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Faster Nucleation of Ice at the Three-Phase Contact Line: Influence of Interfacial Chemistry

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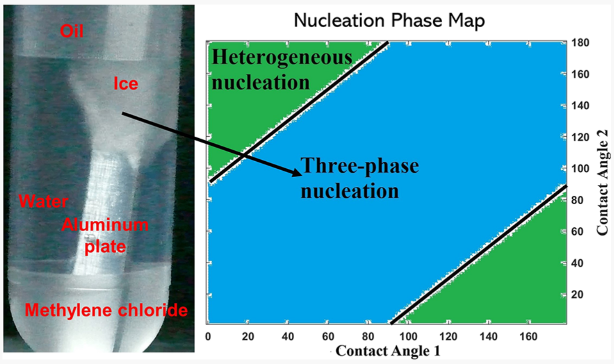
ABSTRACT: Controlling the nucleation of ice is important in many areas including atmospheric sciences, cryopreservation, food science, and infrastructure protection. Presently, we conduct controlled experiments and analysis to uncover the influence of surface chemistry at the three-phase line on ice nucleation. We show that ice nucleation is faster upon replacing the air at the water−air interface with oils like silicone oil and almond oil. We show via statistically meaningful and carefully designed experiments that ice nucleation occurs at a higher temperature at an aluminum−water−silicone oil (or almond oil) interface as compared to an aluminum−water−air interface. We show that the location of ice nucleation can be controlled (in situations with multiple locations for ice nucleation) by controlling the interfacial chemistry at the three-phase line. We develop a model (which utilizes classical nucleation theory) to study the combined influence of two interfaces on a seed crystal of ice originating at the three-phase contact line. This model can evaluate the thermodynamic competition between nucleation at the three -phase line and heterogeneous nucleation at an interface. The model shows that three-phase contact lines usually result in a higher driving force than heterogeneous nucleation, which speeds up nucleation kinetics. Overall, our experiments and modeling uncover several useful insights into the influence of three-phase lines on nucleation during contact freezing.



■ INTRODUCTION

Crystallization of ice impacts applications across engineering and science,[1] along with daily life, in various ways. Water−ice transitions influence earth-scale events (rainfall and melting of polar ice caps) and process phenomena in industrial systems (food preservation, aviation, energy production, infrastructure, etc.) and everyday life (deicing roadways, etc.).[2−6] The process of crystallization consists of two steps: nucleation followed by growth of ice crystals. While the thermodynamic melting point of water is 0 °C, recent MD simulations show that water can exist as a liquid at temperatures as low as −48 °C[7] in the absence of ice nucleation promoting phenomena. Ice nucleation in supercooled water is promoted by surfaces; this is termed heterogeneous nucleation wherein the energy barrier for ice nucleation is lowered by surfaces. Particles in water can also act as heterogeneous nucleation sites. In the complete absence of nucleation sites, homogeneous nucleation of ice will occur, but at higher supercooling levels than those required for heterogeneous nucleation. In this work, we study the influence of three-phase contact lines on ice nucleation and obtain several novel insights from our experiments and modeling. In the rest of this paper, we refer to ice nucleation originating at the three-phase contact line as three-phase nucleation (observed in contact freezing) and ice nucleation originating at the interface of two phases (inside bulk water, as observed in immersion freezing) as heterogeneous nucleation. High-speed visualization allows the identification of three-phase nucleation as opposed to heterogeneous nucleation and has been captured by several research groups including the present research group.[8−11]

The study of nucleation at three-phase contact lines is more than half a century old and is termed contact freezing in the literature.[12] Silver iodide (AgI) is a strong promoter of ice nucleation; it has been observed that AgI particles nucleate ice at a much lower supercooling on direct contact with water drops (the presence of the air−water−AgI line) compared to the case of AgI particles immersed inside the water droplet.[13−16] Shaw et al.[17] reported that ice nuclei trigger faster nucleation of ice when placed on the water−air interface rather than being completely immersed. The benefits of three-phase nucleation have also been observed by the present group during nucleation of gas hydrates,[18−20] which are ice-like solids of gas and water and form at high pressures and temperatures close to 0 °C.

It is noted that contact freezing also refers to ice nucleation when particles nucleate ice upon impact. Ice nucleates at higher

