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Nucleation at contact lines where fluid–fluid interfaces meet solid surfaces

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Abstract

Water droplets that only contact solid particles freeze at higher temperatures than those in which the particle is completely immersed. The difference between the two situations is that only when the particle contacts the droplet is there a contact line where the air–water interface meets the surface of the particle. If the particle is immersed in the droplet the contact line disappears. To try to better understand this we study nucleation in a simple model: the three-state Potts model. This model has the three phases that are required to study nucleation at a contact line. Using computer simulation we calculate exactly the nucleation rates at the contact line, and at interfaces and in the bulk. We find that the nucleation rate at the contact line is orders of magnitude higher than it is anywhere else. Classical nucleation theory calculations suggest that this finding should be generic and so may also be true for much more complex systems, such as ice nucleating in a water droplet. Thus we may have found the nucleation mechanism that underlies the experimental observations.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

In clouds at sub-zero temperatures, the water droplets freeze via heterogeneous nucleation on small solid particles (unless the temperature is very low, below around -30°C) [1]. Remarkably, these particles induce nucleation at higher temperatures (lower supersaturations) when they just contact a water droplet than when they are completely immersed in the droplet [1–4]. The difference between a particle contacting a droplet (figure 1(b)) and being immersed (figure 1(a)), is that when a particle is completely immersed there is no contact line where the air/water interface meets the surface of the solid particle. Thus, the experimental data suggests that removing the contact line dramatically reduces the nucleation rate. Inspired by this, we calculate nucleation rates in simple models that have 2 coexisting phases (models of the air and water phases in the atmosphere) and a model of an inert solid surface of a particle.

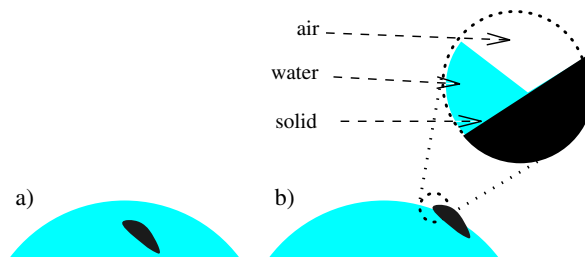


Figure 1. Two schematic cross-sections through a water droplet (cyan) with an impurity particle (black), surrounded by air (white). In (a) the particle is completely immersed in the droplet while in (b) it is at the interface between the droplet and the surrounding air. In (b) an expanded view is shown of the region around the contact line. The contact line is perpendicular to the page and intersects it at the point where the air, water and solid all meet. It therefore runs along the line where three interfaces meet: the air–water, air–solid and water–solid interfaces.

These are the minimal requirements for a contact line. We find that indeed the nucleation rate is much higher along the contact line than it is anywhere else. This finding appears to be rather generic. Therefore nucleation along contact lines may occur not only in clouds but also in other systems with two or more coexisting phases. A possible example of this has been observed in protein solutions [5]. Finally, if we are right in predicting that nucleation occurs along contact lines, then the ice should be observed to grow from where the particle meets the droplet surface.

First-order phase transitions such as freezing start off with nucleation. For example, nucleation of ice is where a microscopic crystalline cluster of water molecules forms and overcomes a free-energy barrier [6, 7]. Nucleation can be either homogeneous or heterogeneous. Homogeneous nucleation is where the nucleus forms in the bulk away from any interfaces, and heterogeneous nucleation occurs when the nucleus forms at an interface (or three interfaces in the case of nucleation at a contact line). Heterogeneous nucleation is expected to have a lower barrier than that for homogeneous nucleation [7].

For a water droplet in the atmosphere and in contact with a solid particle, there are four different environments in which an ice crystal can nucleate, and so four different nucleation barriers. These environments are: (a) in the bulk of the liquid water, (b) at the interface between the water and the surrounding air but away from the particle’s surface, (c) at the particle’s surface inside the bulk of the droplet, and (d) at the contact line where the water–air interface meets the surface of the particle. Here we simulate a simple lattice model, not a model of water, however this model has analogues of all four environments, and nuclei in all four are shown in figure 2. The last of these environments is missing if the particle is completely immersed. The first of these environments corresponds to homogeneous nucleation while nucleation at the others is heterogeneous.

