

Molecular Dynamics Investigation of the Nucleation Barrier and Prefactor in the Freezing of (NaCl)₁₀₈ Clusters

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Received: June 11, 1998

Nucleation rates for the freezing of molten clusters of salt were determined in molecular dynamics simulations at 400, 500, 525, 550, and 580 K. These were analyzed in terms of the free energy of formation of the critical nucleus implied by the classical theory of homogeneous nucleation and by the diffuse interface theory of Granasy. Both the classical prefactor based on activated diffusion across the interface and the Grant–Gunton prefactor were examined. When each formulation of nucleation theory was adjusted to force $J(T)$ to agree with the simulation at 525 K, the calculated rates corresponding to the four combinations of prefactor and exponential factor diverged rapidly from each other as the temperature departed from 525 K. This extreme incompatibility of the different formulations of nucleation theory was due as much to the different prefactors as to the different nucleation barriers. Such an incompatibility has been paid little heed, partly because it is less evident in studies at less extreme supercooling. Of the formulations considered, the classical nucleation theory with the classical prefactor and the diffuse interface theory with the Grant–Gunton prefactor were ruled out by the molecular dynamics simulations in combination with a criterion to estimate freezing rates at the evaporative cooling temperature. Nevertheless, this result, considered in light of the known flaws of the classical nucleation theory, suggests that the Grant–Gunton prefactor is excessively high. Also, the classical prefactor, which is known not to be universally applicable, appears to err in the opposite direction. Although theorists have devoted most of their efforts on nucleation in condensed phases to the free energy barrier, it is clear that refinement of the prefactor is of comparable importance.

Introduction

Unresolved aspects in the theory of homogeneous nucleation in condensed matter stand in the way of physically realistic interpretations of nucleation experiments. It is generally assumed that the rate of production J of critical nuclei can be expressed as

$$J(T) = A \exp(-\Delta G^*/k_B T) \quad (1)$$

where ΔG^* is the free energy barrier to the formation of a critical nucleus of the new phase in a matrix of the old phase and A is a prefactor originally based on the rate of transport of molecules across the boundary separating the two phases.

One possible way to discriminate between alternative theoretical formulations of nucleation theory is to carry out molecular dynamics (MD) simulations of phase changes which are unbiased by preconceptions of properties of the core of the critical nucleus or of properties of the interface between the phases. It has been shown in a number of studies^{1–6} that the classical theory of nucleation (CNT) is only qualitatively correct in its treatment of ΔG^* in taking the free energy barrier to be

$$\Delta G^* = 16\pi\sigma_{sl}^3/[3(\Delta G_v + w')^2] \quad (2)$$

where σ_{sl} and ΔG_v are the interfacial free energy of the solid–liquid boundary per unit area and the free energy of freezing per unit volume, respectively. For a nucleus containing but a handful of molecules, both quantities are assumed to have the values characteristic of bulk phases. The term w' is the work of changing the surface area of the liquid phase due to the

volume change on freezing⁷ (see Appendix). Density functional theory has given significantly different results for several model systems but has yet to be formulated in such a parametrized way that it can be applied to general systems by experimentalists. Granasy, on the other hand, has formulated a diffuse interface theory (DIT)^{8–11} of homogeneous nucleation which is as simple to apply in analyses as the CNT and which, at least in Granasy's hands, seems to be competitive in accuracy to the density functional theory. Regrettably, theorists have not invested as much effort in refining the prefactor as they have in treating ΔG^* . This is unfortunate because deficiencies in the prefactor appear to be comparable in effect to those in the free energy barrier, at least at the deep supercooling characteristic of the new supersonic nucleation experiments and the simulations. The two model prefactors which have been proposed for freezing are the classical prefactor^{12–14} based on the activated diffusion of molecules across the liquid–solid interface and the Grant–Gunton prefactor¹⁵ based on thermal diffusion.

