729 (1975).
- [39] F. Spaepen and R. B. Meyer, Scr. Metall. **10**, 257 (1976).
- [40] D. Holland-Moritz, Int. J. Non-Equilib. Process. **11**, 169 (1998).
- [41] K. F. Kelton, G. W. Lee, A. K. Gangopadhyay, R. W. Hyers, T. J. Rathz, J. R. Rogers, M. B. Robinson, and D. S. Robinson, Phys. Rev. Lett. **90**, 195504 (2003).
- [42] G. W. Lee, A. K. Gangopadhyay, T. K. Croat, T. J. Rathz, R. W. Hyers, J. R. Rogers, and K. F. Kelton, Phys. Rev. B **72**, 174107 (2005).
- [43] D. Turnbull, J. Appl. Phys **21**, 1022 (1950).
- [44] K. Yamaguchi, Y.-C. Song, T. Yoshida, and K. Itagaki, J. Alloys Compd. **452**, 73 (2008).
- [45] K. Kelton and A. Greer, *Nucleation in Condensed Matter: Applications in Materials and Biology*, Pergamon Materials Series, Vol. 15 (Pergamon, 2010).
- [46] I. S. Gutzow and J. W. Schmelzer, *The Vitreous State: Thermodynamics, structure, rheology, and crystallization* (Springer-Verlag Berlin Heidelberg, 2014).

- [47] V. M. Fokin, E. D. Zanotto, N. S. Yuritsyn, and J. W. Schmelzer, *J. Non-Cryst. Solids* **352**, 2681 (2006).
- [48] P. G. Debenedetti, *Metastable liquids: concepts and principles* (Princeton University Press, 1997).
- [49] A. S. Abyzov, V. M. Fokin, N. S. Yuritsyn, A. M. Rodrigues, and J. W. Schmelzer, *J. Non-Cryst. Solids* **462**, 32 (2017).