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Molecular dynamics studies of the transient nucleation regime in the freezing of $(\mathrm{RbCl})_{108}$ clusters

Jinfan Huang and Lawrence S. Bartell*

Department of Chemistry, University of Michigan, 930 N. University Ave., Ann Arbor, MI 48109-1055, USA

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Abstract

The freezing of supercooled liquids in the transient period before a steady state of nucleation is attained has been the subject of a number of theoretical treatments. To our knowledge, no published experimental studies or computer simulations have been carried out in sufficient detail to test definitively the behavior predicted by the various theories. The present molecular dynamics (MD) simulation of 375 nucleation events in small, liquid RbCl clusters, however, yields a reasonably accurate account of the transient region. Despite published criticisms of a 1969 treatment by Kashchiev, it turns out that the behavior observed in the present study agrees with that predicted by Kashchiev. The study also obtains a much more accurate nucleation rate and time lag than reported for MD studies of RbCl previously published in this journal. In addition, it provides estimates of the solid–liquid interfacial free energy and the Grànàsy thickness of the diffuse solid–liquid interface.

Keywords: Transient nucleation; Freezing; Rubidium chloride clusters; Interfacial properties

1. Introduction

Molecular dynamics (MD) simulations have proven to be an effective means to study nucleation. In the course of research on the freezing of clusters of molten salts, molten metals, and molecular liquids [1,2], RbCl was found to nucleate readily and freeze to well-faceted crystals [3,4]. We decided to investigate the phenomenon of nucleation in this system in some detail. Our prior analyses of nucleation had been based on much smaller sets of independent clusters, and had ignored the build-up of nuclei during the transient period before the time lag. In this regime, it takes time for subcritical nuclei to form so that the rate $J(t)$ of production of critical nuclei, N^* in number, per unit volume per unit of time, or

$$J(t) = (\mathrm{d}N^*/\mathrm{d}t)/V \tag{1}$$

is less than J_s, the steady-state nucleation rate that is eventually attained in an isothermal system of such volume that the existence of some nuclei has no influence on further nucleation.

The present investigation takes transient behavior [5] into account for the first time in our analyses, thereby yielding a more accurate picture of the process of freezing. The method of moments applied in analyses is outlined in Section 2, followed by details of the simulations.

2. Computational procedures

2.1. Method of moments

In a set of N_0 clusters undergoing spontaneous nucleation, observed nucleation times are ordered from the lowest to highest, treating the 1st, 2nd,…,lth,…,N_0th times in much the same way as disintegration times in radioactive decays are treated. In the present work, nucleation times were identified in exactly the same way as they were in Refs. [3,4], namely by observing the times associated with the onset of rapid growth of the solid phase in each cluster. The primary difference between the present work and that of Refs. [3,4] is that an enormously larger set of nucleation events was obtained in order to establish nucleation parameters with some precision. All previous analyses of nucleation

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*Corresponding author. Fax: +1-734-647-4865.
E-mail address: ibart@umich.edu (L.S. Bartell).

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in MD simulations of sets of supercooled clusters had been based on an oversimplified rate law, assuming that the decay of the population of liquid clusters followed the first-order expression

$$-\ln[N_l(t)/N_0] = K(t - t_0), \tag{2}$$

where

$$N_l(t) = N_0 - l + 1 \tag{3}$$

is the number of clusters in the set of N_0 clusters which have not yet undergone nucleation before time t of the lth nucleation event, K represents the product $J_s V_c$ with J_s the steady-state nucleation rate, V_c the volume of the clusters, $t > t_0$ the time of nucleation, and t_0, the nucleation time lag. Such a rate law is the same as that for the decay of radioactive nuclei starting at time t_0 but is clearly incorrect for nucleation in the transient period before a steady state is reached.

Refs. [6,7] addressed the problem of how to modify Eq. (2) to take into account the phenomenon of transient nucleation in analyses of MD data for clusters. The most general treatment of transient nucleation that is relatively simple to incorporate into analyses is that of Wu [5]. His method of moments yields an explicit expression for the function $J(t)/J_s$ which he applied to nucleation in the bulk of a large system. We modify it to apply to nucleation in a large set of clusters, by noting that the volume of clusters which have not yet nucleated at a time just before the lth nucleation event totals $N_l V_c$. Therefore, the Wu function can be written for clusters as

$$\frac{J(t)}{J_s} = -\frac{\mathrm{d}N_l/\mathrm{d}t}{J_s N_l V_c} = -\frac{\mathrm{d}\ln[N_l(t)]}{K\,\mathrm{d}t} \tag{4}$$