Recently, a preliminary MD study of nucleation in the freezing of clusters of salt compared the consequences of applying the CNT and the DIT in analyses of the molecular dynamics (MD) results for $J(T)$.¹⁶ It failed to resolve the issue. For one thing, the range of temperature studied was too small. For another, only one model of the prefactor was considered. The present investigation was initiated on the same system to cover a wider range of temperature. It was also undertaken to compare the results of applying the classical prefactor with those of adopting the Grant–Gunton prefactor. As will be discussed subsequently, Broughton and coworkers^{17,18} have shown in simulations of the freezing of Lennard–Jones systems that the

rate of transfer of molecules from the liquid to the solid phase is much less inhibited by the greatly diminished coefficient of diffusion at low temperatures than is implied by the classical prefactor. In this regard the Grant–Gunton prefactor is of interest because it does not imply such a decline of transfer with increasing viscosity. On the other hand, the Grant–Gunton prefactor appears intuitively, at least, to err in the opposite direction at deep supercooling since it tends to increase steadily with cooling. Because the freezing of salt clusters in MD runs takes place at extreme supercooling, it was supposed that the nucleation kinetics might shed some light on which type of prefactor is appropriate for that system.

Computational Details

Molecular dynamics simulations were carried out for (NaCl)₁₀₈ clusters as described in detail in the earlier paper.¹⁶ Clusters with free boundaries were chosen to avoid artifacts of periodic boundary conditions. Computations were performed on an IBM RISC workstation with a modified version of the program MDIONS¹⁹ incorporating the well-known Born–Mayer–Huggins potential function.²⁰ Nucleation temperatures ranged from 400 to 580 K, rates determined in each case from 16 independent nucleation runs.

Details of applying the Grant–Gunton prefactor¹⁵ were discussed in detail in paper 1.¹⁶ There are several variants of the more commonly applied prefactor, the classical prefactor. In its earliest formulation Turnbull and Fisher,¹² and Buckle,¹³ treated it as an activated diffusion via absolute rate theory, inferring the activation energy from the viscosity of the liquid. Bartell and Dibble²¹ sought to incorporate the non-Arrhenius behavior often occurring at low temperatures by translating the Turnbull–Fisher–Buckle Arrhenius formulation into one expressed in terms of viscosity via Eyring’s absolute rate theory of viscosity,²² then extrapolating to the non-Arrhenius regime. Kelton, Greer, and Thompson¹⁴ formulated the prefactor in terms of rate of diffusion. In the present investigation there is little difference between the alternative formulations and we adopt the latter formulation which reduces to

$$A = 16(3/4\pi)^{1/3}(\sigma_{sl}/k_B T)^{1/2} D a^{-2} v_m^{-1/3} \quad (3)$$

for the CNT, where D is the coefficient of diffusion, a is a jump distance across the boundary, and v_m is the volume per molecule. For the DIT the interfacial free energy dependence is replaced by one based on the interfacial thickness.^{8–11} As seems to be the custom in the field, we take the jump distance to be the cube root of the molecular volume. For coefficient of diffusion we used the mean of the value for the cation and anion in the melt.²³

Our assumptions regarding the volume of the salt clusters considered to be effective in nucleation and our criterion to establish the time of nucleation of the individual runs are discussed in detail in paper 1.¹⁶ Rather than using the mean time of nucleation to estimate the nucleation rate we use the slope of the first-order decay of the population of unfrozen clusters. This avoids, to the extent that it can be avoided, the correction for the nucleation time lag. Time lags, in principle, can be determined from the intercept of the decay curve at zero decay. Our intercepts, however, showed no consistent correlation with the temperature.

