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Test of classical nucleation theory in a condensed system

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Definitive tests of nucleation theory in condensed systems do not exist since the required interfacial energies and attachment frequencies are not directly measurable. We present a quantitative test of classical nucleation theory based on numerical modeling of the cluster evolution for multistep annealing treatments in lithium disilicate glass. The classical theory of nucleation is shown to be valid when the critical size is greater than 16–20 molecular formula units.

Nucleation phenomena, where small clusters of a new phase develop and grow in an existing phase, are fundamentally important in many areas of physics, chemistry, and materials science. Although nucleation has been studied extensively, the process is still poorly understood. Existing theories are dependent on generally unmeasurable quantities such as the interfacial energy between the developing cluster and the initial phase, and the molecular attachment frequency. Consequently, quantitative checks of the theories do not exist. This is discussed in detail, for example, by Binder and co-worker.[1,2] We present the first quantitative assessment of the dynamical model for classical nucleation theory in a condensed system, by comparing the results of a computer simulation, based on classical nucleation theory, with experimental measurements made by Kalinina and co-workers[3-8] in a lithium disilicate glass.

Nucleation is usually described by a phenomenological theory, hereafter referred to as the classical theory, where clusters of atoms in the configuration of the transformation product arise as a result of homogeneous fluctuations. In the simplest case, assuming spherical clusters and no stoichiometric difference between the two phases, a cluster containing n molecules is characterized by a free energy, ΔG_n, which is the minimum work required to form the cluster

$$\Delta G_n = n\,\Delta G' + (36\pi)^{1/3}\bar{v}^{2/3}\sigma . \tag{1}$$

Here $\Delta G'$ is the Gibbs free energy per molecule of the new phase, less that of the initial phase, $\bar{v}$ is the molecular volume, and σ is the interfacial energy per unit area.

In the classical theory, the macroscopic values for $\Delta G'$ and σ are used to compute ΔG_n. For small clusters, however, this assumption is probably in error. For the devitrification of a glass, the growth rate of the cluster is assumed to scale with the fluidity of the surrounding phase so that no measurable stress develops around the cluster and stress contributions to the free energy can be ignored. Other contributions to the free energy, ΔG_n, are also assumed to be insignificant for the case discussed here.[9] Since $\Delta G'$ is negative and σ is positive, there exists a critical cluster size, n^*, above which ΔG_n decreases with increasing cluster size. Assuming that the homogeneous medium is in equilibrium, for times less than the critical size formation time, the thermodynamic probability of forming a cluster of size n is proportional to $\exp(-\Delta G_n/k_B T)$. Based on this probability, the equilibrium cluster size distribution is readily determined.

The kinetic model generally assumed for nucleation and growth was developed by Volmer and Weber[10] and Becker and Doring.[11] The cluster evolves in size by adding or losing a single molecule at a time. The time-dependent cluster density $N_{n,t}$ is then determined by solving a system of coupled differential equations of the form,

$$\frac{dN_{n,t}}{dt} = k_{n-1}^{+}N_{n-1,t} - [k_n^{-}N_{n,t} + k_n^{+}N_{n,t}] + k_{n+1}^{-}N_{n+1,t} . \tag{2}$$

Here k_n^+ is the rate of addition of molecules to a cluster of size n, and k_n^- is the rate of loss. Given $N_{n,t}$, the time-dependent nucleation rate is readily determined:

$$I_n(t) = k_n^{+}N_{n,t} - k_{n+1}^{-}N_{n+1,t} . \tag{3}$$

The rate constants in a condensed system are generally defined in terms of an average unbiased molecular jump frequency, γ, at the cluster surface. Following the usual procedure, first outlined by Turnbull and Fisher,[12] the rate constants for spherical clusters are obtained from reaction rate theory:

$$k_n^+ = 4n^{2/3}\gamma \exp\left[-\frac{\delta g_n}{2k_BT}\right], \tag{4a}$$

$$k_n^- = 4(n-1)^{2/3}\gamma \exp\left[+\frac{\delta g_n}{2k_BT}\right], \tag{4b}$$

where δg_n is the free energy of a cluster of $n+1$ molecules less that of a cluster containing n molecules.

The classical theory then involves two quantities that are not generally measurable, i.e., γ and σ. This makes it extremely difficult to test the theory.

We have developed a computer model that simulates directly the cluster evolution to solve the master Eq. (2). We extend that model here to simulate the time-dependent nucleation behavior following various preannealing treatments in a lithium disilicate glass. Since the model has been discussed in detail in previous publications,[9,13–15] we will only briefly describe it here.

In essence, the time is divided into small intervals. The nucleation process is simulated by an algorithm that in each time interval calculates the numbers of clusters making transitions to neighboring sizes and alters the cluster population according to Eq. (2). The number of single molecules, initially set to be Avogadro's number, is altered to take account of the molecules released or absorbed in the cluster transitions.