which expression, upon integrating and incorporating Wu's result, yields

$$-\ln[N_l(t)/N_0] = Kt\left\{1 - \frac{1}{2}\operatorname{erfc}\left(\frac{\ln[(t/t_0)M_R^{1/2}]}{\sqrt{2\ln M_R}}\right)\right\} - Kt_0\left\{1 - \frac{1}{2}\operatorname{erfc}\left(\frac{\ln[(t/t_0)M_R^{-1/2}]}{\sqrt{2\ln M_R}}\right)\right\} \tag{5}$$

provided N_0 is larger enough that $N_l(t)$ can be approximated by a continuous function. In view of the fact that the erfc function decreases rapidly when the time increases beyond t_0, it is evident that Eq. (5) approaches Eq. (2) at large times. A quantity characterizing the gradual buildup of nuclei in the transient regime is a parameter we have chosen to call the "reduced moment", M_R. It is proportional to Wu's first moment M but possesses a more universal nature. Clearly, the lowest value the reduced moment can have is unity. Wu regarded his moment M as a free parameter to be derived in the analysis of experimental data.

Because the quantity $-\ln[N_l(t)/N_0]$ is known exactly in the set of nucleation events while the stochastic nucleation times are a matter of chance, it is appropriate to make the times, t, the uncertain "y" values in least squares analyses. This requires that Eq. (5) be inverted. To a good approximation beyond $g_l \approx 0.03$, the result is [6],

$$t = t_0 + g_l/K - t_0(1 - 0.5/M_R^{2.5}) \times \exp[-1.82(g_l/Kt_0)^{1/2}/(M_R - 1)^{0.41}], \tag{6}$$

where g_l represents the quantity $-\ln[N_l(t)/N_0]$.

2.2. Outline of computational details

Simulations were performed using a modified version of the program MDIONS [8]. Procedures followed those of paper I in this series [3] closely except that the potential function of Dixon and Sangster [9] was adopted instead of the function of Fumi and Tosi [10]. Whereas the Fumi–Tosi potential corresponded to rigid ions, the Dixon–Sangster potential was parameterized to take into account, in a pairwise-additive approximation, the effects of polarization of the ions.

In the simulations, molten clusters were quenched to 600 K. In an attempt to find whether the temperature from which the quenches were initiated had any effect on the nucleation dynamics, 75 clusters were quenched from 940 K, 75 from 920 K, 75 from 910 K, and 150 from 900 K. The latter temperature is approximately the melting point observed in this work for $(\mathrm{RbCl})_{108}$ clusters. Although there appeared to be a small systematic effect, it was not significant statistically. Therefore, all nucleation times were merged into a single set for the kinetic analyses.

Results were interpreted in terms of both the classical nucleation theory [2,11] and Grànàsy's diffuse interface theory [12,13]. Prefactors used did not include one employed in Paper I, namely that of Grant and Gunton [14], because we do not believe its physical basis is relevant to the present simulations. Its main virtue had been that it gives a higher prefactor than the classical prefactor which, in our judgment, tends to be too low. On the other hand, we believe the Grant–Gunton prefactor probably errs excessively in the opposite direction.

3. Results

3.1. Determination of kinetic quantities

In Figs. 1 and 2 are plotted the sorted nucleation times vs. the quantity $-\ln[N_l(t)/N_0]$ for 375 independent liquid $(\mathrm{RbCl})_{108}$ clusters quenched to 600 K. From the limiting slope, intercept, and behavior in the transient regime can be determined the rate, time lag, and reduced moment in accordance with Eqs. (5) and (6). It should