Additional assumptions include the use of certain bulk thermodynamic quantities for salt in place of quantities inferred for a system governed by the potential function adopted. These are identified in the Appendix. We add to our existing results

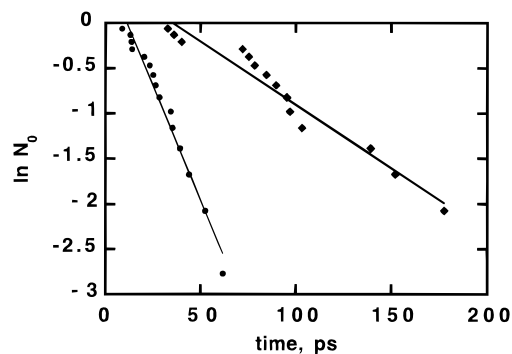


Figure 1. Decay of population of liquid clusters with time from MD runs at 400 K (●) and 580 K (◆).

TABLE 1: Parameters Derived from MD Nucleation Rates via the CNT and DIT with the Classical and Grant–Gunton Prefactors^a

T	CNT		DIT			ξ	
	$\sigma_{sl}(A_{cl})$	$\sigma_{sl}(A_{GG})$	$\delta(A_{cl})$	$\sigma_{sl}(A_{cl})_{\infty}$	$\delta(A_{GG})$		$\sigma_{sl}(A_{GG})$
400	no soln	120.0	no soln		3.30	0.61	
500	62.0	117.7	1.19		2.40	0.82	
525	68.4	117.6	1.22		2.25	0.87	
550	78.8	119.6	1.36		2.22	0.92	
580	80.4	117.8	1.30		1.98	0.99	
$\sim T_m$			(1.33)	150.1	(2.10)	254.0	2.20

^a Interfacial free energies σ_{sl} in mJ/m², interface thicknesses δ and correlation lengths ξ in Å. Quantities in parentheses imposed.

of nucleation runs at 500, 525, and 550 K those calculated at 400 and 589 K.

Results

The optimum cubic shape of the crystalline clusters and the considerable deviation from sphericity of the molten clusters were covered in paper 1.¹⁶ Molten clusters froze to single crystals in all but four runs at the deepest supercooling where twinning was observed. Crystals exhibited 100 faces almost exclusively but grew from the melt at such high velocities that their final shapes included steps, giving the completely frozen clusters a significantly higher mean potential energy than the optimum.

Decay curves for the runs at 400 and 580 K are plotted in Figure 1. A kinetic parameter usually considered to represent the interfacial free energy σ_{sl} of the solid–liquid boundary can be calculated from the nucleation rate if the CNT is applied (via eqs 1 and 2 and the expression for the prefactor adopted for analysis). If the DIT is applied an interfacial thickness parameter, δ , is derived. From it can be estimated the interfacial free energy at temperatures close to the freezing point.^{8–11} Of course, the value of σ_{sl} obtained depends upon the prefactor adopted in the analysis. In Table 1 we list the interfacial free energies corresponding to the various combinations of prefactor and nucleation theory for the runs at the various temperatures. We also list the interfacial thickness parameter of Granasy along with the interfacial correlation length ξ for the Grant–Gunton prefactor according to the prescription proposed in paper 1.¹⁶

Granasy has suggested that the essential difference between the CNT and his DIT is the expectation that the parameter σ_{sl} should be approximately constant over a fair temperature range in the former theory whereas it is the parameter δ that is constant in the latter.²⁴ To assess these expectations we compare the MD nucleation rates with rates calculated according to the CNT (with constant σ_{sl}) and the DIT (with constant δ) in Figure 2.

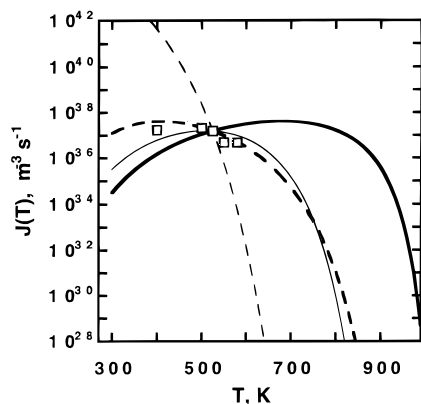


Figure 2. Temperature dependence of rates of homogeneous nucleation. Squares, from molecular dynamics simulations. Heavy solid curve, classical nucleation theory (constant σ_{sl}) with classical prefactor; light solid curve, diffuse interface theory (constant δ) with classical prefactor; heavy dashed curve, classical nucleation theory (constant σ_{sl}) with Grant–Gunton prefactor; light dashed curve, diffuse interface theory (constant δ) with Grant–Gunton prefactor.

