Journal of Crystal Growth 76 (:
North-Holland,

SOLUTE CLUSTERING AND INTERFACIAL TENSION

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Received 30 October 1985; manuscript received in final form 27 March 1986

The effect of surface curvature on surface tension has been included in the theory of homogeneous nucleation to show
certain conditions, cluster formation results in a decrease in Gibbs' free energy. This cluster formation is thus a sponta
and a quasi-equilibrium concentration of clusters of narrow size range may then exist in supersaturated solutior
experimental work suggests the existence of solute clusters in a variety of aqueous solutions. The implications for crysta
and growth theory are discussed.

1. Introduction

The mechanism of homogeneous nucleation is not fully understood but the process requires the spontaneous creation of a solute crystal from a single-phase supersaturated system. In the case of crystallization from solution such a system contains dissolved solute in excess of the equilibrium concentration. It is presumed that in the supersaturated state a series of bimolecular reactions between solute molecules or ions gives rise to ordered "clusters" or "embryos". These are continuously forming and dispersing. Any of these clusters which attain a critical size do not disperse but continue to grow spontaneously, resulting in the formation of crystal nuclei. This process is governed by the following thermodynamic requirements.

The Gibbs free energy of the embryos ΔG is made up of both a surface and a volume term and so is a function of their size; assuming that the embryos are spherical of radius r, it can be written

$$\Delta G = 4\pi r^2 \sigma + \tfrac{4}{3}\pi r^3 \, \Delta G_{\text{v}}. \qquad (1)$$

Here, σ is the surface tension per unit surface area and is a positive quantity. ΔG_{v} is the specific free energy change associated with the liq
phase change. **. It therefore represents
free energy and is a negative quantity.

Fig. 1 illustrates the terms in eq.
function of cluster size. ΔG exhibits a ı
at the critical size r_{c}. Growth of clust
than this critical size results in a decrea
Gibbs free energy; such clusters thus gro

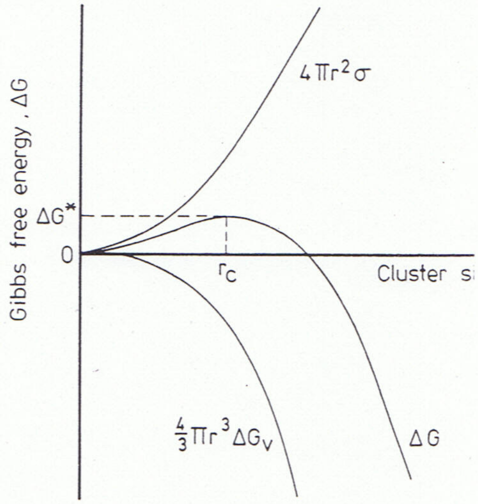

Fig. 1. Free energy change for cluster formation; si:
dent surface tension.

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** Cf. Notation at the end of this paper.

neously and are regarded as nuclei, while clusters smaller than r_c are presumed to disperse. The Gibbs free energy at $r = r_c$, ΔG^*, is the activation energy for nucleation and is incorporated into the formulation of kinetic equations for nucleation.

Thus phase change through nucleation occurs when clusters of solute reach size r_c requiring an activation energy ΔG^*. As the supersaturation is increased, ΔG_v becomes more negative resulting in a smaller critical nucleus size and a lower activation energy. At higher supersaturations, the frequency at which clusters reach critical size is therefore increased and nucleation occurs at a greater frequency.

2. Influence of surface curvature

The above analysis forms the basis of homogeneous nucleation theory. It is, however, based on the assumption that the surface tension remains unchanged regardless of the cluster or nucleus size. Gibbs [1] has shown that surface tension is a function of the curvature of the surface, the effect being highly significant for entities with a very small radius of curvature. This effect results because the phase interface is not dimensionless, but has a significant thickness. When the radius of an entity is of the same order of magnitude as the interfacial thickness, the surface tension is affected [1,2].

In accordance with the equation of Gibbs [1–3] the dependence of surface tension on the interphase potential is

$$\mathrm{d}\sigma = -\Gamma\,\mathrm{d}\mu. \tag{2}$$

Γ is the superficial density of the interfacial region and μ is the chemical potential of the fluid in the homogeneous part of the phase. The interfacial region can be envisaged as shown in fig. 2. The dashed lines enclose the interfacial region of an entity of radius r. The solid line is regarded as the equimolar surface [4], that is, the surface which divides the interfacial region into equimolar regions. The dashed lines mark the boundaries beyond which the two phases have their ambient densities. Γ is defined as the difference between the actual mass of the interfacial region and the mass it would have if each phase maintained its ambient density up to the surface of tension.