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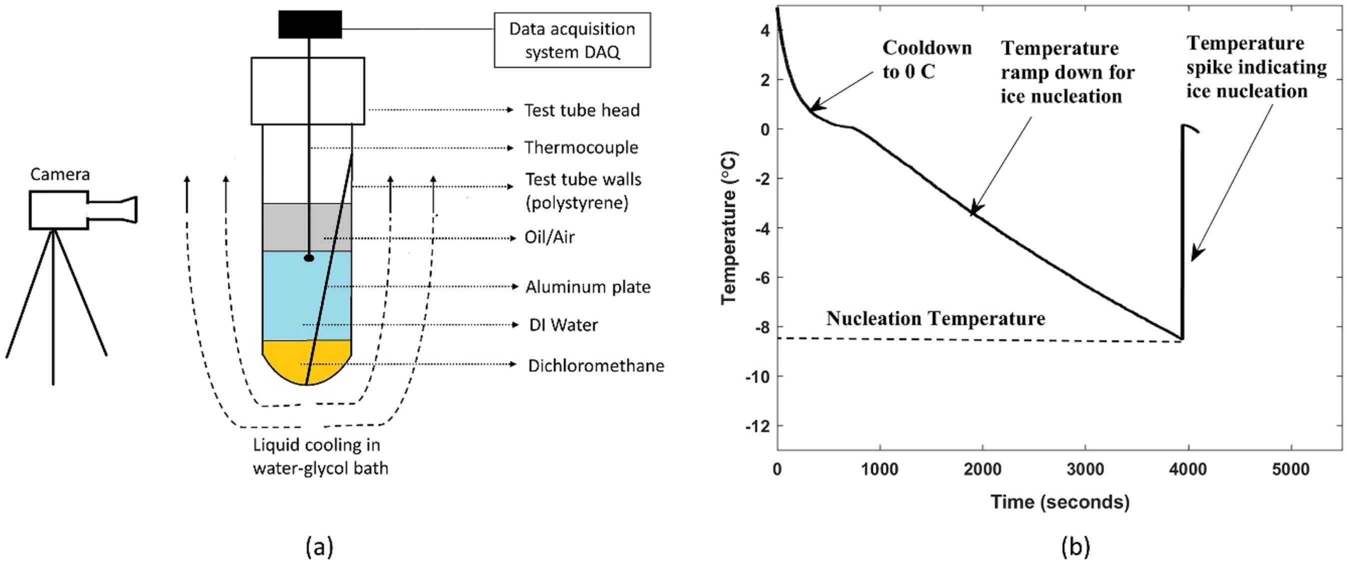

Figure 1. (a) Schematic of the experimental setup and three-fluid system. (b) Illustration of detection of ice nucleation (by a temperature spike) during cooling.

supercooling when particles strike the air−water interface as opposed to contact nucleation where the particles reside on the interface. Such an effect is observed for many particles such as kaolinite, salts, aerosols, and so on, which nucleate ice at a lower supercooling.[21−24] These particles can even be inhibitors like salts, yet they tend to nucleate ice faster on impact. Marcolli et al.[15] referred to this as collisional contact freezing in their review. Hence, it should be understood that impact of particles also influences nucleation, in addition to surface chemistry. The focus of the present work is to capture the influence of surface chemistry alone, on ice nucleation, in the absence of any impact-related influence. Also, it is often argued that discrepancies in temperature can provide localized higher driving force for nucleation.[24] The air−water interface can cool faster than the bulk and therefore nucleate ice faster due to higher supercooling.

Although contact nucleation has been studied for several decades and many theories have been proposed for contact freezing,[25] classical nucleation theory has not been adequately leveraged to explain ice nucleation at three-phase contact lines; this is one motivation for the present work. Classical nucleation theory is widely used to predict nucleation probabilities and has traditionally been used to capture the influence of surface chemistry on ice nucleation. Classical nucleation theory has also been used to study nucleation at water−air interfaces, resulting from particle impact; this is based on a deposition nucleation mechanism.[26,27] In stagnant systems, with particles residing on the interface, Sear[28] and Djikaev−Ruckenstein[29] adopted the Potts model and classical nucleation theory, respectively, to argue that the presence of two interfaces at the triple-phase contact line increases the driving force for nucleation. Recent molecular dynamics (MD) simulations have also captured the promoting influence of multiple interfaces[30,31] on nucleation. *Presently, we adopt classical nucleation theory to study the influence of two interfaces assisting a seed crystal of ice nucleating at the three-phase contact line.* A simple but robust implementation of classical nucleation theory is used to study the influence of surface chemistry and macroscopic contact angles on nucleation at three-phase contact lines. Because the continuum assumptions in classical nucleation theory are not applicable at nanoscales (where nucleation typically occurs), we highlight the trends and scales obtained from the model and do not focus on the magnitude of obtained energy barriers. Importantly, classical nucleation theory explains the results of our presently conducted experiments as well as observations from the literature.

A majority of experimental studies on three-phase contact lines and contact freezing have studied ice formation in water droplets. Presently, we choose a different experimental setup: a column of water in a test tube, since it helps in modulating the surface chemistry without affecting the contact areas. An aluminum plate is placed inside the water column to trigger ice nucleation (because of its high surface energy). *Our statistical measurements show that replacing the fluid above the water column from air to silicone oil (or almond oil) triggers ice nucleation at lower supercooling.* The area of an aluminum plate in contact with water in each case remains unchanged, indicating that nucleation promotion cannot be due to heterogeneous nucleation occurring on the aluminum surface inside bulk water (this is also seen in the experiments). In traditional droplet-on-surface experiments, the influence of contact area and contact line cannot be easily separated, since modulating the surface chemistry at the surface water−air junction will change the contact area of the droplet as well.[10,32,33] The experimental setup adopted in this study decouples these two effects and facilitates a study of the influence of three-phase contact line without significantly changing the area of bulk water in contact with the surface. Another motivator for our experimental setup is that it helps study the contact mode of nucleation as opposed to the collisional contact mode of nucleation as discussed before. Experiments are conducted by using a stagnant aluminum plate and hence there is no influence of impact. In past experiments (where particles are dropped on water droplets), impact and surface chemistry will jointly influence ice nucleation.[16,34] Recently, ice nucleation inhibitors like salts (when dissolved in aqueous phase) have been shown to promote ice nucleation resulting from impact with water droplets.[22] In all such studies, it is not possible to directly decouple the influence of surface chemistry with impact. The present experiments and analysis do not involve impact and facilitate a direct understanding of the role of surface chemistry.

