

Nucleation via an unstable intermediate phase

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The pathway for crystallization from dilute vapors and solutions is often observed to take a detour via a liquid or concentrated-solution phase. For example, in moist subzero air, droplets of liquid water form, which then freeze. In this example and in many others, an intermediate phase (here liquid water) is dramatically accelerating the kinetics of a phase transition between two other phases (water vapor and ice). Here we study this phenomenon via exact computer simulations of a simple lattice model. Surprisingly, we find that the rate of nucleation of the new equilibrium phase is actually fastest when the intermediate phase is slightly unstable in the bulk, i.e., has a slightly higher free energy than the phase we start in. Nucleation occurs at a concave part of the surface and microscopic amounts of the intermediate phase can form there even before the phase is stable in the bulk. As the nucleus of the equilibrium phase is microscopic, this allows nucleation to occur effectively in the intermediate phase before it is stable in the bulk. © 2009 American Institute of Physics. [DOI: 10.1063/1.3205030]

I. INTRODUCTION

A new equilibrium phase often forms by using an intermediate phase as a “stepping stone.” This is particularly true of crystalline phases forming from dilute fluid phases. There a dense fluid phase is the intermediate between the dilute fluid phase we start with and the dense crystal phase that we end in. This phenomenon occurs in a wide range of systems including water, pharmaceuticals, and proteins. In supersaturated subzero water vapor in the Earth’s atmosphere, often, liquid water first forms and then freezes.¹ More complex molecules such as pharmaceuticals,² calcium carbonate,^{3–5} and proteins, such as lysozyme,^{6,7} can also crystallize from dilute solution via a high-concentration intermediate phase. New thermodynamic phases start with the formation of a microscopic nucleus of the new phase. When this process of nucleation is studied carefully, it is almost always found to be heterogeneous,^{1,8–10} i.e., it occurs with the nucleus of the new phase in contact with a surface. Here we will try to understand how an intermediate phase affects phase transformations by studying nucleation at a surface, in a model that has an intermediate phase that can act as a stepping stone.

We take particular inspiration from the study of Galkin and Vekilov.⁷ They studied the nucleation rate of the crystal phase of the protein lysozyme, near a metastable transition where a dilute solution of the protein coexisted with a more concentrated solution phase. Intriguingly, they observed that the nucleation went through a maximum just *before* the metastable transition was reached. Now, since the time of Ostwald, we have appreciated that an intermediate phase can promote nucleation of the most stable phase.^{11,12} Indeed, for this system, Muschol and Rosenberger⁶ and others found that once the concentrated solution appeared the crystal phase nucleates rapidly in this phase. However, Galkin and Vekilov’s observation of a metastable phase transition affecting

nucleation even before it was reached was novel.

When a fluid phase wets a wall, then substantial amounts of this fluid phase can appear at the wall, even before it is stable in the bulk.^{13,14} If the surface is concave, then capillary condensation will also result in substantial amounts of the fluid phase being present when it is slightly thermodynamically unstable in the bulk. Our idea here is that if this surface attracts the intermediate phase, then even before this intermediate phase is stable in the bulk, there will be enough of it at the surface to allow nucleation to occur at the surface in this intermediate phase. This can then explain why the rate of nucleation of the equilibrium phase increases rapidly just before the intermediate phase becomes stable in the bulk.

To explore this idea we wish to obtain reliable results for nucleation at a surface near and at equilibrium with an intermediate phase. So, we define a simple lattice model that has the required three phases. In this model we can control the stabilities of the three phases independently. It is also sufficiently simple that we can calculate nucleation rates exactly. As it is so simple, it allows us to address generic questions about nucleation via an intermediate phase, but it is not a good model for the nucleation in any specific experimental system.

To motivate our model we make some assumptions about the experimental situation we want to understand:

- (1) We assume that the interfacial tension between the nucleating phase and the intermediate phase is lower than the interfacial tension between the nucleating phase and the phase we start in.
- (2) We assume that heterogeneous nucleation will occur first at a point on the surface of an impurity where the nucleation barrier is lowest or near to being the lowest.
- (3) We assume that the surface attracts the intermediate phase sufficiently strongly that the formation of the intermediate phase is not an activated process. The only

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activated process is then the nucleation of the equilibrium phase.

The first assumption essentially defines what we mean by an intermediate phase. The phase is closer to the nucleating phase in some way, e.g., in concentration, and so the interfacial tension is lower. The nucleation barrier is very sensitive to the interfacial tension.^{9,15} The second assumption just states that many possible nucleation sites with different surface chemistries and geometries will be present on the surfaces of impurities and that nucleation will occur at the point where the barrier is lowest. See Refs. 16 and 17 for detailed discussions of this point. We make assumption three partly because we are interested in understanding systems where the intermediate phase is a fluid phase and fluid phases often nucleate easily. The work of Vekilov and co-workers^{18–20} also assumed that nucleation from the intermediate phase was the rate-limiting step. The other part of the reason is for simplicity. Modeling multistep nucleation is complex so for this study we want to only consider nucleation of the equilibrium phase that occurs in one step.

