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Vitaly A. Shneidman

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Communication: On nucleation statistics in small systems

Vitaly A. Shneidman[a)]
Department of Physics, New Jersey Institute of Technology, Newark, New Jersey 07102, USA

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Non-stationary random formation of stable nuclei from a small metastable system is considered. Distribution of waiting times to observe the first nucleus is examined, and it is shown that the steady-state nucleation rate is given by inverse of the standard deviation, which is independent of the post-critical size n where the nucleus is detected. The mean time, on the other hand, is n-sensitive and contains additional information on transient nucleation and growth effects. The method is applied to Monte Carlo data on nucleation in a cold two-dimensional Ising ferromagnet with Metropolis dynamics, where nucleation rates obtained earlier from low-temperature cluster expansions can provide a strict independent test. © *2014 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4891980]

Nucleation in small droplets of liquid metal was studied by Turnbull in early 1950s and the interest in such problems only increased with time, promising an enhanced control over solidification.[1] In present context, the term "small" implies a system where phase transformation is due to a single (at most, a few) nucleation event, as also can be of interest in boiling,[2] ice formation,[3,4] or in biological nucleation.[1,5] In molecular dynamics, small systems are almost standard[6] and attempts to achieve experimentally realistic nucleation barriers can make a system "small" even if it contains up to 10^9 monomers.[7] Similarly, while in the Monte Carlo nucleation studies of lattice dynamics both large and small systems are encountered,[8,9] the latter have a significant advantage of producing less stress on computer memory. At the same time, fluctuations in small systems can be enormous, and efficient statistical methods tailored to specifics of the nucleation problem are required.

The primary goal of most nucleation studies, whether experimental or computational, is the evaluation of the rate, which in neglect of boundary effects can be written as NI with N being the number of monomers in the system and I the specific rate per monomer. In the ideal case of a very high barrier, random nucleation represents a stationary Poisson process, and the rate can be deduced from the average waiting time to observe the first nucleus

$$\bar{t} \approx 1/NI. \tag{1}$$

In reality, however this expression is rarely accurate due to contribution of non-stationary effects and due to the time required for a nucleus to grow to "detectable size" n. In such cases Eq. (1) should be increased by the time lag ("induction time") t_0—a situation well known to experimentalists,[10] even though analytical expressions for $t_0(n)$, which accounts for both transient nucleation and growth, were constructed later. Alternatively, at least in computer studies one can attempt to minimize transient effects by lowering the n value, but then the rate I in Eq. (1) becomes n-dependent and, assuming the validity of the Becker-Döring picture, is modified as[11]

$$I(n)^{-1} = \frac{1}{2I}\mathrm{erfc}\frac{n_* - n}{\Delta} \tag{2}$$

(here n_* is the critical size and Δ is the width of the near-critical region—notations are standard). An analogous expression was suggested[12] based on similarity with the "mean-first-passage time" in the theory of random processes, and by now Eq. (2) became a widely used tool in analysis of nucleation data.[13,14] Nevertheless, one should keep in mind that Eq. (2) at least formally is valid only in the near-critical region, and for some applications large discrepancies have been reported.[14,15] In addition, it is unclear how the "detector" affects nucleation in non-classical cases which allow multiple configurations with the same n (the methods based on Eqs. (1) and (2) were never tested for those few lattice systems where analytical results for the nucleation rate are available). Thus, the present treatment which considers non-stationary effects and larger sizes n well outside of the near-critical region will be complementary to the one given by Eqs. (1) and (2). It will be shown that the "mean waiting time" is not the most adequate way to evaluate the nucleation rate I, and alternatives will be discussed. The treatment will be applied to dynamic Monte Carlo studies of nucleation in an Ising ferromagnet (which is equivalent to lattice gas) where the results of independent low-temperature cluster expansions[16] can provide a rigorous test.

The probability density function (PDF) $w(t)$ for the distribution of waiting times and the cumulative distribution (CDF) $F(t)$ can be related to nucleation parameters as

$$w(t) = j(n,t)e^{-\rho(t)}, \tag{3}$$

$$F(t) = 1 - e^{-\rho(t)}. \tag{4}$$

Here $j(n,t)$ is the nucleation flux with a stationary limit NI and $\rho(t) = \int_0^t dt'\, j\left(n,t'\right)$ with a large-time asymptote $NI(t-t_0)$ where $t_0(n)$ is the aforementioned time lag.

