

Studies on the shape of critical nucleus in homogeneous crystal nucleation

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Abstract : Effect of the critical nucleus shape on the nucleation parameters has been studied by deriving the required formulae (assuming the shape as spherical, cubic and cylindrical) based on classical theory for homogeneous nucleation and calculating the nucleation parameters for ammonium dihydrogen orthophosphate (ADP) and urea nitrate crystals. The present study shows that it would be better to consider the shape of the critical nucleus as cylindrical.

Keywords : Homogeneous crystal nucleation, critical nucleus shape

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1. Introduction

The formation of a crystal in the absence of a seed, involves nucleation. Previous workers have assumed the shape of the critical nucleus in homogeneous crystal nucleation as a sphere and provided the way to determine the various nucleation parameters. However, for many reasons, we cannot restrict this shape to a sphere.

It is necessary to consider the following facts while assuming a shape for the critical nucleus :

- (i) Atoms are not strictly spherical in shape regardless of the minimum energy consideration;
- (ii) Molecules are not spherical in shape-wide variation available;
- (iii) Crystal lattices are not spherical in shape;
- (iv) Grown crystals which are of spherical in shape are very rare;
- (v) Needle (cylindrically shaped) crystals are quite commonly found;

- (vi) Crystals with many flat faces are quite commonly found;
- (vii) In the case of melt growth, liquid (melted substance) solidifies. But, in the case of slow evaporation or slow cooling process, only the excess of solute in the solution solidifies and not the solvent;
- (viii) Using the conventional experiment for determining the induction period (as it is followed in the present study—the direct vision method) and the classical theory for homogeneous nucleation, we obtain only one value for the energy of formation of the critical nucleus (independent of the shape) for a particular supersaturation; *etc.*

Hence, from the above facts, it becomes trivial to restrict the nucleus to a sphere.

In the present investigation, formulae for critical nucleation parameters using the classical theory for homogenous nucleation have been derived by considering the shape of the critical nucleus as a sphere, a cube and a cylinder (assuming different surface energies for flat and curved surfaces). Also, the critical nucleation parameters for ammonium dihydrogen orthophosphate (ADP) and urea nitrate (as representations to inorganic and organic substances respectively) crystals using the induction periods measured by the direct vision method have been determined using the derived formulae and a comparison is made with respect to the nucleus shape.

We present here a report of the work done and discussion of the results obtained.

2. Theory

The free energy change associated with the process of homogeneous nucleation may be considered as follows :

The overall excess free energy (ΔG) between an embryo and solute in the solution is equal to the sum of the surface excess free energy (ΔG_s) and the volume excess free energy (ΔG_v) [1] given by

$$\Delta G = \Delta G_s + \Delta G_v, \quad (1)$$

where ΔG_v is given by

$$\Delta G_v = -\left(\frac{kT}{v}\right) \ln(S). \quad (2)$$

Here k is the Boltzmann's constant, T is the absolute temperature, v is the volume per molecule in solid phase, and S is the supersaturation.

According to Gibb's formulations in terms of surface thermodynamics, the end and lateral surfaces of a cylinder will have different surface energies [1]. We also assume here that there are two kinds of surfaces, *viz.*, curved and flat and they will have different surface energies, *viz.* σ_0 (for flat) and σ (for curved). Also, in order to reduce complexity, we assume same surface energy for all the surfaces in the tetragonal and orthorhombic cases.

The basic relationship of equilibrium between solid and its solution which connects the solubility expressed as the chemical potential to the particle size is the Thomson equation,

$$\mu_d - \mu_\infty = \frac{2\sigma_1 v}{d} \quad (3)$$

where μ_d is the chemical potential of nucleus of dimension d , μ_∞ is the chemical potential of the nucleus of infinite size and σ_1 is the surface free energy. When the crystal attains a size of dimension d , it will be in equilibrium with the solution and under these conditions the chemical potentials of the two co-existing phases are equal. The free energy of formation of the nucleus of the new phase in equilibrium with its solution may be expressed as

$$\Delta G = \frac{A}{(\mu_d - \mu_\infty)^2} \quad (4)$$

where A is a factor which depends on the surface energy. The change in chemical potential is given by [2]

$$\mu_1 - \mu_{10} = \mu_d - \mu_\infty = kT \ln(S), \quad (5)$$

where μ_1 is the chemical potential of supersaturated solution and μ_{10} is the chemical potential of saturated solution.

The frequency of formation of crystal nuclei from their respective supersaturated solutions have been given as [3]

$$J = K \exp\left(\frac{-U_1}{kT}\right) \exp\left(\frac{-\Delta G}{kT}\right) \quad (6)$$

where K is a constant and U_1 is the energy of activation for the molar transition from phase 1 (solution) to phase 2 (crystal).