Based on these assumptions, we define a novel lattice model that has three phases and in which one is an intermediate phase in the sense defined above. We study nucleation in a wedge. Generically, nucleation in a concave geometry is expected to be faster than on a smooth plane^{9,21} and so we have chosen a simple concave geometry: the wedge. As nucleation is faster in a wedge^{9,21} than on a flat surface, nucleation in a wedge will dominate that on flat surfaces.

Below, we start by introducing the model and outlining its bulk and surface phase behaviors. We then present and discuss our results for nucleation. Our final section is a conclusion. Before we introduce the model, we should say that there is another way that an intermediate phase can influence the formation of the equilibrium phase and this is by providing a surface for nucleation of the equilibrium phase. This is different from the situation considered here as nucleation occurs on the surface of an intermediate, not within it. There are numerous examples of one crystalline form of a substance, for example, the equilibrium one, nucleating on another crystalline form of the same substance. For an experimental example of this behavior see the work of Chen *et al.*²² on a substance known as ROY. The molecule commonly known as ROY is named after its red (R), orange (O), and yellow (Y) polymorphs. For simulation studies see the work of Desgranges and Delhommelle.^{23,24}

II. MODEL

In this section we will introduce our simple two-dimensional lattice model. We could not find a model that satisfies all our requirements, so we resorted to defining a new model. The model is defined on a two-dimensional square lattice and the spin on each lattice site can take one of three values: -1 , 0 , and $+1$. We denote the spin on site i by s_i . The coupling between a site and the four nearest-neighbor sites is controlled by a parameter J and favors neighboring pairs of like spins. Thus at low temperatures there are three phases: spin down, spin zero, and spin up. In the spin-down phase the majority of the spins are -1 , while in the spin-zero

and spin-up phases, most spins are 0 or $+1$, respectively. For three spin values there are two independent fields that couple to the spins, altering the relative stabilities of the three phases. We choose fields h_0 and h_1 , which couple to the numbers of spin zeros and spin ups, respectively.

Here we are using a model magnet and magnetic language, although our interest is in crystallization. Our spin-down, spin-zero, and spin-up phases map onto the vapor (or dilute solution), liquid (or concentrated solution), and crystal phases, respectively. Our model will capture the generic mechanism by which an intermediate phase facilitates a phase transition because of the low interfacial tension between the nucleating phase and the intermediate phase. See Refs. 25 and 26 for this effect in homogeneous nucleation.

As nucleation is almost always heterogeneous, i.e., occurs at a surface, we require surfaces in our model. We define surfaces as simple edges of the model, i.e., rows of empty lattice sites, but we do include surface fields, i.e., fields that only couple to spins on lattice sites immediately neighboring the edge. The surface fields are $h_0^{(s)}$ and $h_1^{(s)}$, which couple to spin zeros and spin ones, respectively.

Thus the energy of a lattice of spins is given by

$$H = J \sum_{ij} (s_i - s_j)^2 - h_0 \sum_i \delta(s_i, 0) - h_1 \sum_i \delta(s_i, 1) - h_0^{(s)} \sum_i' \delta(s_i, 0) - h_1^{(s)} \sum_i' \delta(s_i, 1). \quad (1)$$

The sum over pairs ij is over all nearest-neighbor pairs of spins, while the undashed sums over i are over all spins. The dashed sums are over all spins in contact with a surface. With this energy function the energy cost of either an up spin next to zero spin, or a down spin next to a zero spin, is J , while the energy cost of an up spin next to a down spin is $4J$.

We simulate the model using the Metropolis Monte Carlo algorithm. All our nucleation rates are calculated with conventional Glauber Monte Carlo dynamics. For a description of these dynamics see, for example, the textbook of Chandler.²⁷ Briefly, a lattice site is selected at random, then the spin on this site is flipped with equal probability to one of the other two possible values, e.g., if it is a down spin, it is flipped with probability 0.5 to a zero spin and with probability 0.5 to an up spin. If the energy change, ΔE , due to this spin flip is negative, it is always accepted. If the energy change is positive it is accepted with probability $\exp(-\Delta E/kT)$.

These dynamics do not conserve the numbers of spins of a specific type. Our calculations to determine the triple point are done with Kawasaki-type dynamics, in which randomly selected pairs of lattice sites are selected and the spins on them swapped. These dynamics do conserve the numbers of up, zero, and down spins.

