

Two-Dimensional Nucleation of Ice from Supercooled Water

L. H. Seeley and G. T. Seidler*

Department of Physics, University of Washington, Seattle, Washington 98195-1560

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We report the temperature dependent nucleation rates of ice from single water drops supporting aliphatic alcohol Langmuir films. Analysis in the context of a classical theory of heterogeneous nucleation suggests that the critical nucleus is essentially a monolayer, and that the rate-limiting steps in these nucleation processes are therefore not merely influenced by, but instead dictated by, the physics of the water-alcohol interface. Consequently, reduced dimensionality may be much more important in heterogeneous nucleation than has previously been believed.

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Homogeneous nucleation is the initial formation of a stable phase within a uniform, or homogeneous, metastable phase. More commonly, the initial embryo of the stable phase forms adjacent to a catalytic surface through heterogeneous nucleation. Heterogeneous nucleation of the solid phase from supercooled pure liquid or solution has wide-ranging consequences. In addition to its role in metallurgy [1], heterogeneous nucleation also occurs in some fabrications of nanoparticles [2], in calcium oxalate (kidney stone) crystallization in nephrons [3], and in viniculture [4]. Furthermore, the anomalously high glaciation of tropospheric clouds requires that heterogeneous nucleation plays a crucial role in cloud microphysics [5].

A key topic in the theory of nucleation is the geometry of the critical nucleus [6]. Standard nucleation theory has long assumed that the surface of a critical nucleus will have roughly constant curvature [7]. Surprisingly, recent crystallization studies of the protein apoferritin from solution give strong evidence that the critical nucleus is nearly planar in that macromolecular system [8]. We focus here on a very different nucleation phenomenon, the heterogeneous nucleation of a simple molecular crystal from its melt in the presence of significant epitaxial matching between the crystal structure of the solid phase and that of a nucleating surface. Specifically, we report measurements of the temperature dependent nucleation rate of ice from supercooled water samples supporting aliphatic alcohol Langmuir films. We use the classical theory of heterogeneous nucleation to extract thermodynamic parameters from the measured nucleation rates. From these parameters we conclude that both the effective free energy barrier and the molecular kinetics of nucleation are dominated by the physics at the interface. Our results give self-consistent evidence that the critical nucleus in this system is essentially two dimensional.

The ice nucleating properties of aliphatic alcohol Langmuir films were previously investigated by Gavish, Popovitz-Biro, and co-workers [9,10]. In these systems, the alcohol molecules self-assemble at the air-water interface to form a two-dimensional crystalline structure whose unit cell projected onto a plane parallel to the water-alcohol interface closely matches the crystalline structure

of hexagonal ice perpendicular to the c axis. It was observed that the mean freezing temperature, T_f^* , increases with the number of carbons in the alcohol molecules, albeit with a dependence on the parity (even or odd) of the alcohol's chain length. This correlates well with the measured dependence on the chain length of the structural correlation length of the 2D crystalline regions of the Langmuir films [11], and was taken as evidence that epitaxy is important in the nucleation mechanism. The parity dependence is attributed to the orientation of the alcohol headgroup with respect to the molecular tilt angle.

Our apparatus measures the distribution of freezing temperatures for a single water sample on repeated thermal cycling [12–14] and is described in detail in Ref. [14]. As we describe later in this paper, the distribution of freezing temperatures can be easily normalized to provide the temperature dependent nucleation rate. This technique avoids sample-to-sample variations, thus allowing for an accurate characterization of proposed nucleation agents. Sample preparation is carried out under a laminar flow hood. First, a single 10 μL drop of deionized ($\rho \sim 18 \text{ M}\Omega \text{ cm}$) and filtered (pore size 0.2 μm) water is placed at the center of a silanized borosilicate glass substrate. Next, a 1 μL drop of a $2.5 \times 10^{-4} \text{ M}$ solution in chloroform of the alcohol to be tested is added to the water sample. The amount of alcohol reproduces the experimental parameters used in Ref. [10]. If distributed uniformly on the surface, this alcohol content would compose 1.5 monolayers. Finally, after allowing 10 min for evaporation of the chloroform, the sample space is sealed and loaded into our apparatus. We report here the results for water drops supporting Langmuir films of pentacosanol ($\text{C}_{25}\text{H}_{52}\text{O}$, 99%), hexacosanol ($\text{C}_{26}\text{H}_{54}\text{O}$, 99%), heptacosanol ($\text{C}_{27}\text{H}_{56}\text{O}$, 99%), or octacosanol ($\text{C}_{28}\text{H}_{58}\text{O}$, 98%); these samples will be referred to as C25, C26, C27, and C28, respectively.