Calculated rates were forced to pass through the MD rate at 525 K by adjusting σ_{sl} (CNT) or δ (DIT).

Discussion

Derived interfacial free energies listed in Table 1 convey a mixed message. Differences between the various values listed in the table are a reflection of how much larger the Grant–Gunton prefactor is than the classical. The Grant–Gunton prescription requires a much larger value of σ_{sl} to reduce the factor $\exp(-\Delta G^*/k_B T)$ in eq 1 sufficiently to reproduce the MD nucleation rate if the CNT is adopted. By contrast, the classical prefactor is so much smaller that, at 400 K, it becomes *smaller than the nucleation rate* when the difference between observed and calculated nucleation rates is minimized (they cannot be made the same). Such behavior is unphysical. This rules out the classical prefactor whether in combination with the CNT or DIT, at least in the present system at 400 K. Other evidence against the classical prefactor is cited below. Values of σ_{sl} , derived from the nucleation rate can be compared with the value of 115 mJ/m² suggested by the empirical rule of Turnbull²⁵ which makes σ_{sl} proportional to the heat of fusion, ΔH_{fus} at the melting point. The better agreement between this quantity and the value based on the Grant–Gunton prefactor cannot be taken as support for the Grant–Gunton prefactor in combination with the CNT for two reasons. First, Turnbull's relation was calibrated with experimental values based on the CNT with the classical, not the Grant–Gunton, prefactor. Next, Turnbull's calibration was at a much milder supercooling. Some authors have suggested that the proportionality should be between σ_{sl} and $\Delta H_{fus}(T)$ at the nucleation temperature, not $\Delta H_{fus}(T_m)$ at the melting point. Although certain evidence²⁶ suggests that such a temperature correction is exaggerated, it does turn out that such a temperature correction would favor the values based on the classical prefactor over that of the Grant–Gunton factor (excluding, of course the 400 K run). But undermining the relevance of values in either of the CNT columns in Table 1 are the much higher values implied at low supercoolings (where the DIT and the CNT become equivalent and asymptotically correct) calculated by Granasy's prescription utilizing a temperature-independent δ . Indeed, these values are so much higher even than implied by the empirical Turnbull relation as to suggest that the Turnbull proportionality constant does not apply to salt, a system not included in the original calibration. Because

the Turnbull relation has enjoyed a noteworthy popularity in the recent literature, it seemed worthwhile to point out its ambiguous role in diagnoses of the present system.

Likewise, little can be inferred from the interfacial thickness parameter δ of the DIT because its physical significance is not well understood. Proposed to be the distance between the mean surfaces at which the entropy, on the one hand, and the enthalpy change from their values in the old phase to their values in the new, δ is of the order of magnitude of the correlation length ξ . Unlike the correlation length which depends markedly upon the temperature, δ is considered to be constant in freezing transitions according to Granasy. At the present state of the DIT, then, δ does not shed much light on the choice between prefactors. Evidence that is more enlightening is discussed next.

