

Nucleation Rates for High Supersaturations

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A new asymptotic expression for the stationary nucleation flux is obtained. The result provides a nontrivial generalization of the classical expression attributed to Zeldovich, and has a much broader domain of applicability. For extremely high supersaturations when the critical cluster number does not exceed a few units, the preexponential of the nucleation rate exhibits an oscillatory behavior. The latter effect increases for systems with high interfacial tension.

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Introduction.—Nucleation is a typical pathway for an activation decay of a metastable state with an enormous amount of applications ranging from biological [1] to cosmological systems [2]. Although in each specific case a nucleating system exhibits its own individual characteristics, there exist certain universal features which are best captured by the classical theory of Refs. [3] [see also textbook introductions [4,5] into the classical thermodynamics and kinetics of nucleation, respectively]. Those features are the competition between the surface and volume contributions to the free energy when a nucleus is formed, and the possibility to describe the kinetics as a random walk of nuclei in the space of their sizes.

The classical theory emphasizes the asymptotic nature of the nucleation problem which has two large dimensionless parameters—the reduced nucleation barrier W_c/T (Boltzmann constant is taken as 1) and the number of monomers in a critical cluster, n_c . If a certain hierarchy between these two parameters is established, namely $n_c \gg \sqrt{W_c/T} \gg 1$, one can write down an explicit elementary expression for the nucleation rate, known as the Zeldovich approximation (ZA) [3] which has strong similarities to the Kramers flux [6]. Generalizations of the one-dimensional ZA to an infinite dimensional space of the parameters of a nucleus, mostly due to Langer [7], serve as a basis for modern field-theoretic descriptions of nucleation. Within the classical framework [3] time-dependent generalizations of the ZA are available [8,9] with similar (somewhat stronger) requirements of a large barrier and a large critical size.

On the other hand, while the condition of a large barrier is indeed crucial for the formulation of the nucleation problem (otherwise, a “metastable state” is not well defined) the condition of a large n_c is not. In fact, in many experimental situations the latter is quite modest, of the order of 10^1 or even less, in order for nucleation to be observable. Related computer studies, e.g., Ref. [10], often also deal with quite modest values of n_c . Similarly, in a few available “first-principles” (nonclassical) examples of nucleation in lattice systems [11] (which can be considered as a discrete counterpart of field-theoretic nucleation) the reduced barrier is large, but the critical size is a finite

discrete parameter. At the same time, the ZA does not exhibit any nontrivial dependence on n_c which can be scaled out from the preexponential of the nucleation rate, while the exponential part depends only on the barrier.

An alternative would be to consider the stationary flux in terms of exact sums, first introduced into the nucleation problem by Farkas [3]. Those sums, however, formally depend on kinetic coefficients at all cluster sizes and their analytical structure as well as sensitivity to the barrier and n_c appear to be unknown beyond the continuous approximation (which is equivalent to the ZA). Traditionally the ZA was associated with the domain of applicability of an asymptotic treatment and whenever the accuracy of the latter was deemed insufficient the exact expression had been invoked.

The goal of this study, nevertheless, is to show that there exists an intermediate asymptotic regime which extends well beyond the ZA and which describes rather strong discreteness effects. At the same time, similarly to the ZA and in contrast to the exact expression, the flux in this intermediate regime is sensitive only to properties of near-critical clusters. Since the ZA emerges as a large- n_c limit of a more general expression, the analytical structure of the leading corrections to the ZA, as well as the precise domain of its applicability, can be elucidated.

In what follows, the classical “Becker-Döring” nucleation equation, Eq. (1), will be treated as an exact one and asymptotic approximations to the solution of this equation will be constructed. Less formally, since small cluster numbers n will be considered it could be useful to provide some justification of using the classical approach [3] and to understand its potential limitations.

