

Classical nucleation theory with a size dependent interfacial tension: $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$ crystal nucleation

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Manuscript received 25 July 1991

Nucleation rates for lithium disilicate are calculated as a function of temperature using a modified version of the classical nucleation theory which contains a radius dependent surface tension of the form proposed by Tolman. Two different methods are used to find the parameters in the expression for the surface tension. The results are compared with experiment. Also, the effective temperature dependence of the surface tension produced by this procedure is compared with previous results.

The understanding and control of crystal nucleation and growth in polymeric, metallic, inorganic, and biological materials have tremendous importance for a wide range of high technology applications such as optical memories, artificial bones and teeth, low thermal expansion glass ceramics, cryopreservation, etc. Also, the prevention of spontaneous devitrification is required for the production of homogeneous, defect free glasses. Thus, it is essential to gain basic knowledge concerning the kinetics of crystal nucleation through theoretical and experimental studies.

Classical nucleation theory⁽¹⁾ has been used extensively by materials scientists to predict nucleation rates. However, the steady state crystal nucleation rates (I_0) calculated by the theory are many orders of magnitude smaller than the experimental values for inorganic glasses.⁽²⁻⁵⁾ Two main assumptions of the theory could be responsible for its failure to predict experimental nucleation rates accurately.

First, the activation energy for atomic jumps at the interface between the nucleus and the matrix, the kinetic part of the classical expression, is normally associated with that of ordinary diffusion and is eliminated in favour of the shear viscosity through the use of the Stokes-Einstein equation. However, this procedure has not been justified. Recently, a more

rigorous approach, which makes use of the induction times for nucleation instead of viscosity, was suggested and tested.⁽⁶⁾ Neither the magnitude nor the temperature dependence of the nucleation rates were well described by theory when the latter procedure was used. A good fit could be obtained only in the temperature range above the temperature of the maximum nucleation rate. Therefore, discrepancies between theory and experiment were found with both approaches implying that other problems exist with the classical nucleation theory.

Second, capillarity approximation is the assumption that the free energy of a nucleus can be written as the sum of a bulk and surface free energy and that the surface tension (surface energy/area) is that of a flat interface and is independent of nucleus size. However, use of a constant liquid-crystal surface tension produces large discrepancies between measured and predicted I_0 . James⁽²⁾ observed that classical nucleation theory could be made to agree with experimental data by employing a temperature dependent interfacial surface tension whose parameters were fixed by fit to experimental data. Although this procedure has been used by others^(7,8) for different types of materials, the use of a temperature dependent surface tension has been criticised by Oxtoby.⁽⁹⁾

If the critical nucleus is small, then its surface free energy could be quite sensitive to its radius. Tolman⁽¹⁰⁾ and others^(11,12) have developed theories to account for this size dependence and applied them to the nucleation of liquid droplets from a vapour. The objectives of this article are (1) to examine the effect of employing a radius dependent surface tension on the agreement between classical nucleation theory and experiment for $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$ (LS_2) crystal nucleation and (2) to compare the effective temperature dependence introduced by the latter procedure with the one used by James for this system.

Theory

In classical nucleation theory an additive process is assumed where an embryo is enlarged atom by atom until a critical nucleus is assembled. For spherical, stoichiometric nuclei in a viscous matrix, the change in free energy in forming an embryo of radius r , $W(r)$ is given by

$$W(r) = 4\pi r^3 \Delta G_v / 3 + 4\pi r^2 \sigma_\infty \quad (1)$$

where ΔG_v is the free energy difference per unit volume between supercooled liquid and crystal (J/m³) and σ_∞ is the macroscopic surface energy (J/m²). In classical nucleation theory the interfacial tension is assumed to be constant. The steady state nucleation rate, I_o , is given by

$$I_o = A \exp\left(\frac{-\Delta G_d}{RT}\right) \exp\left(\frac{-W^*}{RT}\right) \quad (2)$$

with

$$A = 2Nv^{1/3}(kT\sigma_\infty)^{1/2}/(3\pi\lambda^3) \quad (3)$$

where N is the total number of molecules per unit volume, v is the volume per formula unit, λ is the atomic jump distance, ΔG_d is the activation free energy for transport across the solid-liquid interface (kinetic barrier), and W^* is the work needed to form a mole of nuclei and is given by

$$W^* = 16\pi\sigma_\infty^3/(3\Delta G_v^2). \quad (4)$$

The kinetic barrier is usually, but not invariably, assumed to be related to that for viscous flow. Here, we opt to use this version of classical nucleation theory and Equation (2) therefore simplifies to

$$I_o = \left(\frac{A'T}{\eta}\right) \exp\left(\frac{-W^*}{RT}\right) \quad (5)$$

where η is the viscosity at temperature T , and A' is given by

$$A' = \left(\frac{2}{3\pi}\right) \left(\frac{N_a}{v}\right)^{5/3} \left(\frac{k\sigma_\infty}{T}\right)^{1/2}. \quad (6)$$

In writing Equation (6), following James,⁽²⁾ it has been assumed that $\lambda^3 = v$ and $N = v^{-1}$, N_a is Avogadro's constant, and v is the volume per formula unit.