After preparing supersaturated solutions, there is often a period where no phase change can be observed, the induction period (the time of formation of the first nucleus); then minute nuclei appear and grow into visible crystals. For a given volume of solution, based on the probabilistic approach [4], the frequency of formation of nuclei (in the steady state) is inversely proportional to the induction period (τ):

$$\ln \tau = \ln K^{-1} + \frac{U_1}{kT} + \frac{\Delta G}{kT} \quad (7)$$

For an isotherm, the term U_1/kT is a constant and the equation can be written as

$$\ln \tau = B + \Delta G/kT, \quad (8)$$

where B is a constant.

Applying eqs. (4) and (5) in eq. (8) we get

$$\ln(\tau) = B + \frac{A}{k^3 T^3 \ln^2(S)} = B + \frac{AN^3}{R^3 T^3 \ln^2(S)}, \quad (9)$$

where R is the universal gas constant and N is the Avogadro number.

Eq. (9) suggests a straight line for $\ln(\tau)$ against $1/\ln^2(S)$ with the slope given by

$$m = \frac{AN^3}{R^3T^3}$$

Therefore,

$$A = \frac{mR^3T^3}{N^3} = mk^3T^3. \quad (10)$$

2.1. Spherical nucleus :

The overall excess free energy for a spherical nucleus of radius r can be written as

$$\Delta G = 4\pi r^2\sigma + \frac{4}{3}\pi r^3\Delta G_v, \quad (11)$$

where r is the radius of the sphere. This energy will be maximum for a certain value of r , which is known as critical radius. Nuclei formed with radius greater than this r are stable and decrease their free energy by growing. Differentiating eq. (11) with respect to r and maximizing, we get

$$\frac{\delta\Delta G}{\delta r} = 8\pi r\sigma + 4\pi r^2\Delta G_v = 0. \quad (12)$$

Therefore for the critical nucleus,

$$r = \frac{2\sigma v N}{RT \ln(S)}, \quad (13)$$

$$\Delta G = \frac{mRT}{\ln^2(S)}, \quad (14)$$

$$\sigma = RT \left[\frac{3m}{16\pi v^2 N^3} \right]^{1/3} \quad (15)$$

The number of molecules in the critical nucleus is

$$n = \frac{4}{3}\pi \frac{r^3}{v}. \quad (16)$$

2.2. Cubic nucleus :

The overall excess free energy for a cubic nucleus of edge a can be written as

$$\Delta G = 6a^2\sigma_0 + a^3\Delta G_v. \quad (17)$$

Therefore for the critical nucleus,

$$a = \frac{4\sigma_0 v N}{RT \ln(S)}, \quad (18)$$

$$\Delta G = \frac{mRT}{\ln^2(S)}, \quad (19)$$

$$\sigma_0 = RT \left[\frac{m}{32v^2 N^3} \right]^{1/3} \quad (20)$$

The number of molecules in the critical nucleus is

$$n_c = \frac{a^3}{v} \quad (21)$$

2.3 Tetragonal nucleus :

The overall excess free energy for a tetragonal nucleus of base edge a and height h can be written as

$$\Delta G = 4ah\sigma_0 + 2a^2\sigma_0 + a^2h\Delta G_v \quad (22)$$

Therefore for the critical nucleus,

$$a = \frac{4\sigma_0 v}{kT \ln(S)} \quad (23)$$

$$h = \frac{4\sigma_0 v}{kT \ln(S)} \quad (24)$$

As all the surfaces are flat, the surface free energy, as per our assumption, is same for all the surfaces of a tetragonal nucleus under homogenous condition. This gives us the result $a = h$ and consequently the tetragonal nucleus reduces to a cubic nucleus. So, the critical nucleation parameters are nearly the same as that of a cubic nucleus.

2.4 Orthorhombic nucleus :

The overall excess free energy for an orthorhombic nucleus of edges a , b and c can be written as

$$\Delta G = 2(ab + bc + ca)\sigma_0 + abc\Delta G_v \quad (25)$$

Therefore for the critical nucleus,

$$a = b = c = \frac{-2\sigma_0}{2\sigma_0 + \Delta G_v} \quad (26)$$

As in the case of tetragonal nucleus, here also, the orthorhombic nucleus reduces to a cubic nucleus. So, the critical nucleation parameters are nearly the same as that of a cubic nucleus.