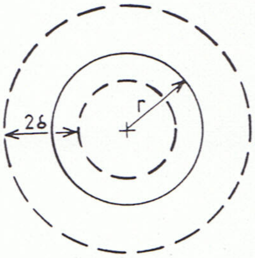

Fig. 2. Interfacial region of a cluster.

For a single component fluid–fluid system, Tolman [2] derived a relationship between the surface tension for an infinite plane and the actual surface tension for small entities as a function of entity radius and interfacial thickness 2δ. The complete derivation is given by Tolman [2] and Ono and Kondo [3]. Here only the results will be quoted. Rasmussen et al. [5] have also considered the effect of cluster radius on surface tension.

Tolman showed that δ is given by

$$\delta = \Gamma/(\rho_1 - \rho_2), \tag{3}$$

where ρ_1 and ρ_2 are the respective phase densities. This expression was derived for an infinite surface but was used in the following equation relating surface tension σ with σ_∞:

$$\ln\frac{\sigma}{\sigma_\infty} = \int_\infty^r \frac{\dfrac{2\delta}{r^2}\left(1 + \dfrac{\delta}{r} + \dfrac{\delta^2}{3r^2}\right)}{1 + \dfrac{2\delta}{r}\left(1 + \dfrac{\delta}{r} + \dfrac{\delta^2}{3r^2}\right)}\,\mathrm{d}r. \tag{4}$$

Tolman solved eq. (4) numerically and showed that the numerical solution could be approximated by

$$\frac{\sigma}{\sigma_\infty} = \frac{1}{1 + 2\delta/r}. \tag{5}$$

However, if $\delta/r \ll 1$, then it can be shown from eq. (4) that

$$\sigma/\sigma_\infty = \exp(-2\delta/r). \tag{6}$$

Further the numerical solution to eq. (4) obtained by Tolman can be approximated for $\delta/r > 0.1$ by

$$\sigma/\sigma_\infty = \exp(-1.3\delta/r). \tag{7}$$

These results predict a substantial decrease in surface tension for very small entities.

Adapting this concept to solid–liquid interfaces and using the above exponential approximation in eq. (1) gives

$$\Delta G = 4\pi r^2 \sigma_\infty \exp(-a\delta/r) + \tfrac{4}{3}\pi r^3 \, \Delta G_v. \tag{8}$$

3. Application

Eq. (8) predicts that entities can be formed more readily at smaller sizes than does eq. (1). For example, fig. 3 is a plot of eq. (8) with $a = 2$ and δ taken as 2.5 nm. Typical values of surface tension for crystals in suspension are of order 10 mJ/m^2 while the critical size of a crystal nucleus is usually of order 10 nm and is related to the bulk free energy change by

$$\Delta G_v = -2\sigma_\infty / r_c. \tag{9}$$

In fig. 3, eq. (9) was used to approximate ΔG_v, using the values of surface tension and critical radius quoted above. This gives $\Delta G_v = -2 \times 10^6$ J/m^3. The plot shows that when the surface tension decrease is taken into account, there can exist a region in the very small size range where cluster formation results in a decrease in Gibbs' free energy. This cluster formation is thus a spontaneous event. However, the size of these clusters is limited because as size increases beyond that corresponding to the minimum (at $r = r_{c_1}$), the Gibbs free energy change increases. A quasi-equilibrium concentration of clusters can therefore be expected to exist in "single-phase" supersaturated solutions and these clusters will have a mean size of order r_{c_1}. From the calculations quoted above it appears that this size is almost an order of magnitude smaller than the critical nucleus size r_c.