In the remainder of this paper we first introduce the simple model we will be using to study nucleation at contact lines. This is the Potts model in two dimensions. We do this in section 2. This model is not of course a faithful model of water, which is the experimental system of interest. However, we are interested in the generic differences between nucleation at a contact line (or contact point in two dimensions), and nucleation either at a single interface or in the bulk. These generic differences are those that directly follow from the fact that a contact line is where three interfaces meet. As we will see when we apply classical nucleation theory to the problem, the presence of these three interfaces dramatically effects nucleation. Having introduced the model we will briefly consider, in section 3, the algorithm used in our computer simulations. This is the, now widely used, forward flux sampling (FFS) algorithm of Allen and

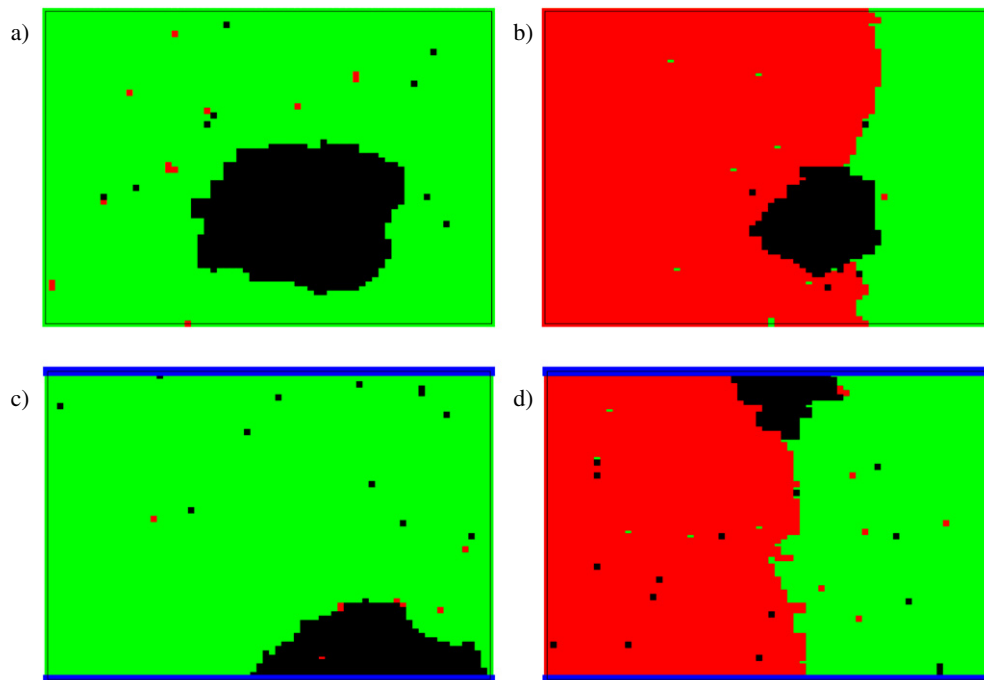


Figure 2. Simulation snapshots of Potts-model systems 70 by 70 lattice sites in size at $J/kT = 1.65$, $h_3/kT = 0.08$. The four snapshots are of nuclei of phase-3 in the four different environments. The nuclei are those for: (a) homogeneous nucleation in phase-1, (b) heterogeneous nucleation at the phase-1/phase-2 interface, (c) heterogeneous nucleation in phase-1 at the surface, and (d) heterogeneous nucleation at the contact point where the phase-1/phase-2 interface meets the surface. Phases 1, 2 and 3 are light green (grey), dark red (grey) and black, respectively. In (c) and (d) (only) there are surfaces composed of fixed spins along the top and bottom of the simulation box; these are shown in dark blue (black lines).

co-workers [10–12]. Then we will present the results of simulation, in section 4, and compare them with the predictions of classical nucleation theory, in section 5. Our final section is a conclusion.

2. A simple model: the Potts model

As modelling water is difficult, and as we want to understand generic features of nucleation from systems of two coexisting phases, we will study a very simple model. It is the two-dimensional three-state Potts model on a square lattice, with nearest-neighbour interactions [8]. This is perhaps the simplest possible model with the required three thermodynamic phases. Our systems will start with two coexisting phases, phases 1 and 2. These phases are the analogues of water and air. Then we will simulate the nucleation of another phase, phase-3, the analogue of ice. Earlier work has already studied homogeneous nucleation in this model [9]. Although the experimental work that inspired our calculations is all on fluids [2, 3, 5], we simulate a simple model magnet. We do so because nucleation is expected to depend only weakly on whether the dynamics are spin flips or particle diffusion.