To solve Eq. (2), it is necessary to assume a finite range of cluster sizes. Approximate solutions based on a Fokker-Planck approximation to Eq. (2) (Refs. 16 and 17) must also consider this; there it is often assumed that only those clusters of energy k_BT about ΔG_{n^*} need be considered. The choice of our upper limit is based on convenience and available computer time. The choice of the lower limit is somewhat ambiguous, however. Besides the obvious difficulties of extending the macroscopic values for $\Delta G'$ and σ to small cluster sizes, there remains the fundamental problem that extremely small clusters of the new phase will be indistinguishable from equilibrium configurational fluctuations in the initial phase. Since we are considering nucleation in a glass, we choose a lower limit of ten atoms since this is the number in the configuration of two edge-sharing octahedra, an atomic arrangement that is extremely unlikely to arise in a dense random-packed liquid.

Lithium disilicate glass is known to nucleate crystals of the same stoichiometry by a homogeneous mechanism.[18] Although glasses of slightly different composition undergo phase separation in the amorphous phase and nucleation of lithium metasilicate prior to the appearance of the lithium disilicate crystal, these complications do not arise when the silicate composition is equal to or greater than the disilicate composition.[19,20]

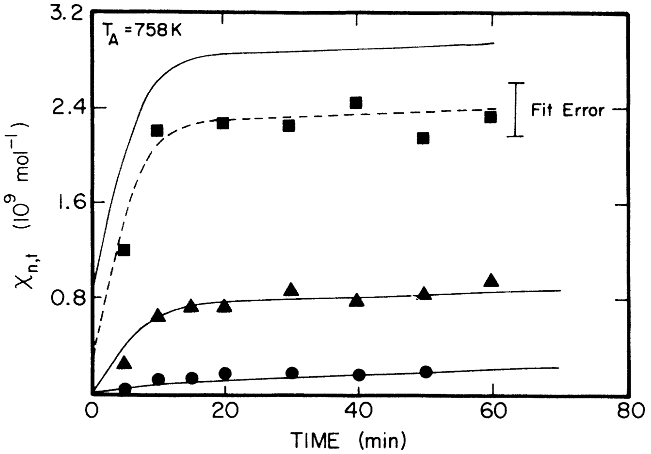

FIG. 1. Simulation (solid line) and experimental number of nuclei, X (solid circles), for lithium disilicate as a function of time at 758 K after annealing at 713 K for 18 h, 724 K for 4.5 h, and 746 K for 45 min. The dashed line is the simulation result for the 713-K anneal after shifting to match the initial number of nuclei. The maximum estimated error of the simulation, based on measurement uncertainties, is indicated.

Kalinina and co-workers[3–8] have measured the time- and temperature-dependent nucleation rates in as-quenched lithium disilicate glass, and the time dependence of the nucleation rate after heat treatments of the glass for different temperatures and times. These data are modeled with the numerical simulation. The upper limit on the cluster distribution is taken to be three times the critical size at the growth temperature. Measured values for the specific heat were used to calculate $\Delta G'$. Following the method described elsewhere,[14] the cluster distribution of the glass is prepared by calculating the cluster evolution as a function of temperature during a quench at the critical cooling rate using Eq. (2). The fit to the measured data was found to be largely independent of the choice of the initial distribution, however. The values for σ and γ, were determined by simultaneously fitting the steady-state nucleation rate and the transient time to steady state as a function of temperature to give a temperature-independent value for $\sigma = 0.146 \pm 0.001$ J/m^2. As expect-

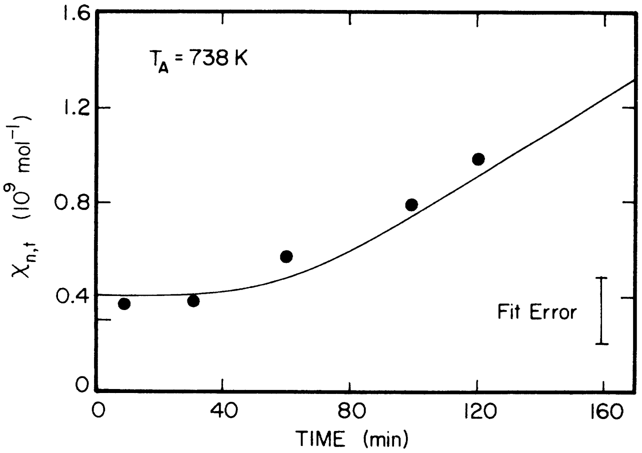

FIG. 2. Simulation (solid line) and experimental (solid circles) values for the number of nuclei, X in lithium disilicate, produced as a function of time at 738 K following a preanneal at 758 K for 143 min.