The most striking result in Figure 2 is the rapid divergence of the calculated $J(T)$ curves from each other as the temperature deviates from the reference temperature. This conspicuous incompatibility of the various formulations of nucleation theory is not only due to the difference between the treatments of the nucleation barriers in the CNT and DIT. Equally important is the contrasting behavior of the prefactors. The reason for the divergence of the prefactors is clear enough. Since the classical prefactor is based on activated molecular jumps, it rapidly decreases with deeper supercooling as the viscosity of the liquid climbs. On the other hand, the Grant–Gunton prefactor is based on the transfer of heat, not of molecules, and thermal conductivity is not a steep function of temperature. It is the correlation length ξ in the Grant–Gunton prefactor that has the largest effect. It decreases substantially as the system cools, sharpening the interface (a result supported by density functional computations^{27–29}) and this increases the prefactor which is inversely proportional to the fourth power of ξ .¹⁵

The molecular dynamics results are insufficiently accurate to lead to a definitive choice of the various theoretical treatments considered. Nevertheless, for the system of salt, at least, Figure 2 would seem to eliminate the CNT with the classical prefactor and the DIT with the Grant–Gunton prefactor. Tempering this conclusion somewhat is the prediction by Turnbull³⁰ and Spaepen³¹ that the negative excess entropy expected for the solid–liquid interface tends to make σ_{sl} increase with temperature. This would tend to rotate the calculated CNT curves clockwise. Whether the effect for salt is significant is completely unknown.

Another source of information has some bearing on possibilities. It is the expected nucleation rate for freezing at the so-called evaporative cooling temperature^{32,33} of clusters of a given material. For salt this temperature is about 880 K.^{12,33} The upper limit of the nucleation rate can be estimated with some confidence from prior experience with clusters. Studies of some five dozen materials led to an empirical criterion,³⁴ later corroborated by kinetic arguments,³⁵ connecting the phase of clusters generated in supersonic flow with thermodynamic quantities. According to this criterion,³⁵ the rate of homogeneous nucleation in salt at the evaporative cooling temperature must be lower than $10^{28} \text{ m}^{-3} \text{ s}^{-1}$. Referring to Figure 2, this would eliminate only the classical nucleation theory with the classical prefactor, an alternative already eliminated by criteria considered previously.

The four choices proposed in the foregoing do not cover the full range of possibilities, of course. For example, an appreciably higher prefactor than given by the classical formulation in combination with the DIT would accord even more favorably with the MD data. In view of the known deficiencies of the CNT^{1–6} it appears that the Grant–Gunton prefactor, which

limits the rate of transfer of molecules to the new phase only by the rate of heat transfer, is excessive. It is not surprising that the CNT, which disregards the thickness of the interface between the solid and liquid phases, appears to be inferior to the DIT which does, in some manner, take the thickness into account. Still, it should be mentioned that there is no known relation between Granasy's thickness parameter δ and other measures of the thickness such as Tolman's δ^{36} and the correlation lengths in the Grant–Gunton¹⁵ and density functional treatments.^{27–29} With respect to prefactors, the work by Broughton and co-workers^{17,18} suggests that the classical prefactor must be inadequate for some systems. That is, the molecular jump rate in an argon-like system at low temperature did not fall off as precipitously as the rate of diffusion. We speculate that one characteristic of liquids which may govern whether activated diffusion or some other bottleneck limits the prefactor is the degree of “fragility” of the liquid.^{37,38}

According to Angell and co-workers, liquids which follow Arrhenius behavior all the way or nearly all the way to the glass temperature are “strong.” They form glasses readily. “Fragile” liquids display deviations from Arrhenius behavior, the more extreme, the greater the degree of “fragility.” Granasy's experience with strong liquids suggests that the classical prefactor applies to them quite well.^{8–11} Fragile liquids can begin to deviate markedly from the Stokes–Einstein (SE) law at deep supercooling, with coefficients of diffusion greatly exceeding those expected from the viscosity.³⁸ A deviation from the classical prefactor in the direction of the Grant–Gunton prefactor is probably characteristic of fragile liquids. But a free-jump (nonactivated) model³⁹ based on Broughton's growth rates¹⁸ does not give as large a prefactor as the Grant–Gunton model. Molten salt is unlikely to be a strong liquid or an extremely fragile one (to our knowledge it has not been quantitatively characterized). But even the deviation of the coefficient of diffusion from that implied by the viscosity via the SE law cannot be the full story because it cannot account for Broughton's results.¹⁸ The reason for the present discussion is to call attention to the unsatisfactory state of the prefactor in nucleation theory and to point out certain complexities in liquid systems that will have to be addressed before theorists can expect to resolve the matter.

