

On the Physics of Ice Nucleation and Growth in Nanoscale

By

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DEDICATION

This dissertation is dedicated to my family for their unyielding love, support, and encouragement.

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I would like to thank many people who helped me to accomplish this research. Dr. Ghasemi my advisor. I am thankful to my lab mates who were a big help during my research. I would like to thank my parents, brothers, and sister who supported me during my education. I also place on record, my sense of gratitude to all who, directly or indirectly, have lent their helping hand in this venture.

ABSTRACT

Fundamental understanding of ice formation on a surface, i.e. heterogeneous formation, is critical to suppress ice accretion on the surfaces. Ice formation on a surface includes two steps of ice nucleation and further ice growth. As water droplet is placed on a sub-zero surface, with a time delay, ice nucleolus form on the surface. Ice nucleation is governed by thermodynamics of ice-water-surface system and it is described by Gibbs energy barrier, ΔG^* , which strongly depends on surface factor, $f(m, x)$. Surface factor is a function of surface geometry, i.e. nano or micro, as well as surface free energy and through manipulating these parameters, ice nucleation can be controlled. After ice nucleation, ice further grows in a process which is controlled through heat transfer. Ice growth could be described by two extreme scenarios. In the first one, ice formation occurs with no airflow around where heat transfer through the substrate determines ice growth rate. In the second scenario, ice growth occurs in an environment with external airflow in which ice growth rate is controlled mainly by convective heat transfer.

Water-ice transformation of few nm nanodroplets plays a critical role in nature including climate change, microphysics of clouds, survival mechanism of animals in cold environments, and a broad spectrum of technologies. In most of these scenarios, water-ice transformation occurs in a heterogeneous mode where nanodroplets are in contact with another medium. Despite computational efforts, experimental probing of this transformation at few nm scales remains unresolved.

Here, we report direct probing of water-ice transformation down to 2 nm scale and the length-scale dependence of transformation temperature through two independent metrologies. The transformation temperature shows a sharp length dependence in nanodroplets smaller than 10 nm and for 2 nm droplet, this temperature falls below the homogenous bulk nucleation limit. The formed ice phase even down to 2 nm is I_h (hexagonal). Contrary to nucleation on curved stiff solid surfaces, ice formation on soft interfaces (omnipresent in nature) could deform the interface leading to suppression of ice nucleation. Considering the interfacial deformation, the findings are in good agreement with predictions of classical nucleation theory. This understanding contributes to a greater knowledge of natural phenomena and rational design of anti-icing systems for aviation, wind energy and infrastructures.

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CHAPTER 1

I. INTRODUCTION

1.1. Background and Motivation

Anti-icing surfaces play a critical role in a broad range of systems including infrastructures and energy systems. At cold climate, the absence of these surfaces can lead to interruption in operation or catastrophic events in power systems (e.g. power towers, power stations, and power lines), transportation systems (e.g. aviation industry and ocean-going vessels) and energy systems (domestic and large power plants), see Fig. I-1. According to Lawrence Berkeley Laboratory, ice storms account for 10% of power transmission outages in US. The financial loss for industries is approximated \$3-5 billion annually. In addition to financial losses, around 3 million people in US every winter suffer from power losses caused by ice storms.

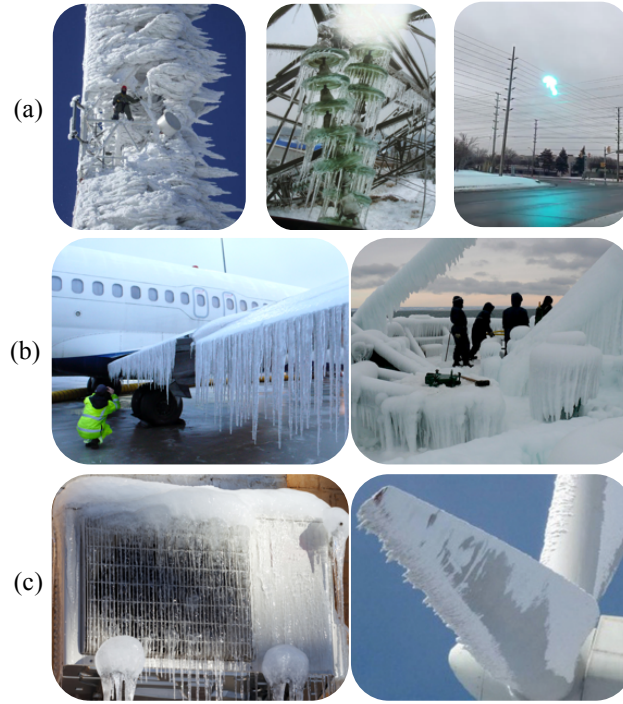


Figure I-1: The importance of icephobic surfaces in a broad spectrum of systems is shown. (a) power systems (b) transportation systems and (c) energy systems.