A first-principles derivation of the Becker-Döring equation remains a challenging problem and even for lattice systems it is usually associated with larger clusters [12] when discreteness effects are not too important. For smaller n it is hard to justify using a macroscopic “surface plus volume” expression for the thermodynamics of a nucleus, which smoothly depends on n , while treating n as a discrete variable when describing kinetics. Conversely, in a few available discrete nonclassical examples [13] one observes a rugged n dependence of the work required to

form a given nucleus, the function $W(n)$ below. In addition, the same number n can correspond to clusters of different shapes with a resulting branching of the nucleation path; in those cases the validity of the one-dimensional random walk picture remains unclear. Nevertheless at least in the stationary treatment there are selected “magic” values of n , for which analogs of a one-dimensional sum, similar to Eq. (3) below, can be written for nonclassical kinetics [13,14]. Those sums have smooth dependences of the contributing values of W on the summation index. This bolsters one’s confidence in a strongly discrete master equation of type (1), which in the spirit of Ref. [3] has smooth coefficients, even if the discrete variable does not necessarily coincide with the number of monomers in a cluster.

The master equation of the classical nucleation problem has the form

$$df_n/dt = j_n - j_{n+1}, \quad j_n = \beta(n-1)f_{n-1} - \alpha(n)f_n. \quad (1)$$

Here f_n is the distribution function of nuclei and j_n is the flux; $\beta(n)$ and $\alpha(n)$ are the gain and loss coefficients, respectively. The latter can be excluded using the detailed balance condition $\alpha(n) = \beta(n-1) \exp\{[W(n) - W(n-1)]/T\}$. The work $W(n)$ (which is expected to be known from thermodynamics) is related to the quasiequilibrium distribution by

$$f_n^{\text{eq}} = A \exp[-W(n)/T] \quad (2)$$

with A being a constant which depends on normalization.

The function $W(n)$ has a maximum at some $n = n_c$ which is the “critical size” and $W_c \equiv W(n_c)$ represents the barrier to nucleation. The value of n_c depends on supersaturation and does not have to be an integer number. If the barrier is large compared to T , for an exponentially long time the depletion of the metastable phase can be neglected and the boundary conditions will be taken as $f_1 = f_1^{\text{eq}} = \text{const}$ and $f_n \rightarrow 0$ for $n \rightarrow \infty$ [for a mathematically controlled study of the role of boundary conditions in the Becker-Döring equation, see Ref. [15]]. Those conditions lead to an n -independent stationary flux

$$J^{-1} = \sum_{n=1}^{\infty} 1/\beta(n)f_n^{\text{eq}} \quad (3)$$

similar to the one originally obtained by Farkas [3].

The continuous approximation to the above sum (and asymptotic evaluation of the resulting integral) is equivalent to the ZA:

$$J^{\text{ZA}} = \frac{\beta(n_c)}{\Delta\sqrt{\pi}} A \exp\left(-\frac{W_c}{T}\right) \quad (4)$$

with $\Delta = \left(-\frac{1}{2T} \frac{d^2 W(n)}{dn^2}\right)^{-1/2}$ at $n = n_c$. The ZA is valid for $W_c/T \gg 1$ and $\Delta \gtrsim 1$; in the latter case a strong inequality is not required, as will be shown below.

When generalizing the ZA, the condition $\Delta \gtrsim 1$ will be relaxed. One still can perform parabolic expansions of $W(n)$ [and also of $\beta(n)$] near n_c , but in a general case the sum (3) cannot be replaced by an integral. One has

$$J^{-1} \simeq \frac{1}{\beta(n_c)} A^{-1} \exp\left(\frac{W_c}{T}\right) \times \sum_{n=1}^{\infty} \exp\left[-\left(\frac{n-n_c}{\Delta_*}\right)^2 - \delta(n-n_c)\right], \quad (5)$$

where $\Delta_* = \Delta/\sqrt{1 + \Delta^2\gamma}$ with $\gamma = \frac{1}{2}(\ln\beta)_c''$ and $\delta = (\ln\beta)_c'$. For a large barrier with $\Delta_* \ll n_c$ and the sum is insensitive to the precise location of the lower boundary which thus can be replaced by a $-\infty$. Then, using the fact that the summation index can be shifted by an arbitrary integer value, one obtains

$$J^{-1} \simeq \frac{A^{-1}}{\beta(n_c)} \exp\left(\frac{W_*}{T}\right) \sum_{k=-\infty}^{\infty} \exp\left[-\left(\frac{k - \{n_*\}}{\Delta_*}\right)^2\right]. \quad (6)$$

