Collapse of Transient Nucleation Fluxes in a Cold Ising Ferromagnet

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We report the time-dependent nucleation fluxes and associated nucleation rates in a metastable Ising ferromagnet on square lattice with Metropolis (Glauber-type) dynamics. It is discovered that, with lowering of the temperature, fluxes collapse into several representative transient curves corresponding to magic cluster sizes. Those can be associated with physical droplets, i.e., long-lived configurations which provide a link with the classical Becker-Döring picture.

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The classical theory of nucleation [1–3] views it as a one-dimensional random walk in the space of nuclei sizes and has an enormous number of applications from condensation of vapors [4] to crystallization of glass-forming melts and glasses [5,6] and, more recently, to biological systems [7]. The corresponding master equation, known as the Becker-Döring equation, has an attractive mathematical structure [8]. In steady state, there is an exact solution [2], and the flux, the ''nucleation rate,'' also can be expressed asymptotically as the product of an exponential term determined by thermodynamics [1] and a kinetic preexponential [3] (similarly to the activation flux in the Kramers problem [9]). The preexponential can be refined to account for discrete number of monomers in a nucleus [10], making the asymptotic flux practically indistinguishable from the exact one. In the time-dependent case, moments of the transient flux can be obtained exactly—see, e.g., Refs. [11,12], and an asymptotic expression for the flux itself also is available [13]. Efficient numerical schemes had been developed to solve the Becker-Döring equation under realistic experimental conditions [14].

Despite the outstanding role of the classical approach, it is a phenomenological one and there remain fundamental questions with respect to its underlying assumptions. It is thus natural to seek additional insight from models where the description of nucleation is close to ''first principles,'' such as the the Ising model in external field [15–21] with various kinds of spin-flip dynamics. Rather surprisingly, even for this well-studied model, the status of the classical approach remains open, and below we associate this with inherent limitations of the stationary treatment. Transient nucleation was discussed in connection with analysis of high-temperature Monte Carlo simulations [22,23] assuming the qualitative validity of the Becker-Döring picture for the Ising model, but, otherwise, the thrust of most of the earlier studies had been the stationary nucleation rate $J_{\rm st}$ or the metastable-state lifetime, usually (depending on precise definition) proportional to $1/J_{\rm st}$.

In the present Letter, the nonclassical transient nucleation rates are obtained for the case of Metropolis dynamics which is of nonconservative, Glauber type. Since at low temperatures this can be done without additional strong assumptions (and without using the Monte Carlo methods), connections with the classical phenomenology, including the limitations of the latter, can be elucidated. The significance of time dependence is increased by the fact that the steady-state treatment allows multiple definitions of a ''nucleus.'' (This flexibility echoes the duality in splitting the nucleation rate into the exponential and preexponential factors [19(b)] and, more generally, the uncertainty of classical-type approximations to the rate if both factors are treated as fitting parameters [24].) The time scale associated with postnucleation growth also emerges naturally in the nonstationary approach, allowing one to estimate the duration of the entire phase transformation.

The method is based on solving a time-dependent kinetic equation in a multidimensional space of cluster configurations assuming noninteracting clusters which evolve due to random gain or loss of a spin. (More complicated events, such as coagulation, can be neglected at small T [16].) The kinetic equation, to the largest possible extent, is cast in the generalized Becker-Döring form, which facilitates the comparison. In particular, at least formally, all exact results for the classical kinetics will have a direct analog in the Ising case.

We consider the standard two-dimensional model on a square lattice solved in equilibrium by Onsager [25], with an added external field h analogous to supersaturation. The following units are used: The Boltzmann constant is taken as 1, and interaction energies between neighboring spins are assumed to be ± 1. The temperature T is much lower than the critical value $T_c = 2.269\ldots$, and the main temperature-dependent variable is $z = \exp(-4/T) \ll 1$. Interactions with external field h are taken as $\pm 4h$, and the field variable is $\delta = \exp(8h/T) \gg 1$; the fields of interest are $h < 1/2$ with $z\delta \ll 1$, corresponding to a stable interface. Metastability is created by all spins originally pointing in the ''wrong'' direction, and the intent of the study is to evaluate the time-dependent nucleation fluxes. Steady-state analytical treatments of this problem are available for both $T \to 0$ [17,18,20] and finite T [20]; symbolic computations [19] provide significant additional help.

