Heterogeneous and Homogeneous Nucleation Compared: Rapid Nucleation on Microscopic Impurities

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We use computer simulation to calculate the rates of both homogeneous nucleation and heterogeneous nucleation on microscopic impurities. We do so in perhaps the simplest model of fluids and magnets: the two-dimensional Ising model. We expect our results to be qualitatively applicable to many simple and complex fluids. We find that heterogeneous nucleation on an impurity that is not only microscopic but also as small as possible, that is, a single fixed spin, is more than four orders of magnitude faster than homogeneous nucleation. The rate of heterogeneous nucleation then increases by a factor of approximately five for each additional fixed spin in the impurity. These results suggest that impurities as small as single molecules can result in homogeneous nucleation being irrelevant due to heterogeneous nucleation on these microscopic impurities being much faster.

1. Introduction

In practice, first-order phase transitions, such as condensation, crystallization, and the reversal of the magnetization direction of a ferromagnet, occur via heterogeneous nucleation.1–4 The nucleus of the new phase forms in contact with an impurity, and the properties of the impurities control the rate of nucleation. Thus, the nature of the impurities present determines the extent of supercooling before nucleation occurs. The disadvantage of this is that typically virtually nothing is known about these impurities, and this makes understanding the microscopic origins of the observed behavior difficult. The advantage is that as nucleation is controlled by impurities the phase transformation can be induced by adding an impurity that is particularly effective at providing a surface for nucleation, see for example refs 5–8.

Here we address the question of how small impurities can be made while remaining active at promoting nucleation. The classical theory of nucleation as extended to heterogeneous nucleation1 predicts that an infinite planar surface, which is wet by the nucleating phase, reduces the barrier to nucleation to zero, but that small and finite surfaces are less effective at reducing the barrier.9 If the surface area of the impurity is small, then its interaction with the nucleus will also be relatively small. This is relevant to experiment as if say it is desired to study homogeneous nucleation then we would like to know how small are the impurities that need to be removed. If very small impurities only promote nucleation rather weakly, then a simple purification procedure that does not remove them will be all that is required to study homogeneous nucleation. However, if even small microscopic impurities strongly promote nucleation, then it may be impossible to purify a sample sufficiently to observe homogeneous nucleation, and we should resign ourselves to only observing phase transitions that occur via heterogeneous nucleation.

We study heterogeneous nucleation using perhaps the simplest and best-studied nontrivial model that has a first-order phase transition: the two-dimensional Ising model. We do this as we are interested in obtaining a qualitative understanding of what to expect for heterogeneous nucleation on impurities. We will study nucleation via computer simulation to obtain exact results for the rate. However, as nucleation is an activated process, it can be extremely slow. Therefore, direct simulations in which the system is simply allowed to evolve until it nucleates can take excessive amounts of time. To avoid this problem, we will use the recently developed exact simulation method of Allen et al.10,11 This provides a straightforward and accurate way of obtaining nucleation rates, even if they span several orders of magnitude. The only previous study of nucleation done using this technique is a study of the homogeneous nucleation of sodium chloride performed by Valariani et al.12

For many years, heterogeneous nucleation has been understood to be the dominant mechanism for nucleation under most circumstances. It has also been understood that the impurities need not be much larger than the nucleus. We refer to impurities comparable in size or smaller than the nucleus as microscopic impurities. In particular, in 1958, Fletcher9 extended Vollmer’s classical nucleation theory (CNT) for heterogeneous nucleation to deal with nucleation on spherical impurities of arbitrary size. More recent theoretical work has been via computer simulations.13–16

There is earlier simulation work that has considered phase transformations in the two-dimensional Ising model. This has almost all been on homogeneous nucleation and growth combined. As far as we are aware, the only one of these studies to have studied homogeneous nucleation, not nucleation and growth, is that of Brendel et al.17 For the parameter values they studied, we find that nucleation is so rapid that it is difficult to define accurate rates, and so we do not compare with their results. Studies of the complete phase transformation, of nucleation and growth, have been made by Rikvold and co-workers,18,19 and Acharyya and Stauffer.20 By contrast, for the three-dimensional Ising model, a careful study of homogeneous nucleation has been performed by Pan and Chandler.21

Heterogeneous nucleation in the low-temperature Ising model has been studied for the specific case of free-boundary conditions by Cirillo and Lebowitz.22 These boundary conditions

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mean that the system does not have an embedded impurity, as ours do, but rather nucleation is easier along the edges of the system and especially at the four corners. Also, they found that, at the low temperatures they studied, there was good agreement between the predictions of CNT and their simulation results. This finding is part of the motivation for us employing classical nucleation theory, which we do in section 3. This follows the next section, which briefly describes the model. Subsequent sections contain our results and a conclusion.