III. BULK EQUILIBRIUM BEHAVIOR

At zero temperature, the bulk equilibrium behavior is simple. There are three phases: the spin-down phase in which all spins are down spins, the spin-zero phase in which they are all zero spins, and the spin-up phase in which they are all

up spins. Which phase is stable depends on the values of the fields h_0 and h_1 . If both are negative the spin-down phase is the equilibrium phase. If at least one is positive then if $h_1 > h_0$ the spin-up phase is the equilibrium phase, while if $h_0 > h_1$ it is the spin-zero phase that is the equilibrium phase.

Here we work only at one fixed temperature: $J/kT=1.5$. This temperature is low in the sense that the phase behavior is similar to that at zero temperature. However, at nonzero temperature, the symmetry between the three bulk phases is broken by the fact that the spin-zero phase has a higher density of flipped spins, i.e., spins that are not of the majority type. The symmetry between the spin-up and spin-down phases is maintained at all temperatures.

At low temperatures most of the spins that are not of the majority species exist as single spins. If a spin is surrounded by down spins then the energy cost of flipping it from down to zero is $4J$. The energy cost of flipping it from down to up is $16J$. Thus the spin-down phase will contain a fraction of approximately $\exp(-4J/kT)$ zero spins plus a much smaller fraction of up spins. The spin-up phase will contain the same fraction of zero spins and the same low fraction of down spins as the spin-down phase has of up spins. The spin-zero phase will have concentrations of approximately $\exp(-4J/kT)$ of both down and up spins. The fact that the spin-zero phase has two species of spins at non-negligible concentrations, while the spin-down and spin-up phases have only one, slightly stabilizes the spin-zero phase with respect to the other two phases.

We quantify this stabilization by determining the triple point at the temperature $J/kT=1.5$. The triple point is where all three phases coexist. The symmetry between the spin-up and spin-down phases means that it must be at $h_1=0$, however, at nonzero temperature $h_0 \neq 0$ at the triple point. By explicitly simulating three-phase coexistence, we find that at the triple point the strength of the field that couples to the zero spins is $h_0^{(tr)}/kT = -0.0026 \pm 0.0004$. This is very small. So, below when deriving approximate expressions we will sometimes approximate it by zero. To obtain an estimated phase diagram at $J/kT=1.5$, we took the calculated triple point and then assumed that the slope of the line separating the spin-up and spin-zero phases in the h_0-h_1 plane is unity, as it is at zero temperature. The result is shown in Fig. 1.

IV. INTERFACES

At zero temperature the interface between the spin-up phase and the spin-zero phase is simple. It is just a line along which up spins and zero spins are adjacent. It therefore has an interfacial tension $\gamma_{+0}=J$. As the temperature increases we expect this interfacial tension to decrease but at the low temperature at which we work we will use this as an estimate for γ_{+0} . The interface between the spin-down and spin-zero phases is related to the interface between the spin-up and spin-zero phases by symmetry and so has the same interfacial tension, $\gamma_{-0}=\gamma_{+0}$.

The interface between the spin-up and spin-down phases is more complex. The energy cost of a line of up spins in contact with down spins is $4J$ per lattice site. However, if the interface has a single zero spin interposed between the up

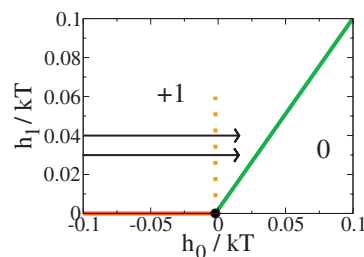


FIG. 1. The $h_1 \geq 0$ part of the phase diagram of our model. Shown are the lines of two equilibrium phase transitions: spin-down/spin-up coexistence (red) and spin-zero/spin-up coexistence (green). Coexistence between all three phases occurs at the triple point, marked by the black circle. Also shown is the metastable spin-down/spin-zero transition (orange dotted line). This transition is between two metastable phases and ends at the point where these phases become unstable with respect to nucleation of the spin-up phase. The location of this point is a little arbitrary as the nucleation rate of the spin-up phase continuously increases with increasing h_1 . Black arrows indicate the axes along which the nucleation rates shown in Fig. 5 are calculated.

and down spins, the cost is $2J-h_0$. Note that at spin-up/spin-down coexistence h_1 must be equal to zero and h_0 must be negative. For $h_0 > -2J$ this is cheaper than an interface where up and down spins are in direct contact. Thus unless h_0 is large and negative the spin-up/spin-down interface will contain a layer of zero spins. Then the interfacial tension at zero temperature is given by $\gamma_{+-}=2J-h_0$. It is a little more than twice the interfacial tension between the spin-zero and either the spin-up or spin-down phase. Above we defined an intermediate phase as one with a lower surface tension to the nucleating phase. As γ_{+0} is approximately half as big as γ_{+-} , the spin-zero phase qualifies as an intermediate phase.

