Oscillations in the nucleation preexponential

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Oscillations in the preexponential of the nucleation rate are due to the discrete nature of small nuclei. An accurate elementary expression to describe such oscillations is derived in the limit of a high nucleation barrier. The result is applied to the standard Becker-Döring equation in two and three dimensions, and to the lowest-energy nucleation path in a cold lattice gas with Glauber and Metropolis dynamics (equivalent to an Ising model on a square lattice) where oscillation effects can be more pronounced.

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I. INTRODUCTION

A typical first-order phase transition starts from *nucleation*, which is the fluctuational formation of microscopic amounts ("droplets") of a new phase. While originally developed in terms of vapor condensation [1–3] and cavitation [4], the classical theory of nucleation (CNT) was later extended to include the crystallization of liquids and glasses, various types of solid-to-solid transformations, polymers, biological systems, etc. [5–8]. A deeper understanding of nucleation fundamentals, of the strong sides and limitations of CNT, will potentially increase control over phase transformations with a resulting effect on multiple applications.

The CNT [1–3] treats nucleation as a random walk of a nucleus in the space of its sizes via a random gain and loss of monomers. Once their number exceeds the critical value n_*, the nucleus grows deterministically towards the new phase. The corresponding nucleation rate J is represented as a product of exponential [1] and preexponential [4] terms. The former became a signature feature of nucleation theories, both classical and beyond [9,10], and can be written as $\exp(-W_*/T)$. Here, W_* is determined by the thermodynamics of the metastable system, being the minimal work to form a critical nucleus and assumed to be large compared to temperature T measured in energy units. The preexponential, on the other hand, is sensitive to kinetics and is more specific for each system under consideration. With a few exceptions of glass forming melts, the exponential term dominates and it is often hard to extract accurate information about the preexponential from experimental data. Thus, there is a strong interest in fully or partly solvable models of nucleation where the rate J can be derived from "first principles," providing information on both preexponential and exponential factors.

One of the simplest yet remarkably realistic examples of nonclassical nucleation is the nonequilibrium Ising model on a square lattice which is equivalent to a supersaturated lattice gas (LG) described later in this paper. As $T \to 0$, the exponential term can be obtained [11] for arbitrary supersaturation s, while for $s \to 0$ the Wulff construction [12] can be used to evaluate the barrier [13] at finite T, thus providing a connection with CNT. Various spin-flip dynamics (Glauber, Metropolis, etc.) can be considered on the background of identical thermodynamics, allowing one to assess the sensitivity of the preexponential to specifics of the kinetics. Other types of dynamics, which can affect both the exponential and preexponential factors, are discussed [14,15].

An intriguing feature of the Ising and LG nucleation is the oscillations of the preexponential as a function of s. First indications came from numerical [16,17] and analytical [18] transfer-matrix studies of the imaginary part of the free energy extrapolated into the metastable region around the Andreev singularity at $s = 0$ [19]. The appearance of oscillations was largely associated with the lattice structure of the Ising model. Due to the complexity of the problem no simple expression for the amplitude of such oscillations could be suggested, although it was correctly conjectured that it should decrease with T [18]. Alternatively, at small but finite T and not too small s, a large number of contributing cluster configurations and transition rates between them can be identified with the resulting equations solved using symbolic computations. Sharp peaks in the inverse preexponential were observed at several integer $1/2s$ for various versions of the spin-flip dynamics [20,21]. Furthermore, at $T \to 0$ the lowest-energy nucleation path was identified [22], allowing one to get an explicit expression for the preexponential at all s. The result, however, contained a nonelementary elliptic function with one real and one imaginary argument with a nonanalytic dependence on s, which prevented an explicit extraction of the leading oscillating asymptote.

The intent of the present paper is to show that oscillations of the preexponential can be accurately described by an elementary function with a clear separation of the supersaturation and temperature dependences. Moreover, it is argued that this function is not restricted to lattice systems but will typically appear in problems where the discrete nature of the nucleus is important, including the CNT. We will use the latter as a starting point for the discussion following the general outline of Ref. [23] extended to an arbitrary dimension d, obtaining an analytical result with a differently structured special function, which allows one to deduce the elementary asymptote responsible for oscillations.

