

Properties of Ice Clusters from an Analysis of Freezing Nucleation[†]

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Properties of the critical clusters that are instrumental in the nucleation of a first-order phase transition can be obtained through the analysis of nucleation rate data. The theoretical tools for doing so are known as nucleation theorems. We consider solid-phase critical clusters forming from a liquid phase, and it is shown that their size and binding energies can be extracted from data gathered at a range of temperatures and pressures. Ice crystal nucleation rates described recently are used to study ice clusters containing several hundred water molecules.

I. Introduction

To understand the properties of matter on very small scales, it is often necessary to devise experiments which amplify microscopic effects into effects on scales more readily accessible to measurement. For example, the presence of nanometer-sized particles in the atmosphere can be detected by inducing the massive condensation of some working fluid onto their surfaces, yielding relatively large droplets which can be detected optically.¹ A similar case is the generation of photons in photomultipliers, and there are many examples² of the detection of trace chemical constituents through chemical amplification.

The nucleation of a phase transition is an amplification process. Nucleation is the process by which a metastable state relaxes toward its true equilibrium state in the given environment. For example, a vapor confined to a box and cooled below its dew point becomes metastable, but cannot easily condense in the absence of foreign particles or wettable surfaces, since the molecular clusters that have to form before bulk condensed phases can appear are actually less stable than the original metastable phase. Hence, they can form only with difficulty, and the condensation is impeded. The relative stability of the clusters depends on the degree of cooling below the dew point (or, equivalently, the elevation of the vapor pressure above the saturated vapor pressure). This means that to drive the transition at a significant rate, the temperature sometimes has to be reduced well below the dew point.

Similarly, liquids can be supercooled. Pure water can be cooled³ to $-45\text{ }^{\circ}\text{C}$ (or less⁴) before ice begins to form. Again, it is the relative instability of tiny clusters of new phase which causes this phenomenon. Purity of the original phase is the key requirement, and often freezing nucleation experiments are conducted using finely divided liquids, either as an emulsion⁵ or an aerosol.^{6–9} In this way, trace impurities, which might aid the freezing process, are confined to a minority of the droplets, and their influence can be minimized.

It is generally agreed that clusters of the new phase with a critical size are instrumental in allowing nucleation to take place. The instability of smaller clusters with respect to the bulk metastable phase is reflected in their tendency to evaporate rather than to grow. However, this tendency is size dependent, and

large clusters prefer to grow, as they should do as they acquire more of the bulk characteristics of the new phase. The critical size is where the mean rates of decay and growth are equal. Once a critical cluster is formed as a result of stochastic fluctuation, it has a high probability of continuing to grow to form a macroscopic “lump” of new phase. Thus, the rate at which crystals, for example, are detected in a supercooled liquid is a reflection of the formation rate of critical clusters. The detected crystals are large, whereas their seeds, the critical clusters, may consist of only a few tens or hundreds of molecules. The properties of these clusters may be investigated by measuring the rate of formation of large crystals, and this is the amplification process alluded to above.

So, if nucleation rates are related to the probability of formation of critical clusters, then what do they tell us about their properties? The answer to this comes from either a kinetic treatment of cluster growth and decay¹⁰ or more general arguments from thermodynamics.^{11,12} Both approaches suggest that the probability of formation of a critical cluster is related to its reversible work of formation starting from the original phase. This in turn is related to thermodynamic properties of the cluster, in particular its energy and entropy, as well as its size. We shall investigate the work of formation in the next section, develop useful theoretical results from this formulation in section III, perform an analysis of data for the freezing of water in section IV, and draw conclusions in section V.

II. Work of Cluster Formation

The work of formation of a cluster of new phase of a given size depends on the constraints applied to the original phase. A convenient set of constraints for considering the creation of clusters in laboratory experiments is to hold constant the volume, temperature, and chemical potential of the system. We consider a permeable box of volume V , which is small enough to make the stochastic formation of more than one molecular cluster within it extremely unlikely. The box permits the insertion of material from an external reservoir at a constant chemical potential μ . The reservoir also maintains the system at a temperature T . The parameters μ and T are chosen so that the true equilibrium state is the solid phase (labeled “new” for generality) but the system is set up containing the liquid (“old”) phase. It remains in metastable equilibrium through the difficulty in creating a critical cluster.

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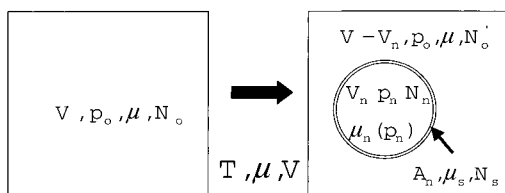


Figure 1. Formation of a cluster in a system with constant volume, temperature, and chemical potential. Refer to the text for the meaning of the symbols.