2.5 Cylindrical nucleus :

The overall excess free energy of a cylindrical nucleus of radius r_c and height h can be written as

$$\Delta G = 2\pi r_c^2 \sigma_0 + 2\pi r_c h \sigma + \pi r_c^2 h \Delta G_v \quad (27)$$

Therefore for the critical nucleus,

$$r_c = \frac{2\sigma v N}{RT \ln(S)} \quad (28)$$

$$h = \frac{4\sigma_0 v N}{RT \ln(S)} \quad (29)$$

$$\Delta G = \frac{mRT}{\ln^2(S)}, \quad (30)$$

$$\sigma_0 = \frac{mk^3T^3}{8\pi\sigma^2v^2}.$$

Substituting the value of σ (for all the surfaces curved as in a sphere) from eq. (15) in the above equation, we get

$$\begin{aligned} \sigma_0 &= RT \left[\frac{m}{18\pi v^2 N^3} \right]^{1/3}, \\ &= \left[\frac{mk^3T^3}{8\pi\sigma_0 v^2} \right]^{1/2}. \end{aligned} \quad (31)$$

Substituting the value of σ_0 (for all the surfaces flat as in a cube) from eq. (20) in the above equation, we get

$$\sigma = \frac{RT}{\sqrt{\pi}} \left[\frac{m}{4v^2 N^3} \right]^{1/3}. \quad (32)$$

The number of molecules in the critical nucleus is

$$n_{c1} = \frac{\pi r_c^2 h}{v}. \quad (33)$$

In a cube, all surfaces are flat. Similarly, in a sphere, the whole surface is curved. So in the limiting conditions, it does not become trivial to substitute the values of σ and σ_0 obtained by considering the shape as spherical and cubic respectively while obtaining the values of σ and σ_0 in the case of cylindrical nucleus.

Using the experimentally observed m and v values various nucleation parameters can be evaluated.

3. Experimental details

Analytical Reagent grade samples of the substances along with doubly distilled water were used in the experimental study of the present work. Urea nitrate was prepared by following the procedures given by Vogel [5]. Aqueous solutions of various supersaturated concentrations were prepared by dissolving the required amount of the substance at temperatures slightly higher than the saturation temperature. Supersaturation was obtained by natural cooling.

The experimental set up used for induction period (τ) measurement consists of two identical nucleation cells (100 ml beakers of corning glass) kept at a constant temperature of 33°C (controlled to an accuracy of $\pm 0.1^\circ\text{C}$). One of the cells was used as dummy (As insertion of thermometer in the experimental cell may disturb the system, this dummy cell was used for keeping the sensitive thermometer). Using a powerful lamp, the cells were illuminated. Supersaturated solutions of equal volume (20 ml in the present work) were taken in the cells at a higher temperature. A sensitive thermometer (accuracy is $\pm 0.1^\circ\text{C}$)

was placed in the dummy cell. As the temperature of the cell reached the experimental temperature (*i.e.*, 33°C), the time was noted. Once the nucleation occurs, it grows quickly and a bright sparkling particle is seen. The time of observation of the sparkling particle in the undisturbed nucleation cell from the time at which the nucleation cell reaches the experimental temperature gives the induction period. It was measured in seconds.

Volume of the solutions taken in the nucleation cell was maintained at 20 ml in all the experiments in the present work. Several nucleation runs were carried out under controlled and unstirred conditions. Reproducible results within an accuracy of $\pm 2.5\%$ were obtained. Experiments were performed with five selected supersaturations, *viz.*, 1.200, 1.225, 1.250, 1.275 and 1.300 for ADP and 1.500, 1.525, 1.550, 1.575 and 1.600 for urea nitrate.

The direct vision method is not very accurate and does not involve rigorous methodology to study nucleation. The nuclei are non-observable even by microscopy; at the observable level, they are already at the growth stage. It is assumed that the time required for the critical nucleus to grow to an observable level is very small when compared to the induction period and is negligible. Despite all these problems, this method was considered for the present study for the reason that no other better method is available to study nucleation in supersaturated solutions of highly soluble substances. Moreover, in order to reduce the inaccuracy, it was taken care that the supersaturated concentration considered should provide the induction period more than 500 seconds at least. The effect of heterogeneous nucleation by dust particles from air was reduced by carrying out the experiment in a relatively dust free space. Also, the effect of heterogeneous nucleation by scratchings on the inner wall of the nucleation cell (glass beaker), was reduced by properly choosing the glass beaker without scratches (tested with a microscope).

4. Results and discussion

The results of measurements of induction period for ADP and urea nitrate crystals are presented in Table 1. The value of τ decreases and hence the nucleation rate increases as the

Table 1. Results of induction period measurements

System	Supersaturation <i>S</i>	τ (sec)	Slope <i>m</i>
ADP	1.200	15480	0.160
	1.225	8280	
	1.250	3480	
	1.275	2160	
	1.300	1020	
Urea nitrate	1.500	4570	1.317
	1.525	2680	
	1.550	1572	
	1.575	945	
	1.600	600	

supersaturated concentration of the aqueous solution increases for both the systems considered in the present study. This is similar to the results obtained by previous workers for their systems [6–11]. Plots of $\ln \tau$ versus $1/\ln^2(S)$ (not shown here) for both the systems considered in the present study are linear as expected by the theory.