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II. RESULTS

The master equation of CNT, also known as the Becker-Döring (BD) equation, can be cast in the form [4]

$$\frac{df_n}{dt} = j_n - j_{n+1}, \quad j_n = \beta_{n-1} f_{n-1}^{\rm eq}\left(\frac{f_{n-1}}{f_{n-1}^{\rm eq}} - \frac{f_n}{f_n^{\rm eq}}\right). \quad (1)$$

Here, $f_n(t)$ is the distribution of nuclei over "sizes" n, the number of monomers in a nucleus, $f_n^{\rm eq}$ is the (quasi)equilibrium distribution which ensures a zero flux j_n in the n space, and β_n is the kinetic gain coefficient. It is assumed that the number of smallest nuclei at $n = 1$ is held fixed with $f_1 = f_1^{\rm eq}$, while clusters at some large $n_{\max}$ are removed without exhausting the system. The latter implies $f_n = 0$ at $n = n_{\max}$ and, without restricting generality, in what follows $n_{\max}$ will be replaced by ∞. With these boundary conditions, Eq. (1) has an exact nonequilibrium steady state solution with a size-independent flux $j_n \equiv J$ [2]. Then one has $f_n/f_n^{\rm eq} = f_{n-1}/f_{n-1}^{\rm eq} - J/\beta_{n-1} f_{n-1}^{\rm eq}$, which can be extended iteratively to give $f_k/f_k^{\rm eq} = 1 - J\sum_{n=1}^{k-1} 1/\beta_n f_n^{\rm eq}$. Since the latter tends to zero as $k \to \infty$, the flux is given by

$$J^{-1} = \sum_{n=1}^{\infty} \frac{1}{\beta_n f_n^{\rm eq}}. \quad (2)$$

Next, CNT assumes that $f_n^{\rm eq}$ can be estimated from macroscopic thermodynamics as $\propto \exp[-W(n)/T]$ with $W(n)$ being the minimal work to form a nucleus; the preexponential of $f_n^{\rm eq}$ can involve a mild function of n, which is however irrelevant to our discussion. The coefficient β_n can be deduced from macroscopic kinetics [4] and both β_n and $W(n)$ are expected to be smooth functions of n [24]. The number of contributing terms in the sum (2) is determined by

$$\Delta_n = \left\{-\frac{1}{2T}\frac{d^2W}{dn^2}\bigg|_*\right\}^{-1/2}, \quad (3)$$

where "$*$" indicates a value obtained at the critical size n_*, and for $\Delta_n \gg 1$ one obtains the flux of CNT,

$$J_{\rm CNT}^{-1} = A_{\rm CNT} f^{\rm eq}(n_*), \quad A_{\rm CNT} = \frac{\Delta_n\sqrt{\pi}}{\beta(n_*)}. \quad (4)$$

Note, however, that for sufficiently low T, despite the smoothness of $W(n)$, the $\exp[-W(n)/T]$ does not have to be smooth. In that case one still can expand $W(n) \simeq W_* - [(n - n_*)/\Delta_n]^2$ near n_* and replace β_n by $\beta(n_*)$, but the summation in Eq. (2) cannot be replaced by integration since Δ_n is not necessarily large. Instead, one can extend the summation to $n = -\infty$, formally obtaining the preexponential relating J^{-1} to $f^{\rm eq}(n_*)$ in terms of an elliptic theta function [25]:

$$A = A_{\rm CNT}\vartheta_3\left(-\pi n_*, e^{-\pi^2\Delta_n^2}\right). \quad (5)$$

The major differences from earlier treatments [22,23] are the structure of the elliptic function where both arguments are real, and its analytic dependence on n_* which simplifies further expansions without losing the delicate oscillation feature [26]. The leading asymptote describing oscillations is then given by

$$A \simeq A_{\rm CNT}\theta(n_*, \Delta_n), \quad (6)$$

with

$$\theta(n_*, \Delta_n) = 1 + 2\cos(2\pi n_*)\exp\left(-\pi^2\Delta_n^2\right), \quad (7)$$

which is the main result of the present paper. In the domain of its applicability $\Delta_n \gtrsim 1/\pi$ this approximation is very accurate since the next correction contains the fourth power of the exponential [25]. Also note the remarkable accuracy of the continuous approximation in CNT when describing the stationary flux for "regular" values of $\Delta_n \gtrsim 1$ due to the large numerical value of π^2 under the exponential in Eq. (7). Discreteness effects and associated oscillations can become detectable, however, for sufficiently large values of the reduced barrier W_*/T.