In the three-state Potts model, each lattice site i has a spin $s_i = 1, 2$ or 3 associated with it. Below a temperature $kT/J = 1.005$ [8] there is coexistence between three phases. Phase-1

is one in which the spins on most lattice sites are spin-ones. Phase-2 is one in which most spins are spin-twos, and so on. J is the coupling between neighbouring spins. k and T are Boltzmann's constant and the temperature, respectively. We want to model the nucleation of the equilibrium phase (phase-3) from a system with two coexisting phases (phases 1 and 2). Thus we introduce fields h_k that couple to spin- k s. Then we set $h_1 = h_2 = 0$ to make phases 1 and 2 equally stable, and make $h_3 > 0$ in order to reduce the free energy of phase-3 and make it the equilibrium phase.

With fields h_k , and fixed spins to model the surface of a particle, the energy E of the Potts model is given by

$$E = -J \sum'_{ij} \delta(s_i, s_j) - \sum_{k=1}^3 h_k \sum_i \delta(s_i, k) - J_s \sum''_{ij} \delta(s_i, s_j), \quad (1)$$

where $\delta(s_i, s_j)$ is the Kronecker delta, which equals one for $s_i = s_j$ and is zero otherwise. To distinguish them from the fixed spins that form surfaces, we refer to the spins that are free to flip as free spins. The first sum is from interactions between free spins, the second sum is the interaction with the fields h_k , and the third is for the interaction between the free spins and the fixed spins of the wall. The dash on the first sum indicates that it is over all nearest-neighbour pairs of free spins, and the double dash over the last sum indicates that it is over all nearest-neighbour pairs of free and fixed spins. In equation (1), J is the strength of the coupling between free spins and J_s is the strength of the coupling between a free spin and one of the fixed spins that compose a surface. Here we consider only $J_s = 0$. Thus the surface does not favour any one of the three phases, and so all contact angles are 90° .

3. Computer simulations

We study the Potts model using Monte Carlo simulations [13]. Simulating nucleation directly is prohibitively slow if the nucleation rate is low. Therefore, we will use the forward flux sampling (FFS) algorithm of Allen and co-workers [10–12]. We have previously used this to study nucleation in the Ising model [14, 15]. It allows us to efficiently calculate very low nucleation rates.

To simulate different environments for the nucleus we vary the boundary conditions. For homogeneous nucleation we employ periodic boundary conditions (PBCs) along both axes. For nucleation at a surface in contact with phase-1, we employ PBCs along one axis and have monolayers of fixed spins along the other two sides. We also employ PBCs along one axis when we study nucleation at the phase-1/phase-2 interface but here along the other axis we force the spins along one side to be spin-ones and along the opposite side we force them to be spin-twos. This forces there to be coexisting phases in the box. To study nucleation at the contact point we combine fixed spins along two sides to form solid surfaces with spins forced to be spin-ones and spin-twos along the other two sides. All our simulations were performed at the low temperature $J/kT = 1.65$. Here the transitions between the phases are strongly first order. Snapshots of nuclei in the four different environments are shown in figure 2. They are all near the top of the barrier. For example, of 1000 independent runs started from the configuration in (a), a fraction 0.54 resulted in the nucleus growing into a bulk phase-3, while the remainder returned to phase-1.

4. Results

Simulations of a box of 70 by 70 lattice sites at $h_3/kT = 0.08$, yields all four nucleation rates. These are: (a) homogeneous nucleation, $8 \times 10^{-30} \pm 5 \times 10^{-30}$; (b) nucleation at the interface

between phases 1 and 2, $1.5 \times 10^{-13} \pm 3 \times 10^{-14}$; (c) nucleation in phase-1 at the surface, $1.9 \times 10^{-16} \pm 6 \times 10^{-17}$; (d) nucleation at the contact point where the interface meets the surface, $9.8 \times 10^{-9} \pm 2 \times 10^{-9}$. These and all other rates are per simulation cycle. The rates are the average over three runs and the error estimates are the standard deviations. A cycle is one attempted spin flip per free lattice site. Due to the symmetry between phases 1 and 2 the rates of homogeneous nucleation and of nucleation at the surface are the same in both phases.

