Hybrid Monte Carlo technique for modeling of crystal nucleation and application to lithium disilicate glass-ceramics

Matthew E. McKenzie[a,*], John C. Mauro[b,*]

[a] Science and Technology Division, Corning Research and Development Corporation, Corning, NY 14831, USA
[b] Department of Materials Science and Engineering, The Pennsylvania State University, University Park, PA 16802, USA

ABSTRACT

We propose a computational method for studying crystal nucleation in glasses and supercooled liquids, combining the techniques of cluster formation via Monte Carlo, Steinhardt order parameter biasing, and an implicit solvation model. Each of these techniques calculates an important contribution to the overall nucleating free energy. This hybrid Monte Carlo technique is applied to the canonical example of a lithium disilicate glass-ceramic, where it is found that the cluster formation and cluster-to-crystal transition energies are approximately equal. The known crystal precursor, lithium metasilicate, has a smaller thermodynamic barrier to nucleation compared to that of lithium disilicate. The solvation energy is small compared to the formation and crystallization energies; yet the metasilicate solvation energy is much lower, indicating easier precipitation compared to the disilicate cluster. Our hybrid Monte Carlo approach is generally applicable to study the nucleation and crystallization processes in any arbitrary glass or supercooled liquid.

1. Introduction & Background

The nucleation phenomenon occurs throughout natural and manufacturing processes ranging from rain droplet formation to glass devitrification. Many reviews, special features, and books have been devoted to explaining the nucleation process [1–15]. There are still unanswered questions in this field, especially pertaining to the physics and chemistry of the nucleating cluster. With classical nucleation theory (CNT), the nucleating cluster is treated as a distinct macroscopic object containing the crystallizing atoms or monomers. The interface between the cluster and the surrounding supersaturated liquid is defined as a vanishingly thin interface. One of the deficiencies of CNT is the capillarity approximation, which states that the interplay between the cluster's surface tension, σ, and the difference in free energy between the liquid and crystal, Δg, completely describes of crystal nucleation free energy, ΔG_N (where N is the number of atoms or monomers). For a spherical cluster of radius r, the nucleating free energy (NFE) is described by:

$$\Delta G_N = 4\pi r^2 \sigma - \frac{4}{3}\pi r^3 \Delta g. \tag{1}$$

The first and second terms on the right-hand side of Eq. (1) are the surface and the growing bulk terms, respectively. Initially, for small clusters, the thermodynamic barrier is dominated by the surface term.

The condition when Eq. (1) reaches an extremum corresponds to the critical cluster size, r_c. The clusters smaller than r_c tend to shrink and dissolve. Once the critical size is met, the cluster becomes thermodynamically stable. This raises another problem with CNT, viz., defining at what size the macroscopic nucleating phase begins. The small length scales associated with nucleation are difficult to probe experimentally since the volume fraction of critical clusters is well below the experimental limits [14,16]. Furthermore, within these small length scales is another possible deficiency of CNT: a lower energy metastable phase that could act as heterogeneous nucleating sites for the stable phase [17,18]. Atomistic simulations could therefore offer some insight into these first steps of cluster nucleation.

Both Monte Carlo (MC) and molecular dynamics (MD) techniques have previously been used to study the nucleation process [19–23]. MC and MD techniques bring particular advantages and disadvantages. For example, MD is efficient for modeling condensed phase systems and has been shown to produce good results in the study of glass-ceramic nucleation [21]. However, the choice of MD can be rather limiting since closed ensembles such as the canonical (NVT) or isothermal-isobaric (NpT) ensemble are typically used. When a closed ensemble is used to describe the cluster growth process, specific atoms or monomers are removed from the surrounding glass or liquid, creating a depletion layer. This method of creating a depletion layer is an artifact of the simulation [9,21,24–26]. The dynamics of this depletion layer would

have a concentration gradient, which sets up a diffusive flux of that particular atom towards the cluster. Similarly, if the cluster dissolves, the concentration gradient would be reversed, setting up a flux of these atoms away from the cluster. This characterizes the typical solvation/dissolution of the pre-critical clusters. Periodic boundaries and constant number of particles results in creating a strong unphysical depletion layer in the phenomenological model [9,21,24–26]. To ensure that the closed system is representative of the nucleation process and that it does not cross periodic boundaries (leading to artificially high rates); one needs to test convergence with different system sizes.

On the other hand, sophisticated MC methods have been developed incorporating different sampling techniques to explore open statistical ensembles, including the grand canonical (µVT) ensemble. These techniques have been successfully applied to a variety of problems, including gas-liquid nucleation [16,20,23,22]. However, a major drawback for application of grand canonical Monte Carlo in condensed phase nucleation is that the translational and particle creation/deletion moves tend to have a high rejection rate due to the close proximity of neighboring atoms. To address this shortcoming, a more sophisticated (biased) MC technique [27,28] or a combined MC-MD algorithm [29,30] would need to be adopted to investigate the fundamental physics of crystal nucleation at the atomic scale.