A single data collection cycle begins with the stabilization of the sample at a temperature of 5 $^\circ\text{C}$. The sample is then cooled to $-20 \text{ }^\circ\text{C}$ at a linear rate of 0.05 $^\circ\text{C}/\text{s}$. During this cooling period the sample freezes and the temperature at the onset of freezing is identified via the latent heat pulse. The sample is then heated to 5 $^\circ\text{C}$ and the cycle is repeated. We present freezing temperature histories for

more than 500 thermal cycles for each of C25 (○) and C26 (●) in the top panel of Fig. 1, and for each of C27 (□) and C28 (■) in the bottom panel. We have previously found that water on a silanized borosilicate glass substrate in the absence of a Langmuir film will not nucleate ice at temperatures above -20°C [12]. Hence neither heterogeneous nucleation on the glass substrate nor homogeneous nucleation ($T_f^* < -30^\circ\text{C}$ [15]) contributes to the nucleation rates for these samples.

There is a qualitative difference between the freezing temperature histories for samples supporting odd- versus even-parity alcohol films. For C25 and C27 the mean nucleation temperature decreases relatively rapidly for the first few hundred data points, then the rate of decrease slows and we observe a period of approximately linear decrease of the mean nucleation temperature with the iteration number. In order to obtain a stationary distribution of freezing temperatures we perform a linear correction to the final 450 freezing events for each of the four freezing temperature histories. This correction leaves the mean freezing temperatures unchanged, but compensates for total drifts of -1.22 , 0.10 , -0.95 , and 0.07°C for C25, C26, C27, and C28, respectively. The positive drifts recorded for C26 and C28 are not statistically significant. The larger, negative drifts for C25 and C27 are statistically significant and we speculate that the origin of these drifts may be linked to the slow evaporation or solution of alcohol molecules, as is often observed in Langmuir monolayers [16]. Following the linear correction, however, there is statistical agreement between the first one-third and last one-third of each of the four data sets. This agreement demonstrates

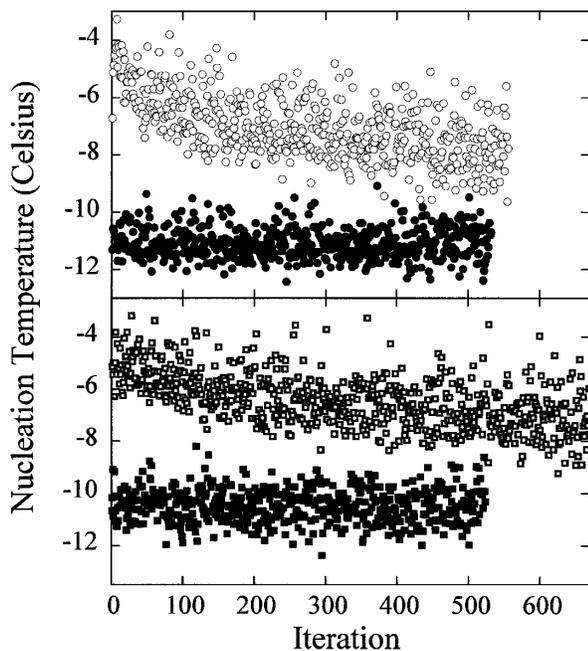


FIG. 1. The nucleation temperature as a function of iteration number for a $10\ \mu\text{L}$ water sample containing 2.5×10^{-10} mol of (○) pentacosanol ($\text{C}_{25}\text{H}_{52}\text{O}$), (●) hexacosanol ($\text{C}_{26}\text{H}_{54}\text{O}$), (□) heptacosanol ($\text{C}_{27}\text{H}_{56}\text{O}$), and (■) octacosanol ($\text{C}_{28}\text{H}_{58}\text{O}$).

that the distribution of nucleation temperatures about the mean remains stable even when the mean nucleation temperature is weakly time dependent.

