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Formation of a metastable phase due to the presence of impurities

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Abstract

Phase transitions into a new phase that is itself metastable are common; instead of the equilibrium phase nucleating, a metastable phase does so. When this occurs the system is sometimes said to be obeying Ostwald's rule. We show how this can happen when there are impurities present that reduce the barrier to heterogeneous nucleation of the metastable phase. We do so by studying a Potts lattice model using Monte Carlo simulation. Thus, which phase forms depends not only on the properties of the different phases but also on the impurities present. Understanding why systems obey Ostwald's rule may therefore require a study of the impurities present.

1. Introduction

On heating glassy silica it crystallizes into a crystalline form called cristobalite, but the equilibrium crystalline form is tridymite [1]. The silica has two crystalline forms and it transforms into the metastable form, not the equilibrium form. Phase transformations into metastable phases are quite common, and systems that do this are sometimes said to obey the Ostwald or Ostwald step rule [2]. Typically the appearance of the less stable phase is ascribed to it being in some way more similar to the original phase it nucleated in than is the equilibrium phase and so having a lower interfacial tension with the original phase. Within classical nucleation theory the nucleation rate is proportional to $\exp(-\gamma^3/h^2)$, where γ is the interfacial tension between the nucleating phase and the phase it is nucleating in and h is proportional to the difference in chemical potential between the nucleating phase and the phase it is nucleating in [1, 3]. Thus, although h will be larger for the nucleation of the equilibrium phase, if the interfacial tension γ for this phase is also larger its rate of nucleation may be slower than that of a metastable phase.

This argument is based on the nucleation of the new phases being homogeneous, i.e., occurring in the bulk. However, the nucleation of most new phases is not homogeneous

but heterogeneous; it takes place in contact with impurities, or with the surface of the container [1, 4–6]. This implies that which phase nucleates first may be influenced by differences in the interactions of the nuclei of the different phases with the impurities present. Here, we use computer simulation and theory to demonstrate that impurities can indeed determine which phase appears. We find that if we start with a system in which the equilibrium phase nucleates, we can change only the nature of the impurity and obtain a system in which the metastable phase nucleates.

We study nucleation in the Potts lattice model [7, 8], via Monte Carlo computer simulation. This model is one of the simplest models that has the three phases we require. Thus we will try to obtain an understanding of the generic features of nucleation under conditions when there is more than one phase that is more stable than the existing phase and when there are impurities present. We hope our conclusions will apply widely to systems where there are competing phases that the system can transform into. The nucleus of a new phase is typically only a few molecules (in the case of the Potts model: spins) across and so even impurities only a few molecules or spins across are large enough to greatly reduce the free-energy barrier to nucleation; see for example [9]. Here we will study impurities only a few spins across, although we could have studied much larger impurities. We defer a systematic study of the effect of varying the impurity size to later work. See, e.g., [10] and references therein for recent simulation work on heterogeneous nucleation.

In the next section we define a simple model that has the required three phases. The third section contains the results of Monte Carlo simulations. These simulations are exact and demonstrate that the nature of the impurity can indeed determine which phase nucleates. Having established this, we do not go on and systematically vary parameters such as the size and shape of the nucleus. Instead, in the fourth section we write down a simple phenomenological theory for the competitive nucleation of two phases, one of which is assisted by an impurity, i.e., the nucleation is heterogeneous, and the other of which is not and so nucleates via homogeneous nucleation. This allows us to calculate how much an impurity needs to reduce the barrier to nucleation in order to determine which phase nucleates, as a function of the density of impurities, the interfacial tensions between the phases etc. The final section is a conclusion, where we discuss the relevance to experiment.

2. Potts model

Consider the three-state Potts model [7] on a simple cubic lattice in three dimensions. On each lattice site i there is a spin s_i that can take one of three values: 1, 2 or 3, and that interacts with its six nearest neighbours. The interaction energy of a pair of neighbouring spins i and j is $-J\delta_{s_i,s_j}$, i.e., the only interaction is between spins that have the same spin value. J is positive, so on cooling the model undergoes a symmetry-breaking transition from a state in which a third of the spins have each spin value to one of three ordered phases, in each of which one of the spin values predominates [7]. These are the spin-one, spin-two and spin-three phases. In the absence of any external fields all three phases have the same free energy. The transition occurs at $J/kT = 0.55$ [8]. k and T are Boltzmann's constant and the temperature, respectively. Here we work solely at the low temperature $J/kT = 0.8$.