To illustrate limitations of the stationary approach, however, consider first the case of $T \to 0$. Here the nucleation path contains only the most compact clusters with the work $W(n)$ having an overall classical (Gibbs) outlook plus sharp sawtooth modulations [20(b)]. The critical nucleus is an $m(m+1)$ rectangle with an extra spin on the longer side, as identified by Neves and Schonmann (NS) [17]. The critical value of m is given by $m(h) = [1/2h]$ (with $[x]$ denoting the largest integer not to exceed x) with the number of spins $n_*(0, h) = m^2(h) + m(h) + 1$. The absolute barrier $W_*^H \equiv W(n_*(0, h))$ determines $J_{\rm st} \propto \exp(-W_*^H/T)$ [17] with a finite preexponential at $T = 0$ [18,20]. Alternatively, one can consider only clusters with a smooth interface as candidates for nuclei with the NS clusters treated as activation complexes. The time scale for an activated transition between neighboring smooth shapes is given by

$$\tau = 1/z\delta \tag{1}$$

and will determine the preexponential, which tends to 0 for $T \to 0$. Nevertheless, the overall estimation for $J_{\rm st}$ will not change due to a smaller barrier $W_*^L = W_*^H + 8h - 4$ [which corresponds to an $m(m+1)$ rectangle]. In other words, $J_{\rm st}$, which is the physical observable, allows two very different interpretations if one tries to identify a droplet. A time-dependent approach, on the other hand, reveals additional time scales which help to select between the two possibilities. The actual calculations, however, are meaningful at $T > 0$ and, regardless of interpretation, can be of independent interest due to the exceptional status of the Ising model.

At nonzero temperatures, one needs to identify clusters beyond the compact shapes, and computer assistance [19,26] is required in a general case. Clusters are distinguished by a class index k, and each class is characterized by a geometric factor $w_k \le 8$ related to the symmetry of a cluster, perimeter P_k, and the number of spins n_k. A (quasi)equilibrium distribution of clusters belonging to a given class k and normalized per empty site ($k = 0$) is then described by $f_k^{\rm eq} = w_k z^{P_k/2} \delta^{n_k}$. The maximum class index has a large value D.

If adding a spin to class i converts it to class k, an integer number $o_{i,k}$ is identified as the number of sites where this addition can take place [26]. Transition rates between classes are then defined as $\beta_{i,k} = o_{i,k}/\max[1, f_i^{\rm eq} w_k / f_k^{\rm eq} w_i]$. This corresponds to Metropolis dynamics, which is asymptotically close to Glauber dynamics for $h \le 1/2$, with $\beta_{i,k}$ being analytical functions of h [20(b)]. An absorbing boundary is placed at $k = D + 1$, and with $n_D - n_*(0, h) \gg 1$ the precise location of that boundary is expected to be insignificant, in analogy with the classical situation [8].

If f_k represents a time-dependent distribution, the kinetic equation is conveniently written in terms of a D-dimensional vector $\vec{v} = (f_1/f_1^{\rm eq}, \ldots, f_D/f_D^{\rm eq})$. Treating $\beta_{i,k}$ as elements of a matrix $\hat{\beta}$, one can construct a "transient matrix" $\hat{T} = \hat{\beta} + \hat{\Phi}^{-1} \cdot \hat{\beta}^T \cdot \hat{\Phi} - \hat{d}$. Here $\hat{\Phi}$ and $\hat{d}$ are two diagonal matrices with nonzero elements $\Phi_{i,i} = f_i^{\rm eq}$ and $d_{i,i} = \sum_{k=1}^{D+1} \beta_{i,k}$, respectively, with $1 \le i \le D$. The time dependence is then governed by an equation

$$\frac{d\vec{v}}{dt} = \hat{T} \cdot \vec{v} + \vec{e}, \qquad \vec{e} = (1, 0, \ldots, 0). \tag{2}$$

The exact solution is formally given by $\vec{v}(t) = \{\hat{I} - \exp(t\hat{T})\} \cdot \vec{v}_{\rm st}$, with $\hat{I}$ being a unitary martix and $\vec{v}_{\rm st} = -(\hat{T}^{-1}) \cdot \vec{e}$. In practice, however, a numerical approach should be used for large D, similarly to the classical situation [14]. A forward update scheme $\vec{v}(t + \epsilon) = \vec{v}(t) + \epsilon[\hat{T} \cdot \vec{v}(t) + \vec{e}]$ does not require an inversion of a large matrix and, in principle, can be employed even if $\vec{v}_{\rm st}$ cannot be obtained.