In case nucleation is described by a phenomenological Becker-Döring equation (BDE), the stationary rate can be estimated from the Zeldovich formula[17] $I \simeq \Delta/(2\tau\sqrt{\pi})\exp(-B)$, asymptotically accurate for a large

a)Electronic mail: vitaly@njit.edu

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dimensionless barrier B. The time constant τ is defined as the inverse of $d\dot{n}/dn$ at $n = n_*$ where $\dot{n}$ is the deterministic growth rate associated a given BDE. Similarly, for a large B the transient flux and $\rho(t)$ are obtained from the matched asymptotic (singular perturbation) solution of the BDE.[18,19] In the growth region with $n - n_* \gg \Delta$ one has[18,19]

$$j(n,t) = NI\ \exp[-e^{-r}]\ ,\ \ r = \frac{t - t_i(n)}{\tau} \tag{5}$$

and

$$\rho(t) = NI\tau\ E_1\left(e^{-r}\right). \tag{6}$$

Here E_1 is the first exponential integral,[20] while the "incubation time" $t_i(n) \gg \tau$ is related to the time lag

$$t_0(n) = t_i(n) + \gamma\tau\ ,\ \ \gamma = 0.5772\ldots \tag{7}$$

and increases with n as $\int dn/\dot{n}$. (For explicit examples of $t_i(n)$ see Ref. 19.) In a large system $\rho(t)$ can be associated with the number of nuclei exceeding size n. The results were independently tested against high-precision numerics,[21,22] and can be used for analysis of nucleation data if the Becker-Döring picture is deemed appropriate.

For a small system with $\epsilon = NI\tau \ll 1$ the characteristic time is large, and one can further simplify the PDF by using the asymptote of the exponential integral and adjusting the constant to preserve normalization. In terms of dimensionless reduced "time" r defined in Eq. (5):

$$w(r) \simeq \epsilon \exp[-e^{-r} - \epsilon r]/\,\Gamma(1+\epsilon). \tag{8}$$

For $\epsilon \to 0$ this becomes a delayed exponential distribution. In original time units one has

$$w(t) \approx NI\Theta(t - t_0)e^{-NI(t-t_0)}. \tag{9}$$

When evaluating the moments of the distribution $\bar{t^k} = \int_0^\infty t^k w(t)\,dt$, the lower integration limit can be replaced by $-\infty$. This allows one to express $\bar{t^k}$ as combinations of t_i and the moments of the reduced time r. In particular, $\bar{t} = t_i + \tau\bar{r}$ and the variance σ^2 is given by $\tau^2(\bar{r^2} - \bar{r}^2)$. The elementary approximation given by Eq. (8) then allows explicit evaluations:

$$\bar{t} = t_0(n) - \gamma\tau - \tau\Psi(I\tau) \simeq \frac{1}{NI} + t_0(n) - \frac{1}{6NI}(\pi\epsilon)^2, \tag{10}$$

$$\sigma = \tau\sqrt{\Psi_1(\epsilon)} \simeq \frac{1}{NI} + \frac{1}{12NI}(\pi\epsilon)^2, \tag{11}$$

with $\Psi(z) = d/dz \ln\Gamma(z)$—the digamma function, and $\Psi_1(z) = d\Psi(z)/dz$. Note that even without the assumption of small ϵ, the standard deviation σ is independent of the cluster size n, which is the main conclusion of this Communication. The leading part of Eq. (11) is expected to be accurate when applied to small systems with $\epsilon \ll 1$, allowing an immediate estimation of the stationary rate $I \simeq 1/N\sigma$. In practice there are several possibilities to evaluate ϵ, either from the fit to the observed $w(t)$, or as τ/σ where τ can be obtained when considering growth and decay of individual nuclei.[23] In the example below, however, I and τ are known independently, so that the accuracy of the approach can be verified.

