Dominant Effect of Heterogeneous Dynamics on Homogenous Crystal Nucleation in Supercooled Liquids

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Understanding the microscopic (molecular) mechanism of crystal nucleation remains intangible. For instance, it is still impossible to predict in which regions of a supercooled liquid nucleation will occur. Moreover, allegedly the Classical Nucleation Theory fails to describe the homogeneous crystal nucleation rates below the glass transition temperature. In this mini-review article, we revisit, critically comment, and link some highly selected recent studies using examples of an oxide glass-former, water, and a metallic alloy on the largely neglected effect of dynamic heterogeneities on crystal nucleation.

Keywords: nucleation, crystallization, dynamic heterogeneity, supercooled liquid, glass

HIGHLIGHTS
- The effect of DHs on nucleation are revisited for water, an oxide, and a metallic glass-former.
- A link between crystal nucleation and dynamic heterogeneities (DHs) is reviewed.
- The dominant role of DHs on nucleation opens up new challenges to the physics of nucleation.

INTRODUCTION: SIGNIFICANCE AND OPEN PROBLEMS

The formation of crystalline clusters or embryos in supercooled liquids (SCL) is stochastic; they statistically appear and disappear within the parent phase and only become sustainable when a critical size is reached. Ubiquitous examples of nucleation-induced crystallization are intracellular freezing, snow precipitation, mineralization, metal solidification, and glass-ceramic formation [1, 2]. On the other hand, the absence of nucleation on the cooling path is a necessary condition for glass formation [3]. However, despite the extraordinary relevance of crystal nucleation in materials and life sciences and technology, due to the extremely small size scales, and either very long or very short time scales, experimental assessment is very challenging, and comprehension of the microscopic details of crystal nucleation remains intangible. Many open questions remain. For instance, will glasses eventually crystallize after sufficiently long times? [3, 4]; is there a link between dynamic heterogeneities (DHs) and nucleation? In which regions of the supercooled liquid nucleation will occur? [5, 6]. We will address this issue here.

However, we will start with another prying opinion on nucleation in glass-forming substances, which has been a matter of vigorous debate. It is related to an alleged failure of the Classical Nucleation Theory (CNT) to describe the magnitudes of nucleation rates and the temperature-dependence of the crystal nucleation rates below the temperature of maximum, \( T_{\text{max}} \), which is close to the glass transition temperature, \( T_g \) [7–9]. Possible explanations for the failure at \( T_{\text{max}} \) have been advanced by different authors (e.g., [9]). They include the (often neglected) effect of elastic stresses on the thermodynamic barrier for nucleation [10] and the variation of the size of the “structural units” with temperature [11], both with limited success.
The discovery and increasing understanding of dynamic heterogeneity—referring to the spatio-temporal fluctuations in local dynamics in supercooled liquids, i.e., the phenomenon of coexisting domains of widely different sizes and agility [12]—provides a promising approach to realize the slowdown of dynamics during vitrification as the temperature decreases toward the glass transition [13–15]. Furthermore, attention has been given to investigate the relationship between structural relaxation and dynamic heterogeneity in glass-forming liquids [16–18]. A recent publication on the possible role of dynamic heterogeneities in crystal nucleation kinetics is of particular interest to this article [19]. Therefore, we will also discuss here whether DH could be important in explaining this alleged breakdown of CNT.

**CASE STUDIES FOR THREE SELECTED SUBSTANCES**

**Lithium Disilicate (Li$_2$O·2SiO$_2$)**

Let us take homogeneous nucleation rate data in the stoichiometric Li$_2$O·2SiO$_2$ supercooled melt—which nucleates in the sample interior, homogeneously—to study the suspected failure of CNT at low temperatures. CNT fits nucleation rate data rather well for temperatures above $T_{\text{max}} \sim T_g$; however, below this temperature, the measured rates allegedly drop off from the extrapolation of the high-temperature CNT fit. This CNT break is not related to the breakdown of the Stokes–Einstein expression, which considers diffusivity to be proportional to viscosity. The proposed explanations for this failure treat the SCL as being structurally and chemically homogeneous.