2. The Ising Model

The model we use is the two-dimensional Ising model on a square lattice with nearest-neighbor interactions. This is the model whose zero-field phase behavior Onsager was able to obtain exactly, and it can be mapped onto a simple lattice-gas model. We will simulate lattices of \( L \) by \( L \) spins with periodic boundary conditions. On each lattice site \( i \) there is a spin \( s_i \) that can take one of two values: \( s_i = \pm 1 \). The energy of a configuration of the spins is given by

\[
E = -J \sum_{i,j} s_i s_j - h \sum s_i
\]  

(1)

The first dashed sum is over all nearest-neighbor pairs of spins, and the second sum is over all spins. The \( h \) is the external field that couples to the spins, and \( J \) is the coupling constant. As the \( s_i \) are dimensionless, both \( J \) and \( h \) have dimensions of energy. Onsager was able to show that at \( h = 0 \), the two-dimensional Ising model undergoes a continuous transition from a disordered phase to one of a pair of ordered phases when \( \sinh(2J/kT) = 1 \), which is at \( JK/T = 0.44 \). The \( k \) and \( T \) are Boltzmann’s constant and the temperature, respectively. The ordered phases are the spin-up and spin-down phases, in which the spins are predominantly up spins and down spins, respectively.

We will use computer simulation to study homogeneous and heterogeneous nucleation of the spin-up phase from the spin-down phase. Thus, we start in the spin-down phase but with \( h > 0 \), and so in the region of the phase diagram where the spin-up phase is the equilibrium phase. However, \( h \) will not be so large that the spin-up phase nucleates very rapidly. Nucleation will be an activated process. These are the conditions under which the spin-down phase is said to be metastable. Heterogeneous nucleation occurs, by definition, on a surface or impurity. We will use an impurity that is a straight line of \( w \) spins fixed to have \( s_i = +1 \). See Figure 1 for a snapshot of a simulation with an impurity \( w = 4 \) spins long. We are interested in the generic features of nucleation at a phase transition, which is why we study a model as simple and well-studied as the Ising model.

3. Classical Nucleation Theory

The standard theory for homogeneous nucleation is CNT. There, the nucleation rate per lattice site is given by

\[
Rate = \nu \exp(-\Delta F^*/kT)
\]  

(2)

where \( \nu \) is an attempt frequency of the order of the spin-flip frequency and \( \Delta F^* \) is the height of the free-energy barrier that must be surmounted. The CNT considers the nucleus to be a droplet whose free energy is just the sum of a bulk term and a surface term. Thus, the free energy of a nucleus \( l \) spins across is given by

\[
\Delta F = -2ht^2 + 4\gamma l
\]  

(3)

where \( \gamma \) is the interfacial tension between the bulk spin-up and spin-down phases. In eq 3, we have assumed the droplet to be square. The droplet with the maximum free energy is found by setting the derivative of eq 3 to zero. It is \( l^* = \gamma / h \) spins across and has a free energy \( \Delta F^* = 2\gamma^2 / h \). The interfacial tension of the two-dimensional Ising model is given by the exact expression derived by Onsager: \( \gamma/kT = 2JK/T - \log[(1 + \exp(-2JK/T))/(1 - \exp(-2JK/T))] \). At \( JK/T = 0.65 \), \( \gamma/kT = 0.74 \).

4. Simulation Methodology

We simulate using the standard Metropolis Monte Carlo method for spins. Each move starts by selecting one of the free spins at random. This spin is then flipped. If this flip lowers the energy, it is always accepted, and if it increases the energy, it is accepted with a probability of \( \exp(-\Delta E/kT) \), where \( \Delta E \) is the energy change due to the spin flip. See ref 23 for an introduction to the Monte Carlo method, and see Figure 1 for a simulation snapshot.

The calculation of nucleation rates via direct means can be prohibitively slow. Here we have calculated rates down to below \( 10^{-12} \). The rates of homogeneous nucleation that we quote are per cycle and per lattice site, and the rates of heterogeneous nucleation are per cycle and per impurity. One cycle is one attempted spin flip per lattice site. The rates are defined in this way, as then if the homogeneous and heterogeneous rate are \( R_{\text{HOMO}} \) and \( R_{\text{HET}} \), respectively, and the concentration of impurities is \( c_i \), the total nucleation rate of a macroscopic system is \( R_{\text{HOMO}} + c_i R_{\text{HET}} \) per lattice site.