To determine the total flux J_n and the exact transient moments $t_k(n) = \int_0^\infty t^k [1 - J_n(t)/J_{\rm st}] dt$ at each size n, we introduce linear operators L_n:

$$L_n[\vec{v}] = \sum_{k, n_k = n} \sum_i \beta_{i,k} f_i^{\rm eq} (v_i - v_k). \tag{3}$$

This gives a generalization of similar classical expressions [11], and with $k = 0, 1$ one has:

$$J_n(t) = L_n[\vec{v}(t)], \qquad t_k(n) = L_n[(-\hat{T})^{-k-1} \cdot \vec{v}_{\rm st}]/J_{\rm st}. \tag{4}$$

The actual calculations were performed for $n_D = 25$ ($h = 0.22$) and $n_D = 30$ ($h = 0.15$). The update scheme was implemented in the MATHEMATICA 5.2 version. Compact clusters with a minimum perimeter $P_k^{\rm min}(n)$ and only those with $P_k \le P_k^{\rm min}(n) + 2$ for a given n were included, with total numbers $D = 3196$ and $D = 6316$, respectively. The selected upper boundaries are sufficiently far from the values of $n_*(0, h)$, respectively, 7 and 13, which are expected to further decrease with temperature [27]. Changes of n_D affected only the upper 2–3 fluxes, and those were excluded from consideration. To control sensitivity of numerics to selected configurations, clusters with $P_k \le P_k^{\rm min}(n) + 4$ were included, with $n_D = 15$ ($D = 5924$), and the maximum changes of $J_{\rm st}$ were within a few percent at $T = 0.8$ (note that at such T the system is still "cold" with a small $z \simeq 0.007$). Correctness of $J_{\rm st}$ (which involves inversion of a large matrix) was verified by their n independence and by small difference from the analytical results of Ref. [20(b)] at the lowest temperature. The outgoing flux J_n can be evaluated for an empty site with $n = 0$, although such calculations are less stable compared to larger n and at low T could be completed only for $h = 0.22$.

Results for $J_n(t)/J_{\rm st}$ are presented in Fig. 1. Note that τ in Eq. (1) (which changes by orders of magnitude) provides a reasonable scale for transient nucleation. This is an indication that rectangular-shaped clusters are indeed

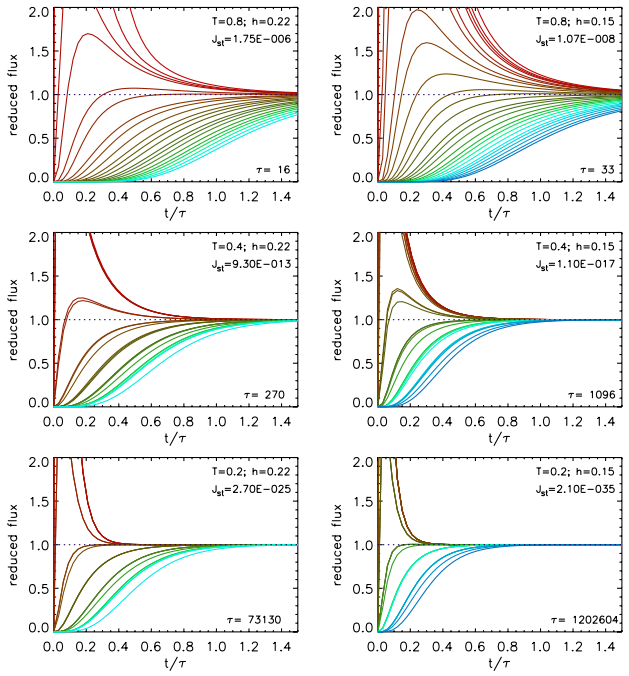

FIG. 1 (color online). Collapse of transient fluxes $J_n(t)/J_{\rm st}$ with lowering of the temperature. Left column: $h = 0.22$, $0 \le n \le 20$. Right column: $h = 0.15$, $1 \le n \le 25$. At higher T, the structure of fluxes is similar to the one in the Becker-Döring model, including the overshoot at subcritical n [4]. At low T, fluxes group into a few representative curves. For $T = 0.2$, $h = 0.22$, the groups are (counterclockwise, from top): $n =$ (0–3), (4, 5) (the two descending curves) and $n =$ (6, 7), 8, (9–11), (12–14), 15, (16–19), 20. For $h = 0.15$, the second group is $n =$ (4–11) (descending), and added groups on the right (due to larger n_D) are $n =$ (20–23), 24, 25. At intermediate $T = 0.4$, similar grouping is observed, although collapse is incomplete; the (4, 5) fluxes for $h = 0.22$ and the (9, 10) and the 11 fluxes for $h = 0.15$ are shown as bell-shaped, rather than descending, curves due to a smaller overshoot at higher T.

good candidates for "droplets," while Neves-Schonmann clusters play the role of activation complexes for slow droplet-to-droplet transitions. When temperature is lowered, collapse of different fluxes to several representative values of n is observed. At the lowest temperature where the effect is the most pronounced, all fluxes group around "proper" n, which correspond to squares ($n = m^2$) and rectangles [$n = m(m + 1)$]. The stand-alone fluxes indicate wrong rectangles $n = (m + 1)(m - 1)$ (the latter have only one-sided connection with the lowest energy path and thus play the role of "metastable traps"). At low temperatures, a primitive model can be constructed, which involves only the aforementioned representative n and which accurately predicts fluxes at proper n [28]. The difference with the Becker-Döring picture, however, is obvious since only selected n are present and three distinct shapes (squares and two types of rectangles) are to be considered.