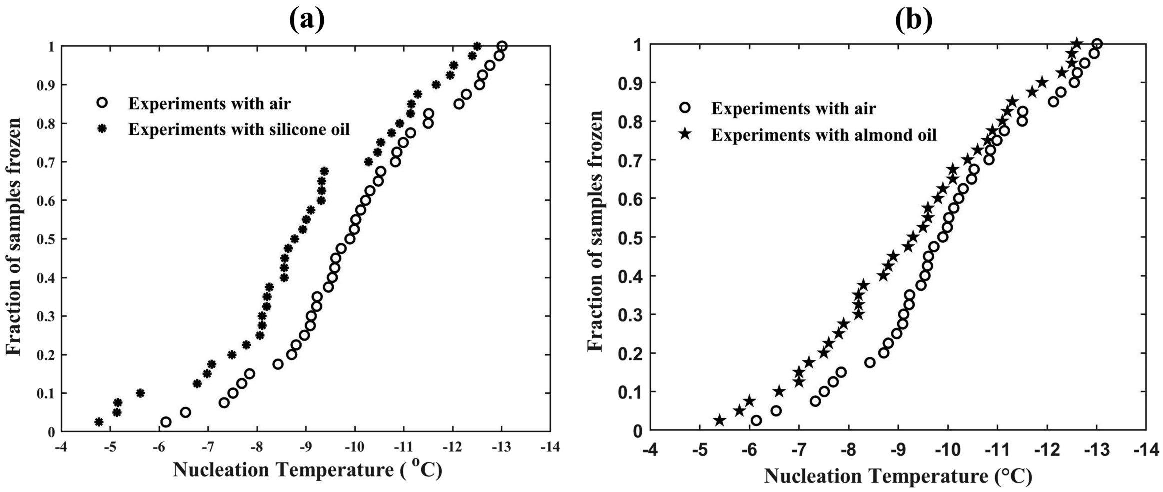

Figure 2. Fraction of test tubes which nucleated ice (probability of nucleation) at a particular nucleation temperature: (a) 40 experiments conducted per fluid with either silicone oil or air as the top fluid; (b) 40 experiments conducted per fluid with either almond oil or air as the top fluid.

■ EXPERIMENTAL SECTION

Materials and Methods. Freezing experiments were done (Figure 1a) in a 17 mm diameter polystyrene test tube containing three immiscible fluids. The bottom fluid is 1 g (about 0.75 mL) of methylene chloride (dichloromethane), followed by 3 g (about 3 mL) of deionized (DI) water on top of it. The fluid above water is either air or 1 g (about 1 mL) of silicone oil/almond oil. All fluids were obtained from Sigma-Aldrich. The specific grade of silicone oil had a viscosity of 50 cSt. The almond oil had a viscosity of about 35 cSt. An aluminum plate (length: 2 in.; width: 0.25 in.; thickness: 0.04 in.) is placed inside the test tube and protrudes into the two fluid−fluid interfaces. The aluminum plate is polished to an average roughness of 200 nm (measured by using an SJ-210 surface probe) and is cleaned with isopropyl alcohol and subsequently flushed with nitrogen gas before experiments. There exists two three-phase contact lines of water with the aluminum plate: one at the top with either silicone oil or almond oil or air and one at the bottom with methylene chloride. The three-fluid setup was adopted primarily to prevent any solid−solid contacts with water where ice nucleation can originate. We note that each experiment was conducted with a new test tube, an aluminum plate, and fluids.

The choice of fluids methylene chloride, silicone oil, and almond oil was based on three factors. First, all three fluids do not mix with water. Second, all the fluids have melting points below −15 °C, which ensures that they do not freeze during experiments. Third, the fluids modify the contact angle of water on aluminum, in accordance with the objectives of this study. Contact angles were measured by using a goniometer from Biolin Scientific. The 20 μL water droplets on aluminum in air have an average contact angle of 91° (average calculated from four measurements, reported as an average of receding and advancing contact angles). On replacing the air by silicone oil or almond oil, the contact angle reduced to 74° and 80°, respectively, at the triple-phase contact lines. Conversely, methylene chloride tends to increase the triple-phase contact angle to 102° at the junction of water−aluminum−methylene chloride. The two oils and methylene chloride thus change the macroscopic contact angle of water on aluminum in opposite directions. Images from contact angle measurements are included in the Supporting Information.