The *per site* rates of homogeneous nucleation, nucleation at the interface, nucleation at the surface, and nucleation at the contact point are $r_{\text{HOMO}} = 2 \times 10^{-33}$, $r_{\text{INT}} = 2 \times 10^{-15}$, $r_{\text{SURF}} = 1 \times 10^{-18}$, and $r_{\text{CONT}} = 5 \times 10^{-9}$, respectively. To obtain rates per site we divided by 70^2 , 70, 140, and 2, respectively. Homogeneous nucleation can occur at any one of the 70^2 sites, so to obtain the rate per site we need to divide the rate for our simulation box by 70^2 . For nucleation along the interface the rate per site is that for the complete box divided by 70 as the interface crosses the box and so has a length of 70 sites, see figure 2(b). For nucleation along a surface, we divided by 140 as our simulation box, see figure 2(c), has surfaces along the top and bottom, and each is 70 spins long. Finally, for nucleation at the contact point we divide by 2 as the simulation box has two contact points.

Having calculated the rates per site we can estimate the total nucleation rate R for a droplet of phase-1 coexisting with a comparable amount of phase-2. If we have N lattice sites in total then we expect the interface to be of order $N^{1/2}$ sites long. Then if the surface has a length N_s lattice sites, the total rate

$$R \approx Nr_{\text{HOMO}} + N^{1/2}r_{\text{INT}} + N_s r_{\text{SURF}} + r_{\text{CONT}}. \quad (2)$$

We expect the length of the surface N_s to be at most comparable to $N^{1/2}$ —it will be much smaller if the particle is much smaller than the droplet. If $N_s \lesssim N^{1/2}$ then as $r_{\text{SURF}} \ll r_{\text{INT}}$ nucleation at the surface is always negligible and can be discounted.

The ratios of the remaining rates are $r_{\text{CONT}}/r_{\text{INT}} \approx 10^6$ and $r_{\text{INT}}/r_{\text{HOMO}} \approx 10^{18}$. Thus, for $N < 10^{12}$ nucleation at the contact point dominates the total nucleation rate. This finding that the nucleation rate can be dominated by nucleation at the contact point is the major result of our calculations. It provides a possible mechanism for the nucleation behaviour that underlies the experimental observations that motivated this study [2, 3]. This is that particles trigger nucleation when in contact with a droplet under conditions at which no nucleation occurs if the particle is immersed in the droplet. Immersing the particle removes the last term in equation (2), and if this is the dominant term in the nucleation rate R , then R can drop from a large to a negligible value, shutting off nucleation. A lower nucleation rate without a contact point means that larger supersaturations are required to achieve a measurable nucleation rate. This is what Shaw and co-workers [2, 3], and others [1, 4] have found for the heterogeneous nucleation of ice from water droplets.

Durant and Shaw [3] list three suggested explanations for the observation that nucleation occurs more readily when a particle just contacts a water droplet than when the particle is completely immersed. However, all three should result in history-dependent nucleation rates. This is not what they observe in their experiments. We suggest that our finding for the simple Potts model, that the nucleation rate is highest where the interface meets the surface is generic, and so is the explanation for the experimental observation in water. Our nucleation rate is not history dependent.

There is a second open question in the nucleation of ice from water, which is also important in atmospheric physics. This is whether, in the absence of particle surfaces, nucleation of ice occurs in the bulk of the liquid water (as in figure 2(a)) or at the interface with air (as in figure 2(b)). Tabazadeh, Djikaev and Reiss (TDR) [16, 17] have suggested that it may occur at the interface but there is no consensus on this [1, 18, 19]. Within the Potts model it is clear that

nucleation at the interface is much (18 orders of magnitude) faster than in the bulk, and this is also true for a model of gold [20]. Thus TDR's suggestion that nucleation at the interface may be much faster than in the bulk, is clearly correct for the Potts model, which suggests that it should at least be taken seriously for water.

5. Classical nucleation theory

To help us better understand the relative sizes of the four rates we turn to classical nucleation theory (CNT). CNT [6, 7] approximates the nucleation rate per site, r , by

$$r = \nu \exp(-\Delta F^*/kT), \quad (3)$$

where ΔF^* is the height of the free-energy barrier to nucleation, and ν is an attempt frequency. We assume that ν changes little from one environment to another and so differences in rates are dominated by differences in barrier heights. For homogeneous nucleation in either phase-1 or phase-2, the free energy of a circular nucleus of radius R is

$$\Delta F = -\pi R^2 h_3 + 2\pi R \gamma, \quad (4)$$

where the first term is the bulk term, the reduction in free energy from forming the more stable phase-3, and the second term is the surface term, the free-energy cost of forming the interface at the edge of the nucleus. The interfacial tension between the two phases $\gamma \approx J$ at the low temperatures we are working at. The maximum in ΔF of equation (4), is the barrier to homogeneous nucleation

$$\Delta F_{\text{HOMO}}^* = \pi \gamma^2 / h_3. \quad (5)$$

It occurs for a critical nucleus of radius $R^* = \gamma / h_3$.