In order to assess the sensitivity of I_o to a size dependent surface tension, the expression

$$\sigma(r) = \sigma_\infty / (1 + 2\delta/r) \quad (7)$$

which was derived by Tolman,⁽¹⁰⁾ is used. In Equation (7), σ_∞ is the surface tension of a flat interface, and 2δ is a positive quantity equivalent to an interatomic distance. It should be noted that Equation (7) is an approximate expression, valid in the limiting case $\delta \ll r$, and that it was derived for the nucleation of a liquid droplet. For example, if $2\delta = r^*$, then Equation (7) overestimates the surface tension by about 8%.⁽¹⁰⁾

At the critical radius the thermodynamic barrier is a maximum, and thus the critical radius, r_c , can be found from $(\partial W/\partial r)_{r_c} = 0$. Using the latter condition

in conjunction with Equations (1) and (7), one obtains

$$\bar{r}_c = \frac{r_c}{\sigma_\infty} = -\left(\alpha + \frac{1}{\Delta G_v}\right) + \sqrt{\left(\alpha + \frac{1}{\Delta G_v}\right)^2 - \alpha\left(\alpha + \frac{3}{\Delta G_v}\right)} \quad (8)$$

where $\alpha = 2\delta/\sigma_\infty$. Hence, the thermodynamic barrier is given by

$$W^* = \sigma_\infty^3 [4\pi\bar{r}_c^3 \Delta G_v / 3 + 4\pi\bar{r}_c^2 \bar{\sigma}(\bar{r}_c)] \quad (9a)$$

$$= \sigma_\infty^3 \bar{W}^*$$

$$\bar{\sigma} = \bar{r}_c / (\bar{r}_c + \alpha) \quad (9b)$$

Determination of surface tension parameters

So far only formal results have been given, since the parameters δ and σ_∞ are not known. Two different methods are used to determine these parameters. In the first, they are fixed by utilising the experimentally determined values of the temperature of maximum nucleation rate, T_m , and the steady state nucleation rate at T_m , $I(T_m)$. Using the logarithm of Equation (5) evaluated at T_m and the equation for T_m which may be derived by taking the temperature derivative of Equation (5) and setting it to zero, one can derive

$$\frac{\sigma_\infty^3}{kT_m} = \left[\frac{-\frac{1}{2} \left(\frac{1}{\bar{\sigma}} \frac{d \ln \bar{\sigma}}{dT} + \frac{1}{T} \right) + \frac{d \ln \eta}{dT}}{\left(\frac{\bar{W}^*}{T} - \frac{d \bar{W}^*}{dT} \right)} \right]_{T=T_m} \quad (10)$$

and

$$\left[\frac{1}{2} \ln \bar{\sigma} - \frac{\sigma_\infty^3 \bar{W}^*}{kT} + \frac{1}{2} \ln \sigma_\infty \right]_{T=T_m} = f(T_m) \quad (11)$$

where

$$f(T_m) = \ln I(T_m) - 1/2 \ln T_m + \ln \eta(T_m) - \ln A'. \quad (12)$$

Since T_m and $I(T_m)$ are determined from experiment and A' can be computed from classical nucleation theory, $f(T_m)$ is easily found. Equation (10) can be employed to eliminate σ_∞ from Equation (11), and the resulting equation can be used to solve for $\bar{\sigma}$. Equations (8) and (9b) can then be used to determine α and \bar{r}_c . Finally, use of Equation (10) allows the determination of σ_∞ .

In the second method the two parameters are obtained by minimising the difference between the calculated and experimentally determined nucleation rates over the entire temperature region in which nucleation occurs. This procedure leads to the following equations which are used to determine α and σ_∞ :

$$\sum_i I_i^2 \left(\frac{1}{6\sigma_\infty^3} - \frac{\bar{W}_i}{kT_i} \right) = 1 \quad (13a)$$

$$\sum_i I_i I_i^e \left(\frac{1}{6\sigma_\infty^3} - \frac{\bar{W}_i}{kT_i} \right)$$

$$\frac{\sum_i I_i^2 \left[\frac{0.5 \frac{\partial \bar{\sigma}}{\partial \alpha}}{\bar{\sigma} \sigma_\infty^3} - \frac{\partial}{\partial \alpha} \left(\frac{\bar{W}_i}{k T_i} \right) \right]}{\sum_i I_i I_i^e \left[\frac{0.5 \frac{\partial \bar{\sigma}}{\partial \alpha}}{\bar{\sigma} \sigma_\infty^3} - \frac{\partial}{\partial \alpha} \left(\frac{\bar{W}_i}{k T_i} \right) \right]} = 1. \quad (13b)$$

In Equations (13) the sum runs over i , which corresponds to a temperature T_i at which a nucleation measurement has been made and I_i^e refers to an experimental value of the nucleation rate. Equations (13) can be solved simultaneously for the determination of α and σ_∞ .