We will consider not the disorder–order transition but transitions between the three ordered phases. To do so we need to consider external fields that break the symmetry between these phases. The three external fields h_k , $k = 1, 2, 3$, couple to the spins via terms $-h_k\delta_{s_i,k}$, i.e., a positive h_k favours the phase with spins predominantly taking the value k . If, for example, the h_k have values $h_3 > h_2 > h_1$, then the spin-three phase is the equilibrium phase and the spin-two phase is more stable than the spin-one phase. We will always start in the spin-one

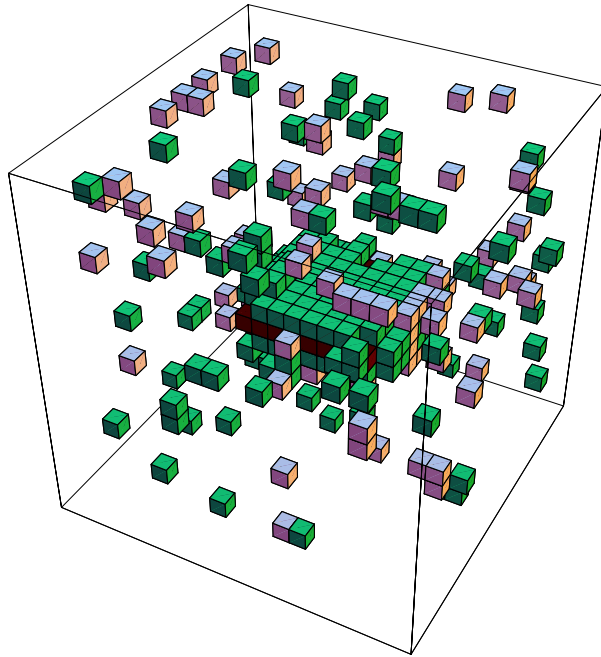


Figure 1. Computer simulation snapshot of a small simulation box 20 spins across. The system is in the spin-one phase at coexistence, $h_1 = h_2 = h_3 = 0$, at a temperature $J/kT = 0.8$. Sites with spins taking the values two and three are filled with green and very pale cubes, respectively. The fixed spins that form the impurity are dark red. The impurity favours the spin-two phase, it is a $p = 2$ impurity, and it is a square monolayer with sides eight spins long. Sites with free spins taking the value one are left empty.

(This figure is in colour only in the electronic version)

phase and always set $h_1 = 0$. Then by increasing h_2 and h_3 from zero we will make both the spin-two and spin-three phases more stable than the spin-one phase.

We also require an impurity that favours either the spin-two or the spin-three phase. We use an impurity that is a square monolayer of 8-by-8 spins that are fixed and that interact with adjacent spins with an energy $-2J\delta_{s_i p}$, where when $p = 2$ ($p = 3$) we have an impurity with a strong affinity for the spin-two (spin-three) phase. See figure 1 for a snapshot showing the impurity. We refer to the spins that can flip between the three values as free spins to distinguish them from the fixed spins that form the impurity. At the temperature we work at the interaction between the fixed spins of the impurity and the free spins is strong enough that if the impurity is expanded into an infinite plane, wetting occurs. See for example [11, 12] for an introduction to wetting. For example, if $p = 2$, at equilibrium at coexistence, $h_1 = h_2 = h_3 = 0$, impurities in either spin-one or spin-three phases are wetted by the spin-two phase. In between the, infinite, impurity and the bulk phase there will be a macroscopic layer of the spin-two phase and then an interface between the spin-two phase and either the spin-one or spin-three phase. We verified this via computer simulation.