Now we consider the reversible formation and growth of a molecular cluster of new phase. Ordering the molecules and changing the density of the material require mechanical work to be provided externally (otherwise, the old phase would not be metastable), and Reiss¹¹ has provided a general formula for this reversible work for a variety of different sets of constraints. For our system, the work of formation is

$$\Delta w = \Delta E - T\Delta S - \mu\Delta N \quad (1)$$

where ΔE , ΔS , and ΔN are, respectively, the changes in internal energy, entropy, and number of molecules in the system brought about by the formation of the cluster.

At this point, we introduce the Gibbs model^{11,13,14} of a cluster: a spherical volume within which the material takes on the properties of the bulk new phase. This is surrounded by old phase, again characterized by old phase bulk properties. This is not at all what a cluster would look like on a microscopic scale, but it is a useful model. The errors in representing the properties of the cluster in this way are taken care of by introducing a surface phase with its own thermodynamic properties. Assuming that the work has created a single Gibbs cluster, the changes in system extensive variables are described by

$$\begin{aligned} \Delta E &= E_n + E_s + E'_o - E_o \\ \Delta S &= S_n + S_s + S'_o - S_o \\ \Delta N &= N_n + N_s + N'_o - N_o \end{aligned} \quad (2)$$

where suffices n, s, and o label the new, surface, and old phases, respectively. E'_o is the energy of the old phase in the system after the cluster has been formed, and E_o is the energy of the old phase in the absence of the cluster. Similar definitions apply to S'_o and S_o and to N'_o and N_o . The model is illustrated in Figure 1.

The work of formation is now written $\Delta w = \Delta\Omega$, where $\Omega = E - TS - \mu N$ is the grand potential (a thermodynamic potential which, as Reiss showed,¹¹ emulates the work of formation for the imposed constraints of constant T , V and μ). Writing the change in Ω in terms of contributions from each phase, we have

$$\begin{aligned} \Delta\Omega &= F_n + F_s + F'_o - F_o - \mu(N_n + N_s + N'_o - N_o) \\ &= (\mu_n N_n - p_n V_n) + F_s + (\mu N'_o - p_o(V - V_n)) - \\ &\quad (\mu N_o - p_o V) - \mu(N_n + N_s + N'_o - N_o) \end{aligned} \quad (3)$$

where $F_n = E_n - TS_n$, etc., and p_n and V_n are the volume and pressure of the new phase. $\Delta\Omega$ simplifies to

$$\Delta\Omega = (\mu_n - \mu)N_n + \Omega_s + (\mu_s - \mu)N_s - (p_n - p_o)V_n \quad (4)$$

where $\Omega_s = F_s - \mu_s N_s$ is the grand potential associated with

the surface phase, also represented by σA_n , where σ is the interfacial free energy and A_n the surface area of the cluster.

We have created reversibly a cluster of new phase and have assigned to it (and its surface) a variety of thermodynamic properties. Note that the volume V_n of the new phase is arbitrary but that surface properties such as σ and N_s take values to make $\Delta\Omega$ independent of where we place the so-called dividing surface between the phases. The requirement that the position of the dividing surface should not affect the thermodynamic properties is an important feature of the Gibbs model.

Having made such a choice and established the thermodynamic properties of each phase in the model, we now focus on the critical cluster, which we identify by its property of unstable equilibrium and, hence, the invariance of the work of formation under variation of unconstrained variables. These are the molecular numbers N_n and N_s and the cluster volume. T , μ , and p_o are held constant. We determine the increment in $\Delta\Omega$ arising from increments in these three quantities:

$$\begin{aligned} d\Delta\Omega &= (\mu_n - \mu)dN_n + d(\sigma A_n) + (\mu_s - \mu)dN_s - \\ &\quad (p_n - p_o)dV_n + N_n d\mu_n + N_s d\mu_s - V_n dp_n \end{aligned} \quad (5)$$

By introducing Gibbs–Duhem relations $N_n d\mu_n = V_n dp_n$ and $N_s d\mu_s = -A_n d\sigma$ (at constant T), we get

$$\begin{aligned} d\Delta\Omega &= (\mu_n - \mu)dN_n + \sigma dA_n + (\mu_s - \mu)dN_s - \\ &\quad (p_n - p_o)dV_n \end{aligned} \quad (6)$$

and so by demanding invariance in the form of $(\partial\Delta\Omega/\partial N_n)_{N_s, V_n} = 0$, etc., for the critical cluster, we obtain the conditions $\mu_n = \mu$, $\mu_s = \mu$, and $p_n - p_o = \sigma dA_n/dV_n$. These are familiar relations for a droplet in chemical and mechanical balance with its surroundings.¹¹ Denoting the properties of the critical cluster with an asterisk, we can now write the work of formation of the critical cluster as

$$\Delta\Omega^* = F_s^* - \mu N_s^* - (p_n^* - p_o)V_n^* \quad (7)$$

Useful relations known as nucleation theorems emerge when we determine the dependence of this work of formation on the external constraints, in this case T and μ .