Having considered the interfaces between the phases, let us consider the interface with the surface. Here we consider only surfaces with $h_0^{(s)}/kT=h_1^{(s)}/kT=1.5$. As this is large and positive, the surface strongly favors the spin-zero and spin-up phases over the spin-down. As the two surface fields are equal the surface does not favor the spin-up phase over the spin-zero phase; the contact angle the spin-up/spin-zero interface makes with the surface is close to 90° .

We will study nucleation in a wedge with a 90° internal angle, i.e., that made by the intersection of two straight-line surfaces, each at an angle of 45° to a plane. See Figs. 2(a), 3(a), and 4(a) for snapshots of 90° wedges far from spin-down/spin-zero coexistence, relatively near to coexistence, and very near coexistence, respectively. We see that as we approach the point (at $h_0 \simeq 0$) where the spin-zero phase coexists with the spin down, the wedge gradually fills with the spin-zero phase. This phenomenon is called filling.²⁸⁻³² It is the wedge analog of wetting at a flat surface.^{13,14}

The phenomenon of filling of wedges is covered in Refs. 28-32. Briefly, if fluctuations are ignored, then there are two competing terms in the free energy. Defining l as being the distance between the point of the wedge and the spin-zero/spin-down interface, one of these terms is linear and the other is quadratic in l . The first term is a surface term and so is linear in l . It is the free-energy cost of the spin-zero/spin-down interface, plus the free energy decrease due to replacing the wall/spin-down interfaces along the sides of the wedge by lower-free-energy wall/spin-zero interfaces. This

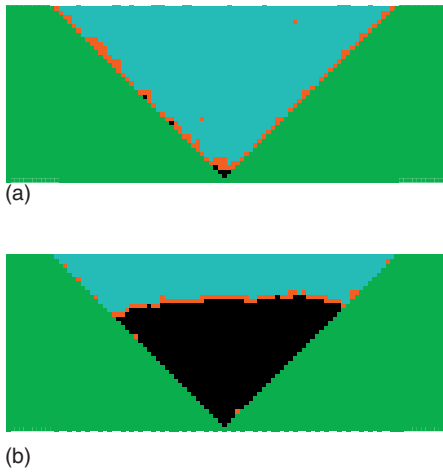


FIG. 2. Snapshots of the wedge at $h_0/kT=-1$, $h_1/kT=0.04$, and $J/kT=1.5$. (a) is the wedge at metastable equilibrium in contact with the bulk spin-down phase. (b) is a snapshot taken during the nucleation. In (b) the nucleus is near the top of the barrier, of 300 simulation runs started from this configuration, a fraction 0.49 went on to form the spin-up phase, and the remainder returned to the metastable state of (a). The configuration has 789 up spins. Shown are 100 by 40 spin parts of the simulation box, which is 150 by 100 sites. Down spins, zero spins, and up spins are cyan, red, and black, respectively. The surface is green.

surface term is negative for wedges that fill and it drives filling. It is opposed by the second term, which is positive and is the cost of filling the wedge to a height l with the spin-zero phase. This term scales as $-l^2 h_0$. Thus as h_0 approaches coexistence from below, the wedge is filled to a height $l \sim 1/(-h_0)$. This assumes that spin-down/spin-zero coexistence is at $h_0=0$. In fact it is of the order of $10^{-3}kT$ lower, see Sec. III, but we ignore this small correction here.

V. FORWARD FLUX SAMPLING

The calculation of nucleation rates via direct means can be prohibitively slow. Here we calculated rates down to be-

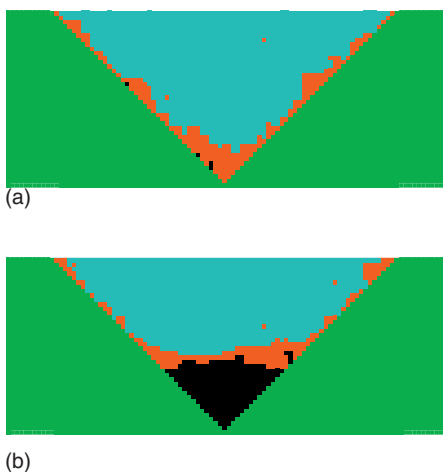


FIG. 3. Snapshots of the wedge at $h_0/kT=-0.15$, $h_1/kT=0.04$, and $J/kT=1.5$. (a) is the wedge at metastable equilibrium in contact with the bulk spin-down phase. (b) is a snapshot taken during the nucleation. In (b) the nucleus is near the top of the barrier, of 300 simulation runs started from this configuration, a fraction 0.51 went on to form the spin-up phase, and the remainder returned to the metastable state of (a). The configuration has 235 up spins. Shown are 100 by 40 spin parts of the simulation box, which is 150 by 100 sites.