We also require estimates for the other three barriers. First, that for heterogeneous nucleation on a surface (see figure 2(c)). Here the nucleus is a semicircle because the contact angle between interface and the surface is 90° . The nucleus is just half the nucleus for homogeneous nucleation and so has half the free energy. Note that the interface along the bottom of the semicircle costs nothing because creating it just involves replacing a phase-1–solid interface by a phase-3–solid interface. These two interfaces have the same interfacial tensions. Thus the nucleation barrier on a smooth surface is

$$\Delta F_{\text{SURF}}^* = \Delta F_{\text{HOMO}}^* / 2. \quad (6)$$

The third barrier we require is that for nucleation at the interface between the two bulk phases (see figure 2(b)). Here due to the symmetry between these two phases, the nucleus is circular and the interface bisects it. Thus, when a nucleus of radius R forms at the interface it replaces a length $2R$ of interface between the two phases. This length of interface has a free energy cost that must be subtracted from the free energy of formation of the nucleus. Thus, the free energy of a nucleus of radius R is

$$\Delta F = -\pi R^2 h_3 + 2(\pi - 1)R\gamma. \quad (7)$$

This yields a smaller critical radius $R_{12}^* = (\gamma/h_3)(1 - 1/\pi)$, and a barrier that is smaller than that for homogeneous nucleation. It is

$$\Delta F_{\text{INT}}^* = \Delta F_{\text{HOMO}}^* (1 - 1/\pi)^2. \quad (8)$$

Finally, we require the barrier for nucleation at the contact point (see figure 2(d)). As with nucleation at the surface in one of the phases, the nucleus is a semicircle. The nucleus is just half the nucleus for nucleation at the interface between the two bulk phases, and so it has half

the free energy. Thus the nucleation barrier at the point where the interface between phases 1 and 2 hits the surface of a particle is

$$\Delta F_{\text{CONT}}^* = \Delta F_{\text{INT}}^*/2 = \Delta F_{\text{HOMO}}^*(1 - 1/\pi)^2/2. \quad (9)$$

All four barriers are of the form a constant times the barrier for homogeneous nucleation, and the constant is smallest for nucleation at the contact point. Therefore, the barrier to nucleation at the contact point is always the lowest of the four barriers. It is always approximately a fifth of the barrier to homogeneous nucleation, and half that of the next smallest barrier, that at the interface. Thus CNT correctly predicts that nucleation is fastest at the contact point.

CNT not only correctly predicts that nucleation is fastest at the contact point, it shows us why. The barrier to nucleation comes from the free energy cost of creating the interface around the nucleus (the bulk term in the free energy is negative and so subtracts from the barrier height). This free-energy cost is the free energy of the interface minus the free energy cost of any pre-existing interface that disappears when the nucleus forms. The contact point is by definition where three interfaces meet and so there are three pre-existing interfaces not one whose free energy is subtracted from the barrier height. These are the phase-1–phase-2, phase-1–solid and phase-2–solid interfaces.

Having found that nucleation is fastest at a contact point (line in three dimensions) we note that contact lines are expected to be common in systems with coexisting fluid phases. Quite generally, small impurity particles tend to collect at interfaces; by doing so they reduce the area of the interface and so its free energy. This is the physics that underlies Pickering emulsions [21]. At the interface the particles will of course create a contact line. Protein solutions provide a possible example of nucleation at a contact line around an impurity particle at an interface. These solutions often phase separate into coexisting dilute and concentrated protein solutions. Crystallization can occur in such solutions. When it does so the crystalline phase has sometimes been observed to appear growing out from the interface between the coexisting phases [5].

In figure 3 we have plotted all four rates as a function of h_3 . All four rates can be well fitted by functions of the CNT form, i.e. $A \exp(-B/h_3)$, where A and B are adjustable constants. The values of B obtained from the fits are consistently smaller than the CNT predictions, e.g. for nucleation at the interface, CNT predicts that $B = 4.0$, whereas fitting gives $B = 2.4$. It appears we are overestimating the interfacial tension γ when we approximate it by J . However, the ratios between the four different values of B obtained from the fits are quite close to the CNT predictions, e.g. CNT predicts that the B for nucleation at the contact point and at the interface should differ by a factor of 2, whereas fitting gives a ratio of 1.8. Thus, although (with our approximation for γ) CNT consistently overpredicts the barrier height, it predicts the trends semiquantitatively. It also correctly predicts the order of the four barrier heights.

