

Homogeneous nucleation theory and experiment: A survey

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Abstract - Theories describing the homogeneous nucleation of a supersaturated vapor are presented, critically discussed, and compared to experiment. Extensions of these theories to nucleation on smooth surfaces, and to nucleation with simultaneous chemical reaction also are described.

INTRODUCTION

There are some phase transitions which occur whenever experimental conditions change such that a new phase becomes more stable. These include evaporation from the surface of a pure liquid and the melting of a pure crystal. However, there are other phase transitions for which this is not the case. Examples of phase changes which often occur at other than equilibrium conditions are condensation of a gas and crystallization of a melt. Gases supersaturate, melts supercool, and they need to nucleate before a new phase can be formed. Melting and boiling (i.e., phase changes which almost always occur at equilibrium) differ from condensation and crystallization because they occur at a free surfaces. If one carefully eliminates all free surfaces, by surrounding a liquid with another liquid whose boiling point¹ is much higher or by heating only the center of a single crystal², both can be superheated extensively.

Phase transitions usually occur in an irreproducible fashion as a result of the variety of heterogeneous nuclei that are present. It is therefore difficult to accurately characterize crucial experimental parameters, except in experiments specifically designed to study homogeneous nucleation or heterogeneous nucleation on homogeneous surfaces.

Homogeneous nucleation is more than just theoreticians' desire to simplify interesting problems until they can be solved. There are a number of "real world" situations in which it is the dominant mechanism for phase transition, e.g., condensation in supersonic nozzles³, explosions which occurs when a cold liquid contacts a much hotter one⁴, formation of heavily microcrystallized ceramics⁵. Furthermore, experimental techniques to study homogenous nucleation^{6,7,8} have advanced significantly in recent years. Today one can measure, to better than one percent, the supersaturations required to cause a gas to condense(11-17). Similarly, one knows the temperatures to which liquids can be superheated¹ to about $\pm 0.5K$.

HOMOGENEOUS NUCLEATION

A snapshot of the molecules present in a supersaturated state would show small clusters of the new phase containing two, three, or more molecules. There also would be occasional clusters containing a larger number of molecules; however, a motion picture of these larger clusters would show that most are very short lived; they grow rapidly and then shrink rapidly. Nucleation occurs when a cluster of two, three, four, or some other small number of particles grows (fluctuates in size) to a size large enough that it then continues to grow rather than shrink.

A critical-sized nucleus is a cluster of a size such that its rate of growth is equal to its rate of decay. Clusters which fluctuate to a size larger than the critical size will probably continue to grow to macroscopic size, while clusters smaller than the critical size most likely will shrink. The nucleation rate is the net number of clusters per unit time which grow larger than the critical size.

In dilute solution, whether gaseous or condensed, the concentration of clusters (dimers, trimers, etc.) is much lower than the concentration of monomers (except when there are strong interatomic forces, e.g., carboxylic acids, metals). Because of their very low concentrations, clusters rarely collide. The assumption that clusters grow only by the addition of *single* molecules is therefore quite accurate. From the principle of microscopic reversibility (i.e., that *at equilibrium* every forward process has to be matched by its corresponding reverse process) it follows that evaporation also occurs one molecule at a time.

The net rate, $J(i)$, at which clusters of size i grow to size $i+1$ is the difference between the rate at which clusters of size i add an additional molecule, and the rate at which clusters of size $i+1$ lose a molecule, that is

$$J(i) = f(i)n(i) - b(i+1)n(i+1) \quad (1)$$

where $f(i)$ represents the forward rate--the rate of addition of molecules to a cluster, $b(i+1)$ is the backward rate--the rate of loss of molecules from a cluster, and $n(i)$ is the concentration of clusters of size i . Each of these quantities, and hence $J(i)$, are functions not only of temperature, cluster size, and pressure, but also can be functions of time.