III. Nucleation Theorems

The nucleation theorem was known empirically for some years before it was derived formally. In 1982, Kashchiev¹⁵ presented a phenomenological proof of a general thermodynamic relationship between the work of formation of a critical cluster and the size of this cluster. He noted that this relationship, or “theorem”, is satisfied by the classical theory of nucleation¹⁶ and showed that it leads to a virtually model-independent relationship between the size of the critical cluster, the nucleation rate, and the chemical potential difference between the old and new phases. Anisimov and co-workers¹⁷ also made use of the relationship, basing its validity upon the law of mass action. In 1993, Viisanen, Strey, and Reiss^{18,19} found that this relationship held quite generally using a statistical mechanical approach for single and multicomponent homogeneous vapor condensation. They noted that the relationship involved the excess in the number of molecules associated with the critical cluster over the number that would be present in the absence of a cluster. Further development was provided by Viisanen, Strey, Laaksonen, and Kulmala.²⁰ Heterogeneous multicomponent droplet nucleation was later treated by Kashchiev.¹⁴ It was Oxtoby and Kashchiev²¹ who in 1994 provided the name “nucleation

theorem” and a rigorous thermodynamic proof. All these developments took place independently of earlier work by Hill,^{22,23} who derived the central relationships in the thermodynamics of critical cluster formation but apparently did not realize their significance regarding the interpretation of experimental data. Inspired by Hill’s work, Ford²⁴ derived in 1996 a relationship between the temperature dependence of the nucleation work and the excess energy of the critical cluster (excess over the new phase). This result was a consequence of the explicit temperature dependence of the nucleation work, rather than the temperature dependence of the chemical potential difference, which had been explored earlier.^{15,21} This second nucleation theorem was developed for droplet nucleation from a single vapor¹⁰ and then extended to multicomponent vapors.²⁵ Luijten et al.²⁶ have gone on to investigate the dependence of the nucleation work on the total pressure for vapor-droplet systems.

Let us develop the central thermodynamic relationships again. Starting from eq 7 and using $dF_s = -S_s dT + \sigma dA_n + \mu_s dN_s$, we obtain

$$d\Delta\Omega^* = -S_s^* dT + \sigma dA_n^* + \mu dN_s^* - \mu dN_s^* - N_s^* d\mu - V_n^* dp_n^* + V_n^* dp_o - (p_n^* - p_o) dV_n^* \quad (8)$$

and through cancellation and a Gibbs–Duhem relation $d\mu = -s_o dT + v_o dp_o$, we get

$$d\Delta\Omega^* = -\left(S_s^* + S_n^* - s_o \frac{\rho_o}{\rho_n} N_n^*\right) dT - \left(N_n^* + N_s^* - \frac{\rho_o}{\rho_n} N_n^*\right) d\mu \quad (9)$$

where ρ_o and ρ_n are the molecular densities in the old and new phases, respectively, $v_o = 1/\rho_o$ is the volume per molecule in the old phase, and s_o is the entropy per molecule in the old phase. This equation is particular to the Gibbs model of a cluster, but it happens to be more general, as can be seen when it is written in the following form:

$$d\Delta\Omega^* = -\Delta S^* dT - \Delta N^* d\mu \quad (10)$$

where ΔS^* and ΔN^* (as defined in eq 2) are the additional entropy and molecular content that are gained by the system through the reversible formation of a critical cluster. We might call eq 10 the Hill relation, since it was first established by Hill in 1962.^{22,23}

The nucleation theorem follows from eq 10:

$$\left(\frac{\partial \Delta\Omega^*}{\partial \mu}\right)_T = -\Delta N^* \quad (11)$$

Since the rate of nucleation J is given by¹⁴ $J = J_0 \exp(-\Delta\Omega^*/kT)$, where k is Boltzmann’s constant, this corresponds to the useful result^{15,18,21}

$$\left(\frac{\partial \ln J}{\partial \mu}\right)_T = \left(\frac{\partial \ln J_0}{\partial \mu}\right)_T + \frac{\Delta N^*}{kT} \quad (12)$$

where J_0 is the so-called kinetic prefactor in the nucleation rate. The dependence of measured isothermal nucleation rates upon the chemical potential of the metastable phase therefore gives us the change in molecular content of the system associated with the creation of a critical cluster.