However, Gupta et al. [19] treated crystal nucleation in a heterogeneous medium using a concept proposed by Stevenson and Wolynes [5]. Grounded on the presence of dynamic heterogeneities in supercooled liquids, they anticipated the existence of a “cross-over” temperature, $T_X$, which might regulate a lower limit for the validity of Classical Theory. $T_X$ is the temperature where the size scales become equal, $\xi (T_X) = r_C(T_X)$, with $\xi$ being the (average) size of the CRR (cooperatively rearranging regions), which characterizes the size scale of relaxation in a dynamically heterogeneous liquid, and $r_C$ is the size of CNT’s critical crystal nucleus, which defines the size scale of the nucleation process. The possible crossover of these two sizes poses an intriguing question for the mechanism of nucleation below $T_X$. Since interactions with the surrounding SCL environment configurationally constrain the structural rearrangements on a scale smaller than $\xi (T)$, structural changes required for nucleation cannot take place in such cooperatively rearranging regions.

Stevenson and Wolynes [5] showed that the calculated values of $T_X$ are close to the glass transition temperatures, $T_g$, of o-terphenyl, and methanol. Using experimental data on the nucleation kinetics in lithium disilicate, Gupta et al. [19] reported for the first time values of $T_X$ for an oxide glass-former. Their findings indicate that $T_X$ is very close to $T_{\text{max}}$, which, in turn, is close to $T_g$, Figure 1.

Based on this finding, Gupta et al. [19] proposed that the anomalous drop of nucleation rates below $T_X$ in this regime is because the size of the CRR, $N_{\text{CRR}}$, controls the critical nucleus size, $N_C$, and the nucleation rate. Hence the mechanism changes around $T_X$. Their discovery linked experimental nucleation kinetics to dynamic heterogeneities in a SCL, suggesting a new opportunity in terms of understanding crystal nucleation in glass-forming liquids.

In a related study, Abyzov et al. [20] proposed another idea, incorporating concepts of spatial heterogeneity of glass-forming liquids for the description of crystal nucleation. They assumed that nucleation takes place only in the high mobility, floppy regions and is suppressed in the solid-like parts of a SCL. They calculated the fraction of liquid-like and solid-like areas as a function of temperature, and thus achieved a satisfactory agreement between the predictions of the CNT and experimental data at temperatures above and below $T_{\text{max}}$. This is a thought-provoking idea; however, it contradicts the Molecular Dynamic simulations of Fitzner et al. [21] and Puosi and Pasturel [22], to be reported in the following sessions, which demonstrated that nucleation takes place in the low mobility regions of the SCL.

**Water**

Water crystallization is likely the most ubiquitous phase transition on Earth. It is known that SCL exhibits dynamical heterogeneity, however, the microscopic connection between
the DH and crystal nucleation was not known until recently. Substantial effort has been focused on understanding the microscopic details of ice nucleation (e.g., [23–27]). While several studies have significantly improved our knowledge of the structural transformation during nucleation, the dynamics of ice nucleation have been scarcely addressed.

From a structural perspective, several investigations highlighted the differences between very mobile and very immobile regions within the liquid [28, 29]. Regarding bond-orientational order [30], have observed a higher degree of tetrahedrality in less mobile regions and 5-membered rings acting as locally preferential structures [31]. It has been under debate whether the immobile or mobile regions could be favored domains for nucleation. However, if there is any preference, it had not been proved for any supercooled liquid until recently. Fitzner et al. [21] filled this important gap through studying supercooled liquid water and ice nucleation by computer simulations to infer in which regions ice nucleation happens preferentially. Figure 2 shows regions of high and low mobility.

**Dynamics of Pre-critical Fluctuations**

The preliminary results of their simulations showed a strong propensity for the pre-critical ice nuclei to form within the most immobile domains. Then they studied the temporal correlation between immobility and clusters prior to their initial time of assembly. They showed that the mobility drops at 1,000 ps before the assembly at 240 K, which is significantly longer than the structural relaxation time of the liquid: $\tau_{\text{liq}} \approx 70$ ps. Besides, this drop takes place earlier than cluster formation and is not as abrupt as the change in structure, which can be related to the increase of an order parameter at about 400 ps before the assembly. This result confirmed that immobility precedes ice-cluster formation by a significant timespan.

**Connection Between Nucleation and Dynamics**

The same authors also reported simulation results that allowed them to sample many nucleation events at high temperatures. Simulation details are given in the original article [21]. Figure 3A shows a snapshot before nucleation from a typical trajectory.
While there are no domains recognized as ice-like, they show large immobile regions in the supercooled liquid. (Figures 3B,C) show similar trajectories after the start of nucleation. The formation of an ice nucleus commences in an immobile domain. Their study further demonstrated that the behavior shown in Figure 3 is typical for all nucleation snapshots.