Relatively little effort has gone into the development of the theory of the prefactor in comparison with the effort devoted to the nucleation barrier, partly because the disagreement between prefactors was not so evident in prior studies at more modest supercoolings. It is to be hoped that new results on nucleation at deep supercooling will provide an incentive for refining the theory.

Acknowledgment. This research was supported by a grant from the National Science Foundation.

Appendix

Physical quantities adopted in the analyses are given in Table 2. The correlation length ξ , envisaged as pertaining to the Cl[−] ion in a fcc lattice, was estimated from the ratio of correlation lengths to lattice constants of the fcc substances Ar, Na, and Pb reported by Oxtoby and Harrowell.⁴⁰ There is a difference of a factor of 2 between the defined correlation lengths of ref 40 and ref 15. The temperature dependence of ξ used in the present investigation was estimated from the results in refs 27–29 and may not persist to the supercoolings encountered here.

TABLE 2: Physical Properties Adopted for NaCl

property	value	ref
T_m , K	1073	a
T_b , K	1730	a
$\Delta H_{\text{fus}}(T_m)$, J/mol	30180	a
$C_p(\text{l}) - C_p(\text{s})$, J/(mol K)	17.5	this research ^b
V_{sol} , m ³ /mol	26.7×10^{-6}	a
V_{liq} , m ³ /mol	31.4×10^{-6}	c
λ , w/(m K)	$0.10 + 0.0008T$	d
ξ , Å	$2.2(T/T_m)^{1.3}$	see Appendix
$D(\text{Na}^+)$, m ² /s	$332 \times 10^{-9} e^{-3955/T}$	23
$D(\text{Cl}^-)$, m ² /s	$302 \times 10^{-9} e^{-4222/T}$	23
σ_{lv} , J/m ²	$0.1906 - 7.125 \times 10^{-4} T$	c
$\log p$, Torr	$20.929 - 11495/T$	
	$-3.526 \log T$	e

^a CRC Handbook of Chemistry and Physics, 63rd ed.; CRC Press: Boca Raton, FL, 1982. ^b Applicable to cluster in range of interest but may not be appropriate to the bulk. ^c International Critical Tables of Numerical Data, Physics, Chemistry, and Technology; McGraw-Hill: New York, 1926–1939. ^d Smirnov, M. V.; Khokhlov, V. A.; Filatov, E. S. *Electrochim. Acta* **1987**, 32, 1019. ^e Barton, J. L.; Bloom, H. J. *Phys. Chem.* **1956**, 60, 1413, information used to estimate the evaporative cooling temperature.

The correction term w' of eq 2 is

$$w' = (2\sigma/r_0)(\rho_l - \rho_s)/\rho_l \quad (4)$$

where $2\sigma/r_0$ is the Laplace pressure exerted by the liquid of density ρ_l , on the solid nucleus of density ρ_s . This correction was made in applying the CNT but was neglected in the DIT because the Granasy formalism has not yet been concerned with it. In calculating the interfacial free energy of the solid–liquid interface at low supercooling, it was assumed, in accordance with Granasy's postulate, that the interface thickness parameter is constant all the way to the melting point. The value was selected to be the mean of the derived values at 550 and 580 K. In the limit at the melting point the DIT and CNT are equivalent so that ΔG^* calculated via the DIT with the δ from the MD runs at lower T can be equated with ΔG^* of eq 2 with $w' = 0$ (because the value pertains to the bulk, not to a small cluster), yielding σ_{sl} .

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