6. Conclusion

The experiments of Shaw and co-workers [2, 3], and others [1, 4], have found that when a particle only contacts a droplet of water it freezes at higher temperatures than when the particle is completely immersed. When the particle only contacts the droplet there is a contact line where the interface between the two coexisting phases meets a solid surface. This is absent if the particle is immersed. Inspired by this we studied nucleation in simple model systems with a contact point, the two-dimensional analogue of a contact line.

We found that the rate was many orders of magnitude larger than at either the surface of a particle or the interface between the coexisting phases. The rate of homogeneous nucleation was found to be extremely low. If we turn to CNT, we can easily understand why the nucleation

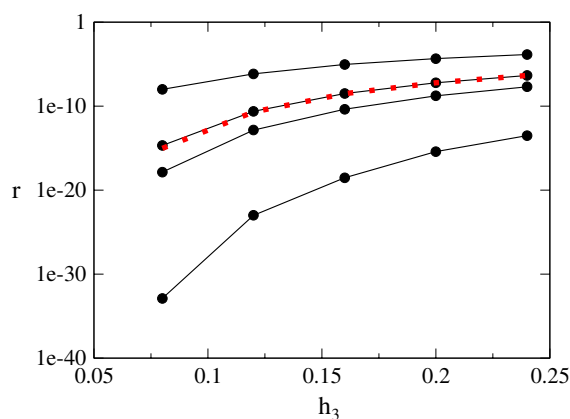


Figure 3. Plots of the nucleation rate per site, r , as a function of the field h_3 , and at a temperature $J/kT = 1.65$. The rates are obtained from simulation. They are the circles, the solid lines connecting them are just to guide the eye. The four nucleation rates are, from bottom to top, r_{HOMO} , r_{SURF} , r_{INT} and r_{CONT} , respectively. The fit of an expression of CNT form to r_{INT} is shown as the dotted (red) curve. Fits to the other rates are of comparable quality but are not shown to avoid cluttering the figure.

barrier is lowest at the contact line. At a contact line three interfaces meet: these are the phase-1/phase-2, phase-1/solid and phase-2/solid interfaces. All three of these interfaces have associated interfacial free-energy costs. As the nucleus expands it reduces the areas of all these interfaces and the corresponding reduction in the interfacial free energy directly contributes to a reduction in the height of the free-energy barrier to nucleation. By contrast, at the interface away from the surface there is only one interface.

The three interfaces will be present, and their total areas (or lengths) will decrease as the nucleus forms, provided only that there is partial not complete wetting. Thus, our conclusion that the nucleation barrier is lowest at the contact line will hold unless there is complete wetting of: (i) the phase-1–solid interface by phase-3, (ii) the phase-2–solid interface by phase 3, (iii) the phase-1–phase-2 interface by phase-3, (iv) the phase-1–phase-3 interface by phase-2, or (v) the phase-2–phase-3 interface by phase-1. If any of (i), (ii) or (iii) is true then as the nucleating phase, phase-3, wets an existing interface in the system then there should be no barrier to nucleation. When (iv) or (v) is true then nucleation would then be more favourable at the surface in contact with phase-2 or phase-1, respectively. If say (iv) is true and phase-2 wets the phase-1–phase-3 interface then moving the nucleus along the surface of a particle from a region in contact with phase-2, to the contact line would not reduce the total area of the phase-1–phase-2 interface as this interface would persist due to wetting of the phase-1–phase-3 interface by phase-2.

Now the volume along the contact line is much less than that at an interface which is turn a very small fraction of that in the bulk. Thus, nucleation at the contact line will only be dominant if the reduction in barrier there is enough to overcome the small volume along the contact line. We cannot calculate the barrier for the nucleation of ice at the contact line where the air–water interface meets the surface of a particle, this would require a very challenging calculation of an accurate model of water and of the particle’s surface. Thus we are unable to predict whether or not Shaw and co-workers [2, 3] should be observing nucleation at a contact line. However, generically the nucleation barrier should be low at a contact line. Therefore, it is certainly physically plausible that Shaw and co-workers, and others, are observing the results of ice nucleation at a contact line.

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