It is not practicable to run simulations for long enough to observe nucleation when for a lattice of around 1000 sites \( 10^{15} \) cycles are needed to observe one nucleation event. Thus, we use the recently developed algorithm of Allen et al.\textsuperscript{10,11} This provides a reasonably simple way to calculate the rate \( R_{AB} \) of a slow process, where a system starts in one phase, call it phase A, then transforms to another phase, phase B. Our phase A is a metastable spin-down phase, while our phase B is the spin-up phase. So that the rate is well-defined, we need to precisely define these two phases. The spin-down phase will have only a few up spins, the vast majority of the spins will be down spins,
while in the spin-up phase the situation is reversed. Thus, the number of up spins varies greatly between these two phases, and because it makes a good order parameter, we denote it by $\lambda$. We define the spin-down phase to consist of those states with no more than $\lambda_A$ up spins, while the spin-up phase consists of states with at least $\lambda_B \gg \lambda_A$ up spins.

Having precisely defined the two phases, the rate

$$R_{AB} = \Phi_1 \prod_{i=1}^{m} p_{i-r_i+1}$$  \hspace{1cm} (4)

where $\Phi_1$ is the flux from phase A to a state with $\lambda_A + \Delta\lambda$ up spins, and $p_{i-r_i+1}$ is the probability that a system with $\lambda_A + i\Delta\lambda$ up spins will go directly to a state with $\lambda_A + (i+1)\Delta\lambda$, without at any point having $\lambda_A$ spins, that is, without returning to phase A. The flux $\Phi_1$ is defined as being the number of times per cycle that the system leaves state A (i.e., the number of up spins increases beyond $\lambda_A$) and reaches a state with $\lambda_A + \Delta\lambda$ up spins. See refs 10 and 11 for details, but note the following: (a) only events when the system reaches a state with $\lambda_A + \Delta\lambda$ up spins for the first time after leaving the phase A are counted, and (b) if at any point the system reaches phase B, that is, the spin-up phase nucleates, then this configuration is discarded, and the system is started again from within phase A and pre-equilibrated before the calculation of $\Phi_1$ is continued. The $m$ is the nearest integer to $(\lambda_B - \lambda_A - \Delta\lambda)/\Delta\lambda$.

In practice, what is done is that the simulation is pre-equilibrated in phase A. A simulation run is then performed, keeping track of the number of times the system goes from within phase A to a state with $\lambda_A + \Delta\lambda$ up spins. Every time it does so with probability $p_n$, the configuration with $\lambda_A + \Delta\lambda$ up spins is stored. Once some large number $n_i$ configurations with this number of up spins has been obtained, the simulation is stopped and $\Phi_1$ is estimated. We typically used $p_n = 0.1$ and $n_i = 10^4$.

Then $p_{i-r_i+1}$ is calculated as follows.\textsuperscript{10,11} One of the $n_i$ stored configurations with $\lambda_A + i\Delta\lambda$ up spins is picked at random. Starting from this configuration, a simulation run is performed until the system either reaches a state with $\lambda_A + (i+1)\Delta\lambda$ up spins, or it returns to phase A. If it reaches a state with $\lambda_A + (i+1)\Delta\lambda$ up spins, this state is stored. This procedure of selecting one of the $n_i$ states at random and then running it until the number of up spins either increases to $\lambda_A + (i+1)\Delta\lambda$ or decreases to $\lambda_A$ is repeated until $n_i$ states have been stored. Then $p_{i-r_i+1}$ is approximated by the fraction of runs that ended with $\lambda_A + (i+1)\Delta\lambda$ up spins. We choose $\lambda_B$ to be sufficiently large that when we start with a configuration with a number $\lambda_A + i\Delta\lambda$ of up spins that is close to $\lambda_B$, the probability $p_{i-r_i+1}$ is very close to one. This is evidence that the boundary for phase B is taken well after the nucleus has crossed the nucleation barrier and where it will grow to form a macroscopic spin-up phase with a probability of almost one. We discuss the choice of the value of $\lambda_A$ in section 5.2, when we discuss checks on the algorithm.