Putting all the interactions together, the energy of a configuration of the spins is

$$H = -J \sum_{i,j}' \delta_{s_i s_j} - \sum_k h_k \sum_i \delta_{s_i k} - 2J \sum_i'' \delta_{s_i p}. \quad (1)$$

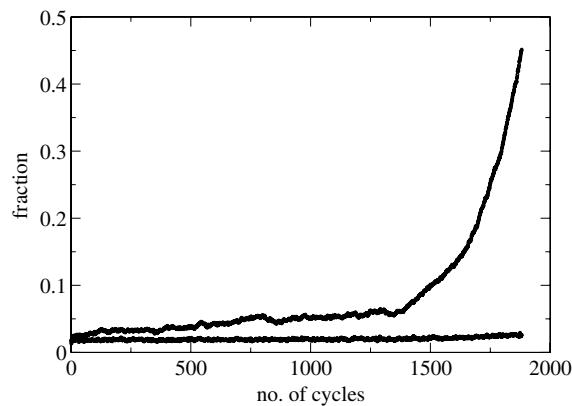


Figure 2. Plot of the fractions of spins taking the values two (top set of points) and three (bottom set). A point is plotted every cycle, i.e., one attempted flip per spin. The simulation is stopped after 1881 cycles as then the spin-two phase has nucleated and grown so that 45% of the spins have the value two. The number of spin-threes fluctuates: on average a little less than 2% of the spins are spin-threes, this corresponds to around 500 spin-threes. This relatively small number fluctuates. The number of spin-twos fluctuates much more.

The first, dashed, sum is over all nearest-neighbour pairs of free spins. The two sums in the middle terms are over the three applied fields and over all spins. The double-dashed sum in the last term is over all free spins adjacent to the impurity.

3. Simulation results

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 to either of the two other spin states with equal probability. If this flip lowers the energy it is always accepted; if it increases the energy it is accepted with a probability that is the exponential of minus the negative of the energy change over kT . See [13] for an introduction to the Monte Carlo method. Our simulations were done on a lattice of 30 by 30 by 30 spins with periodic boundary conditions. This is a somewhat larger lattice than shown in the snapshot of figure 1. The appearance of a new phase was determined by monitoring the fraction of spin-twos and spin-threes. Once the fraction of spin-twos exceeded 45% the simulation was stopped and the spin-two phase was taken to have nucleated. Similarly, if the fraction of spin-threes exceeded 45% the spin-three phase was taken to have nucleated. See figure 2 for a plot of the fractions of spins that were spin-twos and spin-threes as a function of simulation time, for one simulation run. The fraction 45% is arbitrary, varying it even by large amounts does not change the result in almost all cases. Note that then there are over ten thousand spins in the new phase so the nucleus is clearly post-critical, it is extremely unlikely that its growth will stop. In most cases we repeated the simulation five times with the same values of h_2 and h_3 , but near the borderlines between different nucleation behaviours we performed ten simulation runs. If neither the spin-two nor the spin-three phase nucleated within 100 000 cycles, the simulation was abandoned. There the nucleation rate is too low to be measured via direct simulation.

We start all our simulations by setting $h_1 = h_2 = h_3 = 0$ and then equilibrating the system in the spin-one phase. For our first simulations we then instantaneously increased both h_2 and h_3 to 0.2. The spin-two and spin-three phases are then equally stable, and more stable than the spin-one phase. We found that if the simulation box contains a $p = 2$ impurity, which

Table 1. Results of computer simulations of a system of 30^3 Potts spins at $J/kT = 0.8$ with a $p = 2$ square impurity 8 spins along each side. Starting with a system equilibrated in the spin-one phase at $h_1 = h_2 = h_3 = 0$ the system has h_2 and h_3 instantaneously increased to the values shown. Formation of the spin-two phase is indicated by a '2' and formation of the spin-three phase by a '3'. A '0' indicates that neither phase nucleated within 100 000 cycles. The '2/3' indicates that of 10 simulation runs 3 resulted in the spin-two phase and 7 in the spin-three phase. Here the barriers to formation of these two phases are comparable. Finally, 3* indicates that both the spin-three and the spin-two phase nucleated but that it was the fraction of spin-threes that grew to exceed 45%.