The main figures of merit for icephobic surfaces are low freezing temperature, low ice accretion rate, and low ice adhesion. Furthermore, long-term durability of these surfaces should also be considered as another critical factor. A range of surfaces (e.g. superhydrophobic, liquid-infused and hydrated surfaces) are developed to meet these criteria. However, the developed surfaces have either shown incremental improvements in performance or have not satisfied all the required figures of merit. A rational strategy for development of disruptive icephobic surfaces requires a fundamental understanding of physics of ice formation, ice growth and adhesion at the solid-ice interface and the dependence of these physics on the length scale. Thermodynamics of phase change at the solid-water interface governs the freezing temperature, heat transfer governs the ice growth, and the interfacial mechanics govern the ice adhesion at the interface. A

comprehensive body of knowledge on these physics open a path for development of robust icephobic surfaces.

1.2. Ice Nucleation

As a water droplet touches a subzero surface, it starts to freeze and adhere to the surface. Transformation of a water droplet to ice occurs through a two-step process: (1) Ice nucleation and (2) Ice growth.

Ice nucleation temperature, T_N , is defined as the nucleation temperature of a sessile water droplet which is placed on a sub-zero surface where the total system of water droplet, surface and surrounding environment is cooled down in a quasi-equilibrium condition [1]. One could measure ice nucleation temperature, T_N , through an isothermal chamber filled with inert gas, e.g. N_2 . The temperature of this chamber is set to 0°C and a surface is placed in the chamber. At this initial temperature, $30\ \mu\text{L}$ of distilled water is placed on the surface. Temperature of the substrate is probed with a thermometer to assure isothermal condition. The chamber is cooled down at a rate of $1^\circ\text{C}/\text{min}$ and ice nucleation of the droplet is monitored with a high-speed camera during the experiment. Ice nucleation temperature is obtained by recording the temperature at which sudden transparency change of the droplet occurs. T_N is reported as the mean of T_N measured during a set of more than 10 experiments [1, 2]. T_N is a function of Gibbs energy barrier for heterogeneous ice nucleation which is defined as [3]

$$\Delta G^* = \frac{16\pi\gamma_{fw}^3}{3\Delta G_v^2} f(m, x), \quad (1)$$

in which γ_{IW} is interfacial tension of water-ice nucleolus, ΔG_v is the volumetric free energy of phase-change and surface factor, $f(m, x)$, is the parameter that affects Gibbs energy barrier for heterogeneous ice nucleation, varies between 0 and 1, and its value is 1 for homogeneous nucleation. An ice nucleolus is a particle which acts as the nucleus for the formation of ice. The initial embryos of ice are formed from a supercooled mother phase, i.e. water droplet, that transform to ice nucleolus when reach to a critical size, r_c . In this section the focus is mainly on $f(m, x)$ which is governed by the interfacial free energy and geometry of the interfaces. In $f(m, x)$, m is a function of interfacial free energies and is defined as

$$m = \cos \theta = \frac{\gamma_{SW} - \gamma_{SI}}{\gamma_{IW}}, \quad (2)$$

where γ_{SW} denotes the solid-water interfacial free energy, γ_{SI} denotes the solid-ice interfacial free energy and γ_{IW} denotes the water-ice interfacial free energy. These interfaces are illustrated in Figure I-2.

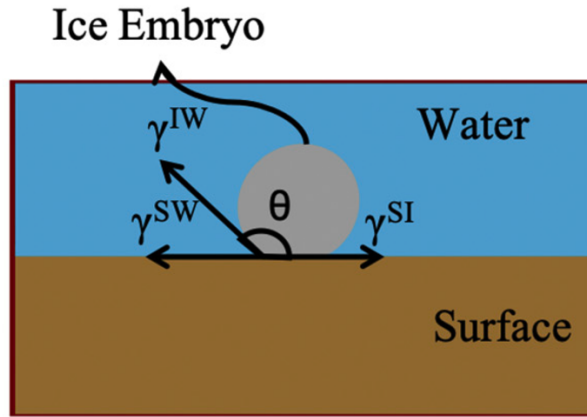


Figure I-2: Ice nucleolus on a subzero substrate and the involved interfaces are shown. The value of m is equal to $\cos \theta$ [5].

Also, x which is a function of surface geometry is defined as

$$x = \frac{R}{r_c}, \quad (3)$$

where R is radius of features at the surface and r_c is the critical nucleolus radius. r_c is defined in Eq. (4) and its typical value could vary from 1.53 to 4.47 nm for temperature range of -30 to -10°C [3, 4]:

$$r_c = \frac{2\gamma_{lw}}{\Delta G_{f,v}}, \quad (4)$$

$$\Delta G_{f,v} = \Delta H_{f,v} \frac{T_m - T}{T_m}, \quad (5)$$

$$\text{and } \gamma_{lw} = 23.24 \left(\frac{T}{235.8} \right)^{0.35}. \quad (6)$$