A further consequence of eq 10 is

$$\left(\frac{\partial \Delta\Omega^*}{\partial T}\right)_\mu = -\Delta S^* \quad (13)$$

and this relation is a key step on the way toward the derivation of the second nucleation theorem.^{24,10} Note that it explores the full temperature dependence of the nucleation work. The temperature dependence of the nucleation work which arises from the temperature dependence of the difference in chemical potential between the old and new phases was explored as a consequence of eq 11 by Kashchiev¹⁵ and Oxtoby and Kashchiev.²¹ Equation 13 also includes any explicit temperature dependence.

Let us express $d\Delta\Omega^*$ in terms of the pressure and temperature of the metastable phase instead. We have $d\mu = -s_o dT + v_o dp_o$, and so

$$d\Delta\Omega^* = -(\Delta S^* - \Delta N^* s_o) dT - \Delta N^* v_o dp_o \quad (14)$$

Furthermore

$$\begin{aligned} -T^2 d\left(\frac{\Delta\Omega^*}{T}\right) &= \Delta\Omega^* dT - T d\Delta\Omega^* \\ &= (E_s^* - TS_s^* - \mu N_s^* - (p_n^* - p_o)V_n^*) dT + \\ &\quad T(S_n^* + S_s^* - (N_n^* + N_s^*)s_o) dT + \\ &\quad \Delta N^* v_o T dp_o \end{aligned} \quad (15)$$

which simplifies to

$$\begin{aligned} -T^2 d\left(\frac{\Delta\Omega^*}{T}\right) &= (E_n^* + E_s^* - h_o(N_n^* + N_s^*) + p_o V_n^*) dT + \\ &\quad \Delta N^* v_o T dp_o \\ &= \left(\left(E_n^* + E_s^* - \frac{\rho_o N_n^* e_o}{\rho_n} \right) - \right. \\ &\quad \left. \left(N_n^* + N_s^* - \frac{\rho_o N_n^*}{\rho_n} \right) h_o \right) dT + \Delta N^* v_o T dp_o \\ &= (\Delta E^* - h_o \Delta N^*) dT + \Delta N^* v_o T dp_o \end{aligned} \quad (16)$$

where ΔE^* is the energy gained by the system through the creation of the critical cluster, as defined by eq 2, and $h_o = \mu + s_o T$ is the enthalpy per molecule of the old phase.

The final line in eq 16 demonstrates the generality of the result beyond the Gibbs model. We can now write down results that are particularly useful for analyzing nucleation rate data gathered for a range of temperatures and pressures:

$$\left(\frac{\partial \Delta\Omega^*}{\partial p_o}\right)_T = -v_o \Delta N^* \quad (17)$$

and

$$\left(\frac{\partial(\Delta\Omega^*/T)}{\partial T}\right)_{p_o} = -\frac{1}{T^2}(\Delta E^* - h_o \Delta N^*) \quad (18)$$

Equation 17 is simply a restatement of eq 11 and has been derived before.^{27,14} Similar results regarding the pressure dependence of nucleation rates have also been proved and exploited,²⁶ and the significance of the pressure dependence was speculated upon some years ago.²⁸ Equation 18 is new and offers the possibility of obtaining information about the excess energy of the critical cluster from knowledge of the temperature dependence of the nucleation rate of freezing at constant pressure. It is an analogue of the second nucleation theorem derived for droplet nucleation from vapors,^{24,10} the difference being that in that case the derivative is taken with vapor supersaturation held constant, while in eq 17 it is the pressure.

Temperature and pressure are convenient control variables for the collection of nucleation rate data for freezing. The mathematical complementarity of eqs 17 and 18 is clear.

IV. Data Analysis

The nucleation rate for freezing can be written^{29,30} in the form

$$J = \left[\rho_o \frac{kT}{h} \exp(-\Delta g_a/kT) \right] \exp(-\Delta \Omega^*/kT) \quad (19)$$

where h is Planck's constant and Δg_a is the free energy of activation for molecular diffusion in the old phase. The terms in square brackets therefore are a representation of J_0 . The temperature and pressure dependence of Δg_a has been investigated by Jeffrey and Austin,³¹ and we use their formulation here. Other parametrizations³² do not include the pressure dependence that we need. It turns out that partial derivatives of $\ln J_0$ account for about 10% of the magnitude of the partial derivatives of $\ln J$, and so it is important to consider them in the analysis.