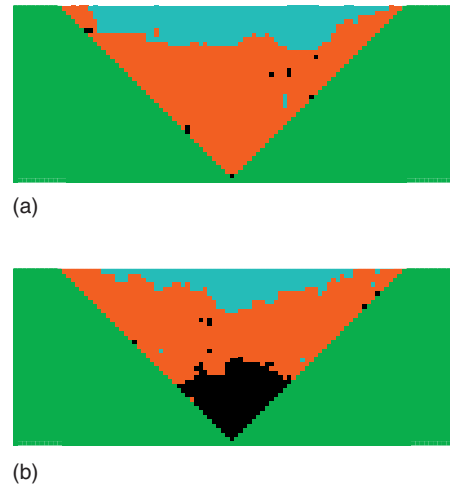


FIG. 4. Snapshots of the wedge at $h_0/kT=-0.025$, $h_1/kT=0.04$, and $J/kT=1.5$. (a) is the wedge at metastable equilibrium in contact with the bulk spin-down phase. (b) is a snapshot taken during the nucleation. Here the nucleus is near the top of the barrier, of 300 simulation runs started from this configuration, a fraction 0.55 went on to form the spin-up phase, and the remainder returned to the metastable state of (a). The snapshot configuration has 265 up spins. Shown are 100 by 40 spin parts of the simulation box, which is 150 by 100 sites.

low 10^{-27} . The rates of nucleation we quote are per cycle. One cycle is one attempted spin flip per lattice site. It is not practicable to run simulations for 10^{27} cycles. Thus we use the recently developed forward flux sampling (FFS) algorithm of Allen *et al.*^{33,34} This provides a reasonably simple way to calculate the rate r of an activated process where a system starts in one phase, call it phase A, then transforms to another phase, phase B. Our phase A is a wedge in contact with either the spin-down or the spin-zero bulk phase. Phase B is the equilibrium spin-up phase. So that the rate is well defined we need to precisely define these two phases. The spin-down and spin-zero phases will have only a few up spins, while in the spin-up phase the vast majority of the spins are up spins. Thus the total number of up spins varies greatly between these two phases and so it makes a good order parameter, we denote it by λ . We define the spin-down phase to consist of those states with no more than λ_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

$$r = \Phi_1 \prod_{i=1}^m p_{i \rightarrow i+1}, \quad (2)$$

where Φ_1 is the flux from phase A to a state with $\lambda_A + \Delta\lambda$ up spins and $p_{i \rightarrow i+1}$ is the probability that a system with $\lambda_A + i\Delta\lambda$ up spins will go directly to state with $\lambda_A + (i+1)\Delta\lambda$ up spins without at any point having $\leq \lambda_A$ spins, i.e., without returning to phase A. The flux Φ_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 λ_A) and reaches a state with $\lambda_A + \Delta\lambda$ up spins. See Refs. 33 and 34 for details but note: (a) only events when the system reaches a state with $\lambda_A + \Delta\lambda$ up spins for the *first* time after leaving phase A are counted and (b) if at any point the system reaches phase B, i.e., the spin-up phase nucleates, then this configuration is

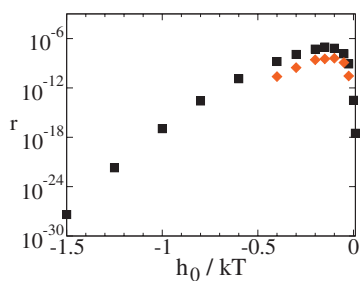


FIG. 5. The nucleation rate per cycle, r , in a wedge, as a function of h_0/kT . A cycle is one attempted spin flip per lattice site. For the black squares the driving force for nucleation is kept fixed at $h_1/kT=0.04$, while for the red diamonds $h_1/kT=0.03$. The square and diamond symbols are the mean nucleation rates from three simulation runs. The error bars, which are the standard deviation of the three runs, are smaller than the symbol size. All rates are for lattices of 150 by 100 lattice sites.

discarded and the system started again from within phase A and pre-equilibrated before the calculation of Φ_1 is continued. 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_s , the configuration with $\lambda_A + \Delta\lambda$ up spins is stored. Once some large number n_s configurations with this number of up spins has been obtained the simulation is stopped and Φ_1 is estimated. We typically used $p_s = 0.2$ and $n_s = 250$.

Then $p_{i \rightarrow i+1}$ is calculated as follows.^{33,34} One of the n_s 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. We repeat this procedure of selecting one of the n_s 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 λ_A , until n_s states have been stored. Then $p_{i \rightarrow i+1}$ is approximated by the fraction of runs that ended with $\lambda_A + (i+1)\Delta\lambda$ up spins. We choose λ_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 λ_B , the probability $p_{i \rightarrow i+1}$ 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.