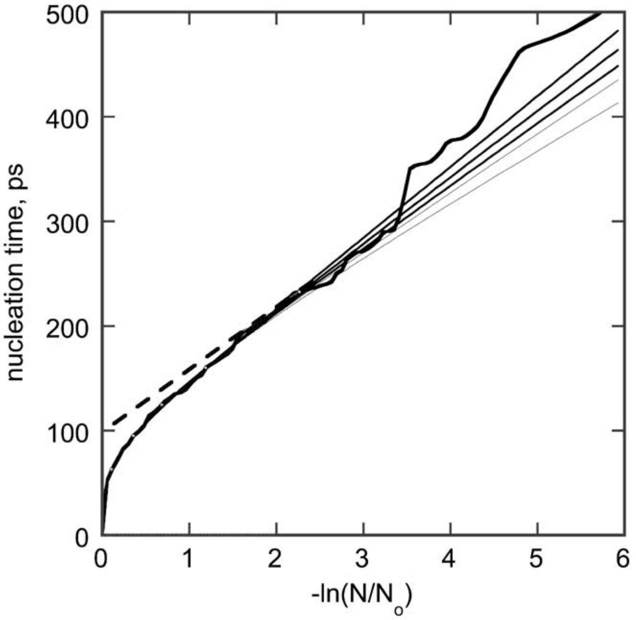

Fig. 1. Heavy curve, 375 nucleation times as a function of $-\ln(N/N_0)$. Lighter solid curves portray a family of calculated nucleation times based on least squares fits of all of the observed times, assuming, top to bottom, reduced moments of 1.1, 1.3, 1.6, 2.0, and 3.2. The severe deviations of the observed times from calculated times at large values of $-\ln(N/N_0)$ is a consequence of the large uncertainty in the stochastic times in the region where nucleation events are very rare. The dashed line corresponds to a reduced moment of unity whose intercept is the nucleation time lag. This line was constructed from the kinetic data obtained in the least squares analysis of all nucleation times together with the reduced moment derived from an examination of the transient region (see Fig. 2).

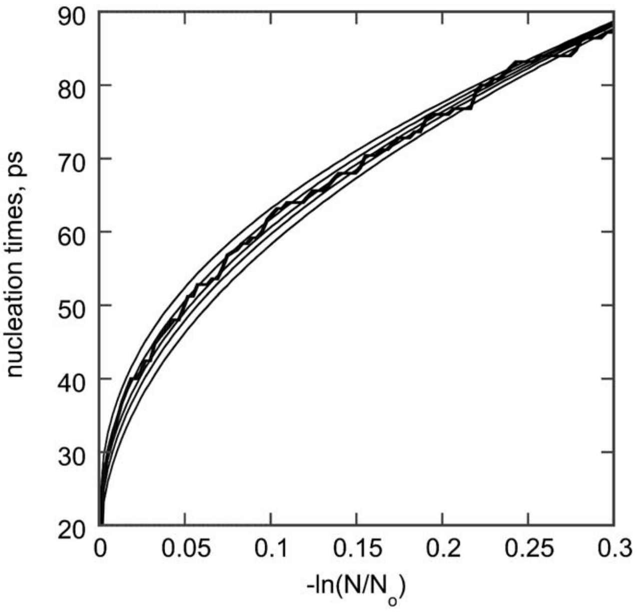

Fig. 2. Heavy curve, times of nucleation for the first 25% of the nucleation events, namely, the region of transient nucleation. Solid curves, a family of calculated nucleation times based on least squares fits of all 375 observed times assuming, top to bottom, reduced moments of 1.3, 1.4, 1.5, 1.6, and 1.8. The best fit is for a moment of 1.48. Note that the line for $M_R = 1.0$ is off-scale in this plot.

be noted that the irregular nucleation times plotted in Fig. 1 beyond a value of 3.5 for the abscissa span a region in which points have become very sparse and far apart (and, hence, this region is not weighted heavily in an optimally weighted least squares analysis). Put in a different way, 25% of the nucleation times are found within the first 5% of the range of the abscissa plotted in Fig. 1, and 19% are found in the second 5%. By contrast, only 3 nucleation events (0.8%) occur in the last 20% of the range. Analyses of the entire set of times are used to derive the nucleation rate and time lag, each analysis being carried out for one member of a set of assumed reduced moments. Ideally, the reduced moment giving the best fit of the times shown in Fig. 1 might be expected to correspond to the expectation value of the moment.

In practice [6,7], it has been found to be more reliable to constrain the rate and time lag by fitting the *entire* set of data, as stated above, and to infer the reduced moment by finding the best fit of observed and calculated curves *in the transient region* (roughly the first 25% of the nucleation times). Such a comparison is illustrated in Fig. 2, where calculated nucleation times cover a much narrower range of reduced moments than the calculated times portrayed in Fig. 1. Results so determined are $2.16(0.15) \times 10^{36}\,\mathrm{m}^{-3}\,\mathrm{s}^{-1}$ for the nucleation rate, 98.6(8.7) ps for the time lag, and 1.48(0.18) for the (dimensionless) reduced moment, with standard deviations shown in parentheses.