The test tubes containing the fluids, aluminum plate, and a thermocouple were then sealed off by using caps with water-repellant sealants (from 3M) and completely immersed inside a 75 L water−glycol cooling bath (Polyscience). The test tubes were first thermally equilibrated at just above 0 °C (±0.2 °C). The temperature was then ramped down linearly at the rate of 0.15 °C/min until the onset of ice nucleation. The onset of nucleation was determined by a temperature spike (due to the release of latent heat) near the upper interface of water−air/silicone oil/almond oil (Figure 1b). The temperature was continuously monitored by a T-type exposed thermocouple of stainless steel (0.5 mm bead diameter) placed very close to the interface on the water side. Continuous data acquisition for the thermocouples was enabled by using a NI DAQ connected though a MATLAB user interface. Along with these experiments, separate nucleation experiments were also conducted with the test tubes cooled in air inside an environmental chamber (ESPEC); these experiments were conducted to visualize nucleation locations using a Nikon DSLR D850 camera.

Results and Discussion. Forty experiments were conducted for silicone oil, almond oil, and air each as the top fluids (for a total of 120 experiments overall). Each experiment resulted in the measurement of one nucleation temperature, and each experiment was conducted with a new aluminum plate, fluids, and a clean test tube (to minimize cross-contamination). Significant differences were observed in the nucleation temperature for the three fluids on the top. Figure 2 shows the fraction of test tubes that nucleated ice at various temperatures. Figure 2a compares the nucleation resulting from silicone oil versus air, whereas Figure 2b compares the nucleation resulting from almond oil versus air. The fraction of tubes frozen (or the nucleation probability) is calculated as the number of tubes frozen at a particular temperature divided by the total number of tubes (40). Therefore, each data point on the plot represents one nucleation event. Faster nucleation of ice (or higher temperature of nucleation) was consistently observed for silicone oil (and almond oil) on top of the water column (compared to air). For example, at a temperature of −9 °C, the fraction of samples nucleated for the case of air is 0.25, whereas that for silicone oil is about 0.5. It is noted that the difference in nucleation temperatures between air and silicone oil/almond oil reduced at temperatures below −10 °C. Overall, experiments with two different oils show similar trends and a noticeable difference in nucleation temperatures in the presence of oils as compared to the case of air.

These experiments clearly show the influence of interfacial chemistry on modulating ice nucleation. As mentioned previously, the area of the aluminum plate inside bulk water is the same in all cases. Faster nucleation can thus be attributed to the variation in surface properties at the three-phase contact line. Traditionally, for the droplets-on-surface setup, these two effects cannot be easily separated as any change in the contact angle would change the contact area of the droplet with the surface. To illustrate, a droplet residing on an aluminum surface in air flattens out when the air is replaced with oil; this changes both the contact area and the contact angle significantly. However, in the current experimental setup replacing air with oil (above the water column) changes the contact angle at the interface significantly, without changing the contact area of the water with the metal surface. Therefore, our experimental methodology allows us to isolate the influence of these two contributors: contact angle and contact area. The findings of these experiments are also validated with the analytical model developed in the next section.

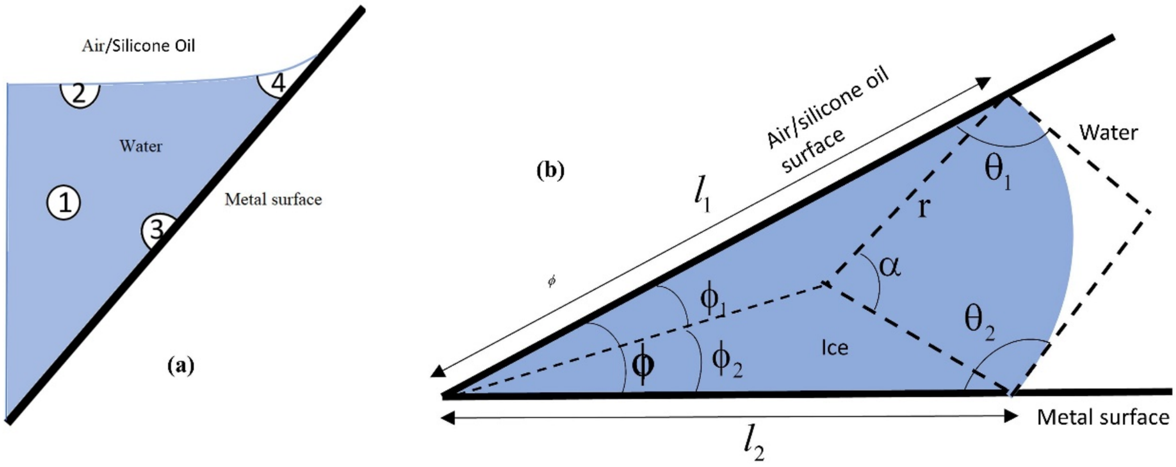

Figure 3. (a) Various sites for ice nucleation in our experiments. (b) Schematic of the two-interface model for ice nucleation.