5. Results

The results of calculations using the technique of Allen et al.\textsuperscript{10,11} are shown in Figure 2. Results are shown as a function of impurity length $w$, for $h/kT = 0.05$ and $J/kT = 0.65$. Unless otherwise indicated, $L = 45$. The $w = 0$ rates are for homogeneous nucleation. Clearly, even impurities of one or a few fixed spins dramatically increase the rate of nucleation. Indeed, perhaps the most striking feature of the nucleation rate data of Figure 2 is that the rate of heterogeneous nucleation for a single fixed spin, $w = 1$, is $20 000$ times higher than the rate per site of homogeneous nucleation. Even the smallest possible impurity increases the rate by more than four orders of magnitude. Larger impurities increase the rate by even larger amounts; for example, nucleation at an impurity six sites long is almost eight orders of magnitude faster than at a site in the bulk. This implies that if impurities six sites long are present homogeneous nucleation will be the dominant form of nucleation only if these impurities occur at a concentration of much less than one per 100 million sites.

Also shown in Figure 2 is a fit to the simulation data of the function $\exp(-f_0 - f_m)$, with $f_0$ and $f_1$ as the fitting parameters. This is the dashed line in Figure 2, with $f_0 = 20.28$ and $f_1 = -1.58$. The increase in rate when $w$ increases by one is equivalent to a decrease in the free-energy barrier to heterogeneous nucleation of $1.58kT$. Each site added to the impurity adds two to the length of the interface between the impurity and the surroundings. When an impurity is engulfed by a growing nucleus, this interface goes from an interface between fixed up spins and the spin-down phase to an interface between fixed up spins and the spin-up phase. We expect the interfacial free energies per unit length of these two interfaces to differ by approximately $\gamma$, and then incrementing $w$ by one increments the barrier by approximately $-2\gamma = -1.5$ at $J/kT = 0.65$. Thus, the figure of $-1.58kT$ we obtained for $f_1$ is very reasonable.

The simulation rates of Figure 2 were obtained on lattices $L = 45$ sites across, with $\lambda_B = 550$ and $\Delta\lambda = 4$. For each point, either four or six simulation runs, each of $n_i = 10^4$ configurations, were performed. We estimated the statistical errors in the rates from the standard deviation of the rates obtained in the individual runs, and in each case, the errors were no larger than the symbol size shown. $\lambda_A$, which defines the maximum number of up spins in the spin-down state from which the up-spin phase nucleates, was varied with $w$. For $w = 0$, we took $\lambda_A = 40$, while for $w = 6$, we took $\lambda_A = 100$. $\lambda_A$ was increased to take account of the fact that as $w$ increases, an increasing number of up spins are adsorbed onto the impurity in the spin-down phase. For each value of $w$, $\lambda_A$ was set at such a value that, in an unconstrained simulation, fluctuations in the number of up spins were rare, so constraining the spin-down phase to have no more than $\lambda_A$ up spins is a very weak constraint. However, $\lambda_A$ and $\Delta\lambda$ cannot be made too large, as then the flux $\Phi_1$ is very low and, therefore, time-consuming to estimate in the simulations. See section 5.2 for further details.

5.1. Comparison with CNT. Our simulations at $J/kT = 0.65$ and $h/kT = 0.05$ give a rate of homogeneous nucleation per
site and per cycle of $3.3 \times 10^{-13}$, CNT predicts a free-energy barrier of $\Delta F^* = 22kT$, and then, if we set $v = 1/\text{cycle in eq 2}$, we obtain a CNT prediction of a rate of $2.8 \times 10^{-10}$. This is three orders of magnitude too fast, but this level of agreement is not surprising given the exponentially small nature of the rates. Three orders of magnitude corresponds to an error in a free-energy barrier of around 7$kT$, so the error in the free-energy barrier is only about 30%.

The most striking feature of the nucleation rate data of Figure 2 is that the rate of heterogeneous nucleation at a single fixed spin, $w = 1$, is 20000 times higher than the rate per site of homogeneous nucleation. We can try to understand this large increase by estimating the difference in the free-energy barrier between nucleation with and without an impurity: $\Delta F_{\text{HET}}^* - \Delta F_{\text{HOMO}}^*$. Then we approximate the ratio $R_{\text{HET}}/R_{\text{HOMO}}$ of the rates of heterogeneous and homogeneous nucleation by

$$
\frac{R_{\text{HET}}}{R_{\text{HOMO}}} = (l^*)^2 \exp[-(\Delta F_{\text{HET}}^* - \Delta F_{\text{HOMO}}^*)/kT] \quad (5)
$$