$h_2 =$	0.1	0.2	0.3	0.4
$h_3 =$				
0.2	0	2	2	2
0.3	0	2	2	2
0.4	3	2/3	2	2
0.5	3	3	3*	2

has an affinity for the spin-two phase, then the spin-two phase nucleates, whereas if the box contains a $p = 3$ impurity, then the spin-three phase appears¹. If h_3 is increased to 0.3, keeping $h_2 = 0.2$, then with a $p = 2$ impurity the spin-two phase still appears not the spin-three phase, even though the spin-three phase is now more stable. As we expect if at $h_2 = 0.2$, $h_3 = 0.3$, the $p = 2$ impurity is replaced by a $p = 3$ impurity it is the spin-three phase that appears. So, it is the impurity that is controlling which phase appears. This is the key result of this work. In table 1 along the diagonal, i.e., $h_2 = h_3$, and also even for $h_2 = h_3 - 0.1$, it is always the spin-two phase that appears. However, returning to a system with a $p = 2$ impurity, if while h_2 is kept at 0.2, h_3 is further increased to 0.5, it is the spin-three phase that nucleates. As the stability of the equilibrium phase with respect to that of the metastable phase is increased, by increasing $h_3 - h_2$, beyond a certain limit our impurity no longer controls the phase that forms. For $h_2 = 0.2$ and $h_3 = 0.5$, $p = 2$ and $p = 3$ impurities both result in the spin-three phase forming. Results for a number of different values of h_2 and h_3 , are given in table 1. These results are for a $p = 2$ impurity. Of course, due to the symmetry of the model, results for a $p = 3$ impurity can be obtained by simply swapping the labels 2 and 3 in table 1.

Stranski and Totomanow [14] argued that when a system is in a phase which has a higher free energy than more than one other phase the phase that nucleates is the one with the lowest nucleation barrier. We agree, but as nucleation is typically heterogeneous, which phase has the lowest barrier will depend on what impurities are present, as well as on properties of the phase itself. As an example, consider increasing the size of the impurity. If the impurity is expanded into an infinite plane, then it will be wetted by the spin-two phase. Thus, if the impurity is large enough then the spin-two phase will nucleate effectively at $h_2 = 0$ as already at this value of h_2 a macroscopic wetting layer of the spin-two phase will be present on the surface of a macroscopic impurity. Thus, if such a large impurity is present the spin-three phase will only get a chance to nucleate in the spin-one phase if the spin-two phase is actually higher in free energy than the spin-one phase, $h_2 < 0$. Note that if h_3 is sufficiently large the spin-three phase may of course nucleate from the spin-two phase.

¹ When one solid nucleates on a defect in another solid phase, the free energy of the nucleus, and hence of course the nucleation barrier, will depend on the orientation of the lattice planes in the crystalline nucleus with respect both to the phase it is nucleating in and the orientation of the defect. Our simple Potts model with $h_2 = h_3$ is a simple model of a solid that can nucleate in only two discrete orientations with respect to the parent phase. Then a $p = 2$ impurity is a simple model of a defect that favours the spin-two 'orientation'. Defect controlled orientation of the nucleating phase has been observed in experiment, see for example the work of Furuhashi and Maki [18] who find that the orientation of the defects controls the orientation of the face-centred cubic phase that nucleates in a body-centred cubic phase of a titanium alloy.

4. Phenomenological theory for the competitive nucleation of two phases

A sufficiently large impurity with a surface wetted by a new phase can reduce the nucleation barrier to zero, even at coexistence, where the barrier to homogeneous nucleation is divergent [3]. Alternatively, if a dilute impurity does not prefer the nucleating phase it will not participate in nucleation. Denoting the barriers to homogeneous and heterogeneous nucleation by ΔF_{HOMO}^* and ΔF_{HET}^* , respectively, the magnitude of the difference δ is then defined by $\Delta F_{\text{HET}}^* = \Delta F_{\text{HOMO}}^* - \delta$; it is the free energy difference between the critical nuclei. For a sufficiently large impurity with a surface that is wetted when the surface is infinite, δ can be made arbitrarily large. It can also be effectively zero. Note that δ will in general be a complex function of h_2 and h_3 because impurities will change the shape and size of the critical nucleus.