Results and discussion

Crystal nucleation in LS₂ glass was chosen for study since there are viscosity,⁽¹³⁾ thermodynamic,⁽²⁾ and nucleation rate^(4,13-15) data available for a reliable test of the theory. Table 1 shows the physical parameters and thermodynamic data used in the calculations. The surface tension parameters and the values of the critical radii at T_m computed by the fitting schemes described above are shown in Table 2. Also, the critical radii and flat interface values of the surface tension are shown for calculations in which the surface tension is taken as constant and temperature dependent, but radius independent.⁽²⁾

One may observe that although the critical radii predicted by the use of a constant and size dependent surface tension do not differ significantly, the computed liquid-crystal surface tensions for a flat interface are much larger for the radius dependent σ . Using the results of Table 2 and the data given in Table 1, nucleation rates were computed as a function of temperature. Figure 1 compares the temperature dependence of the normalised nucleation rate found from experiment with two different calculated values.

Table 1. Physical parameters and thermodynamic data for LS₂

Parameter	Value
Heat of melting	57 300 J/mole
Melting point	1307 K
Molar volume	61.4 × 10 ⁻⁶ m ³ /mole
log ₁₀ η	1.81 + 1346.6/(T - 594.8) Pa s; T (K)
ΔG _m (molar free energy difference between liquid and crystal)	-(53 370 - 39.37T) J/mole

Table 2. Surface tension parameters and critical radius

Parameter	SIG	MAX	IFIT	SIG(T)
δ (m)	—	3.70 × 10 ⁻¹⁰	3.66 × 10 ⁻¹⁰	—
σ _∞ (J/m ²)	0.207	0.278	0.277	0.196
r _c at T _m (m)	10.26 × 10 ⁻¹⁰	9.40 × 10 ⁻¹⁰	9.41 × 10 ⁻¹⁰	7.27 × 10 ⁻¹⁰

SIG: constant value of surface tension
 MAX: Tolman parameters fit via fixing position and magnitude of I to agree with experiment at maximum
 IFIT: Tolman parameters fitted by minimising $(I - I^e)^2$
 SIG(T): temperature dependent surface tension used by James

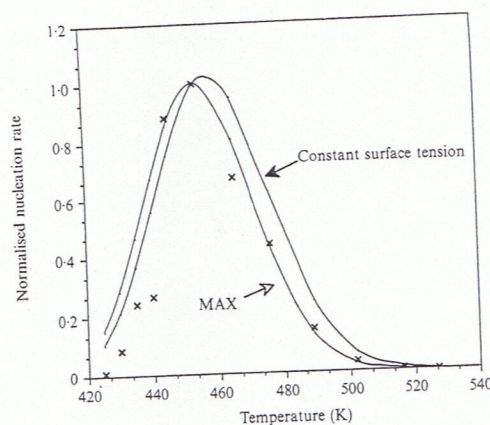


Figure 1. Comparison of temperature dependence of experimental and calculated normalised nucleation rates
 × experimental values
 — calculated values with constant surface tension and Tolman parameters fitted by MAX procedure

It may be noted that although the agreement between computed and measured rates is generally good, both calculated curves deviate somewhat from experiment, particularly in the lower temperature portion of the nucleation regime. A more comprehensive comparison between calculated and experimental results is summarised in Table 3, where the notation employed is the same as that used in Table 2. For each element in this table with two entries, the second value corresponds to the use of the prefactor, A' , computed from Equation (6) and the first to the use of the approximation $A' = k/(3\pi v^2)$: I_{\max} is the calculated value of the maximum nucleation rate. One sees that the use of classical nucleation theory with a constant surface tension predicts a nucleation rate which is orders of magnitude too small; and this has been observed previously for LS₂.^(3,4) The second and third row entries (variance of I/I_{\max} and I) show the errors in the normalised and actual computed nucleation rates. Several features of these results warrant comment. First, it is apparent that all calculations are quite insensitive to the use of the approximate A' . Next, one observes that although the use of a constant surface tension produces huge errors in the magnitude of I , the predicted temperature dependence of I is about as good as or better than those obtained from the variable surface tension calculations. Finally, one finds that the use of a temperature dependent surface tension gives a somewhat better fit to the data than those found using the size dependence. However, it should be realized that the MAX calculation utilises less experimental information, and thus is expected