The single impurity can be anywhere within the nucleus. Thus, the nucleus can form anywhere within an area of $l^*(l^* - w + 1)$ if the impurity is allowed to be at the edge of the nucleus. This introduces a factor of $l^*(l^* - w + 1)$ into the nucleation rate per impurity. But $l^*(l^* - w + 1) \approx (l^*)^2$ as $l^*$ is considerably larger than $w$, and as the theory is so crude, we use the simpler expression. We will use the CNT estimate $l^* = 15$, at $JkT = 0.65$ and $h/kT = 0.05$. Now, the energy change of adsorbing the nucleus onto a single fixed up spin will be close to $8J$, and so we approximate the free-energy change $\Delta F_{\text{HET}}^* - \Delta F_{\text{HOMO}}^* = 8J$. Then we have that, from eq 5, the ratio $R_{\text{HET}}/R_{\text{HOMO}} \approx 40000$. This overestimates the true increase by a factor of two, but this is rather good agreement given the crude nature of our approximation.

Assuming that the physics behind this approximation is reasonable, we will now briefly consider its application to the three-dimensional Ising model at low temperatures. By low temperature, we mean far below the critical temperature at $JkT = 0.22$.$^{25}$ In three dimensions, CNT gives a free energy of a cubic nucleus $l$ up spins as $-2hl^3 + 12l^2$, at low temperatures where the interfacial tension is approximately $2l$. The free-energy barrier and critical size are then $\Delta F^* = 64f l^3/h^2$ and $l^* = 4Jh/l$, respectively. At the low temperature $JkT = 0.8$ and the field $h/kT = 1$, the barrier and size are $\Delta F^* = 33kT$ and $l^* = 3.2$. At 33$kT$, the free-energy barrier to nucleation is predicted to be very high. At a single fixed up spin, the rate of nucleation is increased by a factor $R_{\text{HET}}/R_{\text{HOMO}} = (l^*)^3 \exp[(12J/kT) \approx 5 \times 10^6]$. This is larger than we found in the two-dimensional system that was nearer its critical point. Clearly, very large ratios are easily accessible.

5.2. Checks on Simulations. To check that the rates predicted by simulations using the method of Allen and co-workers$^{10,11}$ were correct, we performed a number of checks. The first type of check was a comparison of the rates calculated with this method with the rates calculated via direct simulations. The first system chosen was the system with a $w = 6$ impurity, as the rate was highest there and determining the nucleation rate via direct simulations is only feasible for relatively rapid nucleation. Determining the rate via direct simulations is straightforward. A system is equilibrated and then a simulation is run until the spin-up phase nucleates, that is, until the number of up spins reaches $\lambda = 550$. These two steps are then repeated many times, and the rate is simply one over the mean time to nucleate. For an impurity of length $w = 6$ at $JkT = 0.65$ and $h/kT = 0.05$, the rate obtained via direct simulation is $1.6 \times 10^{-5} \pm 0.1 \times 10^{-5}$. Here, the error estimate is the standard deviation of the rates measured from six different runs, in each of which the spin-up phase nucleated 250 times. Six runs, each of $n_1 = 10^4$ configurations, using the Allen et al. method yielded a rate $1.56 \times 10^{-5} \pm 0.03 \times 10^{-5}$. The rates from the different methods are the same within the statistical errors.

To check the Allen et al. method for homogeneous nucleation, simulations were performed at $JkT = 0.65$ and $h/kT = 0.1$. At this higher value of $h$, the rate of homogeneous nucleation is high enough to be measured by direct simulations. These give a rate of $1.47 \times 10^{-5} \pm 0.06 \times 10^{-5}$. The Allen et al. method gave a rate of $1.51 \times 10^{-5} \pm 0.09 \times 10^{-5}$. Again, they agree.

To check for system-size effects, rates were also calculated using the Allen et al. method for systems more than and fewer than 45 lattice sites across. Our simulations at $JkT = 0.65$ and $h/kT = 0.05$ with $L = 45$ gave a rate of homogeneous nucleation per site and per cycle of $3.3 \times 10^{-13} \pm 0.3 \times 10^{-13}$. For systems $L = 64$ spins across, 6 simulations each of $n_1 = 10^4$ configurations gave a rate of homogeneous nucleation of $3.0 \times 10^{-13} \pm 1 \times 10^{-13}$, while 6 simulations of lattices $L = 32$ spins across and each of $n_1 = 10^4$ configurations gave a rate of homogeneous nucleation of $2.9 \times 10^{-13} \pm 0.2 \times 10^{-13}$. The rates obtained for the three different sizes of lattice agree within their uncertainties. Also, simulations were performed with an impurity $w = 6$ spins long. The rates obtained with the method of Allen et al. for lattices $L = 32, 45$, and 64 spins across were $1.57 \times 10^{-5} \pm 0.03 \times 10^{-5}, 1.56 \times 10^{-5} \pm 0.03 \times 10^{-5}$, and $1.6 \times 10^{-5} \pm 0.3 \times 10^{-5}$, respectively.