### Structural Hallmarks of Nucleating Regions
Fitzner et al. [21] have also analyzed the distribution of primitive rings in the regions of extreme mobility (MI and MM as defined in Figure 2B). The MI regions have a ring distribution shaped peaked around 6 ± 1 members, whereas the distribution for the MM domains is much broader. Moreover, the percentage of fully H-bonded rings is much higher in the MI region. In particular, an abundance of six 1-membered hydrogen-bonded rings can be considered as the critical structural characteristic of the MI domains in the liquid. Since, if regarded in isolation, most of the 6-membered rings in the MI domains are seen as ice-like, which is the sign of the relative orientation between rings that is different from the crystal, and therefore the missing component in forming ice. Since this was observed in the MI region, which shows a reduced diffusivity, the authors suggested that the mechanism of the initial formation of ice-like clusters is collective. This is consistent with a picture of ring reorientation rather than single-particle attachments through diffusive motion.

In conclusion, Fitzner et al. [21] have clearly shown that ice nuclei are born in immobile regions of the SCL water, and that there is an incubation time when the particle mobility drops before any structural change. Additionally, the ring distribution is the structural hallmark of DH.

### Metallic Glass, Cu5Zr
Along the same line of thought, Puosi and Pasturel [22] used MD simulations to infer the mechanism underlying crystal nucleation in a supercooled metal, Cu5Zr, which is known to show crystal and non-crystalline (local) order based on icosahedral
symmetry. Figure 4A shows a crossover temperature, $T_s$. They found that the supercooled liquid undergoes a breakdown of the Stokes-Einstein relation at this temperature that coincides with the emergence of spatially heterogeneous dynamics. This coincidence of $T_s$ with the breakdown of the SE equation is also very relevant to condensed matter science.

They showed that the origin of these phenomena is related to an increase of icosahedral symmetry during cooling. They also revealed that crystal nucleation could be detected by MD near the glass transition temperature and occurs in domains of high icosahedral symmetry. The underlying nucleation mechanism was thus linked to the slow regions of DH. The crystallization pathways were described as follows: (i) formation of heterogeneities in the supercooled liquid below $T_s$ (ii) slow regions of DH having a high degree of icosahedral symmetry acting as nucleation ancestors (Figure 4B).

These findings corroborate those reported by Fitzner et al. [21] for nucleation of ice and allowed them to quantify how the non-uniform nature of supercooled liquids influences the theory.

**FINAL REMARKS AND OPEN CHALLENGES**

In summary, the above-discussed research works on recent MD simulations show that homogeneous nucleation in Cu$_{32}$Zr and H$_2$O happens in the largest, most immobile regions that arise from heterogeneous dynamics in supercooled liquids. We are not aware of other studies on this particular topic; therefore, it could be educational and relevant to test these novel findings with other substances.

Using a different approach, the alleged breakdown of the CNT below $T_{max}$ could be explained for Li$_2$O.2SiO$_2$ by the fact that the (calculated) average size of the CRR becomes larger than the (calculated) critical nucleus size, and starts to control the nucleation process below this temperature. This hypothesis still needs to be confirmed for other materials that show homogeneous nucleation on laboratory time scales. Possible candidates are BaO.2SiO$_2$, Na$_2$O.2CaO.3SiO$_2$, 2Na$_2$O.1CaO.3SiO$_2$, and Li$_2$O.2B$_2$O$_3$ [32].

One suggestion for future research is that it could be extremely revealing to obtain by MD simulations the average CRR size and the critical nucleus size vs. temperature for other substances. Such work could contribute to generalize or not the predicted crossover. Possible substances could be, for instance, BaS [33] and Lennard-Jones [34], for which excellent potentials exist and spontaneous homogeneous nucleation and the critical nucleus size can be detected by MD at a wide range of supercoolings. In this way, one could perhaps link the findings resulting from calculations performed for lithium disilicate with the MD simulation results for Cu$_{32}$Zr and H$_2$O.

These three original articles connecting the crystal nucleation phenomenon to the non-uniform nature of supercooled liquids open up new questions to the physics of nucleation. We thus hope this mini-review article paves the way for future research on this most relevant topic.

**AUTHOR CONTRIBUTIONS**

EZ has written the first draft. Both authors have polished, reviewed, and prepared the final manuscript.

**FUNDING**

This study was financed by the CNPq, and the São Paulo State Research Foundation support (FAPESP) grant numbers 15/13314-9 and 2013/07793-6.

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**Conflict of Interest:** The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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