Several models have been proposed to describe the way in which a planar substrate acts as an agent for heterogeneous nucleation [17–19]. The simplest of these models describes a growing ice nucleus as a spherical cap [17] with a constant, well-defined contact angle, θ_{SL} , and a sharp interface with a constant interfacial energy, γ_{SL} . The contact angle depends on the relative interfacial energies involved via $\cos\theta_{SL} = (\gamma_{UL} - \gamma_{US})/\gamma_{SL}$, where γ_{UL} , γ_{US} , and γ_{SL} are the substrate-liquid, substrate-solid, and solid-liquid interfacial energies, respectively. It is useful to define the critical height, $h^* = R^*(1 - \cos\theta_{SL})$, of the spherical cap ice nucleus, where $R^* = 2\gamma_{SL}v_iT_m/q(T_m - T)$. The temperature dependent nucleation rate is [17,19]

$$R(T) = J_0 \exp\left(\frac{-\Delta G^*(T)}{kT}\right) = J_0 \exp\left(\frac{-\Gamma}{T(T_m - T)^2}\right), \quad (1)$$

where

$$\Gamma = \frac{16\pi f(\theta_{SL})\gamma_{SL}^3 v_i^2 T_m^2}{3q^2 k}, \quad (2)$$

and where J_0 is the prefactor (discussed below), ΔG^* is the free energy excess of a critical nucleus, $\gamma_{SL} = 29\ \text{ergs cm}^{-2}$ is the solid-liquid interfacial energy [20], $v_i = 1.09\ \text{cm}^3\ \text{g}^{-1}$ is the specific volume of the ice phase, $T_m = 273.15\ \text{K}$ is the melting temperature, $q = 33.3\ \text{ergs g}^{-1}$ is the latent heat of fusion, k is Boltzmann's constant, and

$$f(\theta_{SL}) = (2 + \cos\theta_{SL})(1 - \cos\theta_{SL})^2/4 \quad (3)$$

is the appropriate geometric factor for the spherical cap model as described in detail elsewhere [17,19]. No general agreement exists for the exact temperature and curvature dependences of γ_{SL} and q [21]. Here, we will use the equilibrium values at bulk coexistence [20,22]. While a full discussion of this topic is beyond the scope of this Letter, we note that incorporating the proposed temperature dependence from a recent review by Pruppacher [22] will only strengthen the conclusions described here. In the standard approach, J_0 for condensed systems is proportional to the number of molecules in contact with the substrate, the surface area of a critical nucleus, the molecular vibration frequency, and a Boltzmann factor for the activation barrier for the addition of a single molecule to a critical nucleus [7]. While J_0 is certainly temperature dependent, this temperature dependence is negligible compared to that from the Boltzmann factor for ΔG^* in Eq. (1).

For each data set we bin the freezing temperature distribution into 15 temperature bins of widths $\{\Delta T_i\}$, centered on temperatures $\{T_i\}$, and containing $\{n_i\}$ freezing events. The nucleation rate is then

$$R(T_i) = rn_i/\Delta T_i \left(\frac{n_i}{2} + \sum_{j>i} n_j \right), \quad (4)$$

where r is the cooling rate. The resulting $R(T_i)$ are shown for each of the four samples in Fig. 2. The errors are based on binomial statistics. The solid curves are linear least squares fits to

$$\log_{10}[R(T)] = \log_{10}(J_0) - \frac{\Gamma}{2.303T(T_m - T)^2} \quad (5)$$

in the two parameters, $\log_{10}(J_0)$ and Γ . We present the best-fit values and uncertainties for $\log_{10}(J_0)$ and Γ in Table I. Also given in Table I are $\log_{10}(J_0)$ and Γ for homogeneous nucleation, where Γ is given by Eq. (2) with $f(\theta_{SL}) = 1$ and where $\log_{10}(J_0)$ extracted from homogeneous nucleation results [15]. Finally, we also present $\log_{10}(J_0)$ and Γ for the control sample, a water drop on a silanized borosilicate glass substrate without any Langmuir film [12]. There are clear, systematic trends in both parameters as one proceeds from homogeneous nucleation to heterogeneous nucleation in the absence of epitaxy and to heterogeneous nucleation in the presence of epitaxy.