VI. NUCLEATION

We calculated nucleation rates of the spin-up phase in the wedge, using FFS. The results are plotted in Fig. 5. Each rate is the average of three runs. The standard deviations of the rates are smaller than the symbol sizes. In order to see how proximity to the metastable spin-down/spin-zero bulk transition affects nucleation of the spin-up phase, we varied h_0 at fixed $h_1/kT=0.04$ and 0.03 . Thus the supersaturation of the equilibrium phase, the spin-up phase, is constant. In the phase diagram in Fig. 1 this corresponds to moving horizontally to the right. Supersaturation increases vertically in Fig.

1. At these values of h_1 , the metastable spin-down/spin-zero transition will occur very close to its value at $h_1=0$, i.e., very near $h_0^{(tr)}/kT=-0.0026$.

At $h_0/kT=-1.5$, the intermediate, spin-zero phase is far from its region of stability and we find a nucleation rate $r = 4 \times 10^{-28} \pm 2 \times 10^{-28}$. At $h_0=0$, the nucleation rate of the spin-up phase from the spin-zero phase is $r = 3 \times 10^{-14} \pm 2 \times 10^{-14}$. Thus nucleation from the spin-zero phase is 14 orders of magnitude faster. The lower interfacial tension between the nucleus and the spin-zero phase dramatically reduces the nucleation barrier and so speeds up nucleation by 14 orders of magnitude.

This nucleation rate of 4×10^{-14} applies to wedges in contact with *both* bulk phases at spin-down/spin-zero coexistence. This is because a wedge in contact with the bulk spin-down phase at coexistence with the spin-zero phase is filled with the spin-zero phase. This is the wedge analog of wetting.^{13,14}

So, nucleating from the bulk spin-zero phase dramatically increases the nucleation rate. However, increasing the stability of the spin-zero phase beyond coexistence with the spin-down phase actually decreases the nucleation rate, see Fig. 5. As the nucleation occurs in the spin-zero phase, stabilizing this phase reduces the nucleation rate. The rate will decrease rapidly until $h_0=h_1$, at which point the spin-zero phase is the equilibrium phase and nucleation of the spin-up phase will stop.

The observation that the rate of nucleation is much higher in the intermediate phase is neither new nor surprising. However, in Fig. 5, we see that the nucleation rate increases rapidly then goes through a maximum *before* the spin-zero phase becomes stable in the bulk. Clearly, to maximize its effect on the nucleation rate, we want the spin-zero phase to be almost but not quite stable in the bulk. This observation is, on first sight, quite surprising. We will now try to understand its origin.

Let us start with the system where the spin-zero phase is far from stable, $h_0/kT=-1$. Here the metastable wedge contains only a few zero spins, there is no significant filling of the wedge; see Fig. 2(a). The nucleus forms with an interface containing the expected layer of zero spins between the spin-up phase and the spin-down phase; see Fig. 2(b). Now let us look at nucleation very near to where the spin-zero phase coexists with the spin-down phase, see Fig. 4. Here if we compare the snapshots before, Fig. 4(a), and during nucleation, Fig. 4(b), we see that the nucleus is forming *in* the spin-zero phase. The wedge was filled with the spin-zero phase up to a height greater than that of the critical nucleus—the nucleus that determines the rate. Thus we see here that the intermediate phase is present in the wedge in sufficient quantities to allow nucleation to occur in it. This is before it is stable in the bulk. As the nucleation occurs at the surface, the point where the bulk phase becomes stable is not the important point. The most important is whether there is a large enough amount at the surface to allow nucleation to occur in this phase. This is the key finding of this paper.

The nucleation rate has a clear maximum near $h_0/kT=-0.15$ for $h_1/kT=0.04$ and near $h_0/kT=-0.1$ for $h_1/kT=0.03$. Our first guess at the mechanism that underlies this

maximum is that it comes from a competition of two factors. The first factor is that the nucleation rate is larger in the spin-zero phase due to γ_{+0} being much smaller than γ_{+-} . The second is that as the spin-zero phase becomes more stable, the nucleation rate decreases. If we combine these two factors then we expect the nucleation rate to be maximal when we are just near enough to $h_0=0$ to allow enough spin-zero phase to form in the wedge to accommodate the critical nucleus. Further increasing h_0 should reduce the nucleation rate.

However, if we look at the system at the maximum in the rate, Fig. 3, we see that the critical nucleus is much larger than the droplet of the spin-zero phase present in the metastable state [shown in Fig. 3(a)]. Now, we should note that the interface height is observed to fluctuate strongly in the simulations. In other snapshots at $h_0/kT=-0.15$, the droplet of the spin-zero phase is larger than in the snapshot in Fig. 3(a). For an explanation of this observation we turn to the work on fluids in wedges,^{28–32} in particular, that of Parry *et al.*^{29,31} Parry *et al.* showed that as coexistence is approached the fluctuations in the height of the interface are comparable to the height itself. These findings are supported by the computer-simulation results of Albano *et al.*³² Parry *et al.*^{29,31} showed that if fluctuations are taken into account the mean height still scales as $1/(-h_0)$, but so do the fluctuations in the height.^{29,31,32} This implies that the free energy cost of moving the interface by an amount of the order of its own height is only of the order kT . These large fluctuations may allow nucleation to occur largely within the spin-zero phase even when the mean interfacial height is less than the height of the nucleus. If so, then this will act to push the maximum in the rate farther from $h_0=0$ and so may explain why the nucleation rate reaches its maximum when the mean filling of the wedge is significantly less than the size of the critical nucleus.