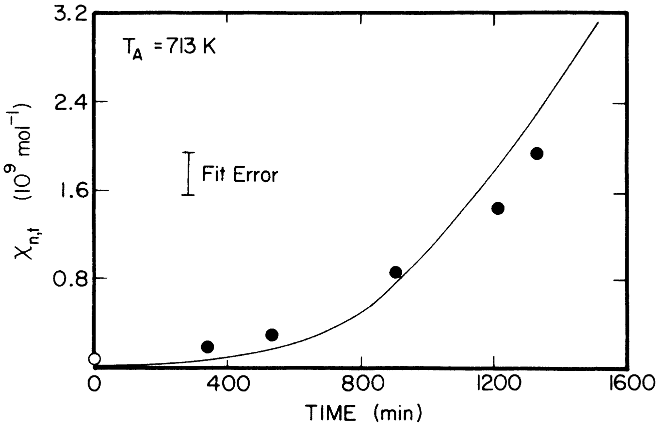

FIG. 3. Simulation (solid line) and experimental (solid circles) values for the number of nuclei χ in lithium disilicate, produced as a function of time at 713 K following a preanneal at 738 K for 50 min.

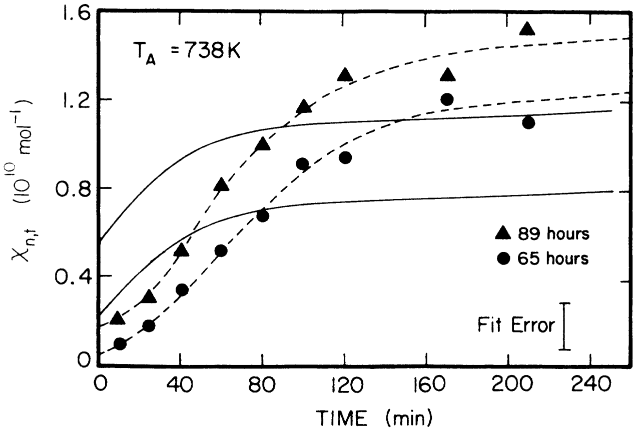

FIG. 4. Simulation (solid line) and experimental (solid circles, dashed line is a guide for the eye) values for the number of nuclei, χ in lithium disilicate, produced as a function of time at 738 K following a preanneal treatment at 703 K for 89 h, and 65 h.

ed, γ was found to scale with the measured values of the viscosity.[21] Using these values for σ, $\Delta G'$, and γ, the time and temperature behavior of the nucleation rates following preannealing treatments at various temperatures for different times were then calculated with no adjustable parameters and compared with the experimental measurements.

In Fig. 1, the measured values for the number of nuclei, χ, produced as a function of annealing time at 758 K following preannealing treatments at 713, 724, and 746 K are shown with the results of the numerical simulation. The agreement between experiment and theory is generally good. The disagreement with the 713 K preannealing treatment is consistent with a spread of approximately 15% in the steady-state nucleation rates at 713 K, obtained in different samples by Kalinina and co-workers. By adjusting I^s (713 K) to correct the initial number of nuclei, the agreement is greatly improved (dashed line). Such scatter in the experimental measurements will lead to uncertainties in the fitting parameters used for this simulation and will give rise to variations in the simulation results shown in Figs. 1-4. The error bars shown in these figures are an estimate, based on these uncertainties, of the maximum error expected for the total number of nuclei produced. It was not possible to refine these estimates since experimental errors were not reported by Kalinina and co-workers. The computational error of the model (e.g., round-off errors) is of the order of the width of the line.

Figure 2 shows good agreement between the predicted and measured values for the number of nuclei produced as a function of annealing time at 738 K following a preannealing treatment at 758 K. Good agreement is also obtained for an annealing treatment at 713 K following a preannealing treatment at 738 K (Fig. 3).

Figure 4 shows the number of nuclei produced at 738 K after preannealing at 703 K for 65 h and 89 h. The agreement between the measurements and the simulation is poor and cannot be explained by errors in the experimental measurements of the steady-state values. The initial temperature dependence is too low, the magnitude of change is too large, and the time dependence is wrong. The critical size predicted from Eq. (1) is approximately 16 molecular units at 703 K. The lower limit for the cluster distribution was reduced to one to check its effect on these simulations. When σ and γ were readjusted to match the steady-state nucleation rates and transient times, the results were identical to those shown in Fig. 1-4. This suggests that the observed disagreement must arise from a substantial misinterpretation of the experimental results or from the inability of the classical theory to deal with the small clusters dominant at the lower temperature. We are reexamining the experimental data for the low-temperature anneals to see if a reasonable variation of the fitting parameters will substantially improve upon the agreement between theory and experiment.

A possible refinement of the classical theory is to permit $\Delta G'$, σ, and/or $k_n^{\pm}$ to be functions of the cluster size and interfacial curvature. While it is true that these kinetic and thermodynamic terms were fit to the steady state nucleation rate and transient time, the multistep annealing experiments sample dynamic behavior at much smaller cluster sizes. Assuming the simple size dependence for the surface energy suggested by Tolman,[22] we find a difference in the time-dependent behavior shown in Figs. 1-4, if σ_0 and γ are matched to the $I^s(T)$ and $\tau(T)$. It may be possible to refine the size dependence of σ by better fitting the data shown in Fig. 4; we are investigating this.

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