Finally, the algorithm relies on defining the A and B states via $\lambda_A$ and $\lambda_B$. We set $\lambda_B$ such that the probability that a state with close to or more than $\lambda_B$ up spins is very low. Then our rate will have essentially no dependence on the value of $\lambda_B$. The choice of value for $\lambda_A$ is a more delicate problem. Too small a value will constrain the system, and so we will be studying nucleation from a system that is not representative of a freely fluctuating metastable spin-down phase. Too large a value makes the flux $\Phi$ very small, and then the efficiency gain of the technique of Allen et al. over direct simulation is reduced. We set $\lambda_A$ to values such that on average at least a few hundred or a few thousand cycles passed between successive times at which the number of up spins reaches $\lambda_A$. However, we did not make the time between these successive times much bigger than this in order that $\Phi$ could be computed rapidly. For homogeneous nucleation for $L = 45$, the simulation results of Figure 2 employed $\lambda_A = 40$ and yielded $3.3 \times 10^{-13} \pm 0.3 \times 10^{-13}$, whereas reducing $\lambda_A$ to 36 yielded a rate of $3.0 \times 10^{-13} \pm 0.1 \times 10^{-13}$. Thus, this check shows no sign that our results depend on $\lambda_A$.

6. Conclusion

We have used computer simulation to obtain essentially exact rates of homogeneous and heterogeneous nucleation in the two-dimensional Ising model. Our most striking observation was that a single fixed up spin increases the nucleation rate by a factor of 20 000. This was at $JkT = 0.65$, which corresponds to about two-thirds of the critical temperature, and at a field $h/kT = 0.05$. We then found that the simple, CNT-like approximation of eq 5 predicted this increase quite well.

This theory essentially predicts that heterogeneous nucleation at an impurity of a single molecule is faster by a factor that has two parts. The first is $\exp(2D\lambda_A/kT)$, where $D$ is the dimensionality, and $\Delta \gamma_I$ is the difference between the interfacial energy of the impurity-metastable-phase interface and the interfacial
energy of the impurity-nucleating-phase interface. The second is the size of the critical nucleus. The first factor can easily be very large: for a difference in the interfacial energies of $2kT$, it is over 100,000. Thus, nucleation at even the smallest impurities can be much faster than at a point in the bulk. The total rate of heterogeneous nucleation can, therefore, be much higher than that of homogeneous nucleation, even if there is only a low concentration of single-molecule-sized impurities present. This is consistent with the observation that nucleation is usually heterogeneous, not homogeneous,\textsuperscript{1–4} and that even intensive purification procedures fail to remove enough of the impurities to allow homogeneous nucleation to be observed. Thus, scientists studying water resorted to studying emulsions of droplets only microns across as a result of the difficulty of removing enough of the impurities from larger volumes.\textsuperscript{1,26}

We studied a simple model in two dimensions and with one type of dynamics: the system evolved via single spin flips. However, we expect our conclusions to be quite generic, that is, to apply to a wide range of systems, including systems in three dimensions and systems with particles that diffuse, not spins that flip. This expectation is based on the observation that, for activated processes such as nucleation, the variation in the rate is at least qualitatively described by CNT. This theory predicts that this variation is largely controlled by the variation in the height of the barrier. The barrier height is a quasi-thermodynamic object and so does not depend on the details of the dynamics. Also, our simple theory for this barrier height agreed reasonably well with our simulation results and predicts large impurity effects in three dimensions if the interfacial tensions are not too small.

As heterogeneous nucleation is so difficult to get rid of in favor of homogeneous nucleation, and as first-order phase transformations are so common and so important, it is surprising that so little fundamental work has been done on heterogeneous nucleation. Future work could consider not only the size of the impurity but also its shape, as well as studying more detailed and, hence, realistic models. The effects both of the size of spherical nucleants\textsuperscript{9} and of the shape\textsuperscript{27} have been considered by Fletcher within CNT. More recently, Cacciuto et al.\textsuperscript{15} studied the nucleation of hard spheres at surfaces of varying curvatures. Hard spheres are a good model of some simple colloidal systems.

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References and Notes

(1) Debenedetti, P. G. 