Of the main interest for applications is the nucleation rate, i.e., the flux for some $n > n_*$ from which deterministic growth of nuclei can be started. Within the classical picture of Refs. [1–3], one has for a high barrier [13]

$$J(n, t) = J_{\rm st} \exp(-e^{-x}), \qquad x = [t - t_0(n)]/t_{\rm rel} + \gamma, \tag{5}$$

with $\gamma = 0.5772\ldots$, the Euler constant. The "relaxation time" can further be related to the transient moments [29]

$$t_{\rm rel} = \frac{\sqrt{6}}{\pi}\sqrt{2t_1(n) - t_0^2(n)}. \tag{6}$$

A similar transient shape will be used (without a rigorous justification) in the present nonclassical situation in order to scale the data. For each field, the largest available proper n were considered, respectively, $n = 20$ for $h = 0.22$ and $n = 25$ for $h = 0.15$, and $t_{\rm rel}$ was evaluated using Eqs. (4) and (6). Results fit reasonably the double-exponential curve for all temperatures and fields, as in Fig. 2, and together with $J_{\rm st}$ listed in Fig. 1 provide a predictive description of the transient nucleation rate. Since relatively high temperatures (up to $0.35T_c$) were considered, the obtained data could test the accuracy of Monte Carlo simulations, which are potentially vulnerable for extremely rare nucleation events. Furthermore, for temperatures and fields which are too low for direct Monte Carlo studies, the obtained transient expressions can provide the (non-Poissonian) rate of injection of nuclei, which can be further grown using faster schemes [30], describing the entire phase transformation. Since the growth rate is of the order of $1/\tau$, the time scale for the transformation follows from the standard Kolmogorov-Avrami estimation $(J_{\rm st}/\tau^2)^{-1/3}$, which is expected to be much larger than τ, leading to a requirement $W_*^L \gg 3T$.

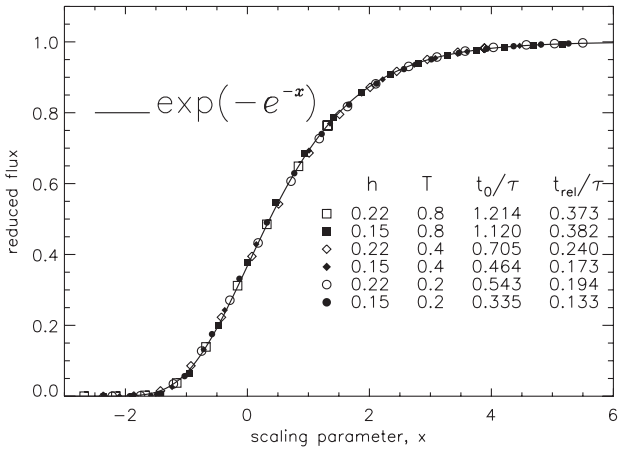

FIG. 2. Reduced nucleation rates [fluxes $J_n(t)/J_{\rm st}$ at the largest n in Fig. 1] vs the scaling parameter $x = [t - t_0]/t_{\rm rel} + 0.5772\ldots$ at different temperatures and fields. The parameters t_0 and $t_{\rm rel}$ can be calculated from exact expressions (see text) and are indicated in the legend. Scaled data closely follow the double-exponential shape (solid line) expected from the Becker-Döring model [13].

In summary, the study provides the first explicit expressions for the nonclassical transient nucleation rates. Such results are important since, in many practical situations, there is just not enough time for the steady-state nucleation to be established (due to depletion of the mother phase by growing nuclei, their interactions with each other, etc.). From a more fundamental point, there exist inherent limitations of the steady-state approach to the nucleation problem, and time-dependent studies provide a much deeper insight into connections with the classical picture. The most interesting feature is the observed collapse of fluxes around selected ''magic'' cluster numbers, indicating the presence of long-living dropletlike structures. The latter effect is not restricted to the dynamic Ising model considered in the study but is expected for any low-temperature nucleating system where a nucleus can have a smooth interface with exponentially slow attachment kinetics.

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