Consider non-classical nucleation in a two-dimensional Ising model on a square lattice with nearest-neighbor interactions and Metropolis dynamics. The model is standard for Monte Carlo (MC) simulations.[8,24] The treatment is restricted to the "cold" region corresponding to 0.35 of the critical temperature. While simulations take longer here, there is a unique opportunity to compare the MC results and the statistical analysis to accurate estimations of the rate I and transient fluxes $j(n, t)/N$, which can be obtained using symbolic computations and matrix methods.[16] Next, although the Becker-Döring picture formally is not applicable due to the presence of "magic numbers" and due to branching of the nucleation path, the general double-exponential shape of the transient flux remains accurate.[16] This bolsters the justification of the approach. The parameters t_0 and τ have to be evaluated directly, however, using the aforementioned symbolic and matrix methods. Here we will use $I = 1.75 \times 10^{-6}$, $\tau = 6.134$, corresponding to dimensionless field ("supersaturation") of 0.22, and $t_0 = 19.964$ for $n = 20$.[16]

The MC scheme was similar to the one used before,[9] updated for *Mathematica 9*. A typical lattice had dimensions $N = 141 \times 141 \simeq 20\,000$, corresponding to $\epsilon \simeq 0.2$. The system was prepared with all spins pointing "down" while the external field favored the "up" direction. On each step a spin was randomly selected for an attempted flip. After each N steps the time t was increased by $+1$ and the Hoshen-Kopelman algorithm was used to identify the largest cluster with n spins. Once n reached a selected "detection limit" the corresponding t was recorded as the "waiting time," and the simulation run was restarted. Typically, 1000 data were generated in each case, with about 3% expected error when finding the mean.

The values of n in Fig. 1 were selected as perfect squares, reflecting the shape of a bulk nucleus at low temperatures. The standard deviation (SD) indeed remains near-constant at $a = \sqrt{n} > 3$, and is in good agreement with the inverse of the independently calculated "first-principle" nucleation rate.

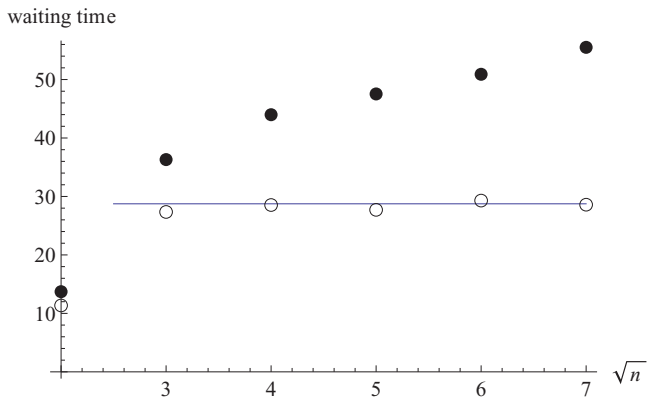

FIG. 1. Monte Carlo (MC) data for the mean of waiting times (solid symbols) and their standard deviation (open symbols) as functions of the "size" n (number of spins) in a detectable cluster on a square lattice with $N \simeq 20\,000$. The horizontal straight line is $1/NI$ with I found from low-temperature cluster expansions.[16]

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Rapid decay of the SD at smaller n indicates the vicinity of the critical size. Within the Becker-Döring picture one expects the SD to drop to 1/2 of its value at $n = n_*$ for small ϵ. In principle, this could serve as an indicator of n_*, much more accurate than the one given by Eq. (2) since the average waiting time does not tend to a constant at large n. The $\bar{t}$ values still can be used to estimate the rate I, but measurements for two different lattices are required. Neglecting the small-ϵ corrections, one has $I \simeq (1/N_1 - 1/N_2)/\left[\bar{t}_1(n) - \bar{t}_2(n)\right]$, with $I = 1.87 \times 10^{-6}$ if data for $N_1 = 141 \times 141$, $N_2 = 200 \times 200$, and $n = 20$ are used; in general, the expected error is quadratic in ϵ evaluated for the larger lattice.