3.2. Derivation of interfacial free energy and interfacial thickness

As described in detail in paper I [3], an excess free energy per unit area can be derived for the liquid-to-solid interface from the steady-state nucleation rate by applying the classical nucleation theory (CNT). In view of the inexactness of the CNT, there are ambiguities in the result. In the Gibbs model [15,16] of the structural fluctuations corresponding to nuclei, what is taken to be the critical nucleus is a fictional, quasi-spherical element of solid with thermodynamic properties of the *bulk-like* phase having the same chemical potential as possessed by the actual structural fluctuation corresponding to the nucleus. With the Gibbs convention, the interfacial free energy derived is $\sigma_{sl} = 0.052\,\mathrm{J/m^2}$. Alternatively, if the actual structural fluctuation itself is considered, adopting the heat capacities of the liquid and solid cluster rather than those of the bulk, our estimate for the interfacial free energy is $0.048\,\mathrm{J/m^2}$, a result differing little from the former one. This difference cannot be taken as a true uncertainty, however, because of the approximate nature of the CNT. If, on the other hand, the interfacial thickness defined by Grànàsy's diffuse interface theory (DIT) is derived (see paper I [3] for details), the choice of heat capacities makes a larger difference. The Grànàsy thickness according to the Gibbs model is $\delta = 1.56\,\text{Å}$ in comparison with the alternative value of 1.96 Å. Here it is well to point out that while the Grànàsy thickness δ derived from the nucleation rate yields a physically plausible value for the interface thickness, it bears no direct connection with either the well-known Tolman δ [17] or the diffuseness of the order parameter corresponding to the profile of the solid–liquid density difference.

4. Discussion

4.1. Comparison of the present results with the results of the prior study

A direct comparison cannot be made precisely because a polarization component was added to the potential function of the present study, a component which was neglected in the earlier investigation [3]. The effect of polarization should be to increase the free energy barrier to nucleation and thereby decrease the nucleation rate [18]. Nevertheless, the rate determined in the present work is three-fold *higher* than in the earlier study. The time lag is also considerably longer. The effect of neglecting the reduced moment in the earlier treatment would be expected to result in a lower rate and time lag but not by as large an amount as seen. Moreover, statistics based on this neglect, i.e., based on the application of Eq. (2) instead of Eq. (5), give an unrealistically low estimate of uncertainties. The principal reason [6,7] for the substantial differences is the much smaller sample size of 17 independent clusters in the earlier study vs. 375 in the present. To be fair, it should be pointed out that a treatment to account properly for the transient regime was not available in the prior study.

According to the classical nucleation theory as applied to the present system, the three-fold difference between the present and earlier nucleation rates should only make an 8% difference in the derived interfacial free energy. Therefore, within the limits of validity of the CNT, the interfacial free energy is less subject to error than the kinetic parameters upon which it is based.

4.2. Interfacial properties

Whether the derived interfacial free energy is reasonable or not can be addressed by comparing it with an empirical relation found by Turnbull [19] to apply to a number of substances. He discovered that the interfacial free energies he had acquired for substances composed of approximately spherical molecules were proportional to heats of fusion per unit area of the interface, or

$$\sigma_{sl} \approx k_T \Delta\bar{H}_{\text{fus}}/(\bar{V}_s^2 N_A)^{1/3}, \tag{7}$$

where k_T is a proportionality constant with a value of about 0.45 for metals and 0.32 for a series of metalloids and non-metals. Eq. (7) does not apply to long-chain molecules [20]. Although Turnbull's observed interfacial free energies had been based on the CNT approximation, they had been determined at shallow supercoolings where the CNT is most accurate. Turnbull's relation has been applied many times in the literature by other workers who, however, disagree upon whether the heat of fusion is supposed to correspond to the value at the melting point or to that at the temperature of supercooling. If we use the latter convention with the Gibbs bulk-like fluctuation model for σ_{sl}, we obtain a value for k_T of 0.32. This proves little but it does suggest that the value of σ_{sl} is plausible.

It is worth pointing out that potassium iodide and rubidium chloride might be expected to yield similar results, because each contains a relatively large ion and a mid-sized ion, and the melting points and heats of fusion are similar. This is found to be the case [21]. Comparisons of the former with the later at comparable temperatures are, for the interfacial free energy (0.046 vs. 0.048 J/m^2) and for the DIT interface thickness (2.3 vs. 2.0 Å) according, in each case, to the cluster heat capacities. Cluster heat capacities for the crystalline phase are very nearly the same as those for the bulk crystalline phase but for the liquid phase, cluster heat capacities are much larger, consistent with their much larger coefficients of thermal expansion (see Ref. [22]).