A convenient equation which contains all the nucleation information can be readily derived by defining a recursive relation⁹

$$Z(i+1) \equiv \frac{Z(i) b(i+1)}{f(i+1)} \quad \text{for } i > 1 \quad \text{and} \quad Z(1) = 1 \quad (2)$$

This recursive relation is easily solved yielding

$$Z(i) = \prod_{j=1}^i \frac{b(j)}{f(j)} \quad (3)$$

Multiplying Eq. (1) by $Z(i)$ and summing, one obtains

$$\sum_{i=1}^{\bar{i}} J(i) Z(i) = \sum_{i=1}^{\bar{i}} [f(i) n(i) Z(i) - f(i+1) n(i+1) Z(i+1)] \quad (4)$$

Note that the two terms on the right-hand side are identical except that their indices differ by unity. On summing, successive terms cancel and Eq. (5) simplifies to

$$\sum_{i=1}^{\bar{i}} J(i) Z(i) = f(1) n(1) - f(\bar{i}+1) n(\bar{i}+1) Z(\bar{i}+1) \quad (5)$$

By carrying out the summation to sufficiently large \bar{i} , the last term on the right-hand side becomes negligible compared to the first because $Z(i+1)$ rapidly goes to zero as i becomes large. This can be seen from Eq. (4). The quotient $b(i)/f(i)$ is the ratio of the number of clusters of size i that shrink to those that grow. At any supersaturation there is a critical size i^* , defined as that size for which this ratio is unity. For all sizes smaller than the critical size the ratio is greater than one, while for all sizes larger than the critical size this ratio is less than one. Since there are only a finite number of sizes smaller than the critical size (and $b(i)/f(i)$ is finite for all i) the product of $b(i)/f(i)$ over all i can be made arbitrarily small by making i arbitrarily large. Furthermore, in most cases of interest, a steady state is rapidly established. Thus, J becomes a constant for all sizes, can be factored out of the summation, and one obtains

$$J = f(1) n(1) \left/ \left[1 + \sum_{i=2}^{\bar{i}} \prod_{j=2}^i \frac{b(j)}{f(j)} \right] \right. \quad (6)$$

To proceed further, one needs explicit expressions for the backward rate $b(i)$ and the forward rate $f(i)$.

Consider the condensation of a one-component supersaturated gas. The forward rate, that is the rate that impinging molecules condense, is the product of $a(i)$, the surface area of the cluster, β , the rate per unit area at which molecules impinge on the surface, and α , the condensation coefficient, i.e.,

$$f(i) = a(i) \beta \alpha \quad (7)$$

For an ideal gas, the impingement rate of molecules on a cluster is

$$\beta = \frac{P}{\sqrt{2\pi m k T}} \quad (8)$$

The condensation coefficient α is a complicated and unknown function of cluster size. However, its effect on the nucleation rate is relatively small since, as will be shown later, the nucleation rate depends primarily on a ratio of backward to forward rates and in this ratio α cancels.

The backward rate is the rate at which molecules leave a cluster. This is much more uncertain. I will now present two different approaches to obtaining it, first by using the Kelvin equation, and then using one's knowledge of the distribution of clusters in a saturated vapor. For single component - single process nucleation, these give essentially identical results. The Kelvin equation states that the partial pressure of a vapor in equilibrium with a liquid drop of radius r is

$$P_K(r) = P_e \exp\left[\frac{2\sigma v}{kTr}\right] \quad (9)$$

where P_e is the vapor pressure above a flat surface of the same liquid, σ is the surface tension of a flat surface of the same liquid, v is its molecular volume, k is Boltzmann's constant and T is the temperature. If one makes the assumption that a cluster of i molecules is a droplet of radius r , surface area $4\pi r^2$, volume $4/3\pi r^3$, and of the same density as normal liquid, i.e. $4/3\pi r^3 = iv$, then the rate at which ideal gas molecules leave such a cluster is, $b(i)$ is given by

$$b(i) = \frac{a(i) P_K(r) \alpha}{\sqrt{2\pi m k T}} \quad \text{and} \quad \frac{b(i)}{f(i)} = \frac{P_K(r)}{P} \quad (10)$$

Substituting Eqs. (9) and (10) into Eq. (6) and converting from using the radius, r , to number of molecules in the cluster, i , as the size variable and using the above assumption one obtains

$$J = f(1)n(1) \left/ 1 + \sum_{i=2}^{\bar{i}} \left[S^{-i} \exp\left(\gamma \sum_{j=2}^i j^{-1/3}\right) \right] \right. \quad \text{where} \quad \gamma = \left(\frac{32\pi}{3}\right)^{1/3} \sigma v^{2/3} / kT \quad \text{and} \quad S \equiv \frac{P}{P_e} \quad (11)$$