Here $\{n_*\}$ is the “fractional part” of the critical size $n_* = n_c - \Delta_*^2\delta/2$ adjusted for the n dependence of β and the corrected barrier is defined as $W_* = W_c + T\Delta_*^2\delta^2/4$.

Introducing one imaginary and one real parameter

$$z = i\{n_*\}/\Delta_*^2, \quad q = \exp(-1/\Delta_*^2) \quad (7)$$

one can express the above sum in terms of an elliptic theta function $\vartheta_3(z, q)$ as defined in Ref. [16]. Thus,

$$J \simeq A\beta(n_c)q^{-\{n_*\}^2} [\vartheta_3(z, q)]^{-1} \exp\left(-\frac{W_*}{T}\right). \quad (8)$$

This is the main result of the present work. Note the oscillatory behavior of the preexponential as a function of n_* if all other parameters are fixed. In reality, oscillations can be masked by the n_c dependence of other parameters and are expected to be observable only for small Δ_* (which implies either a small n_c or a large barrier $W_c/T \gg n_c^2$).

Transition to the ZA will be considered for integer n_* using an identity

$$\vartheta_3(0, q) = \sqrt{2K(m)/\pi}, \quad (9)$$

where $K(m)$ is an elliptic integral [16] and m is related to q by

$$q = \exp[-\pi K(1-m)/K(m)]. \quad (10)$$

Continuous limit is approached for $m \rightarrow 1$ where $K(m)$ logarithmically diverges. Expanding both expressions near $m = 1$ and using the definition of q in Eq. (7), one obtains

$$J \simeq \frac{\beta(n_c)}{\Delta_*\sqrt{\pi}} A \exp\left(-\frac{W_*}{T}\right) (1 - 2e^{-\Delta_*^2\pi^2} + \dots). \quad (11)$$

The leading term corresponds to the ZA corrected for n dependence of β within the continuous approximation. The next term in Eq. (11) describes the discreteness effects.

Note the exceptionally small numerical values of the latter even for $\Delta_* \approx 1$.

In the opposite case of $\Delta_* \ll 1$ when the discreteness effects dominate, at most two terms (and for nonspecial values of the supersaturation only one term) contribute to the sum (6), which explains an oscillatory behavior as a function of n_c . There is a limit of how small the latter can be for the approximation to remain accurate, namely $n_c \geq (W_c/T)^{1/3}$, but in practice this corresponds to a few units and is a much weaker restriction compared to the one used in the ZA.

For numerical illustration, and to understand for which systems deviation from the ZA can be important, consider the standard three-dimensional nucleation with interface-limited kinetics

$$W(n) = W_c[3(n/n_c)^{2/3} - 2(n/n_c)], \quad \beta(n) \propto n^{2/3}. \quad (12)$$

The value of Δ in this case is $n_c(W_c/3T)^{-1/2}$. Formally, W_c and n_c can be treated as independent parameters, but in a real system both are determined by the supersaturation. One can define a dimensionless interfacial energy $\rho = (16\pi/3)^{1/3}v^{2/3}\sigma/T$, where v is the molecular volume of the new phase and σ is the interfacial tension, and a dimensionless supersaturation $s = (\mu_1 - \mu_2)/T$ with $\mu_{1,2}$ being the chemical potentials of the metastable and stable phases, respectively. Then, one has $W_c/T = \rho^3/s^2$ and $n_c = 2\rho^3/s^3$ with ρ being near-constant for a given material (e.g., ρ is about 4 for water and 24 for mercury at room temperature, and values can be larger at small T , as in solid-to-solid transformations).