We now turn to the freezing data that are to be analyzed. Koop et al.³³ have recently compiled a range of data for the freezing of ice from pure water and aqueous solutions of various salts. They proposed a parametrization for the homogeneous freezing rate as a function of the liquid water activity or, equivalently, the liquid water chemical potential. This is supported by the observation that data for solutions of various salts, and at various pressures, collapse onto a single curve of freezing temperature against activity. Since the chemical potential of water is known as a function of temperature and pressure, the equations used by Koop et al.³³ provide the freezing rate as a function of temperature and pressure, which is just what we need. We focus here on the freezing of pure water and leave for a later study the consideration of ice formation from aqueous solutions.

The suggested equation for J (in units of $\text{cm}^{-3} \text{s}^{-1}$) is

$$\log_{10} J = -906.7 + 8502\Delta a_w - 26924(\Delta a_w)^2 + 29180(\Delta a_w)^3 \quad (20)$$

where $\Delta a_w = \exp(\eta/kT) - a_i$, and

$$\eta = \left(v_w \left(p_o - \frac{1}{2} \kappa_w p_o^2 - \frac{1}{6} \frac{\partial \kappa_w}{\partial p_o} p_o^3 \right) - v_i \left(p_o - \frac{1}{2} \kappa_i p_o^2 - \frac{1}{6} \frac{\partial \kappa_i}{\partial p_o} p_o^3 \right) \right) \quad (21)$$

v_i and v_w are the molecular volumes in pure ice and liquid water at zero pressure, respectively, κ_i and κ_w are the isothermal compressibilities, also at zero pressure, $\partial \kappa_{i,w}/\partial p_o$ are their partial derivatives with respect to pressure, and $a_i = \exp((\mu_w - \mu_i)/kT)$, where μ_w and μ_i are the chemical potentials of liquid water and ice, respectively, again at zero pressure.

The properties of water are given by Koop et al.³³ as

$$v_w = \frac{10^{-6}}{N_A} (-230.76 - 0.1478T + 4099.2/T + 48.8341 \ln T)$$

$$v_i = \frac{10^{-6}}{N_A} (19.43 - 2.2 \times 10^{-3}T + 1.08 \times 10^{-5}T^2)$$

$$\mu_i - \mu_w = \frac{1}{N_A} (210368 + 131.438T - 3.32373 \times$$

$$10^6/T - 41729.1 \ln T) \quad (22)$$

all in SI units, with N_A equal to Avogadro's number, and $\kappa_w =$

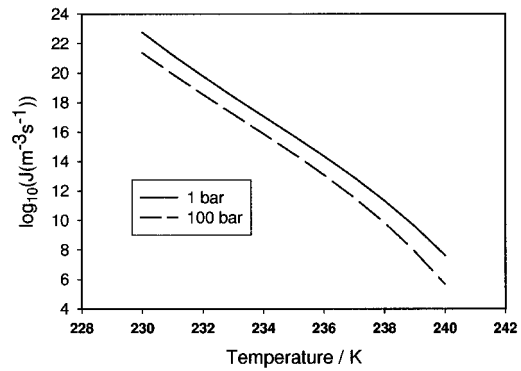


Figure 2. Dependence of freezing nucleation rate upon temperature and pressure, according to the Koop et al.³³ parametrization.

1.6 GPa^{-1} , $\kappa_i = 0.22 \text{ GPa}^{-1}$, $\partial \kappa_w/\partial p_o = -8.8 \text{ GPa}^{-2}$, and $\partial \kappa_i/\partial p_o = -0.17 \text{ GPa}^{-2}$. The equations provide nucleation rates as a function of temperature and pressure, as illustrated in Figure 2.

It is straightforward to evaluate the numerical derivatives of $\ln J$ with respect to T and p_o and to obtain the critical cluster properties with the aid of the given properties of water.

We now need to consider how to present these cluster properties. The analysis provides ΔE^* and ΔN^* , and these are model-independent quantities associated with the formation of the critical cluster. On the other hand, it is illuminating to focus on the Gibbs model of a cluster and to calculate its size in terms of N_n^* and N_s^* . These quantities depend on the position of the dividing surface, but it is possible to choose a position where the molecular content of the surface phase is zero. This is the equimolar dividing surface.^{13,14} Then eq 17 gives¹⁴

$$\left(\frac{\partial \ln J}{\partial p_o} \right)_T = \left(\frac{\partial \ln J_0}{\partial p_o} \right)_T + N_{n,EDS}^* \frac{(v_w - v_i)}{kT} \quad (23)$$

where we have made the approximation that the new phase density ρ_n (at pressure p_n) is given by $1/v_i$. We shall refer to $N_{n,EDS}^*$ as the critical cluster size i^* (in molecules).