4.3. Time lag

The spontaneous behavior of the molecules undergoing nucleation in the supercooled clusters produced fleeting structural fluctuations that resulted in a gradual buildup of embryos. As a consequence of this process there was a time lag before a steady state of nucleation was attained. The value of the time lag derived from the MD simulations was 99 ps, as reported in the previous section. This value was based on the estimate of the reduced moment inferred from the observed nucleation times in the transient region. The duration of the derived time lag depends sensitively upon the reduced moment adopted. For example, over the range of moments 1.3, 1.4, 1.5, 1.6, and 1.8 represented in the calculated curves of Fig. 2, the corresponding least squares time lags derived from the nucleation data were 82, 91, 101, 111, and 137 ps. It is of interest to compare the derived time lag with a theoretical prediction.

A number of theoretical treatments of the nucleation time lag have appeared. In a review of such theories by Kelton, Greer, and Thompson (KGT) [23], the treatment of Kashchiev [24] was singled out as being the best of those considered. Kashchiev derived the following relation for the time lag, as expressed in terms of the KGT approximation for the probability of attachment of a molecule in the mother phase to a nucleus

$$t_0 = [kT(n^*)^{1/3} v_m^{2/3}]/(6D\Delta g) \tag{8}$$

where n^* is the number of molecules in the critical nucleus, v_m is the volume per molecule of the solid, D is the coefficient of diffusion in the melt, and Δg, the free energy of fusion per molecule. If the classical nucleation theory is used to give a value for the size of the critical nucleus, a non-rigorous approximation moderated by the fact that n^* appears only to the 1/3 power, Eq. (8) reduces to

$$t_0 \approx \tfrac{1}{3}\left(\frac{4\pi}{3}\right)^{1/3}\left(\frac{v_{\mathrm{m}}^{4/3} kT\sigma_{sl}}{D\Delta g^2}\right), \tag{9}$$

Inasmuch as the physical properties in Eq. (9) were not in any way used to derive the time lag from the kinetic data of the MD simulations, it is of interest to find whether Kashchiev's expression predicts a value of the same order of magnitude as that found in the simulations. If the quantities listed in Table 1 of the appendix are inserted into Eq. (9), the result is 99 ps if the (Gibbs) bulk-like properties are used or 123 ps if the cluster properties are used. It is noteworthy that these values are close to the values derived from the simulations. As noted by KGT [23], some of the other theoretical treatments had differed by more than a factor of 4 from Kashchiev's.

4.4. Reduced moment

Finally, it is worthwhile to discuss the reduced moment. Wu [5], in his treatment of moments, provided no guidelines regarding the value to be expected, and simply suggested that the moment be determined by experiment. We know of no reports of such determinations by experiment or by simulation. On the other hand, Kashchiev's treatment [24] provided more specific detail than Wu's about the transient period in which nuclei materialize and disappear. His treatment says nothing explicitly about the reduced moment but a comparison with Wu's theory yields a value of almost exactly $M_{\mathrm{R}} = 1.4$ (see Ref. [6]). In discussing alternative treatments of transient nucleation, Wu criticized Kashchiev's approach as being based on rather severe approximations. Therefore, because of the so-far unknown behavior of the buildup of nuclei before the steady state, and in view of the uncertain validity of the Kashchiev treatment, it is of interest that the present investigation does provide a result characterizing the transient regime. The simulations of the freezing of small rubidium chloride clusters yield a value for the reduced moment of 1.48(0.18) agreeing, within its uncertainty, with the Kashchiev value. Whether that result will apply to larger clusters and to clusters of different composition is currently being explored in this laboratory.

Table 1
Physical properties adopted in calculations

Properties	Value or expression	Ref.
T_{m} (K)	996	[25]
$\Delta\bar{H}_{\mathrm{fus}}$ (J/mol)	23723	[25]
$\Delta C_{\mathrm{p}}^{\mathrm{bulk}}$ [$\mathrm{s}\rightarrow l$] (J/mol K)	14.86–0.01041 T	[25]
$\Delta C_{\mathrm{p}}^{\mathrm{cluster}}$ [$\mathrm{s}\rightarrow l$] (J/mol K)	$27.90–1.377 \times 10^{-5}$ T	This work
V_{solid} (m^3/mol)	4.32×10^{-5}	CRC handbook
V_{liquid} (m^3/mol)	5.79×10^{-5}	CRC handbook
D $(\mathrm{RbCl})_{\mathrm{liquid}}$ (m^2/s)[a]	$2.09 \times 10^{-7}\exp(-3883/\mathrm{T})$	[3]
σ_{lv} (J/m^2)	$0.145–6.979\,10^{-5}$ T	[26]

[a] Note that this value is based on the potential of Ref. [3], not that of the present work.

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Appendix A

Physical constants adopted in the present analysis differed somewhat from those in Paper I (3), partly because better values were found in the literature and partly because of updated computations in the present work. The updated constants are listed in Table 1.

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