We would like to explore the nucleation behaviour for the parameter space composed of the driving forces for nucleation of the spin-two and spin-three phases, h_2 and h_3 , and the effect of the impurity, δ . For simplicity, we will only consider $p = 2$ impurities that favour the spin-two phase, and we will neglect homogeneous nucleation of the spin-two phase. Thus we will consider only the competition between homogeneous nucleation of the spin-three phase and heterogeneous nucleation of the spin-two phase. It is easy to relax this constraint but it introduces additional variables without changing the qualitative nature of the behaviour. Exploring the parameter space via computer simulation would be very laborious but fortunately classical nucleation theory [3] should be accurate enough for this purpose. Classical nucleation theory has been shown to be very reasonable for homogeneous nucleation in the Ising model well below this model's critical temperature, where the transition is strongly first order as it is here; see for example [15] and references therein.

We will start with the classical nucleation theory [3] for homogeneous nucleation of the spin-three phase in the spin-one phase. Although this is a little inaccurate we consider nuclei to be always perfectly cubic, i.e., to consist of λ by λ by λ spins. The free energy change on forming a nucleus is just the sum of a bulk term from creating a volume λ^3 of the spin-three phase and a surface term from creating $6\lambda^2$ of spin-three–spin-one interface. Then the free energy of a nucleus of the spin-three phase is [3]

$$\Delta F_3 = -\lambda^3 h_3 + 6\lambda^2 J, \quad (2)$$

where we used the low temperature approximation for the interfacial tension between the spin-one and spin-three phases $\gamma \simeq J$. The rate is determined by the free energy of the nucleus, equation (2), at the top of the barrier, which is $\Delta F_3^* = 32J^3/h_3^2$. The rate of homogeneous nucleation of the spin-three phase, per lattice site, r_3 , is then [3]

$$r_3 = \nu \exp[-32J^3/(h_3^2 kT)], \quad (3)$$

where ν is an attempt frequency; it is of the same order as the frequency of spin flips at a site. The rate of homogeneous nucleation of the spin-two phase is just that given by equation (3) with the field h_2 replacing h_3 . The interfacial tension between the spin-one and spin-two phases will be very similar to that between the spin-one and the spin-three phases at these low temperatures. Then, according to the definition of δ the barrier to heterogeneous nucleation of the spin-two phase is $\Delta F_2^* = 32J^3/h_2^2 - \delta$. The rate of heterogeneous nucleation of the spin-two phase, per lattice site, r_2 , is therefore

$$r_2 = \nu \rho_i \exp[-32J^3/(h_2^2 kT) + \delta/kT], \quad (4)$$

where ρ_i is the number of impurities divided by the number of sites. We expect the density of impurities to be very low so we fix $\rho_i = 10^{-6}$. Also, for an impurity of specific material, size etc, δ will be a function of h_2 and h_3 . We ignore this dependence here and treat δ as simply

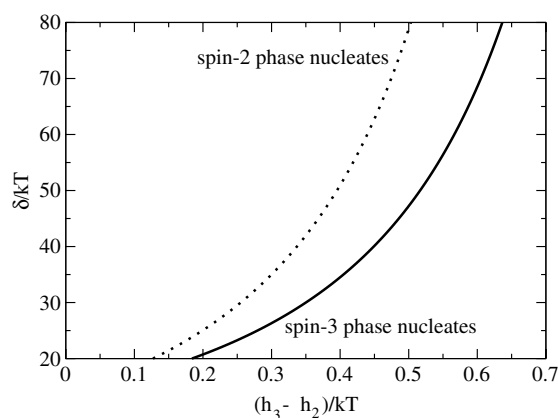


Figure 3. Plot showing the conditions where the spin-two phase nucleates first, above the curve, and, where the spin-three phase nucleates first, below the curve. Each of the two curves gives the value of δ at which the nucleation rates of the two phases are the same, as a function of $h_3 - h_2$. In the case of the solid curve the two rates equal $10^{-6}\nu$ whereas for the dotted curve the rate equals $10^{-8}\nu$. The impurity concentration $\rho = 10^{-6}$.

a shift in the nucleation barrier. Having determined how large a shift is needed we can then work back to estimate the properties the impurity must have in order to generate it.