As for the right-hand side of eq 18, it is convenient to write the term in brackets in the form

$$\Delta E^* - h_o \Delta N^* = E_x^* - (N_n^* + N_s^*) L_f + p_o (V_n^* - (N_n^* + N_s^*) v_n) \quad (24)$$

where $L_f = h_o - h_n$ is the latent heat of fusion per molecule and h_n and v_n are the enthalpy and volume per molecule in the new phase at the pressure p_o . E_x^* is termed the excess energy, defined by

$$E_x^* = E_n^* + E_s^* - (N_n^* + N_s^*) e_n \quad (25)$$

where e_n is the energy per molecule in the new phase at pressure p_o . The excess energy is the energy of the cluster minus the energy the component molecules would have in the bulk new phase at the same temperature and pressure. The last term in eq 24 can be neglected, since $p_o v_n \sim 10^{-3} kT$ at room temperature and pressure for a condensed phase, and because $(N_n^* + N_s^*)$ is less than 10^3 in the calculations to be described shortly and $V_n^* \leq (N_n^* + N_s^*) v_n$, the last term is probably no larger than kT . If we now focus on the cluster defined by the equimolar dividing surface, then

$$\left(\frac{\partial \ln J}{\partial T} \right)_{p_o} = \left(\frac{\partial \ln J_0}{\partial T} \right)_{p_o} + \frac{1}{kT^2} (E_x^* - i^* L_f) \quad (26)$$

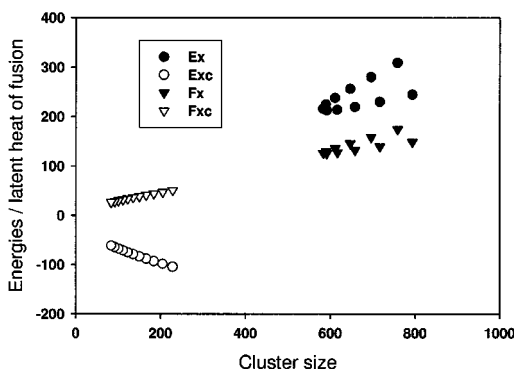


Figure 3. Excess energies and free energies, for clusters of critical size, extracted from data (Ex and Fx) and calculated from the classical theory (Exc and Fxc). The temperature ranges from 230 to 240 K. All energies are shown in units of the latent heat of fusion per molecule L_f evaluated at the appropriate temperature.

The temperature derivatives of J_0 are available from the Jeffrey and Austin parametrization³¹ of Δg_a , and the (temperature dependent) molecular latent heat of fusion of water is obtainable from

$$h_o - h_n = -T^2 \left(\frac{\partial((\mu_w - \mu_i)/T)}{\partial T} \right)_{p_o} \quad (27)$$

and eq 22. Hence, the excess energy of the critical cluster (defined according to the equimolar dividing surface) may be extracted. It is the cluster energy minus the energy the component molecules would have in a bulk new phase at the same temperature and pressure as the original phase. It is a useful quantity to consider since in the limit of large cluster size, it may be identified with the surface energy. For smaller clusters, which might not possess any similarity to the bulk condensed phase, it is not so straightforward to identify it. Nevertheless, it controls the temperature dependence of the nucleation rate.

Using the nucleation data and material properties provided by Koop et al.³³ and Jeffrey and Austin,³¹ together with eqs 23 and 26, a plot of excess energy against cluster size can be constructed, as in Figure 3. The points labeled Ex are the excess energies, normalized by the molecular latent heat of fusion L_f , which is on the order of 0.042 eV. They have been obtained for temperatures in the range 230–240 K and for a pressure of 10^5 Pa.

The critical cluster sizes lie in the region of 600–800 molecules. Each point corresponds to a critical cluster at a particular temperature, and this might explain why some clusters do not have a unique excess energy. However, the higher excess energies refer to clusters at lower temperatures, which is perhaps counterintuitive. Alternatively, the results may be a consequence of the manner in which the data have been fitted, and the true temperature dependence of E_x might be smaller. We shall come to the possibility of inaccuracies in the fits to data at the end of this section. In any case, the results certainly suggest that the excess energy for a cluster of about 600 molecules lies in the region of $200L_f$. This is very reasonable if one takes the view that the cluster is globular, with the center very much like bulk ice and with about $(36\pi)^{1/3}N_n^{2/3}$ of the molecules residing at the surface,¹⁶ in a bonding environment halfway between that of the ice and water phases. The excess energy would then be about $350 \times (L_f/2)$ or $175L_f$, in reasonable agreement with the data. Furthermore, the excess energy rises with size, which reflects the increase in surface area.