Here we only considered heterogeneous nucleation. It is easy to rule out homogeneous nucleation. The classical nucleation theory prediction for the barrier to homogeneous nucleation in two dimensions is $\Delta F^*/kT = \pi\gamma_{+0}^2/h_1$. This is for nucleation in the bulk spin-zero phase when it coexists with the spin-down phase: at $h_0=0$. The barrier in the spin-down phase will be much larger and so the nucleation rate will be much slower. At $h_1/kT=0.04$ and taking $\gamma_{+0}=J$, we have a nucleation barrier of $177kT$. This is far too large to see nucleation. The nucleation barrier in wedges is lower than on flat surfaces,^{9,21} so nucleation will also be much slower on a flat surface than in our wedge.

Finally, note that the nucleation rates for $h_0 < 0$ are all for nucleation from a wedge in contact with a bulk spin-down phase while those for $h_0 > 0$ are for nucleation from a wedge in contact with a bulk spin-up phase. The nucleation rate at h_0 is, as far as we can tell, continuous: there is no jump in rate as the bulk transition is crossed. This is consistent with earlier work on flat surfaces.³⁵

A. Comparison with experiment

In our simple model we are able to vary the stability of the intermediate phase while keeping the supersaturation

constant. However, in experimental systems, for example, in the protein solutions studied by Galkin and Vekilov,⁷ this is not possible. Indeed in these experiments we expect that, as they varied the temperature, the supersaturation with respect to the equilibrium protein crystal varied more rapidly than did the stability of the intermediate concentrated-solution phase.

The argument for this starts with the Clausius–Clapeyron equations for the two phase transitions: $d \ln \Pi_{sx}/dT = \Delta h_{sx}/kT^2$ and $d \ln \Pi_{ss}/dT = \Delta h_{ss}/kT^2$. Here Π_{sx} and Π_{ss} are the osmotic pressures at solution/crystal and dilute-solution/concentrated-solution coexistence, respectively. The enthalpies of the crystal-to-solution and concentrated-solution-to-dilute-solution transitions are Δh_{sx} and Δh_{ss} , respectively. The Clausius–Clapeyron equations relate the rate of change of the pressure at coexistence to this enthalpy change of the phase transition. The enthalpy change on dissolution of a crystal will almost certainly be larger than that on dissolution of the concentrated-solution phase and so the osmotic pressure of the solution that coexists with the crystal will drop more rapidly as the temperature decreases. As the osmotic pressure of a dilute solution is related to its chemical potential by $\mu = kT \ln(\Pi/kT)$, this implies that the chemical potential of the crystal decreases faster as the temperature decreases.

The fact that in the experiments of Galkin and Vekilov⁷ the supersaturation was varying more rapidly than the stability of the intermediate phase means that we should not conclude that the maximum in the nucleation rate we find has the same origin as their maximum. If, starting at the maximum in the nucleation rate, we increase both h_0 and h_1 at the same rate, instead of increasing h_0 while keeping h_1 fixed, we find that the nucleation rate rapidly increases. There is then no maximum in the rate. However, the rapid increase in nucleation rate due to filling still occurs when h_1 increases at the same time as h_0 approaches 0.

Vekilov and co-workers developed and studied models of the effect of the fluid-fluid transition on the homogeneous nucleation of the crystalline phase of lysozyme.^{18–20} The study of Pan *et al.*¹⁹ in particular employed a two-step nucleation process to explain the maximum in the nucleation rate as a function of temperature. Within this model the decrease in nucleation rate comes not from a term in the free energy, i.e., not from the nucleation barrier, but from a slow down of the dynamics. We believe that this purely dynamic effect remains the most likely explanation for the slow down in nucleation rate after the maximum.

