

Phase Transformation near the Classical Limit of Stability

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Successful theories of phase transformation processes include classical nucleation theory, which envisions a local equilibrium between coexisting phases, and nonequilibrium kinetic cluster theories. Using computer simulations of the magnetization reversal of the Ising model in three different ensembles we make quantitative connections between these physical pictures. We show that the critical nucleus size of classical nucleation theory is strongly correlated with a dynamical measure of metastability, and that the metastable phase persists to thermodynamic conditions previously thought of as unstable.

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Introduction.—The mechanism by which a material transforms from one stable phase to another after a change of thermodynamic conditions is of great theoretical and practical importance [1,2]. Despite the long-standing interest in this fundamental process several key aspects remain poorly understood, particularly the behavior close to the classical limit of stability [3,4]. Our understanding of the transformation mechanism is based on two seemingly different physical pictures. Classical nucleation theory (CNT) envisions droplets of the new stable phase that are in local equilibrium with an environment similar to the formerly stable phase. This picture leads to an expression for the free energy $\Delta F(N)$ of a droplet as a function of its size N , with corresponding droplet densities

$$\rho_{ce}(N) \propto \exp(-\beta\Delta F(N)), \quad (1)$$

where $\beta = 1/k_B T$. Here we have added the subscript “ce” to emphasize that these densities can be computed only in a constrained equilibrium in which the transformation process cannot progress to completion.

Cluster dynamics theories, on the other hand, model the time evolution of droplet populations through a set of coupled kinetic equations that represent cluster processes such as coagulation or dissociation. These equations are of the form

$$\frac{\partial \rho_t(N)}{\partial t} = \sum_{\sigma} \nu_N(\sigma) R(\sigma), \quad (2)$$

where $\rho_t(N)$ is the density of N -mers at time t , the sum is over all possible elementary processes σ , $R(\sigma)$ is the reaction rate, and $\nu_N(\sigma)$ is the stoichiometric number of N -mers in the reaction σ [5]. These theories rely on the assumption that the size N is sufficient to describe the cluster growth dynamics, for which there is numerical evidence [1,6,7]. To solve this set of equations the rates $R(\sigma)$ must be specified. In addition to several heuristic arguments one generally requires these rates to obey detailed balance with respect to the distribution (1) so that $\rho_{ce}(N)$ is the time invariant solution of (2). The validity of

this assumption is not clear *a priori*. While the underlying microscopic dynamics obeys detailed balance with respect to the equilibrium distribution of microstates, it is not obvious whether the transition rates between clusters of different sizes obey any balance condition, let alone detailed balance with respect to $\rho_{ce}(N)$. We are not aware of any explicit verification of this crucial assumption.

Solving the infinite set (2) of coupled equations is exceedingly complex. To compute experimentally relevant quantities such as the nucleation rate it is common to consider a hypothetical process in which clusters are removed from the system when they reach a threshold size N_{\max} ; i.e., one introduces an absorbing boundary in N space. Together with a corresponding source term for small clusters one then solves for the time-independent steady-state solution $\rho_{ss}(N)$ of (2). This steady state entails a net flux towards larger droplets.

The relationship between the densities ρ_{ce} , ρ_t and ρ_{ss} and their respective ensembles is of fundamental importance to our understanding of phase transformation processes. While some of these have been computed for various model systems [7–13] we are not aware of any study that measures all three densities for the same system and thermodynamic conditions. In this Letter we report such measurements for the change in magnetization of the Ising model after reversal of the external field. These measurements allow us to establish quantitative connections between the different physical pictures outlined above. We focus on two questions that could not be addressed by considering only one of these ensembles. First we investigate whether the nonequilibrium rates $R(\sigma)$ obey detailed balance with respect to the constrained equilibrium distribution (1). We find that this is indeed the case for the dominant cluster growth process. Second we study whether the key quantity of CNT, the critical nucleus size N_c defined as the location of the maximum in $\Delta F(N)$, is relevant to the dynamics of clusters. We confirm this assumption, and use a novel dynamical measure of cluster growth to locate the limit of stability. Our findings

suggest that droplets remain metastable even at thermodynamic conditions that were previously believed to be unstable.