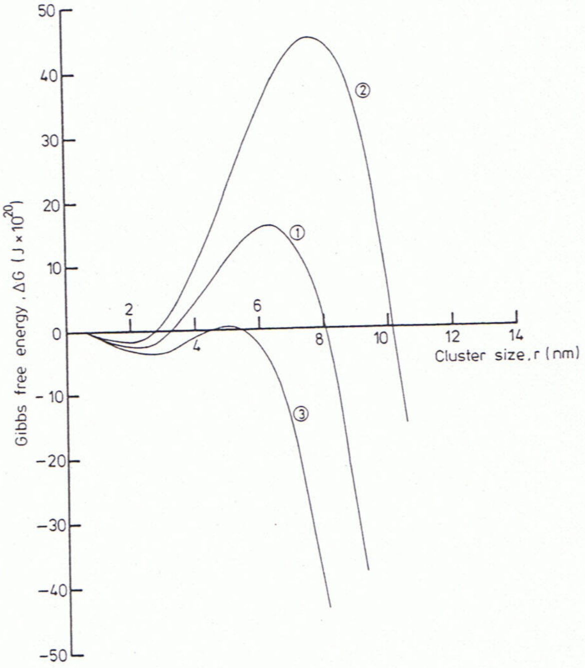

Fig. 3. Free energy change for cluster formation incorporating size dependent surface tension. Curves 2 and 3 correspond to values of ΔG_v 10% less and 10% greater, respectively, than the value used to calculate curve 1.

Fig. 3 also shows the free energy change as a function of size for several values of ΔG_v. As supersaturation increases ΔG_v becomes more negative, that is $|\Delta G_v|$ increases. In consequence r_{c_1} increases while r_c decreases. At some high supersaturation these values ultimately coincide.

4. Discussion

Evidence for the existence of clusters in NaNO$_3$ solutions has been reported by Hussmann, Larson and Berglund [6]. Using Raman spectroscopy, they showed that species exhibiting the Raman spectra of solid state NaNO$_3$ existed in small concentrations in undersaturated as well as in supersaturated solutions. The fraction of the solute in solution which existed in this state increased with increasing concentration. The technique could not, however, give any information concerning the size of the individual clusters.

Recent work by Larson and Garside [7] has confirmed that supersaturated solutions develop concentration gradients in a gravitational force field. Using a quasi-equilibrium model based on uniform molal free energy of a species, they were able to show that, if such clusters exist, a concentration gradient should develop in the solution. Estimates of the size of clusters in critic acid, urea, NaNO$_3$ and K$_2$SO$_4$ solutions were made and were generally between 1 and 10 nm, each cluster containing the order of 10^3 molecules. Chang and Myerson [8], using measurements of solute diffusivity, concluded that diffusion in concentrated and supersaturated solutions was influenced by cluster formation.

The presence of clusters of the size and number indicated by the experimental work cited above and the theoretical derivation in the present paper has important implications in the development of a proper description of the mechanisms of both primary and secondary nucleation. It would be expected that observed homogeneous nucleation in very highly supersaturated solutions would be highly dependent upon the degree of agitation of the solution. If large (say ~ 10 nm) clusters were present slight convective currents or mechanical agitation would increase greatly the probability of several (say 2–10) clusters coming into contact, coalescing and becoming larger than the critical size. Massive nucleation at the onset of agitation could be explained by such a mechanism. At some very high degree of agitation nucleation may be decreased because of the high shear forces separating clusters; such behaviour has been reported by Mullin and Raven [9]. In highly supersaturated solutions it could be that Brownian motion may be sufficient to produce primary nucleation. Nucleation produced by such a mechanism would require a considerable time to occur but this may be the limiting step giving rise to observed nucleation induction times.

Clearly primary nucleation, however initiated, must be a sensitive function of the convective currents in the solution whether or not these are mechanically induced. Once macroparticles are formed convective currents, developed because of the particle movement induced by gravitational forces, is probably sufficient to sustain and increase nucleation as long as supersaturation is sufficiently high.

If it is accepted that an "equilibrium" concentration of clusters of sizes 1–10 nm exists in highly soluble supersaturated solutions it must be expected that they play an important role in crystal growth. It would be expected that they are the species diffusing to the surface of a growing crystal and upon their arrival at the surface one would expect a "queueing-up" of the clusters in a random orientation at the surface. This would result in a substantial solute layer needing to reorder itself so as to fit into the crystal lattice. It seems reasonable that this layer provides the major source of secondary nuclei produced by crystal–crystal or crystal–apparatus contact.

Acknowledgements

The authors acknowledge the support of the SERC through the provision of a Visiting Fellowship and of the Iowa State University Faculty Leave program for providing the opportunity for this collaboration.

Notation

a	Constant
ΔG	Gibbs free energy
ΔG_v	Specific volume free energy
r	Cluster radius
r_c	Critical cluster radius
r_{c_1}	Cluster radius
Γ	Specific density of interface
δ	Half interfacial thickness
μ	Chemical potential
ρ_1	Density of cluster
ρ_2	Density of solution
σ	Surface tension per unit area
σ_∞	Surface tension per unit area of flat interface

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