In addition to the above quantitative findings on nucleation probability, the experiments also provided direct information about nucleation locations. Very interestingly, nucleation was always observed to initiate at the aluminum−water−air/silicone oil/almond oil three-phase contact line and never on the aluminum−water−methylene chloride contact line (as seen in Video S1 and Video S2). It is pointed out that there was no temperature difference between these two locations. Nucleation never originated on the polystyrene−water−methylene chloride contact line due to the higher contact angle of water on the aluminum surface in air/silicone oil/almond oil. This is also captured in the model developed in this paper. It is also noted that there are a couple of other contact lines on the inner surface of the polystyrene test tube: the polystyrene−water−air/silicone oil/almond oil contact line and the polystyrene−water−methylene chloride contact line. Nucleation always originated on the aluminum surface because of its higher surface energy. Nucleation was never seen to originate on the walls of the polystyrene test tube, even though the temperature in that region is expected to be slightly lower than the rest of the test tube, because of its proximity to the coolant. This is contrary to some articles in the literature which claim that lower temperatures at three-phase contact lines result in faster nucleation.[24] It is noted that such studies[24] are based on droplet-on-surface experiments where only one contact line is present. Recent thermal simulations also show the influence of temperature nonuniformity on ice nucleation to be insignificant (especially on high surface energy hydrophilic surfaces like those in this study).[35] Our observations clearly show that surface chemistry plays a vital role in ice nucleation kinetics at the three-phase line.

We briefly discuss the uncertainty in measurements in our experiments. The uncertainty from instrumentation that is associated with the temperature measurement (thermocouples) and data acquisition is ±0.2 °C. Details of the uncertainty calculations are available in the Supporting Information. The thermocouples are fixed at the same location in each experiment; hence, any uncertainties in temperature due to spatial variation in location will be insignificant. Fluids are poured in on a weight basis with maximum uncertainties of ±0.05 g. All data points in Figure 2a for the comparison between silicone oil and air fall outside the uncertainty bands of the two fluids. However, for the case of almond oil and air (Figure 2b), some data points below −10 °C overlap within the uncertainties of each other. Other than the uncertainty due to the experimental setup, uncertainties in nucleation rate arise due to the stochasticity of the nucleation process, which follows a Poisson statistic.[36−38] Based on 40 samples or events, maximum uncertainties in nucleation rate can be ±30% based on a 95% confidence interval (equations are provided in the Supporting Information).

■ MODELING

Methods. Classical nucleation theory predicts a higher driving force for heterogeneous ice nucleation than homogeneous nucleation due to the presence of a surface with high surface energy. For the case of ice nucleation originating at three-phase contact lines, a seed crystal of ice is influenced by two interfaces present at the three-phase contact line instead of one interface (for heterogeneous nucleation at the interface of two fluids). This can result in a larger driving force for ice nucleation as shown below. Sear[28] proposed a two-surface setup for three phase nucleation, and Djikaev and Ruckenstein[29] modeled the influence of two surfaces using classical nucleation theory. They concluded that the presence of an extra surface reduces the energy needed to form the critical ice nucleus. Djikaev and Ruckenstein[29] model considered a hexagonal structure of ice crystal growing between two surfaces. The work of formation was modeled by using the Helmholtz free energy. Because of the consideration of hexagonal structure, all angles between the surfaces were fixed at 120°. Multiple MD simulations based on recent studies[31,32] also show the enhancing influence of more than one surface on ice nucleation.

Presently, we develop a simple, yet robust formulation based on classical nucleation theory to explain our results. Using geometrical considerations, we derive analytical solutions (to the extent possible) and detail the physical implications of our theory. The ice nucleation situation in our experiments is shown in Figure 3a, which details four possible nucleation locations. Site 1 corresponds to homogeneous nucleation, which will have the lowest driving force. Sites 2 and 3 correspond to heterogeneous nucleation with site 3 being preferred due to the high surface energy of the metal surface. Site 4 corresponds to three-phase nucleation where ice nucleus originates at the three-phase contact line, assisted by two interfaces. Our modeling compares the competition between sites 3 and 4 and shows that three-phase nucleation is a more preferred nucleation location in most scenarios.

In the present model, a generalized formulation is developed considering a seed crystal of ice growing in between two surfaces as shown in Figure 3b. The two surfaces form an angle ϕ and have different surface energies. The growing volume of ice forms contact angles θ_1 and θ_2 with the two surfaces. Heterogeneous nucleation is simply a special case of this formulation. Choosing $\phi = 180°$ and $\theta_1 = \theta_2$ reduces Figure 3b to a flat surface with the same surface energy throughout (heterogeneous nucleation). There are three major assumptions in the model. First, the model is formulated in a 2D geometry for capturing the underlying physics in significant detail. Second, ice grows in between the two surfaces with the growing ice−water interface assumed to be an arc of a circle. This is a common assumption which stems from a surface-tension-dominated interface. Third, line tensions arising at three-phase contact lines are not included in the model, as exact scales of line tension are debated in the literature.[39] Previous formulations have either excluded line tension or assumed them to be insignificant in comparison to the surface energies.[28,29] Angles α, ϕ_1, and ϕ_2 in Figure 3b define the internal angles present in the geometry. l_1, l_2, r, and L are the contact lengths of the ice volume on the two surfaces, the radius of