Model and ensembles.—We consider the Ising model on a cubic lattice of volume V , i.e., a set of spin variables $s_i = \pm 1$, $1 \leq i \leq V$, with energy function $E = -h \sum_i s_i - J \sum_{\langle i,j \rangle} s_i s_j$, where the second sum includes all pairs of nearest-neighbor lattice sites. Our calculations are performed at $J/k_B T = 0.369$, or 0.6 times the critical temperature. We propagate the system by flipping a randomly selected spin with probability $\min\{1, \exp(-\Delta E/k_B T)\}$, where ΔE is the change in energy due to the flip.

We are interested in the transformation of the “down” ($s_i = -1$) phase to the “up” ($s_i = 1$) phase after a quench to positive values of the field h . We define a cluster as a collection of nearest-neighbor up spins, other definitions can be found in the literature [1,14]. For a given spin configuration we define M_N as the number of clusters of size N .

We compute the mean cluster densities $\rho_X(N) = \langle M_N \rangle_X / V$ in three different ensembles, specified by the subscript X , corresponding to the three physical pictures outlined in the introduction. The first is the constrained equilibrium ensemble envisioned in CNT. This ensemble can be sampled in simulations by rejecting spin flips that would create a cluster of a size larger than a chosen threshold N_{\max} , which frustrates global phase transformation. The average cluster density $\rho_{ce}(N)$ computed in this ensemble can be used to calculate the droplet free energy [8]

$$F(N) = -k_B T \ln \rho_{ce}(N), \quad (3)$$

which implies (1) after setting $\Delta F(N) = F(N) - F(1)$.

Figure 1 shows these free energy profiles for a wide range of quench depths. These results confirm the fundamental prediction of CNT. In particular, $\Delta F(N)$ has a single maximum that defines the critical nucleus size N_c . The regularity of these profiles establishes the validity of CNT up to quench depths $h/J \approx 0.8$, even though earlier

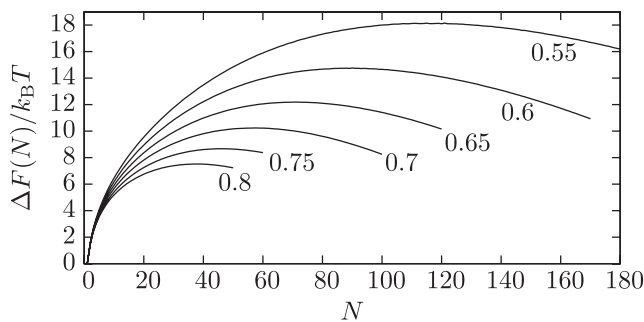


FIG. 1. Droplet free energy for various quench depths h/J as indicated in the figure. $\Delta F(N)$ has a single maximum at the critical nucleus size N_c and a corresponding activation barrier $\Delta F(N_c)$, which both decrease with increasing quench depth.

studies suggested a breakdown of CNT under these conditions [4,15].

The range of thermodynamic conditions for which we can compute $\Delta F(N)$ using this method is limited by the magnitude of the energy barrier at small quench depths, which necessitates the use of advanced sampling techniques [7]. At large quench depths, on the other hand, the average density of up spins $\sum_{N=1}^{N_{\max}} N \rho_{ce}(N)$ becomes sufficiently large so that the assumptions of independent cluster populations, employed in the derivation of (3), no longer holds. In this case the crowding of droplets induces additional many-body interactions, which lead to a N_{\max} dependence of $\Delta F(N)$. If this dependence becomes significant for values of N_{\max} smaller than or comparable to N_c , the free energy profile of an individual droplet can no longer be computed by this method.

The second ensemble corresponds to the time-dependent growth of domains following the reversal of the field. Ensemble averages, denoted by $\langle \cdot \cdot \cdot \rangle_t$, depend explicitly on the time t since the process was initiated. Figure 2 shows the droplet densities $\rho_t(N)$ during the initial stages of nucleation. These functions are monotonically decreasing, and for fixed N the cluster densities converge to a time-independent value. Importantly, this density is different from the CNT prediction $\rho_{ce}(N) = \exp(-\beta F(N))$. These densities coincide for small cluster sizes up to approximately N_c , where $\rho_{ce}(N)$ has a minimum while $\rho_t(N)$ remains monotonic. This comparison shows explicitly that droplets smaller than N_c are indeed in local equilibrium with their environment, as envisioned in CNT. These clusters repeatedly grow and shrink and hence sample the metastable equilibrium distribution. Clusters larger than N_c , on the other hand, predominantly grow and are no longer in equilibrium.

The densities shown in Fig. 2 are intensive quantities and do not depend on the system volume. The probability of observing a nucleation event in a single trajectory, however, depends on how V compares to $\exp(\beta F(N_c))$, and thus changes qualitatively as one varies either the

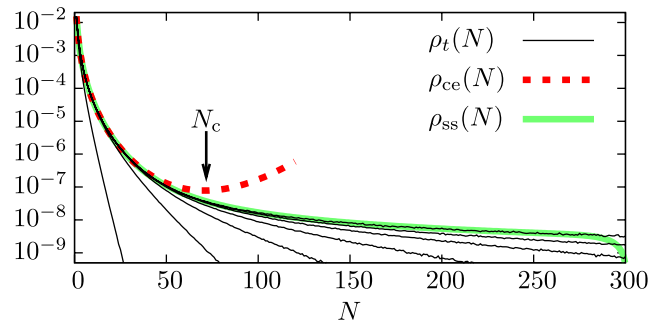


FIG. 2 (color online). Droplet densities computed in three different ensembles for a quench to $h/J = 0.65$. ρ_{ce} is the constrained equilibrium density ($N_{\max} = 120$), ρ_t the time-dependent density for $t = 2, 10, 20, 30, 40, 50, 100$ (left to right), and ρ_{ss} the steady-state density ($N_{\max} = 300$).

quench depth or the simulation size. In particular, at any quench depth one is likely to observe more than one critical nucleus in the simulation box when the volume V is larger than $2\rho_t(N_c)^{-1}$. The appearance of several growing droplets is hence not sufficient evidence by itself for a breakdown of CNT or the onset of collective dynamical effects [3,4]. For $V < \rho_t(N_c)^{-1}$, on the other hand, one observes the spontaneous formation of droplets of those intermediate sizes N for which $V\rho_t(N) \geq 1$ [4]. This too is consistent with CNT because $\rho_{ce}(N) \approx \rho_t(N)$ for $N < N_c$. In this case the average time for the first nucleation event to occur anywhere in the system is a decreasing function of V [2].

The third ensemble we consider is that of the steady state, which we generate in our simulations by replacing droplets with down spins when their size exceeds a threshold value N_{\max} . The cluster density $\rho_{ss}(N)$ computed in this ensemble is also shown in Fig. 2. We find that over a wide range of N the steady-state density equals the limiting density of the corresponding time-dependent system. For cluster sizes close to N_{\max} , however, $\rho_{ss}(N)$ is significantly depleted relative to $\rho_t(N)$ at late times. This behavior can be understood within the framework of kinetic theories of cluster dynamics. Consider the population of clusters of a size close to N_{\max} . In the nonequilibrium ensemble, this population is diminished by growth to larger clusters, and replenished by shrinkage of such clusters. In the steady-state ensemble the rate of such growth processes remains unchanged, whereas the shrinkage of clusters larger than N_{\max} is suppressed, which leads to a lower steady-state density. This behavior is similar to that observed in diffusive processes in the presence of an absorbing wall. In this Letter we will focus on observables sufficiently far away from the boundary, where the late-time behavior of the time-dependent ensemble is recovered.

Results.—To compute the rate constants that appear in (2) we need to characterize all possible processes σ that change the cluster densities $\rho(N)$. Let s be the spin state of

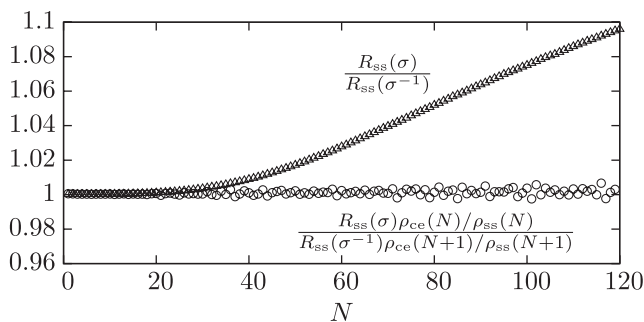


FIG. 3. Ratio of the forward and reverse rate of the process $\sigma = (-1, 1, N)$, i.e., the growth of a droplet of size N to $N + 1$, at quench depth $h/J = 0.65$. In the steady-state ensemble the growth rate exceeds that of the inverse process (triangles). Applying the same rate constants to the constrained equilibrium densities results in approximately equal forward and reverse rates (circles).

a lattice site before a flip. For $s = -1$ ($s = 1$) let m be the number of unique nearest-neighbor clusters before (after) the flip, and N_1, \dots, N_m be their sizes. For definiteness we require that $N_i \leq N_j$ for $1 \leq i \leq j \leq m$. These numbers uniquely define the reaction σ , which we therefore write as (s, m, N_1, \dots, N_m) . For example, the process $(-1, 1, N)$ corresponds to the growth of a cluster of size N to $N + 1$, whereas the process $(1, 2, N_1, N_2)$ is the dissociation of a droplet of size $N_1 + N_2 + 1$ into two clusters of size N_1 and N_2 . The process $\sigma^{-1} = (-s, m, N_1, \dots, N_m)$ is the inverse process of σ . The stoichiometric number of N -mers in the reaction σ can be written as $\nu_N(\sigma) = -s(\delta_{1+\sum_{i=1}^m N_i, N} - \sum_{i=1}^m \delta_{N, N_i})$. Limiting the sum in (2) to only those processes with $m = 1$ one recovers the classical Becker-Döring equation [1,16].

We calculate the reaction rates $R_{ss}(\sigma)$ in the steady-state ensemble by monitoring how many times the process σ occurs per unit volume and unit time. These rates do not observe detailed balance due to the presence of a net flux towards larger clusters (Fig. 3). The rate of the growth process $N \rightarrow N + 1$ is larger than the rate of the reverse process, and their ratio increases with droplet size N .

Dynamical theories of cluster growth assume that these rates obey detailed balance with respect to the density (1). To test this assumption we calculate what the rates would be in the constrained equilibrium ensemble, using the kinetic information from the steady-state calculation. Assuming first order kinetics, we compute these rates as $R_{ss}(\sigma)\rho_{ce}(N)/\rho_{ss}(N)$ for the $N \rightarrow N + 1$ reaction, and $R_{ss}(\sigma^{-1})\rho_{ce}(N + 1)/\rho_{ss}(N + 1)$ for the reverse process. These rates are indeed equal within the accuracy of our simulations (Fig. 3). This numerical verification of one of the key assumptions of kinetic theories of cluster growth validates their extensive use in the field of phase transformation studies.

We now turn our attention to the critical nucleus size N_c . In CNT this size separates droplets that are likely to shrink from those that are likely to grow. From its definition it is not obvious whether this size is significant for the dynamics of the transformation process. Previous studies have shown that droplets of size N_c , generated from an equilibrium distribution, have approximately equal probabilities of growing and shrinking [7], thereby confirming the main prediction of CNT. In experimental realizations of the transformation process, however, droplets of size N_c may already be out of equilibrium, as seen in Fig. 2. A direct comparison between the constrained equilibrium quantity N_c and the actual cluster dynamics is hence still needed.

For computational convenience we work again in the steady-state ensemble. We define the net growth rate of droplets of size N as

$$\omega(N) = \sum_{\sigma} \left(\delta_{s,-1} \sum_{i=1}^m \delta_{N_i, N} - \delta_{s,1} \delta_{1+\sum_{i=1}^m N_i, N} \right) R_{ss}(\sigma),$$

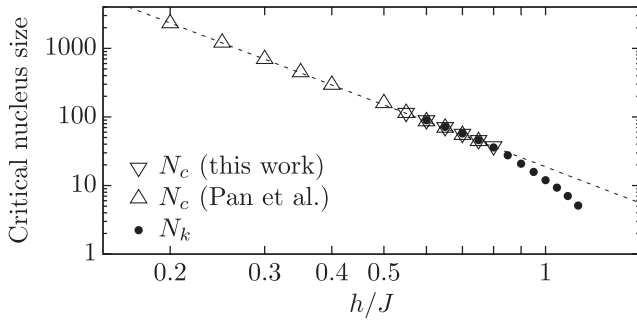


FIG. 4. Comparison of the critical nucleus size N_c , defined as the location of the maximum in $\Delta F(N)$, with the cluster size N_k at which a droplet has equal probability of growing and shrinking. Data for N_c at shallow quench depths are taken from Ref. [18]. The dashed line is a fit to the CNT prediction $N_c \propto h^{-3}$.

where the first term takes into account coagulation processes that involve droplets of size N , and the second term counts processes involving the dissociation of droplets of size N . We define N_k as the droplet size for which $\omega(N_k) = 0$ [17]. A droplet of size N_k hence has equal probabilities of growing and shrinking in the steady-state ensemble.