For an extremely large barrier an opposite, strongly discrete limit with $\Delta_n \ll 1$ is approached when the inverse flux is dominated by at most two terms $J^{-1} \simeq 1/\beta_{[n_*]} f_{[n_*]}^{\rm eq} + 1/\beta_{[n_*+1]} f_{[n_*+1]}^{\rm eq}$ (where $[x]$ denotes the largest integer not to exceed x). For a fixed barrier and variable n_* the reduced preexponential $A/A_{\rm CNT}$ peaks at $1/\Delta_n\sqrt{\pi}$ near integer values of n_*. At semi-integer values of n_* the reduced preexponential dips to exponentially small $2\exp(-1/4\Delta_n^2)/\Delta_n\sqrt{\pi}$ due to the overestimation of the barrier by the continuous CNT. Obviously, the approximation (7) is invalid in this limit although it correctly locates both peaks and dips; the general Eq. (5) is expected to remain accurate.

For illustration and numerical verification of Eq. (7), consider a d-dimensional version of the CNT with the Gibbs barrier $W(n) = W_*[d(n/n_*)^{1-1/d} - (d-1)n/n_*]$. Interface-limited kinetics will be assumed with $\beta_n \propto n^{1-1/d}$. The parameter Δ_n takes the form $\Delta_n = n_*[W_*(1-1/d)/2T]^{-1/2}$ which specifies both the classical preexponential $A_{\rm CNT}$ and the oscillating correction in Eq. (7). (We will not consider here the strongly discrete limit $\Delta_n \ll 1$ since the required values of the barrier are unrealistically high). Note that the amplitude of the oscillating correction depends on the barrier and dimension only via Δ_n, thus certain scaling can be expected if different systems have an identical "dimensionalized barrier" $B = (1-1/d)W_*/T$. Alternatively, the preexponential A can be obtained from the exact flux, Eq. (2), as $A = J^{-1}\exp(-W_*/T)$ which can be used to test the accuracy of the approximation, as in Fig. 1. Accuracy is reasonable and most likely could be further improved by including a linear term in the approximation of β_n near n_* [23]. The aforementioned scaling also is clearly observed.

We now apply the approach to lattice gas (LG) which is a collection of particles on a square lattice, with nearest neighbors linked by bonds with energies $-\phi$. The LG has a chemical potential $\mu < 0$ with supersaturation $s = (\mu + 2\phi)/2\phi$ which determines the metastable thermodynamics of the system. This is equivalent to a nonequilibrium Ising model with up and down spins representing particles and empty sites of LG, respectively, with energies of spin-spin interactions given by $\pm\phi/4$ and external field ϕs. Several types of dynamics will be considered. In the simplest "LG dynamics" new particles are randomly added into the system at a constant (unit) rate regardless of the state of the neighboring sites, while the rate of disappearance of a particle follows from a detailed balance. This mimics the above-mentioned CNT models with an attachment rate proportional to the area of the

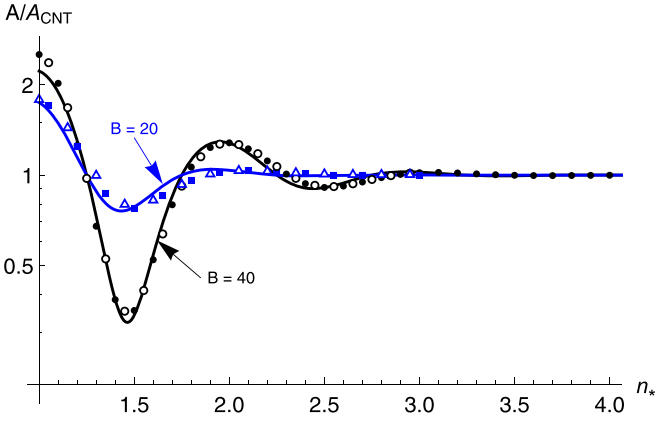

FIG. 1. Preexponential of the inverse nucleation rate in the standard Becker-Döring equation in $d = 2$- and $d = 3$-dimensional systems with "dimensionalized barrier" $B = (1 - 1/d)W_*/T$. Results based on exact Eq. (2) are shown by solid ($d = 2$) and open ($d = 3$) symbols. Lines are the asymptotic approximation, Eq. (7), identical at different dimensions if barrier B is the same.