The nucleation prefactor, J_0 , for each of C25 to C28 is more than 30 orders of magnitude smaller than that for homogeneous nucleation. We propose that this disparity can be largely accounted for by three factors, each of which suggests the importance of reduced dimensionality in the nucleation event. First, the homogeneous nucleation prefactor depends linearly on the total number of molecules in the metastable phase. In contrast, the heterogeneous nucleation prefactor depends linearly on only the number of

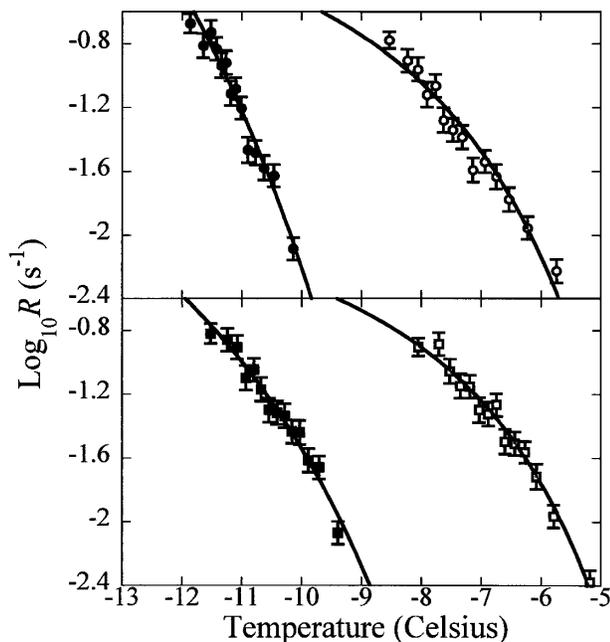


FIG. 2. The freezing rate as a function of temperature for a 10 μL water sample containing 2.5×10^{-10} mol of (○) pentacosanol ($\text{C}_{25}\text{H}_{52}\text{O}$), (●) hexacosanol ($\text{C}_{26}\text{H}_{54}\text{O}$), (□) heptacosanol ($\text{C}_{27}\text{H}_{56}\text{O}$), and (■) octacosanol ($\text{C}_{28}\text{H}_{58}\text{O}$). As described in the text the solid lines represent the best-fit curves of Eq. (5) to the experimental data.

molecules in contact with the substrate. For our sample geometry, this distinction explains a reduction by a factor of 10^{-7} in J_0 . Second, J_0 depends linearly on the rate of molecular kinetics at the critical nucleus boundary [7], and these rates should be roughly proportional to the diffusion constant of water molecules. Molecular dipole forces between the Langmuir film and the interfacial water molecules will in general hinder diffusion in the direction normal to the water/alcohol interface. Assuming that the molecular diffusion processes responsible for the growth of a critical nucleus are largely confined to the interfacial plane, we can use measured surface diffusion values for water on a representative amorphous hydrophilic substrate—porous silica [23]—to estimate an additional factor of 10^{-15} reduction in J_0 . Third, interfacial ordering is expected at the interface of a disordered phase with a commensurate substrate [24]. Surface diffraction measurements have demonstrated the existence of differing degrees of structural correlation in the first few monolayers of water adjacent to epitaxial substrates such as mica [25] or aliphatic alcohol Langmuir films [11]. Consequently, the rate-limiting step in the nucleation process likely involves the coarsening of weakly ordered two-dimensional ice domains. Since coarsening is a strongly collective process, a further decrease in the effective single molecule diffusion constant and, consequently, J_0 is quite reasonable.