Table 3. Calculated nucleation rate quantities

	SIG	MAX	IFIT	SIG(T)
I_{\max} (m ⁻³ s ⁻¹)	0.311 × 10 ⁻¹⁶ 1.32 × 10 ⁻¹⁶	4.25 × 10 ⁻⁹ 4.25 × 10 ⁻⁹	3.63 × 10 ⁻⁹ 3.61 × 10 ⁻⁹	— 3.24 × 10 ⁻⁹
Variance of I/I_{\max}	0.02376 0.02341	0.02594 0.02626	0.02598 0.02693	— 0.02269
Variance of I	0.4262 × 10 ¹⁹ 0.4262 × 10 ¹⁹	0.4692 × 10 ¹⁸ 0.4750 × 10 ¹⁸	0.3399 × 10 ¹⁸ 0.3498 × 10 ¹⁸	— 0.3155 × 10 ¹⁸

to be less accurate. Also, both computations with a radius dependent surface tension employed an approximate form of the Tolman equation, and the small differences between the SIG(T) and IFIT results might therefore be attributable to this fact.

To illustrate the link between these two approaches the effective temperature dependence of the surface tension, due to radius dependence, was computed and compared with the one employed by James. The results are shown in Figure 2. The slopes of the two curves are virtually identical, but the magnitude of the surface tension from the Tolman calculation is about 6% higher at each temperature. However, the approximate form of the Tolman equation overestimates the value of the surface tension at T_{max} by about 7.5%. Thus, there appears to be a close connection between the postulated temperature dependence of the surface tension and the radius dependence of the surface tension.

Summary and conclusions

Nucleation rates as a function of temperature were computed for LS_2 crystal nucleation using a modified classical nucleation theory containing a simple radius dependent surface tension proposed by Tolman. The unknown parameters in the Tolman expression were fitted by comparison to experiment in two different manners. Both procedures yielded similar results for these parameters, and thus gave comparable results for the predicted nucleation rates. In general, the agreement between such calculations and experiment was found to be quite good, except for some divergence in the lower portion of the nucleation regime. However, the major difficulty is that there is no independent verification of the physical reality of these calculations. If the parameters in the Tolman expression for the surface tension could be determined without recourse to the use of experimental nucleation data and the good agreement between theoretical and

experimental $I(T)$ were maintained, then one could confidently assert that the most glaring deficiency of standard classical nucleation theory is its neglect of the radius dependence of surface tension. Although one notes that the calculated parameters in the Tolman expression found in the present work are of reasonable magnitude, one cannot make the latter assertion with confidence. However, from the results of this work one may conclude that the neglect of the radius dependence of the surface tension is a possible (perhaps even plausible) source of major difficulty with classical nucleation theory. One should note (see Table 2) that classical nucleation theory and the Tolman type calculations predict significantly different values for the interfacial tension of a flat liquid-crystal interface. Thus, if one could measure the surface tension between the liquid and crystal at the melting point, then one might be able to reach a definitive conclusion.

Finally, the present approach was compared with the one used by James, who employed a temperature dependent surface tension in order to produce a correction to classical nucleation theory. An effective temperature dependence of σ was calculated by using its determined radius dependence. It was shown that the temperature dependence of the surface tension which we obtained was virtually identical to the one employed by James, but the magnitude of James's was about 6% less. However, we indicated that the approximate Tolman formula, in the relevant size regime, overestimated the actual surface by roughly this amount. Hence, it seems quite likely that the temperature variation in the surface tension is merely a reflection of the radius dependence of the surface tension.

Acknowledgement

Gratitude is expressed to the Jet Propulsion Laboratory and the NASA Division of Microgravity Science and Applications for partial financial support of this work.

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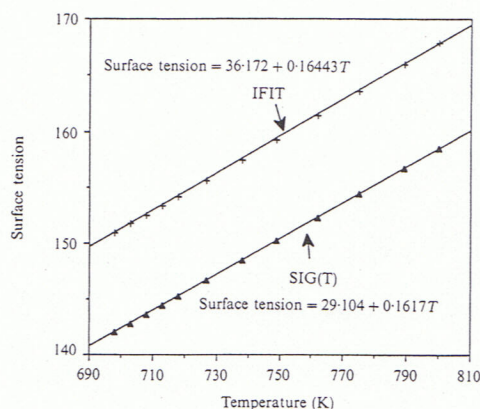


Figure 2. Comparison of temperature dependence of surface tension used by James and effective temperature dependence of surface tension found using a radius dependent surface tension