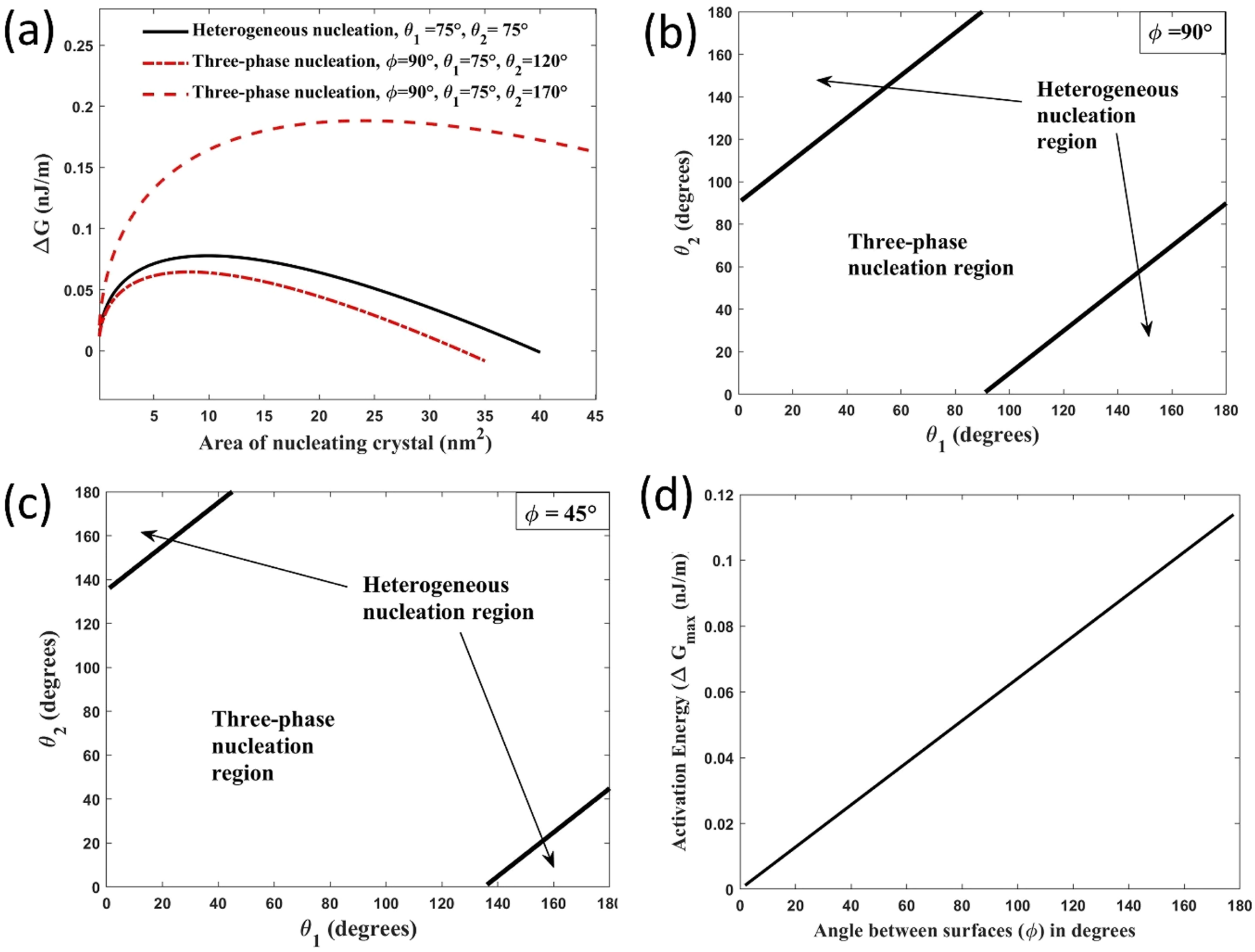

Figure 4. (a) Dependence of activation energy of three-phase and heterogeneous nucleation for various combination of angles. (b) Nucleation phase map for angle between surfaces (Figure 3b) as 90°. (c) Nucleation phase map for angle between surfaces (Figure 3b) as 45°. (d) Variation of activation energy with the angle between the surfaces (value of θ_1 and θ_2 is 90°).

the circular arc, and the length of the arc, respectively. Geometrical considerations result in the following relations:

$$\alpha = \theta_1 + \theta_2 + \phi - \pi, \quad \phi_2 = \cot^{-1}\left(\cot\phi + \frac{\cos\theta_1}{\sin\phi\cos\theta_2}\right),$$
$$\phi_1 = \phi - \phi_2, \quad r = \left| l_1 \frac{\sin\phi_1}{\cos(\phi_1 + \theta_1)} \right|,$$
$$l_2 = \left| r \frac{\cos(\theta_2 + \phi_2)}{\sin\phi_2} \right|, \quad L = |\alpha r| \tag{1}$$

The preceding relations can be used to obtain the area of the nucleating ice crystal A as

$$A = \frac{1}{2}\alpha r^2 - \frac{1}{2}l_1 r\cos\theta_1 - \frac{1}{2}l_2 r\cos\theta_2 \tag{2}$$

Because this is a 2D system, all depths into the plane of the paper are considered to be unity. The Gibbs free energy for the crystallization process is the sum of contributions from the bulk and surface free energies as given in eq 3. The derivation of eq 3 is included in the Supporting Information.