With increasing s both the barrier and the critical size decrease, but n_c decreases faster leading to stronger discreteness effects (smaller $\Delta \sim s^{-2}$). Limitations come from the fact that n_c at least must remain larger than 1 and the reduced barrier should exceed several units to ensure a sufficient lifetime of a metastable state. A large ρ is required in order to get into the discrete regime. Otherwise, there will be no oscillatory behavior in the ratio J/J^{ZA} and a small deviation from unity mostly can be accounted for within the continuous approximation (which is of less interest in the present context). A typical situation with large ρ is shown in Fig. 1 where the aforementioned ratio exhibits noticeable oscillations. Note the accuracy of the analytical expression even if the deviation from the ZA is strong.

From an analytical standpoint the value of the obtained result is that it follows directly from the exact sum (3), bypassing the issue of a continuous approximation of the original Eq. (1) [17–19] and allowing one to account for strong discreteness effects which such approximations are unable to reproduce to a full extent. In contrast to conventional wisdom when the asymptotic nature of the nucleation problem is associated with the possibility to replace Eq. (1) with some Fokker-Planck equation(s), it appears

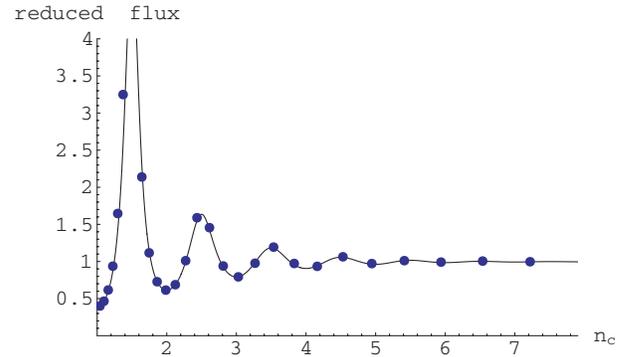


FIG. 1 (color online). Reduced nucleation flux J/J^{ZA} as a function of $n_c = 2\rho^3/s^3$, s being the dimensionless supersaturation. Parameter ρ was chosen as 100 to ensure noticeable oscillations. Solid line—elliptic theta-function approximation, Eq. (8). Symbols—exact (numerical) data.

that the condition $W_c/T \gg 1$ is less restrictive and allows one to examine much smaller values of the critical cluster number n_c .

In summary, a novel asymptotic nucleation regime, which takes place for a high barrier but moderate values of the critical size, has been identified. The flux, Eq. (8), can be obtained analytically within the framework of the classical nucleation theory. The result is valid in a much broader domain of supersaturations than the standard Zeldovich approximation (ZA) and has the latter as a limit when the supersaturation is small. Similarly to the ZA the result depends only of the properties of near-critical nuclei and thus has the same degree of universality. However, the dependences on the barrier and on the critical size are not separated anymore but are combined into a two-parametric special function $\vartheta_3(z, q)$. Oscillatory behavior of the pre-exponential of the flux has certain similarities with the one observed in a strongly nonclassical nucleation in a lattice gas driven by Glauber-type dynamics [13,20] where nucleation can be described by multidimensional generalizations of the Becker-Döring equations in the space of cluster configurations. Technically different approaches to nucleation in lattice systems, as well as different dynamics and lattice symmetries, were considered in Refs. [21,22], and an analogous structure of the preexponential is expected. In this context, one notes the power of the classical approach [3] in capturing at least some of the more general nucleation features, in the present case the nontrivial sensitivity of kinetics to the discrete nature of the number of monomers in a critical nucleus. In practical applications the obtained expression is expected to be of value for materials with high dimensionless interfacial energy when the critical size is small and the ZA can be inaccurate.

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