Equation (11) must be solved numerically, but this can be easily accomplished on a small computer. We shall call this the Kelvin solution. There is another way of obtaining the rate of nucleation.¹⁰ Consider what happens whenever the number density of solute molecules (i.e. molecules which can condense) is much smaller than the number density of solvent molecules (i.e. molecules which are otherwise uninvolved in the nucleation process except that their presence maintains thermal equilibrium). In such cases, the backward rate $b(i+1)$, although it can be a complicated function of temperature and cluster size, is independent of the concentration of the nucleating species, i.e., the solute. Thus one can obtain $b(i+1)$ by realizing that at true equilibrium, (i.e., in a *saturated* vapor) the nucleation rate $J(i)$ is zero for *all* i and therefore from Eq. (1) one finds that:

$$b(i+1) = b_e(i+1) = \frac{f_e(i)n_e(i)}{n_e(i+1)} \quad (12)$$

where the subscript e is used to remind the reader that these concentrations and forward rates refer to those found at *saturation*, not those in the actual nucleating vapor. Equation (12) can be substituted into Eq. (6) to obtain the desired answer. A simplification occurs when $f(i)/f_e(i)$ is independent of the size of the cluster. This is usually the case and occurs when the forward rate is a product of terms which are either size independent or whose size dependence is independent of supersaturation. Assuming so, and using Eqs. (7) and (8) one obtains

$$J = \frac{1}{\sum_{i=1}^{\bar{i}} \left[a(i) \beta \alpha n_e(i) \left(\frac{P}{P_e}\right)^i \right]^{i-1}} \quad (13)$$

Equation (13) can be written in the standard form of classical nucleation theory by making the additional assumption that the equilibrium cluster distribution is defined by

$$n_e(i) = N \exp\left[-\frac{W(i)}{kT}\right] \quad (14)$$

where N is a normalization constant and $W(i)$ is the reversible work required to form a cluster of size i .

One should note that as usually written, Classical Theory is internally inconsistent because N , the normalization constant, is assumed equal to the number of *monomers* that are present, i.e., P/kT , and $W(i)$ is assumed equal to the product of the area of the cluster and the surface tension of a flat liquid surface of the same temperature and composition as the nucleus, i.e. ($W(i) = \sigma a(i)$). Applying these two assumptions simultaneously leads to the internal inconsistency that this expression for cluster size of 1 does not return the number of monomers present. One can impose self-consistency by dividing $n(i)$ by $n(1)$ and obtain

$$n_e(i) = n_e(1) \exp \left[-\frac{W(i) - W(1)}{kT} \right] \quad (15)$$

If one maintains the assumptions that $W(i) = \sigma a(i)$ and that all clusters are spherical and of normal liquid density all the way down to a cluster size of one, the result is:¹

$$n_e(i) = n_e(1) \exp[-\theta (i^{2/3} - 1)] \quad \text{where} \quad \theta = 4\pi \left(\frac{3v}{4\pi} \right)^{2/3} / kT \quad (16)$$

Of course it may be unreasonable to make such an assumption about the work that is required to form a monomer. However this assumption also *can be viewed* as the simplest approximation for the *radius dependence* of the surface free energy, and it does provide a smoothly changing value for σ from that measured for a flat surface to that appropriate for a monomer, i.e. zero. Using Eq. (17) changes Classical Theory by an extra term, $\exp(\theta)/S$, where S is the supersaturation.¹¹ From the supersaturation dependence alone, one cannot decide which version of Classical Theory is better since in both cases agreement was very good. However, one can make a judgement based on Figure 1. It shows that a temperature dependent correction is required for quantitative agreement between experimental results and theoretical predictions for n -nonane. The very short dash line uses the Kelvin approach, the middle length dash line uses the internally consistent form of Classical Theory and the long dash line uses traditional Classical Theory. (The actual data is included with the long dash line to show the experimental scatter, which is the same for each line since the experimental data is the same.) One can see that the temperature dependent multiplicative correction which is required to cause agreement with experiment varies much less with temperature when internal consistency is imposed on Classical Theory and the correction varies even slightly less when the Kelvin approach is used. In the above case its value varies by about six orders of magnitude, from 10^1 to 10^7 at 232 K and 314 K respectively, for the internally consistent Classical Theory, but by nine orders of magnitude, from 10^{-5} to 10^4 at 232 K and 314 K respectively for the original version. This strong decrease in variation with temperature suggests that the self-consistent version is superior. In addition, note that the numerical value which is calculated by the internally consistent form of Classical Theory is very close to that calculated by the Kelvin approach. These differences, at most a factor of 2 (which decreases with increasing cluster size), are very small compared to the up to 6 orders of magnitude difference from traditional Classical Nucleation Theory. The Kelvin approach provides the best predictions of experimental results. However, if one desires a closed form of nucleation theory rather than the numerical solution, obtained in less than tenths of seconds with a personal computer, one can use the internally consistent form of Classical Theory.