VII. CONCLUSION

It has been known since the 19th century that phase transformations such as crystallization can proceed via hopping from one phase to another and then on to the final equilibrium phase. Ostwald postulated that when we start in a phase that has a higher bulk free energy than more than one other phase, it is not the most stable phase that nucleates, but the one that is closest in free energy to the starting phase.^{11,12} If the equilibrium phase then nucleates from this intermedi-

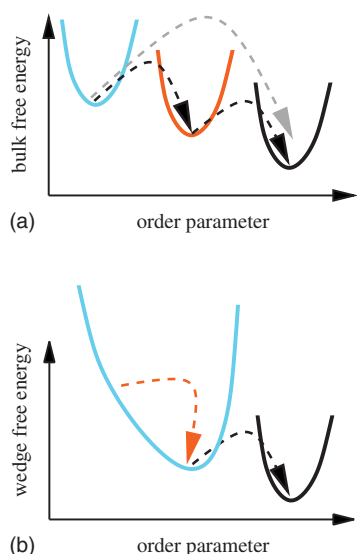


FIG. 6. (a) Schematic of the bulk free energy as a function of an order parameter. The system has three phases with successively lower free energies: the starting phase (blue), an intermediate phase (red), and the equilibrium phase (black). If we start in the highest free energy phase, blue, and we hop from bulk phase to bulk phase, we can reach the equilibrium phase in two ways. The first is directly, the curly gray arrow. The second is the one that the system will take if it follows Ostwald's rule. It is a two-step path via the intermediate bulk phase and it is shown by the curly black arrows. (b) Schematic of the free energy of a wedge as a function of an order parameter. Here nucleation proceeds via filling of the wedge with the intermediate phase, the red arrow, followed by nucleation of the equilibrium phase, the black arrow.

ate phase, then we have the path indicated by the two black curly arrows in Fig. 6(a). This idea of Ostwald's is both simple and intuitive.

However, it considers only bulk phases. The nucleus of a new phase is microscopic and so does not require an intermediate phase to be present in bulk amounts, microscopic amounts are sufficient. Also, in typical experiments, nucleation occurs at a surface. At surfaces, particularly where they are concave, microscopic amounts of a phase can form even before it is stable in the bulk. Depending on the surface geometry this is called wetting, filling, or capillary condensation.

Here we studied heterogeneous nucleation and found that even before the intermediate phase was stable in the bulk, enough formed in our wedge to speed up nucleation by many orders of magnitude. See Fig. 6(b) for a schematic of the process of nucleation in a wedge. Now, if a surface attracts a fluid phase, then concave parts of this surface will always fill with the fluid phase before it is stable in the bulk. This is a general observation and will apply to liquid water, concentrated protein solutions, etc. So, we expect that in a wide range of systems, nucleation will occur in these filled concave parts of surfaces even before the fluid phase is stable in the bulk. Careful experiments on these systems should see a rapid increase in the nucleation rate just before the intermediate phase becomes stable in the bulk. This is our key prediction. It should be borne in mind that although generically the nucleation rate should increase rapidly as the intermediate phase approaches stability, this nucleation rate may be so small that no nucleation is observed. In order to ob-

serve the predicted rapid increase in rate, the intermediate phase must be neither at supersaturations that are so low that the nucleation rate is effectively zero, nor at supersaturations that are so high that nucleation occurs before we get near it. The supersaturation at which the intermediate phase becomes stable varies widely from one system to another.

Nucleation via an intermediate phase can easily be rather complex. The formation of both the intermediate phase and the equilibrium phase could be activated processes. If this process occurs at a surface, surface phase transitions can be rate limiting,^{36,37} and if nucleation occurs in a pore, then even the nucleation of one phase can occur in two steps.³⁸ Because of this, we cannot hope to study all possible ways an intermediate phase may affect the nucleation of a new equilibrium phase. Thus we chose a simple model in which the formation of the intermediate phase is not activated. If formation of the intermediate phase is activated then the behavior may be different from the behavior we observe. Future work could study this case.

In our simple model we can vary the stability of the intermediate phase independently of the supersaturation with respect to the equilibrium phase. We exploited this to see how the rate of nucleation varied at constant supersaturation, but at varying stability of the intermediate phase. However, in experiment, when a parameter such as the temperature is varied, the stabilities of both the intermediate and the equilibrium phase are changed. For example, in the work of Galkin and Vekilov,⁷ the supersaturation is increasing rapidly as the system is cooled to the point at which the intermediate phase is stable in the bulk. This increase in supersaturation will tend to superimpose a rapid increase in the rate on the behavior seen in Fig. 5. We assume the typical result will be a very rapidly increasing nucleation rate with no maximum.

In lysozyme solutions it is well known that nucleation becomes rapid when the intermediate concentrated-solution phase appears.⁶ This association is also seen in other systems.^{2,39,40} However, other than in the work of Vekilov and co-workers^{7,18-20} there is less appreciation of the fact that the nucleation can dramatically increase before the intermediate phase is stable in the bulk. However, this is what we found in our essentially exact simulations and it should be quite generic. The challenge in experiment may be to observe this intermediate phase as it is only required in microscopic amounts at a surface and may exist for a short time if the growth rate of the equilibrium phase is fast. Lysozyme crystals grow slowly,⁴¹ which facilitates seeing the metastable concentrated-solution phase in this system.

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