As a starting point for our analysis of Γ , we follow the usual assumption in classical nucleation theory that the various thermodynamic quantities on the right-hand side of Eq. (2) are the same for heterogeneous and homogeneous nucleation so that any changes in Γ are due to changes in the shape of the critical nucleus, i.e., due to changes in $f(\theta_{SL})$ away from $f(\theta_{SL}) = 1$ for homogeneous nucleation. The small geometric term which appears in theoretical expressions for J_0 [19] is ignored here. We present in Table I the resulting values of $f(\theta_{SL})$, θ_{SL} , R^* , and h^* . Most importantly, note that h^* ranges between 4 and 7 \AA , whereas by comparison the spacing between molecular bilayers along the c axis in hexagonal ice is 3.65 \AA . This is strong qualitative evidence for the existence of a two-dimensional rate-limiting step, and is consistent with previous assertions that the spherical cap model must break down for contact angles less than 30° [26]. The interpretation is necessarily qualitative because the thermodynamic quantities on the right-hand side of Eq. (2) are certainly not the same for the first monolayer against the substrate as for the homogeneous case. However, the result for h^* still serves as a reliable bound on the extent of the critical nucleus outside of the range of strong interaction between the water and the Langmuir films.

Before concluding, we briefly compare our results with the only previous study of ice nucleation kinetics for water supporting Langmuir monolayers. Contrary to our work, that study [27] used a semiquantitative comparison of nucleation in the presence and absence of an alcohol monolayer to conclude that the alcohol monolayer did not significantly lower Γ but instead increased J_0 . However,

TABLE I. Nucleation parameters extracted from the best-fit curves shown in Fig. 2 for the following samples: C25 pentacosanol ($C_{25}H_{52}O$), C26 hexacosanol ($C_{26}H_{54}O$), C27 heptacosanol ($C_{27}H_{56}O$), C28 octacosanol ($C_{28}H_{58}O$), silanized borosilicate glass control, as well as approximate values for homogeneous nucleation. Included in this table are the best-fit values and errors of the prefactor, J_0 , and the energy barrier scaling factor, Γ , as well as the mean nucleation temperature, T_f^* , the heterogeneous scaling factor, $f(\theta_{SL})$, the contact angle, θ_{SL} , the critical radius of curvature, R^* , and the height of the critical nucleus, h^* .

Sample	C25	C26	C27	C28	Control	Homogeneous
$\text{Log}_{10}J_0$	0.4	3.4	0.2	1.7	18.3	35
$\sigma_{\text{Log}_{10}J_0}$	0.3	0.8	0.3	0.6	3.0	—
Γ (K^3)	5.6×10^4	3.4×10^5	4.4×10^4	1.9×10^5	5.6×10^6	2.4×10^7
σ_Γ (K^3)	9.0×10^3	5.7×10^4	7.3×10^3	3.9×10^4	1.1×10^6	—
χ_ν^2, ν	1.63, 12	1.24, 12	0.61, 12	0.71, 12	0.82, 13	—
T_f^* ($^\circ\text{C}$)	-7.3	-11.1	-6.7	-10.5	-22.8	-35.0
$f(\theta_{SL})$	0.0023	0.014	0.0018	0.0081	0.233	1.0
θ_{SL}	19°	31°	18°	28°	68°	180°
R^* (\AA)	79	47	83	50	23	15
h^* (\AA)	4.3	6.7	4.1	5.8	14	—

we believe that the results of that study are inconclusive because the control sample had an appreciable nucleation rate at temperatures above -8°C , requiring strong heterogeneous nucleation by unknown contaminants.

In conclusion, we report the temperature dependent ice nucleation rates for single water drops supporting aliphatic alcohol Langmuir films. Classical analysis requires an anomalously low prefactor and a monolayer-scale thickness for the nucleation geometry. These results self-consistently imply that nucleation in this system is dominated by the physics at the interface. Consequently, surface phenomena in general and epitaxy in particular may play a much stronger and more complex role in heterogeneous nucleation than has previously been believed. We hope that these results will motivate theoretical interest in heterogeneous nucleation at epitaxial substrates. For example, this problem may be addressable by recent advances in nucleation simulations [28].

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*Author to whom correspondence should be addressed.

Electronic address: seidler@phys.washington.edu

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