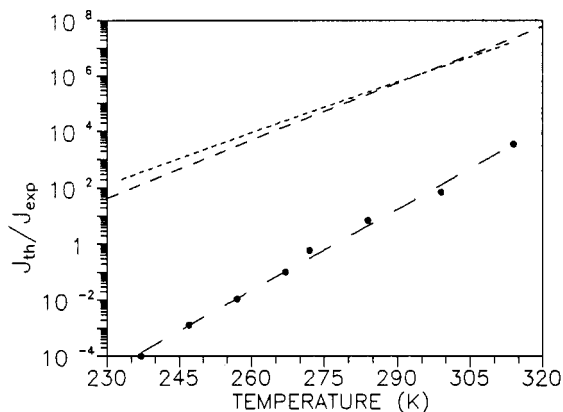


Figure 1

The general solution for the nucleation rate given by Eq. 6 can be used for other more complex nucleation systems, e.g. when clusters can grow and decay by more than one mechanism. Consider the nucleation and growth of condensate nuclei on smooth surfaces, e.g. an immiscible liquid.¹² Figure 2 shows this can occur by the addition of molecules both from the vapor and from molecules adsorbed on the substrate.

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For such a system, one can find the number of clusters containing i molecules per unit area of substrate surface at equilibrium, assuming, as in other nucleation theories, that Eq. 14 is valid. Using

thermodynamic arguments, one obtains

$$n_e(i) = n_e(1) \exp[-(\sigma_{vc} a_{vc} + \sigma_{cs} a_{cs} - \sigma_{vs} a_{vs}) / kT_s] \quad (17)$$

A condensate cluster can grow by direct condensation from the vapor at a rate of β molecules per unit interfacial area per unit time and by condensation from the adsorbed molecules at a rate of α molecules per unit circumferential length per unit time. They can shrink by evaporation of molecules to the vapor and by evaporation of molecules to the adsorbed layer at rates of γ and δ respectively. Thus, the net rate at which clusters containing i molecules become clusters containing $i+1$ molecules is

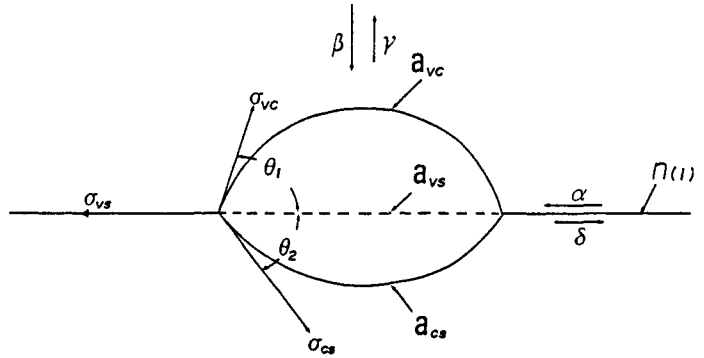


Figure 2

$$J(i) = [\beta a_o i^{2/3} + \alpha l_o i^{1/3}] n(i) - [\gamma a_o (i+1)^{2/3} + \delta l_o (i+1)^{1/3}] n(i+1) \quad (18)$$

where a_o and l_o are the surface area of the cluster in contact with the vapor and the cluster circumference at the substrate cluster border. Note that even though Eq. 18 appears complicated it is in the form of Eq. 1. In an analogous manner to the development of Eq. 12, one may solve for the backward rate for any dilute condition by solving for it at equilibrium, i.e. when the partial pressure of condensate molecules in the vapor phase is equal to its equilibrium vapor pressure.