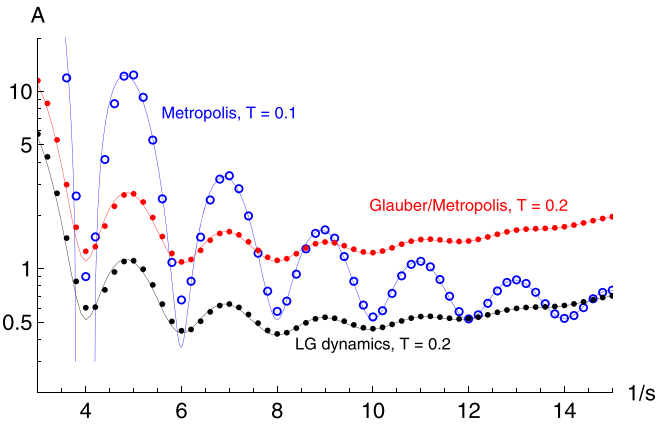

FIG. 2. Preexponential of the inverse nucleation rate for the lowest-energy path in a lattice gas (LG) for three types of spin-flip dynamics at $T = 0.1$ and $T = 0.2$ (with $\phi = 4$). Symbols: from Eqs. (9) and (10); thin solid lines: approximations by elementary Eqs. (7) and (13). The approximations are accurate for small-to-moderate oscillations but break down when those are large (as for the Metropolis dynamics at $T = 0.1$ near $1/s = 4$ and 6, when an elliptic function approximation should be used instead—see text). There is no visual difference between the Glauber and Metropolis dynamics for the low temperatures considered.

interface, and in a slightly modified version the LG dynamics has been used for various crystallization applications [27–29]. In contrast, in the more familiar Glauber and Metropolis dynamics both "down-up" and "up-down" spin flips are sensitive to their surroundings. Nevertheless, since all three models rely on a detailed balance with equivalent energy changes, the results are qualitatively similar. In particular, with the same barrier to nucleation [11] and thus the same exponential term, the models have a similar piecewise constant structure of the preexponential at $T \to 0$ and noninteger $1/2s$ [22,30,31].

In order to extract the oscillating part of the preexponential, we first single out the exponential term in the inverse nucleation rate, $\exp(W^*_{\rm Wulff}/T)$, consistent with the CNT. The availability of the barrier $W^*_{\rm Wulff}/T$ follows from the Wulff construction [12] based on the anisotropic interfacial tension provided by the exact Onsager solution [32] for the square lattice Ising model. One has

$$W^*_{\rm Wulff} = \frac{\phi}{2s}\left(\frac{\sigma_{\rm eff}(T)}{\sigma_{\rm eff}(0)}\right)^2. \tag{8}$$

Here, $\sigma_{\rm eff}$ [13] is the equivalent surface tension of a circular nucleus, with $\sigma_{\rm eff}(0) = 4\phi\sqrt{\pi}$ when the actual nucleus is a perfect square. The surface tension goes to zero at $T_c \simeq 2.269\,\phi/4$, the critical temperature, and we will be considering small $T \ll T_c$.

The preexponential A of the inverse rate will be defined from

$$J^{-1} = A\tau_0 \exp\left(\frac{W^*_{\rm Wulff}}{T}\right), \tag{9}$$

where the timescale $\tau_0 = \exp[\phi(1 - 2s)/T]$ related to the propagation of a low-temperature interface is introduced for convenience. In order to evaluate the nucleation rate J we first identify the lowest-energy nucleation path [22], which brings the problem closer to the one-dimensional random walk of CNT. There is still branching of the path due to the presence of distinct configurations with identical energies. The electric analogy (with J^{-1} similar to the equivalent resistance of the chain) is applied in order to simplify the branching parts, so that the problem is reduced to finding the resistance of a one-dimensional chain. This is already quite analogous to CNT although the values of individual resistances in the chain do not follow the simple BD pattern. Unifying the results of Ref. [22] for different types of spin-flip dynamics, one has at $s < 1/2$ an expression structured similarly to Eq. (2):

$$J^{-1} \simeq \sum_{m=1}^{\infty} g(m)\left[\exp\left(\frac{W_p(m)}{T}\right) + \exp\left(\frac{W_s(m+1)}{T}\right)\right]. \tag{10}$$