This behavior can be contrasted with the predictions of classical nucleation theory.³⁴ This is based on the Gibbs cluster model with a surface tension equal to the plane interface value, chosen here to be³² $\sigma = 10^{-3} (28 + 0.25(T - 273))$ J m⁻². Classical nucleation theory suggests that $\ln(J/J_0) = -16\pi\sigma^3 v_n^2 / (3kT(\mu - \mu_n^0)^2)$, where μ_n^0 and v_n are the chemical potential and the molecular volume for the new phase at pressure p_o . When this expression is inserted into eqs 23 and 26, we obtain critical sizes which are on the order of 100 and excess energies which are negative, as shown by the points labeled Exc in Figure 3. It is hard to see how having a cluster which is more strongly bound than its component molecules would be in bulk ice is compatible with the classical picture of the cluster as a scaled down version of a crystal with bulk material properties. It is a symptom of the failure of the classical theory of freezing to account for experimental data.

It is possible to go further and extract the excess free energy of the critical cluster. We have

$$\begin{aligned} -kT \ln(J/J_0) &= \Delta\Omega^* = F_s^* - \mu N_s^* - (p_n^* - p_o)V_n^* \\ &= \Delta F^* - \mu\Delta N^* \\ &= F_x^* - (N_n^* + N_s^*)\Delta\mu + p_o(V_n^* - (N_n^* + N_s^*)v_n) \end{aligned} \quad (28)$$

where $\Delta\mu = \mu - \mu_n^0$, with μ_n^0 again referring to the chemical potential of the new phase at the pressure of the old phase. For the water data, $\Delta\mu = \mu_w - \mu_i$. Also, $F_x^* = F_n^* + F_s^* - (N_n^* + N_s^*)f_n$, with f_n equal to the free energy per molecule in the new phase at the pressure p_o . It is the excess free energy; the free energy of the cluster minus the free energy its component molecules would have in a bulk new phase at the pressure of the old phase.

The second line in eq 28 demonstrates the generality of the result. The last line, once the final term has been neglected (following arguments similar to those used with regard to eq 24) and when the equimolar dividing surface has been chosen, is equivalent to the familiar result¹⁶

$$\Delta\Omega^* = F_x^* - i^*\Delta\mu \quad (29)$$

In the classical theory of nucleation, F_x would be represented by σA_n , with σ given by the plane surface interfacial free energy and A_n by the surface area of a sphere of volume i^*v_n . By inserting data for J and using the Jeffrey and Austin model³¹ to evaluate J_0 , eqs 28 and 29 can be used to extract the excess free energy of the critical cluster. These values are plotted in Figure 3 and labeled Fx. Once again, the results are satisfactory: they lie below the excess energies, implying a positive cluster excess entropy $S_x^* = (E_x^* - F_x^*)/T$ to be expected of globular clusters of new phase with disorder at the surface. Furthermore, the excess free energy and the excess entropy both increase with cluster size.

The same analysis can be done for classical nucleation theory, yielding the excess free energies labeled in Figure 3 as Fxc. In contrast to the excess energies these are positive. Clearly, the classical theory implies a negative excess entropy, which again is rather inconsistent with the classical picture. It is striking, however, that the excess free energy, when extrapolated up to the cluster sizes which really appear to be acting as the critical nuclei, is not dissimilar to the extracted excess free energies labeled Fx. Equivalently, the extracted free energies may be used to calculate an effective surface tension σ_{eff} which is compared with the bulk surface tension in Figure 4. This is in

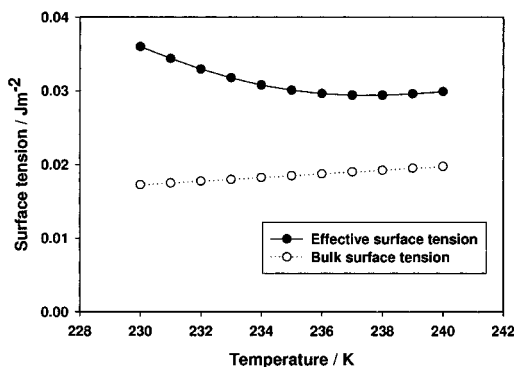


Figure 4. Effective surface tension which can account for the nucleation data when used within the framework of the classical theory and with the physical properties of water specified by Koop et al.³³ and Jeffrey and Austin.³¹ Note that the critical clusters used to generate the effective surface tension are larger at the highest and lowest temperatures than at the middle of the range so that the plot reflects a possible size dependence as well as temperature dependence.