$$\Delta G = -\frac{A}{V_l}\Delta H_{\text{fusion}}\left(1 - \frac{T}{T_f}\right) + (L - l_1\cos\theta_1 - l_2\cos\theta_2)\gamma_{\text{sl}} \tag{3}$$

where V_i is the molar volume of the crystallizing ice, ΔH_{fusion} is the enthalpy change for liquid to solid transition, T_f is the thermodynamic freezing temperature, T is the experimental nucleation temperature, and γ_{sl} is the surface energy at the crystallizing ice−water interface. Values of the ice−water surface tension, γ_{sl}, are typically of the order of 30 mJ/m^2.[40,41] Values of T = 266 K, T_f = 273.15 K, and $V_l = 1.96 \times 10^{-5}$ m^3/mol were used for the simulations. For the ice−water surface energy, a value of γ_{sl} = 24 mJ/m^2 was used for the simulations, adjusted to a nucleation temperature of T = 266 K, using the equation $\gamma_{\text{sl}} = 23.24\left(\frac{T}{235.8}\right)^{0.35}$ from Nemec.[42] It should be noted the unit of ΔG is energy per unit length because of the 2D formulation. More details on the equations and solutions are available in the Supporting Information.

Results and Discussion. A comparison of three-phase nucleation to heterogeneous nucleation predicts that for certain combination of angles ϕ, θ_1, and θ_2 three-phase nucleation is favored over heterogeneous nucleation. The preferred nucleation mode corresponds to lower activation energy required to form the critical nucleus of ice. The activation energy is defined as the maximum of Gibbs free energy during nucleation. Figure 4a shows the evolution of Gibbs free energy versus the area of the nucleating crystal of ice. The three lines show one case of heterogeneous nucleation and two cases of three-phase nucleation. In Figure 4a, θ_2 is varied while ϕ = 90° and θ_1 =

75° are fixed. For θ_2 = 120°, three-phase nucleation is favored over heterogeneous nucleation (due to the lower activation energy of three-phase nucleation). For θ_2 = 170°, heterogeneous nucleation is more favorable. As mentioned previously, θ_1 and θ_2 are the contact angle of the ice nucleus on the two surfaces. Figure 4a shows that three-phase nucleation is thermodynamically more favorable for ice-philic surfaces whereas heterogeneous nucleation can be more favorable for ice-phobic surfaces (ice-philic surfaces refer to low contact angles of ice nucleus on a surface and ice-phobic the opposite).

A deeper investigation into the competition between three-phase nucleation and heterogeneous nucleation reveals that three-phase nucleation is thermodynamically favorable for many more situations than heterogeneous nucleation. Figure 4b can be considered as the nucleation phase map and shows the preferred nucleation mode as a function of the angles θ_1 and θ_2 for angle between the interfaces ϕ = 90°. Classical nucleation theory predicts that three-phase nucleation is energetically more favorable than heterogeneous nucleation for most combinations of θ_1 and θ_2, as clearly seen in Figure 4b. The angle between the two surfaces, ϕ in the model, can be experimentally correlated to the contact angle of water on aluminum surface in the presence of a third medium (Figure 3a). The value of ϕ was ~90°, based on the measured contact angle of water on aluminum in air. It should be noted that the inclination of the plate has little effect on the angle between the two interfaces and is largely determined by the contact angle of water on the surface. Although it is difficult to measure or obtain accurate data on the surface energies of ice−aluminum interfaces (which will determine the contact angles θ_1 and θ_2), heterogeneous nucleation would be preferred only for the situation where one surface is very hydrophilic and the other surface is very hydrophobic, which are unlikely in real situations. This is expected because a very hydrophilic surface tends to favor a heterogeneous nucleation on the surface whereas the other hydrophobic surface increases the activation energy of three-phase nucleation. Values of contact angles for a seed crystal of ice on different interfaces are not well-known; however, it is generally far less than 180°.[43] Therefore, classical nucleation theory predicts that the nucleation of ice on an aluminum surface in the presence of air prefers three-phase nucleation, which is observed in our experiments and has also been reported in several other studies.[8−11]

A similar phase diagram which compares three-phase nucleation with heterogeneous nucleation (Figure 4c) shows the case for ϕ = 45°, i.e., a more hydrophilic surface. For such surfaces, the region where three-phase nucleation is more favorable remains much larger than the region where heterogeneous nucleation is preferred. From an empirical observation, it is interesting to note that the lines in Figures 4b and 4c which demarcate the regions between three-phase nucleation and heterogeneous nucleation closely correspond to the equation $|\theta_1 - \theta_2| = \pi - \phi$. This empirical equation predicts that the region for three-phase nucleation will be much larger than that for heterogeneous nucleation for low value of ϕ. In other words, if a surface is more hydrophilic and exhibits a low contact angle with water, the stability region for three-phase nucleation increases (as in Figures 4b and 4c). Our modeling thus predicts that heterogeneous nucleation will be preferred for a combination of one very ice-philic and another very ice-phobic surface, wherein nucleation will not originate on the three-phase contact line; rather, it will nucleate inside bulk water on one of the interfaces (provided there are no other three-phase contact lines in the system).