Let us consider systems where the difference $h_3 - h_2$ is fixed, so the spin-three phase is a fixed amount more stable. Then $h_3 - h_2$ is one parameter, δ is the other. Having fixed both these parameters we can start with $h_2 = h_3 = 0$ and then increase h_2 and h_3 in parallel until the nucleation rate of either the spin-two, equation (4), or the spin-three, equation (3), phase becomes appreciable. The phase whose nucleation rate is the first to become appreciable will then be the one that appears. It is a little arbitrary what nucleation rate we consider to be appreciable, we select values of 10^{-6} and $10^{-8}\nu$ per site as trial values. We can then divide the parameter space of systems in the $(h_3 - h_2)$ - δ plane into a region where on increasing h_3 and h_2 at fixed $h_3 - h_2$ the rate of nucleation of the spin-two phase equals 10^{-6} or $10^{-8}\nu$ first or a region where that of the spin-three phase is the first to hit one of these values. We have done so and plotted the results in figure 3; the solid and dashed curves separate the two regions for the different nucleation rates. We see that as δ increases the spin-two phase appears first even for larger and larger values of $h_3 - h_2$, i.e., even when the spin-three phase is more and more stable relative to the spin-two phase. Impurities that strongly favour the metastable spin-two phase, i.e., ones with large values of δ , result in the spin-two phase pre-empting the spin-three phase even when the spin-three phase is significantly more stable. This is true even for very low impurity densities ρ . They cause this less stable phase to appear. Note that in figure 3, $\delta \geq 20$, so our neglect of homogeneous nucleation is always reasonable as the rate of homogeneous nucleation is at least a factor $10^6 \exp(-20) \ll 1$ smaller than the rate of heterogeneous nucleation. Also, the trend seen in figure 3 from nucleation of the spin-two phase to nucleation of the spin-three phase as $h_3 - h_2$ is increased is just the same as that in the results of table 1. A given impurity only controls nucleation, in the sense of causing the metastable phase to appear, if the difference in stability between the metastable phase and the equilibrium phase is not too great.

Note that for the Potts model, formation of the spin-two phase slows down formation of the spin-three phase. This is because the interfacial tension between the spin-two and the spin-three phases will be very similar to that between the spin-two and spin-three phases; both will be $\simeq J$ at the low temperatures we are working at, but the driving force for nucleation from the spin-two phase is only $h_3 - h_2$ not h_3 . In other systems, for example alkanes [16], formation

of a metastable phase may accelerate the formation of the equilibrium phase. See [17] for a theoretical description of that effect.

5. Conclusion

It has been known since Ostwald's time in the nineteenth century that when a phase has a higher free energy than two or more other phases it is often not the equilibrium one of these other phases that appears but a metastable one [1]. This was based on experimental observations. Here we have used computer simulation and a simple theory, and seen that which phase appears can be controlled by the impurities that are present. It may be that a system contains impurities that strongly favour a metastable phase. If so, then the metastable phase may nucleate on these impurities under conditions where the equilibrium phase does not nucleate, because the barrier to nucleation of the equilibrium phase is too high. Thus, if we are to understand why a system obeys Ostwald's rule, we may need to consider the effect of the impurities present. It should be noted that the usual explanation for Ostwald's rule, that the interfacial tension for the metastable phase is lower than for the equilibrium phase, is not applicable here: these two interfacial tensions will be very similar for the low temperature Potts model.

Here, we used Monte Carlo simulation to study heterogeneous nucleation. Currently, experimental data are interpreted using the classical nucleation theory of heterogeneous nucleation [1, 4], but this is often unsatisfactory; see for example [5]. Some of the assumptions that underlie the classical nucleation theory of heterogeneous nucleation are known to be poor, particularly when the impurity strongly attracts the new phase [5]. Thus computer simulation, which does not make these assumptions, is useful. Experimental systems can be mapped onto the current simple model or generalizations of it if the supersaturations and interfacial tensions are known. Even if the impurities in the experimental system are uncharacterized, then simulations can be performed with a range of impurities in order to make plausible estimates of how strongly the impurities in the experimental system are interacting with the nuclei.

Acknowledgments

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