Here, there are two types of the energies W: the primary ones with

$$W_p(m) = \phi[2m + 2 - 2s(m^2 + m + 1)] \tag{11}$$

corresponding to $m \times (m + 1)$ rectangles with an extra spin on the longer side (which determine the critical cluster as $T \to 0$ [11]), and the secondary ones

$$W_s(m) = \phi[2m + 1 - 2s(m^2 + 1)] \tag{12}$$

representing a square with an extra spin. The coefficients $g(m)$ depend on spin-flip dynamics [22]: $g(m) = 1/8m$ for the LG dynamics, $g(m) = 3/(8m + 4)$ for the Metropolis, and $[3 + \exp(-2\phi s/T)]/[8m + 4/(1 + \exp(-2\phi s/T)/2)]$ for the Glauber dynamics, respectively.

Once the primary and secondary contributions in Eq. (10) are separated, the problem becomes similar to two independent BD cases with the summation over n replaced by a summation over m which identify the "magic numbers" of spins $n = m^2 + m + 1$ and $n = m^2 + 1$, respectively. The final result is expressed through the same function θ as in Eq. (7).

With our definition of the preexponential one has

$$A \simeq \Delta_m \sqrt{\pi} \exp\left[\frac{\phi}{2sT}\left(1 - \frac{\sigma_{\rm eff}(T)^2}{\sigma_{\rm eff}(0)^2}\right)\right] \times \left[g\left(m_* - \frac{1}{2}\right) e^{\phi s/2T}\theta\left(m_* - \frac{1}{2}, \Delta_m\right) + g(m_*)\theta(m_*, \Delta_m)\right], \quad (13)$$

with the critical size $m_* = 1/2s$ associated with perfect squares and corresponding spread of contributing terms in the series

$$\Delta_m = \left\{-\frac{1}{2T}\frac{d^2 W_s}{dm^2}\bigg|_*\right\}^{-1/2} = \left(\frac{T}{2\phi s}\right)^{1/2}. \quad (14)$$

The oscillating part inside the square brackets in Eq. (13) is given by $2[g(m_*) - g(m_* - 1/2)e^{\phi s/2T}]e^{-\pi^2\Delta_m^2}\cos(2\pi m_*)$. Note the minus sign since contributions from the squares and the rectangles come in opposite phases. Due to the dominant factor $e^{-\pi^2\Delta_m^2}$ the oscillation amplitude decreases with temperature approximately exponentially.

Equation (13) is shown by solid lines in Fig. 2. Generally, this approximation is accurate if compared to "exact" (within the lowest-energy path) results shown by symbols. The breakdown of the approximation near the minima of A is expected only for large s at small T when the oscillation amplitude becomes large, as for the Metropolis dynamics at $T = 0.1$. In such cases the accuracy of Eq. (13) can be restored by replacing $\theta(m_*, \Delta_m)$ by $\vartheta_3(m_*, \Delta_m)$ and making a similar replacement for $\theta(m_* - \frac{1}{2}, \Delta_m)$.

III. SUMMARY

In summary, fast oscillations of nucleation preexponential as a function of inverse supersaturation appear to represent a ubiquitous effect which is due to the discrete nature of nuclei. The effect can be accurately described by an elementary function which can be deduced directly from the Becker-Döring model where discreteness stems from the finite number n of molecules in a nucleus. The same function, only with parameters dependent not on n but on "magic numbers" corresponding to locally extremal energies of nuclei, also appears in nonclassical systems, which was illustrated by examining the lowest-energy nucleation path in a lattice gas. The oscillation effect gets more pronounced at lower temperatures and higher supersaturations, and should be included when high precision of the nucleation rate prediction is required.

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