The ADP ($\text{NH}_4\text{H}_2\text{PO}_4$) crystal has tetragonal structure with tetramolecular unit cell having the dimensions [12] given as $a = b = 7.510$ and $c = 7.564$ Å. The urea nitrate ($\text{CH}_4\text{N}_2\cdot\text{HNO}_3$) crystal has monoclinic structure with tetramolecular unit cell having the dimensions (ASTM file) given as : $a = 9.50$, $b = 8.20$ and $c = 7.54$ Å; $\beta = 124^\circ$.

The critical nucleation parameters obtained in our study are presented in Tables 2 to 4. It is observed that the values of r , n , a , n_c , r_c , h , n_c , and ΔG (same for all the three shapes considered since the experimentally observed slope m value is common) decrease when the supersaturation increases. This result is similar to that observed by previous workers for their systems considering the nucleus shape as spherical [6–11].

Table 2. Critical nucleation parameters when the nuclei are assumed to be spherical

System	S	ΔG (kJ/mole)	σ (mJ/m ²)	r (nm)	n
ADP	1.200	12.246	3.985	0.104	53
	1.225	9.880		0.992	38
	1.250	8.175		0.902	29
	1.275	6.897		0.828	22
	1.300	5.914		0.767	18
Urea nitrate	1.500	20.426	7.380	1.048	40
	1.525	18.854		1.006	35
	1.550	17.479		0.969	31
	1.575	16.267		0.935	28
	1.600	15.192		0.904	25

Table 3. Critical nucleation parameters when the nuclei are assumed to be cubic.

System	S	ΔG (kJ/mole)	σ_0 (mJ/m ²)	a (nm)	n_c
ADP	1.200	12.246	3.212	1.779	53
	1.225	9.880		1.598	38
	1.250	8.175		1.454	29
	1.275	6.897		1.335	22
	1.300	5.914		1.336	18
Urea nitrate	1.500	20.426	5.946	1.688	40
	1.525	18.854		1.622	35
	1.550	17.479		1.562	31
	1.575	16.267		1.507	28
	1.600	15.192		1.456	25

Table 4. Critical nucleation parameters when the nuclei are assumed to be cylindrical.

System	S	ΔG (kJ/mole)	σ (mJ/m ²)	σ_0 (mJ/m ²)	r_c (nm)	h (nm)	n_{c1}
ADP	1.200	12.246	3.625	2.657	1.004	1.472	44
	1.225	9.880			0.902	1.322	32
	1.250	8.175			0.820	1.202	24
	1.275	6.897			0.753	1.104	18
	1.300	5.914			0.698	1.023	15
Urea nitrate	1.500	20.426	6.708	4.890	0.952	1.388	33
	1.525	18.854			0.915	1.333	29
	1.550	17.479			0.881	1.284	26
	1.575	16.267			0.850	1.239	22
	1.600	15.192			0.821	1.197	21

Reasonable sizes for the critical nucleus have been observed for all the three shapes considered in the present study. The order of the number of molecules in the critical nucleus is spherical = cubic > cylindrical. This shows that the nucleus becomes critical with less number of molecules when the nucleus is cylindrical in shape. Consequently, the cylindrical shape is better to be considered than the other ones (spherical and cubic).

During the study of nucleation, both theoretical and experimental difficulties are encountered. The major theoretical difficulty arises from the fact that the size of the nucleus is too small to be treated by the thermodynamic theories and too large to be dealt with the atomic concepts. Since the critical nuclei are so small, accurate measurements are not really feasible and calculated values depend very much on assumptions made, many of which cannot as yet be independently tested. The inferences drawn from observations are therefore indirect.

5. Conclusion

Induction period measurements have been done for ADP (an inorganic substance) and urea nitrate (an organic substance) by the direct vision method at 33°C with five selected supersaturations. Derivation of the required formulae and calculation of the critical nucleation parameters based on the classical theory for homogeneous nucleation by considering the shape of the critical nucleus as spherical, cubic and cylindrical have been done.

The classical theory for homogeneous crystal nucleation is well explained by the experimentally observed linear relationship between $\ln \tau$ and $1/\ln^2(S)$. Calculation of the number of molecules present in the critical nucleus show that it would be better to consider the shape of the critical nucleus as cylindrical than the other shapes (spherical and cubic).

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