It has been postulated [31,32] that crystal nucleation in glassy systems could be studied through use of a Gibbs Monte Carlo approach. A comparable approach, Grand Canonical Monte Carlo (GCMC), has previously been implemented by Chen et al. [19] to study water vapor to liquid nucleation. However, computational efficiency is still a major concern for Monte Carlo-based modeling of condensed phase systems at the atomic scale. Instead of applying brute-force computation, here we consider the various contributions to the fundamental NFE equation and choose specific techniques that are most appropriate for each term. Tanaka [33] divided the crystallization process into two separate parts, the crystal bond orientation and translational ordering (density fluctuations), showing that these are critical steps in the pathway for crystal nucleation in liquids. Specifically, a nucleating cluster would precipitate from the liquid phase by density fluctuations (cluster formation), and eventually become a stable crystal by local bond orientation (cluster to crystal transition). As the nucleation process occurs, the solvent interacts with the cluster. Applying an implicit solvation model to the cluster, one could use GCMC in the condensed phase and maintain its computational efficiency by only simulating only the important cluster formation physics. The work of crystal formation, *W*, is a function of these three variables:

$$W = Cluster\ Formation + Cluster\ to\ Crystal\ Transition$$
$$+\ Cluster\ Solvation \tag{2}$$

It should be mentioned that the strain energy, being the density difference between the developing cluster and surrounding glass melt, would increase the barrier to nucleation. For lithium disilicate the strain energy is near zero at the maximum nucleating temperature ($T = 732$ K) [34]. Since the strain energy increases as the temperature decreases, this method may be lacking lack in such cases. Following Eq. (2), the Methods section is divided according into three discrete subsections for each of these three contributions. The hybrid GCMC technique [19,20] is used [23,22] to (a) create the cluster, (b) calculate the energy needed to transform the cluster into a crystal [35,36], and (c) apply an implicit glass solvation model [37]. Using this approach to estimate the nucleation thermodynamic barrier, we focus our simulations on a [18,38,32,39,8,40,3,41,18,42] lithium disilicate glass-ceramic system.

Glasses near the stoichiometric lithium disilicate (Li_2O $2SiO_2$) composition nucleate both lithium metasilicate (Li_2O SiO_2) and lithium disilicate crystals [18]. It has been postulated that the metasilicate phase is a metastable precursor precipitate [41,43]. From the literature, it is clear that the lithium metasilicate phase is transient, lasting only a

few hours at nucleating temperatures around 454 °C and disappears during higher growth stage heat cycles. Soares et al. [18] showed that the formation of the metasilicate does not play a role in the lithium disilicate nucleation pathway. However, why does the metasilicate phase precipitate first and how does its thermodynamic landscape compare to that of the disilicate?

2. Methods

2.1. Cluster formation

Determining how the atoms form into a cluster uses a well-established grand canonical Monte Carlo code named General Nucleation [44]. The details of the code can be found in Refs. [19,20,22,23,45]; here, we will just review a few of the key highlights of the program. The approach utilizes the grand canonical ensemble (similar to the Gibbs approach) with some added features of the Aggregation-Volume-Bias Monte Carlo (AVBMC) and Histogram-Reweighting (HR) [19] techniques with a self-adaptive umbrella sampling (US) algorithm [20]. For our test case of lithium disilicate nucleation [39], the internal glass-ceramic nucleation rate occurs on the order of 10^{10} nuclei/m³/sec; for the smaller length scale afforded by simulation this can be translated to 10^{-8} nuclei/nm³/ns! Since nucleation is therefore a very rare event, it is intractable to solve this problem by any conventional simulation approaches, regardless of the size of the supercomputer. This emphasizes the importance of accessing long-time scale events, which must overcome large free energy barriers. This leads to the low probability of cluster formation near the critical nucleus size and hence the low probability of precipitating a new crystalline phase. To circumvent this problem, one can employ an umbrella sampling (US) free energy-based method [46]. In this case, the General Nucleation Monte Carlo code [44] samples the cluster size distribution evenly, and the umbrella potential is chosen to be the additive inverse of the nucleating cluster free energy, which is solved iteratively.

However, there is another difficulty when modeling a liquid-solid system with nano-heterogeneities. Relaxation in undercooled liquids is facilitated by "cooperatively rearranging regions" (CRR) in the system [47,48,49]. The liquid has a continuum of cluster-like semi-relaxed fluctuating structural species in which the energetic and entropic factors can differ greatly. If one models this by force-driven diffusion used in molecular dynamics [50] or random displacement moves applied by Metropolis Monte Carlo [51], the simulation techniques lack the ability to model the balance between the entropic factor (e.g., cluster formation/growth) and the energetic term (e.g., cluster shrinkage), leading to problems when simulating the microphase evolution of the system. The AVBMC approach has been developed to tackle this problem where the space surrounding the cluster is divided into associating (V_{in}) and non-associating (V_{out}) volumes that allow the transfer of atoms between the microphase regions. The volume term (the entropic factor, viz., a ratio of the associating and non-associating volumes) and the Boltzmann weighting factor (the energetic contribution, $\exp(-\Delta E/kT)$) are used in the transition probability to enhance the sampling for the MC particle addition/subtraction moves.

When the AVBMC move is selected, one of two possible routes could be executed based on equal probabilities: (1) cluster addition (out → in), or (2) cluster subtraction (in → out). Then a target particle *j* is randomly selected in the cluster. If this is a cluster addition move, then the code randomly selects a particle from the ideal liquid phase and places it inside the V_{in} volume near *j*. If this is a cluster subtraction move, the code randomly chooses a particle from within the V_{in} region of *j*. Then the energy change between the current configuration *A* and the trial configuration *B* is calculated, i.e., $\Delta E = E_B - E_A$. Let us define N_{in} as the total number of particles in the V_{in} regions of the cluster, which sums to $N - 1$ (*N* is the total particles of the cluster, as *j* is excluded), and μ is the chemical potential of the liquid phase. The trial move is accepted with the following probabilities: