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Validity of classical nucleation theory for Ising models

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While the classical nucleation theory (CNT) is widely used to predict the rate of first-order phase transitions, its validity has been questioned due to discrepancies with experiments. We systematically test the individual components of CNT by computer simulations of the Ising models and confirm its fundamental assumptions under a wide range of conditions ($h=0.01$–$0.13J$, $T=0.44$–$0.84T_c$ in two-dimensions and $h=0.30$–$0.60J$, $T=0.48$–$0.62T_c$ in three dimensions). First, CNT accurately predicts the nucleation rate if the correct droplet free energy is provided. Furthermore, theoretical prediction of droplet free energy matches numerical results very well in the two-dimensional (2D) Ising model, if appropriate correction terms are added. This establishes the 2D Ising model as an important reference point where existing theories can predict nucleation rate accurately with no adjustable parameters.

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Nucleation has been the subject of intense research because it plays an important role in the dynamics of most first-order phase transitions [1–3]. For many decades, our understanding of nucleation has been dominated by the classical nucleation theory (CNT) [4,5], because it correctly captures the qualitative features of the nucleation process, and predicts the nucleation rate based on bulk material properties. However, the nucleation rate predicted by CNT often disagrees with experimental measurements [2], and this discrepancy has stimulated the search for improved theoretical models [6–9]. In addition, the fitting parameters, such as surface tension, often introduced when comparing with experiments, prevent a rigorous test of CNT [3]. Computer simulation of the Ising model has been repeatedly used to test nucleation theories [10–16], with the advantage that the surface free energy can be obtained very accurately and extrinsic artifacts such as impurity can be completely removed. Both agreement and disagreement between CNT and computer simulations have been reported. Unfortunately, it is still not clear what causes the discrepancy between CNT predictions and computer simulations of the Ising model, the simplest and most thoroughly studied model for first-order phase transitions.

A widely used form of CNT is the Becker-Döring theory [4], which predicts the nucleation rate by considering the spontaneous formation of droplets of the stable phase in the background of the metastable phase. The theory has two parts that can be tested separately. In part I, CNT assumes that the system can be coarse grained into a one-dimensional (1D) Markov chain characterized by the size n of the largest droplet. The steady-state solution of the Markov chain predicts the nucleation rate to be

$$I = f_c^+ \Gamma \exp\left(-\frac{F_c}{k_B T}\right) \tag{1}$$

where k_B is Boltzmann's constant, T is temperature and F_c is the maximum of the droplet free energy $F(n)$ [17]. The preexponential factors will be discussed later. In part II, CNT assumes that the droplet free-energy function can be written as

$$F(n) = \sigma S - \Delta\mu n \tag{2}$$

where σ is the macroscopic surface tension and $\Delta\mu$ is the chemical-potential difference between the two phases. S is the surface area of a droplet. When discrepancy is observed between CNT predictions and computer simulations, it is important to know whether part I or part II (or both) is responsible so that the theory can be modified appropriately.

In this study, we tested part I and part II of CNT separately on homogeneous nucleation in both two-dimensional (2D) and three-dimensional (3D) Ising models. Part I of CNT is confirmed by excellent agreement between the nucleation rate computed from the forward flux sampling [18,19] method and that given by Eq. (1), in which F_c is computed by umbrella sampling [20]. The agreement is observed over a wide range of conditions where the nucleation rate varies by 40 orders of magnitude. The committor probability distribution of droplets with critical size n_c is sharply peaked at 50% in the 2D Ising model, further confirming the droplet size n as a good reaction coordinate. On the other hand, part II of CNT does not agree with the umbrella sampling results. For the 2D Ising model, excellent agreement is recovered if a logarithmic term $\frac{5}{4}k_B T \ln n$ and a constant are added to Eq. (2). Both terms can be derived analytically from existing theories [7,21]. This work establishes the 2D Ising model as a reference point where CNT, with appropriate corrections, predicts the nucleation rate accurately without any fitting parameters.

The Ising model is described by the Hamiltonian

$$H = -J\sum_{\langle i,j\rangle} s_i s_j - h\sum_i s_i \tag{3}$$

where J is the coupling constant and h is the external magnetic field. The spin variable s_i at site i can be either $+1$ (up) or -1 (down), and the sum $\Sigma_{\langle i,j\rangle}$ is over nearest neighbors of the spin lattice. In our simulations, we set $J=1$, $h>0$ and start with a metastable state in which $s_i=-1$ for most of the

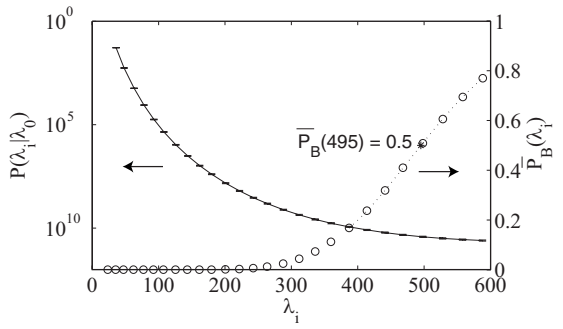

FIG. 1. The probability $P(\lambda_i|\lambda_0)$ (solid line) of reaching interface λ_i from λ_0 and average committor probability $\overline{P_B}(\lambda_i)$ (circles) over interface λ_i at $(k_BT,h)=(1.5,0.05)$ for the 2D Ising model. The 50% committor point is marked by $*$.

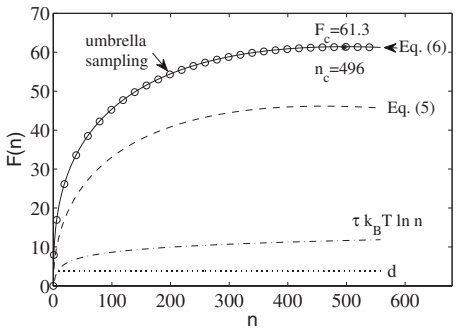

FIG. 2. Droplet free energy $F(n)$ of the 2D Ising model at $(k_BT,h)=(1.5,0.05)$ obtained by umbrella sampling (circles) is compared with Eq. (5) (dashed line) and Eq. (6) (solid line). $\frac{5}{4}k_BT\ln n$ (dash-dot line) and d (dotted line) from Eq. (6) are also plotted. The maximum of $F(n)$ is marked by $*$.

spins. The dynamics follows the Metropolis single-spin-flip Monte Carlo (MC) algorithm with random choice of trial spin. The simulation time step is measured in units of MC step per site (MCSS). The 2D model consists of a 100×100 square lattice and the 3D model consists of a $32\times32\times32$ simple-cubic lattice. Periodic boundary conditions are applied to all directions, in order to model homogeneous nucleation.

In order to test part I of CNT, which predicts the nucleation rate by assuming the system can be coarse grained to a 1D Markov chain, we must have an independent way to compute the nucleation rate without relying on this assumption. It is also important to sample a wide range of (T,h) conditions and collect sufficient statistics for every condition. This precludes the use of brute-force Monte Carlo simulations, which become very inefficient when the nucleation rate is low. The method we choose is forward flux sampling (FFS) [18]. It has been developed to sample rare events in nonequilibrium systems which do not need to obey detailed balance. The transition rate I has also been proven to be independent of the choice of the order parameter [19], as long as it distinguishes the initial and final states of the transition.

In FFS, a series of interfaces is defined in the phase space to separate the initial state A and the final state B, through an order parameter λ. Here λ is the size of the largest droplet. State A is defined as the phase-space region in which $\lambda<\lambda_A$, while state B corresponds to $\lambda>\lambda_n$. The interfaces between A and B are defined as hypersurfaces on which $\lambda=\lambda_i$, $i=0,1,2,\ldots,n-1$, $\lambda_A<\lambda_0<\cdots<\lambda_n$. The transition rate I from A to B is given by

$$I = I_0 P(\lambda_n|\lambda_0) \tag{4}$$

where I_0 is the average flux across the interface $\lambda=\lambda_0$ (i.e., leaving state A). $P(\lambda_n|\lambda_0)$ is the probability that a trajectory leaving interface λ_0 will reach interface λ_n without returning to state A. It is calculated by multiplying together $P(\lambda_{i+1}|\lambda_i)$, $i=0,1,\ldots,n-1$, each computed from MC simulations starting at interface λ_i.

As an example, Fig. 1(a) plots $P(\lambda_i|\lambda_0)$ for the 2D Ising model at $(k_BT,h)=(1.5,0.05)$. Here we choose $\lambda_0=24$ and $\lambda_n=1200$. We find $I_0=1.45\times10^{-8}$ MCSS^{-1} from a brute-force Monte Carlo simulation with 10^7 MCSS. 15 000 configurations are then collected at each interface λ_i, from which we obtain $P(\lambda_n|\lambda_0)=1.92\times10^{-11}$. Following Eq. (4), the nucleation rate is $I^{\mathrm{FFS}}=2.78\times10^{-19}$ MCSS^{-1}.[22]

To compare this result with part I of CNT, we need to compute all the terms on the right-hand side of Eq. (1). First, we compute the droplet free energy $F(n)$ by umbrella sampling, using the size of the largest droplet as the order parameter and a parabolic bias function, $0.1k_BT(n-\bar{n})^2$, where $\bar{n}$ is the center of each window [20]. The result for $(k_BT,h)=(1.5,0.05)$ is plotted in Fig. 2. The maximum occurs at $n_c=496$ giving a free-energy barrier of $F_c=61.3$. The second derivative of $F(n)$ gives the Zeldovich factor [23], $\Gamma=0.0033$, defined as $\Gamma\equiv(\eta/2\pi k_BT)^{1/2}$ where $\eta=-\partial^2F(n)/\partial n^2|_{n=n_c}$.

f_c^+ is the effective attachment rate of single spins to the critical droplet. To compute f_c^+, we collect an ensemble configurations from umbrella sampling, when the bias potential is centered at the critical droplet size. Using each configuration as an initial condition, we run Monte Carlo simulations and observe the droplet size fluctuation with time. The effective attachment rate is obtained from $f_c^+=\langle\Delta n^2(t)\rangle/(2t)$, where $\langle\Delta n^2(t)\rangle$ is the mean-square fluctuation of the droplet size, averaged over the ensemble. At $(k_BT,h)=(1.5,0.05)$, we obtain $f_c^+=39.1$ MCSS^{-1}.

Inserting the values of f_c^+, Γ, and F_c into Eq. (1), we find CNT prediction of the nucleation rate $I^{\mathrm{BD}}=2.37\times10^{-19}$ MCSS^{-1}. This is very close to the rate $I^{\mathrm{FFS}}=2.78\times10^{-19}$ MCSS^{-1} computed from FFS.

We have computed the nucleation rate using these two methods over a wide range of conditions: $h=0.01$–0.13, $T=0.44$–$0.84T_c$ for two dimensions and $h=0.30$–0.60, $T=0.48$–$0.62T_c$ for three dimensions, where T_c is the critical temperature at zero field ($k_BT_c=2.269$ in two dimensions and 4.512 in three dimensions). The nucleation rate over these conditions spans more than 40 (20) orders of magnitude for the 2D (3D) Ising model, but the results of the two methods closely match each other, as shown in Fig. 3. Under most conditions, the rates predicted by the two methods are within 50% of each other. This strongly confirms that for the purpose of computing the nucleation rate, it is valid to coarse grain the Ising model to a 1D Markov chain using the size of

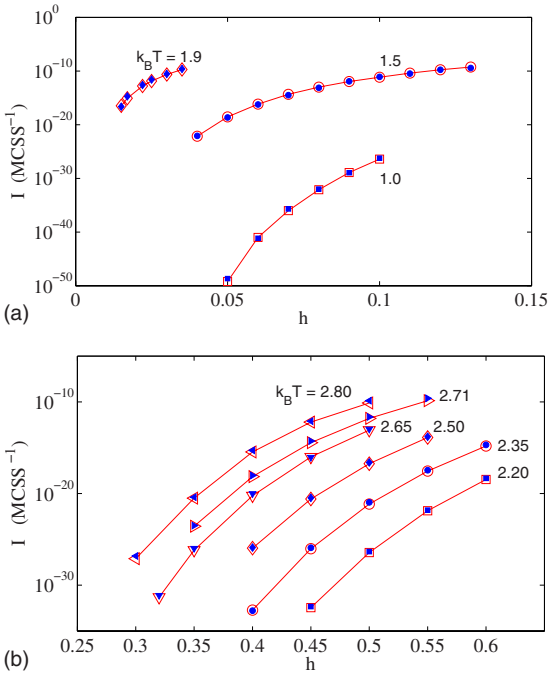

FIG. 3. (Color online) The nucleation rate I computed by FFS (open symbols) and CNT (filled symbols) using free energies obtained from umbrella sampling in the (a) 2D and (b) 3D Ising models.

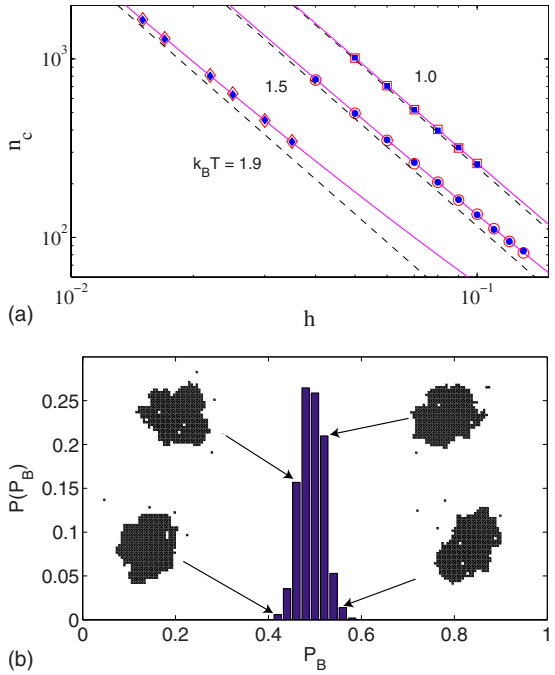

FIG. 4. (Color online) (a) The critical droplet size n_c obtained from FFS (filled symbols) and umbrella sampling (open symbols). n_c predicted by CNT, Eq. (5) (dotted line) and by Eq. (6) (solid line) are plotted for comparison. (b) Committor distribution of an ensemble of configurations all with droplet size $n=n_c=495$ at $(k_BT,h)=(1.5,0.05)$ for the 2D Ising model. Insets show typical droplet shapes at different committor probabilities. Contrary to the assumption in CNT, the droplet shape is not circular.

the largest droplet as the reaction coordinate. Detailed balance [16] between neighboring states along the Markov chain, as is assumed in the derivation of Eq. (1), is also confirmed.

Part I of CNT assumes that the size of the largest droplet is a good reaction coordinate for the nucleation process. To test the quality of this reaction coordinate, we perform the following two calculations on the committor probability, which is the probability that a spin configuration will reach state B before reaching state A. First, we compute the average committor probability $\overline{P_B}(\lambda)$ over each interface $\lambda=\lambda_i$ in our FFS simulation, and determine the critical droplet size n_c^{FFS} at which $\overline{P_B}(n_c^{\mathrm{FFS}})=0.5$. For all (T,h) conditions in this study, n_c^{FFS} matches the maximum point n_c^{US} of the free energy obtained from umbrella sampling within 2%. The data for the 2D Ising model are shown in Fig. 4(a).

Second, we perform a more stringent test of the distribution of committor probability P_B within an ensemble extracted from umbrella sampling, in which the largest droplet in all configurations has size n_c. If n were a perfect reaction coordinate, then all configurations in this ensemble should have P_B exactly equal to 0.5. Figure 4(b) shows that at $k_BT=1.5$ and $h=0.05$, P_B in this ensemble is sharply peaked at 0.5. 95% of these spin configurations have P_B values within the range of 0.45 to 0.55. This is a direct evidence that the largest droplet size is an excellent reaction coordinate for the nucleation process in the 2D Ising model. The spread of P_B in the 3D Ising model is about twice the width of the 2D Ising model, consistent with a previous report [15].

We now turn to part II of CNT, and examine the validity of the classical expression of the droplet free energy, Eq. (2). The 2D Ising model is ideal for this test because the surface free energy σ is known analytically as a function of temperature [14,24]. Following the definition of the effective surface tension in [14], Eq. (2) becomes

$$F(n) = 2\sqrt{\pi n}\sigma_{\mathrm{eff}}(T) - 2hn, \tag{5}$$

where we have used $\Delta\mu \approx 2h$ [25]. As shown in Fig. 2, significant discrepancy exists between the CNT expression of $F(n)$ and our umbrella sampling results. Furthermore, the maximum of Eq. (5) predicts that the size of the critical droplet would be $n_c=\pi\sigma_{\mathrm{eff}}^2(T)/(4h^2)$. This is significantly smaller than our numerical results, as shown in Fig. 4(a).

We find that agreement can be restored if two correction terms are added to the free-energy expression, i.e.,

$$F(n) = 2\sqrt{\pi n}\sigma_{\mathrm{eff}}(T) - 2hn + \tau k_BT \ln n + d(T). \tag{6}$$

The logarithmic correction term originates from Langer's field theory which accounts for the shape fluctuation of the critical droplet, and $\tau=\frac{5}{4}$ for the 2D Ising model [7,21,26]. The term $d(T)=8-2\sqrt{\pi}\sigma_{\mathrm{eff}}(T)$ is added so that the free energy of an isolated spin, $F(1)=8$ is correctly captured [27]. With these two correction terms, Eq. (6) agrees with our umbrella sampling data over all conditions within 1% for the 2D Ising model. This confirms that macroscopic surface tension can be used to describe the free energy of very small droplets, as long as the two correction terms are added.

Without these two correction terms, CNT would severely underestimate the free-energy barrier (see Fig. 2) and overestimate the nucleation rate by many orders of magnitude. While previous studies [6–8] have suggested that the $\tau k_B T \ln n$ correction term improves the description of the droplet free energy, this is the direct confirmation of the field-theoretic prediction [7,21,28], $\tau = \frac{5}{4}$ in two dimensions, over a wide range of (T,h) conditions. In addition, our results show the importance of correctly accounting for the temperature dependence of surface tension, σ_{eff}. The neglect of this temperature dependence has contributed to the discrepancy between CNT predictions and numerical results on the nucleation rate in both 2D and 3D Ising models [12,13,15].

In summary, we have confirmed part I of CNT in 2D and 3D Ising models, which means that it can predict the nucleation rate accurately, if the correct droplet free energy is used. On the other hand, part II of CNT concerning the droplet free energy is inaccurate. In two dimensions, the classical expression of droplet free energy can be brought to excellent agreement with numerical results, as long as two corrections terms are added. This establishes the 2D Ising model as an important reference point where existing nucleation theory can accurately predict nucleation rate without any adjustable parameters. Further investigation is needed to find out why the field-theoretic correction works so well in two dimensions, but not in three dimensions.

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