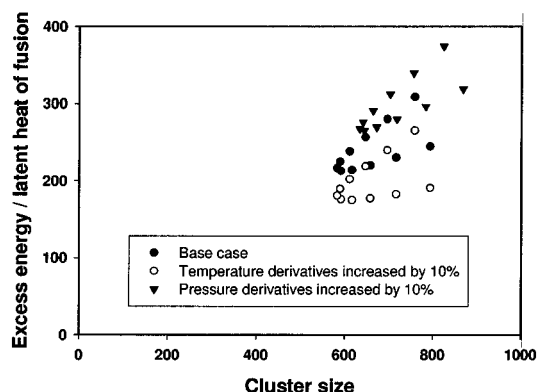


Figure 5. Changes in the plot of excess energy against cluster size when $(\partial \ln J/\partial T)_{p_0}$ is multiplied by 1.1 (open circles), or when $(\partial \ln J/\partial p_0)_T$ is multiplied by 1.1 (triangles), compared to an unperturbed case shown as filled circles.

contrast to the rather greater differences between the classical excess energy and extracted values. Note, however, that the effective surface tension might be reflecting a size dependence as well as the temperature dependence given. The critical sizes in the middle of the temperature range are smaller than those at the extremities.

There is one more aspect to consider in this analysis, and that is the sensitivity of the results to any inaccuracies that might exist either in the Koop et al.³³ fit to the freezing nucleation rate or in the fits to physical data that have been inserted into the theoretical formulas. We have examined this in the following simple way. If we multiply the numerical derivatives of $\ln J$ with respect to temperature at constant pressure by a uniform factor of 1.1, the values of excess energy change by about 20%, as shown in Figure 5 as open circles. Similarly, if we multiply the numerical derivatives with respect to pressure at constant temperature by a factor 1.1, then the plot of excess energy against size changes to the triangular points. We believe that such factors overestimate the uncertainty in the fits made by Koop et al.³³ so that our uncertainty in excess energy at a specific cluster size is within 20%. In light of this, we cannot be definite about the apparent variation in cluster excess energy with temperature discussed earlier.

V. Conclusions

We have used the thermodynamics of critical cluster formation to study the properties of small ice clusters in supercooled

water. The key eq 10 indicates how the work of formation depends on the external chemical potential and temperature. The dependence on the applied pressure and temperature can then be expressed in eq 16. The analysis produces information about the fluctuations in energy and molecular content associated with the formation of a critical cluster of the new phase within the system. These fluctuations have been interpreted using the Gibbs model of a cluster so that we can deduce the size, excess energy, and free energy of a critical cluster, the one which is equally likely to grow or to decay in the prevailing conditions.

We have studied freezing nucleation data parametrized by Koop et al.³³ The results of the analysis seem to be physically reasonable, in that the excess quantities are consistent with a model of the clusters as compact objects. Thus, a cluster of 600 water molecules has an excess energy of $200L_f$, with an uncertainty of probably less than 20%, where L_f is the molecular latent heat of fusion, and this is consistent with a roughly spherical ice crystallite with about 350 molecules lying at the surface. It would be instructive to compare these conclusions with simulations of water crystallization.³⁵ In any case, the present analysis offers a unique experimental viewpoint on the properties of small ice clusters in supercooled water.

In contrast, the same analysis of rates predicted by the classical theory of freezing nucleation produces odd features, such as negative excess energies. The classical critical sizes are also far smaller than the critical sizes suggested by the data. This merely reflects the failure of classical theory to account for the rate of homogeneous freezing.³² We have estimated an effective ice–water surface tension which can account for the data, when used in conjunction with physical data provided by Koop et al.³³ and Jeffrey and Austin.³¹ This might be useful for calculations of the freezing of water droplets in the atmosphere.^{29,30,34,36}

In carefully designed nucleation experiments, the rate of production of micron-sized crystals, detectable experimentally, corresponds to the rate of formation of critical clusters, which are usually far too small to be seen. Systems with such an amplification of a microscopic event are often deliberately engineered in the laboratory to gain insight into events on the microscopic scale. The familiar process of the nucleation of a phase transition is a good example of such a system.

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