The average waiting time can also indicate the critical size $a_* = \sqrt{n_*}$ if one uses an explicit expression for $t_i(a)$ as a fit function. For example, in the case of non-conserved dynamics and neglecting the discrete structure of n, one has[19,23] $t_i(a) = \tau[const + \ln(a/a_* - 1) + a/a_*]$, where the *const* is logarithmically sensitive to the nucleation barrier and also depends on the dimensionality of the system. A similar structure is then expected for $\bar{t}(a)$, which can be fitted to data in Fig. 1 at $a \geq 3$ to give $a_* \approx 2.15$. The latter is reasonably close to $a_* = \sqrt{5} \simeq 2.24$ from Refs. 16 and 25, although there are subtle issues in identifying the "first-principle" critical size with its phenomenological "Becker-Döring" counterpart.[16,25] The phenomenological barrier B can be deduced from the Zeldovich expression for the rate. In two dimensions one has $B = \frac{1}{2}\mathbf{W}[a_*^4/(2\pi I^2\tau^2)] \approx 10.5$ where $\mathbf{W}[z]$ is the Lambert W function.

The PDF of waiting times at $n = 20$ is shown in Fig. 2. Correspondence between MC and analytics is reasonable; for small ϵ the general asymptotic expression, which involves a special function, indeed can be accurately approximated by a simpler Eq. (8). The delayed exponential distribution, which ignores the smallest transient time scale τ but accounts for the time lag $t_0(n)$, is inaccurate in terms of PDF but would give almost correct average and SD. The complementary CDF $1 - F(t)$ is shown in Fig. 3 which compares MC data to the general asymptotic expression $\exp[-\epsilon E_1(e^{-r})]$. The correspondence is decent if one keeps in mind the absence of matching parameters.

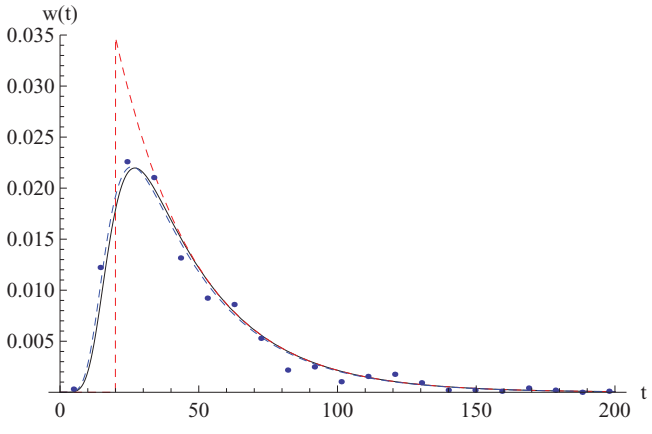

FIG. 2. The probability distribution function (PDF) for the waiting times. Symbols—MC data (binned) on the same lattice as in Fig. 1. Lines: solid—from Eqs. (3), (5), and (6); smooth dashed—elementary approximation, Eq. (8); sharp dashed—delayed exponential, Eq. (9). No matching parameters were used.

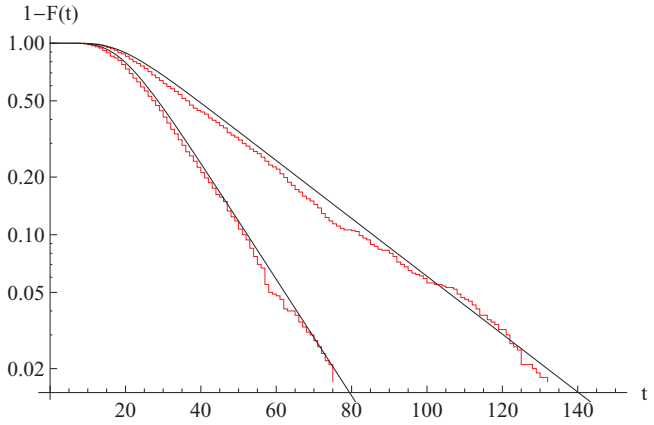

FIG. 3. Complementary CDF for two square lattices with $N = 40\,000$ (left) and $N \simeq 20\,000$ (right). Step-like lines—from MC simulations; smooth solid lines—from Eqs. (4) and (6).

In summary, the mean of waiting times to observe the first nucleus contains useful information on both steady state and on transient nucleation, and is sensitive to the "detection size" n. In contrast, the standard deviation is practically n-independent in the growth region, and is close to the inverse of the stationary nucleation rate, allowing a more efficient evaluation of the latter. The full distribution of waiting times also was considered, and the statistical approach was verified for a cold Ising ferromagnet where independent "first-principle" data are available.

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