Figure 4 shows N_c and N_k for a large range of thermodynamic conditions. We find excellent agreement between these quantities over the range of quench conditions for which both can be computed. This provides explicit evidence that the CNT quantity N_c is useful to characterize the dynamics of cluster growth. For very deep quenches we find that N_k is smaller than the CNT prediction, presumably due to the previously discussed crowding of droplets. Surprisingly we find that clusters remain dynamically metastable up to a quench depth $h/J = 1.18$, which is significantly deeper than previous estimates of the limit of stability [4,18]. For even deeper quenches the growth rate $\omega(N)$ is positive for all droplet sizes, which implies that a monomer already exceeds the critical size.

In summary, we have studied the magnetization reversal in the nonconserved Ising model in three different ensembles, corresponding to the physical pictures embodied in standard theories of phase transformation processes. This allows us to make quantitative connections between these pictures, and to compute observables that are not accessible by computations in only one ensemble. We have provided evidence that the cluster dynamics obeys detailed balance with respect to the constrained equilibrium densities, which is a fundamental and previously untested assumption in kinetic theories of droplet growth. We have also shown that the critical nucleus size, as computed within the CNT framework, correlates very well with a

dynamical measure of droplet stability. These findings validate the assumptions underlying the classical theories of phase transformation processes. We show that the dynamically defined critical nucleus size decreases smoothly up to the limit of stability, which is located at unexpectedly deep quenches.

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- [1] J.D. Gunton, M. San Miguel, and P.S. Sahni, *The Dynamics of First Order Phase Transitions*, edited by C. Domb and J.L. Lebowitz, Phase Transitions and Critical Phenomena Vol. 8 (Academic Press, London, 1983), pp. 269–467.
 - [2] P.G. Debenedetti. *Metastable Liquids* (Princeton University Press, Princeton, NJ, 1996).
 - [3] F. Trudu, D. Donadio, and M. Parrinello, Phys. Rev. Lett. **97**, 105701 (2006).
 - [4] P. Bhimalapuram, S. Chakrabarty, and B. Bagchi, Phys. Rev. Lett. **98**, 206104 (2007).
 - [5] We follow the convention that the stoichiometric number $\nu_N(\sigma)$ is negative for reactants and positive for products.
 - [6] K. Binder and D. Stauffer, Adv. Phys. **25**, 343 (1976).
 - [7] A. C. Pan and D. Chandler, J. Phys. Chem. B **108**, 19681 (2004).
 - [8] P. R. ten Wolde and D. Frenkel, J. Chem. Phys. **109**, 9901 (1998).
 - [9] K. Binder and H. Müller-Krumbhaar, Phys. Rev. B **9**, 2328 (1974).
 - [10] J. Schmelzer and D. P. Landau, Int. J. Mod. Phys. C **12**, 345 (2001).
 - [11] D. Stauffer, A. Coniglio, and D. W. Heermann, Phys. Rev. Lett. **49**, 1299 (1982).
 - [12] D. W. Heermann, A. Coniglio, W. Klein, and D. Stauffer, J. Stat. Phys. **36**, 447 (1984).
 - [13] S. Toxvaerd, J. Chem. Phys. **115**, 8913 (2001).
 - [14] K. Binder, Ann. Phys. (N.Y.) **98**, 390 (1976).
 - [15] L. Maibaum, Phys. Rev. Lett. **101**, 019601 (2008).
 - [16] R. Becker and W. Döring, Ann. Phys. (Leipzig) **416**, 719 (1935).
 - [17] For quench depths up to $h/J \approx 0.8$ the net growth rate changes its sign only once. Since $\omega(N)$ is defined only for integer values, we compute N_k by interpolating $\omega(N)$ in the vicinity of this change. For larger quench depths $\omega(N)$ has an additional node at very small droplet sizes $N \lesssim 2$. In these cases we take N_k to be larger of the two, corresponding to the largest marginally stable cluster.
 - [18] A. C. Pan, T. J. Rappl, D. Chandler, and N. P. Balsara, J. Phys. Chem. B **110**, 3692 (2006).