$$b(i) = b_e(i) = [\beta_e a_o (i-1)^{2/3} + \alpha_e l_o (i-1)^{1/3}] n_e(i-1) / n_e(i) \quad (19)$$

Substituting into Eq. 6 one obtains the nucleation rate

$$J = \frac{(\beta a_o + \alpha l_o) n(1)}{\sum_{i=1}^{\bar{i}} \frac{n_e(1)}{n_e(i)} \prod_{j=2}^i \frac{\beta_e a_o (j-1)^{2/3} + \alpha_e l_o (j-1)^{1/3}}{\beta a_o j^{2/3} + \alpha l_o j^{1/3}}} \quad (20)$$

We have thus obtained an expression for the steady state rate of nucleation of droplets of the condensing material in terms of the arrival rates of molecules from the vapor and from the adsorbed surface phase and in terms of the concentration of clusters that would exist on the surface if the partial pressure of the condensing material were equal to its equilibrium vapor pressure.

Other, even more complex multiple processes are possible. Consider the condensation which occurs as a result of a chemical reaction. If clusters of the condensing substance can themselves serve as sites for the reaction, then again there are two forward processes; the clusters can grow by arrival of the reaction product, and the cluster can grow by arrival of the reactants followed by reaction on (or in) the cluster. The corresponding backward processes also occur. Elaboration of these ideas and their application to the condensation of SiO_2 has been published.¹³

An even more complex example is the nucleation process which occurs in the claddings of fuel rods in nuclear reactors. Energetic neutrons knock atoms from their lattice sites, creating high concentrations of vacancies and of interstitial atoms. The vacancies can cluster and grow to become voids, typically 50 to 100 Å in diameter. The interstitial atoms also nucleate and form interstitial loops, that is an extra plane of atoms growing radially. These structural defects lead to swelling and warping of the fuel rods.

The description of this nucleation phenomenon is more complicated because the vacancies and interstitials are matter and antimatter to each other. Not only can they combine directly with each other to produce nothing (except a release of energy), but each can also combine with clusters of the opposite species to make the cluster smaller by one unit. Furthermore, the clusters are capable of evaporating not only the

self specie, but also the opposite specie. In the limit that vacancies and interstitials arrive at a void at the same rate, no growth occurs. The forward and backward rates are now the sum of two terms:

$$f(x) = [\beta^v + \gamma^i(x)] a(x) \quad \text{and} \quad b(x) = [\beta^i + \gamma^v(x)] a(x) \quad (21)$$

where β^v is the condensation rate (per unit area) of vacancies, $a(x)$ is the surface area of a vacancy cluster, $\gamma^i(x)$ is the rate (per unit area) at which a cluster composed of x vacancies emits an interstitial atom, β^i is the condensation rate (per unit area), and $\gamma^v(x)$ is the rate of emission of vacancies from a cluster containing x vacancies.

For the determination of the emission terms, detailed balance can be used again in an even more restricted sense. For the metal at the same temperature but with equilibrium concentrations of both vacancies and interstitials, not only is it true that $J(x)=0$ and therefore $f_e(x)n_e(x) = b_e(x+1)n_e(x+1)$, but also that the fluxes in cluster space caused by vacancies and interstitials must separately be equal to zero (i.e. at equilibrium the vacancy condensation is balanced by the vacancy emission). Thus

$$\begin{aligned} \beta_e^v a(x) n_e(x) &= \gamma_e^v(x+1) a(x+1) n_e(x+1) \quad \text{and} \\ \beta_e^i a(x+1) n_e(x+1) &= \gamma_e^i(x) a(x) n_e(x) \end{aligned} \quad (22)$$

Solving Eq. X and Y for $\gamma^i(x)$ and $\gamma^v(x)$, substituting into eq. w and using eq. 6 we obtain

$$J = [\beta^v + \gamma^i(1)] a(1) n(1) \left/ \left[1 + \sum_{i=2}^{\bar{i}} \prod_{j=2}^i \frac{\beta^i a(j) + \beta_e^v a(j-1) n_e(j-1)/n_e(j)}{\beta^v a(j) + \beta_e^i a(j+1) n_e(j+1)/n_e(j)} \right] \right. \quad (23)$$

In addition to the ideas presented here, the reader is referred to two recent additional views of homogeneous nucleation.^{14,15}

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