Figure 4d shows the influence of the angle between the surfaces (ϕ) on the activation energy of nucleation. θ_1 and θ_2 are chosen to be 90°, and the angle between the surfaces is varied from 0 to 180°. Figure 4d shows that the activation energy increases almost linearly with ϕ. Therefore, classical nucleation theory predicts faster nucleation if the contact angle is smaller at the triple-phase contact. It is noted that we have chosen a random value for θ_1 and θ_2 as 90° (for Figure 4d). A similar trend is observed for all values within the range 60°−120° for both angles. This trend is validated by our current experiments, where faster nucleation is clearly observed (Figure 2) by reducing the contact angle of water on aluminum via replacing air with silicone oil or almond oil. Hence, our experimental observations are captured well by the current model.

Finally, we address the influence of nucleation kinetics-related considerations in our present experiments, noting that our analysis and results were solely based on thermodynamics-related considerations. Djikaev and Ruckenstein[29] accounted for the nucleation rate of contact freezing based on thermodynamics only, as was pointed out by Ladino Moreno et al.[25] Presently, we briefly comment on the consideration of the kinetics-related factors. The nucleation rate flux, defined as the nucleation rate per unit area, is given as $J = A\exp(-\Delta G_{\max}/kT)$, where the pre-exponential factor $A = zf^*C_0$ depends on the kinetic properties near the nucleation site (z is the Zeldovich factor, f^* is associated with interface geometry, and C_0 is the concentration of nucleation sites). Because nucleation occurs in the liquid water phase, the kinetic factors z and f^* are similar. For homogeneous versus heterogeneous nucleation, the concentration of nucleation sites is significantly different due to the presence of a surface in the latter, as explained in Kaschiev.[44] Because three-phase nucleation also depends on surfaces, we expect the pre-exponential factor for three-phase nucleation to be similar to that for heterogeneous nucleation. Hence, the present experimental results can be attributed to favorable thermodynamics instead of kinetics-related considerations.

We briefly discuss other phenomena and theories that could influence the present experimental results. Pressure perturbation has been proposed as a promoting mechanism, wherein the impact of particles causes a pressure fluctuation resulting in thermodynamically favorable conditions for ice nucleation.[45] However, pressure perturbations assist nucleation only where there is an impact of particles, agitation,[46] the presence of electric fields,[47] the presence of acoustic waves,[48] and so on. In our experiments, the system is stagnant with no forced external excitation; therefore, pressure perturbation is unlikely to promote ice nucleation at the three-phase contact line. Interestingly, for the case of homogeneous nucleation, Koop et al.[49] showed that the pressure difference across the water−air interface and the concentration of solute in water are physically connected and uniquely determine the homogeneous ice nucleation rate. Recently, Pandey et al.[50] proposed a different effect that ice-nucleating proteins induce ordering in the water structure near the three-phase contact line which accelerates ice nucleation.

Researchers have also shown that nanostructures on the surface influence three-phase nucleation versus heterogeneous nucleation. Gurganus et al.[11] reported that the presence of nanoscale structures on the surface triggered heterogeneous nucleation in the bulk two-phase surface contact with the water droplet (instead of the three-phase line), whereas the absence of small structures at nanoscales induced nucleation at the triple-phase contact line of the system. Several related articles suggest that the presence of nanostructures or surfaces in nanoscale vicinity of each other triggers nucleation on the surface itself, whereas the absence of such nanostructures induces nucleation at the triple-phase contact line in the system.[11,51,52] The presence of surface nanostructures accelerating ice nucleation was also observed by Zhang et al.[53] in MD simulations. Recently, Hussain and Haji-Akbari[30] used MD simulations to show that the presence of two adjacent surfaces at nanoscale distances induced much faster ice nucleation. Our work agrees with all such studies wherein the presence of two surfaces speeds up ice nucleation, as explained by our model.

■ CONCLUSIONS

We summarize and highlight four key findings of this study. First, nucleation kinetics can be changed by altering the surface chemistry at the three-phase contact line. We experimentally observed faster nucleation of a water column by changing the surface chemistry at the three-phase contact line of water−air−aluminum. Second, ice nucleation always originated on the aluminum−water−air/silicone oil/almond oil three-phase contact line, suggesting that it should be possible to control nucleation location. There were other three-phase lines in the system, namely the aluminum−water−methylene chloride line and three-phase lines associated with the hydrophobic walls of polystyrene. However, no ice nucleation was observed at those locations. Third, modeling shows the importance of considering the influence of two interfaces on ice nucleation at three-phase contact lines. Lastly, classical nucleation theory shows that there is competition between three-phase nucleation and heterogeneous nucleation, and the former is preferred in most scenarios. In summary, this study explores the influence of surface chemistry on ice nucleation and shows that the presence of extra interfaces can significantly accelerate nucleation.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.langmuir.1c02044.

Additional details on contact angle measurements, modeling, and uncertainty analysis (PDF)

Video S1: origin of ice nucleation on the three-phase contact line of water−aluminum−air (MP4)

Video S2: origin of ice nucleation on the three-phase contact line of water−aluminum−silicone oil (MP4)

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Notes

The authors declare no competing financial interest.

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