As discussed, $f(m, x)$ equal to 1 indicates homogeneous nucleation limit and $f(m, x)$ equal to 0 indicates ice nucleation without sub-cooling. If $m = 1$ and $x > 1$, f approaches zero in which case there is no sub-cooling. In order to achieve $m = 1$, $\gamma_{sw} \geq \gamma_{sl} + \gamma_{wl}$ should be satisfied. If $m = 1$ and $x < 1$, then $0 < f < 1$. In this condition, suppression of ice nucleation which is a result of nano-scale confinement occurs. $f(m, x)$ is analytically derived for two types of surfaces. For convex surfaces, $f(m, x)$ is defined as Eq. (7) and plotted in Figure I-3, as

$$f(m, x) = \frac{1}{2} \left\{ 1 + \left(\frac{1-mx}{g_v} \right)^3 + x^3 \left[2 - 3 \left(\frac{x-m}{g_v} \right) + \left(\frac{x-m}{g_v} \right)^3 \right] + 3mx^2 \left(\frac{x-m}{g_v} - 1 \right) \right\} \quad (7)$$

$$\text{and } g_v = (1 + x^2 - 2mx)^{1/2}. \quad (8)$$

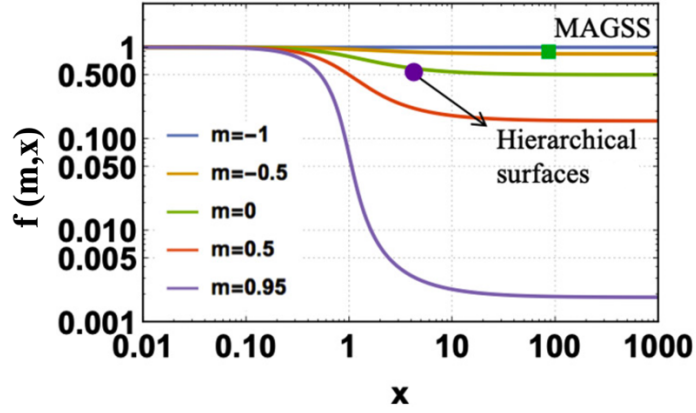


Figure I-3: The surface factor plotted verses different values of x and m for convex surfaces.

Also, for concave surfaces $f(m, x)$ is defined by Eq. (9) and plotted in Figure I-4, as

$$f(m, x) = \frac{1}{2} \left\{ 1 - \left(\frac{1+mx}{g_c} \right)^3 - x^3 \left[2 - 3 \left(\frac{x+m}{g_c} \right) + \left(\frac{x+m}{g_c} \right)^3 \right] + 3mx^2 \left(\frac{x+m}{g_c} - 1 \right) \right\} \quad (9)$$

$$\text{and } g_c = (1 + x^2 + 2mx)^{1/2}. \quad (10)$$

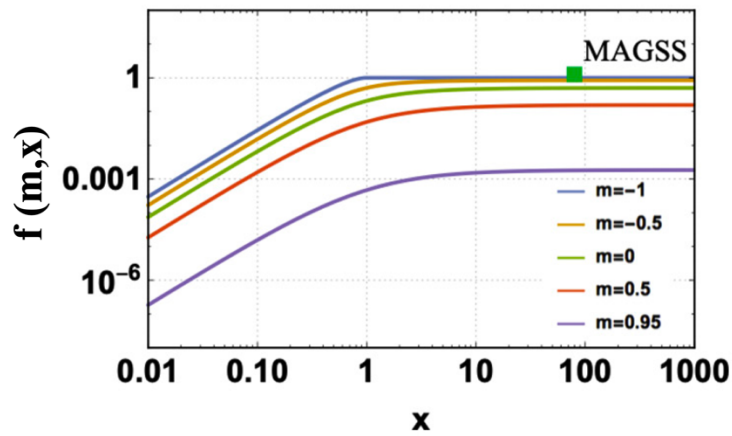


Figure I-4: The surface factor plotted verses different values of x and m for concave surfaces.

For x values larger than 10, $f(m, x)$ becomes independent of x and only depends on m in contrast for x values less than 10, e.g. when R is the order of r_c , $f(m, x)$ depends on x as well [5].

Ice nucleation on a surface depends on the roughness and structure of the surface, i.e. nano or micro surfaces. For example, for $x < 10$, ice nucleation on the surface depends on the roughness and structure of the surface, while for $x > 10$, surface structure has nothing to do with ice nucleation. In this case, ice nucleation only depends on the interfacial free energies, m . As an example, nano-grooves on a surface can suppress ice nucleation [6]. Taking all the aforementioned arguments into account, it stands to reason that tuning surface free energy, m parameter, through different mechanisms is a way to increase ice nucleation energy barrier, especially where the geometry of surface does not affect ice nucleation energy barrier.

On the effect of surface free energy on ice nucleation, according to Eq. (6), γ_{IW} only depends on temperature. Therefore, difference of solid-water surface free energy and solid-ice surface free energy, $(\gamma_{SW} - \gamma_{SI})$ is a determining factor in the value of m and as a result in ice nucleation phenomenon (see Eq. (2)). One of the widely used approaches in the literature is to reduce solid-air interfacial free energy, γ_{sa} . For example, adding functional groups which have high bond dissociation energies, e.g. $-\text{CF}_3$ and $-\text{CHF}_2$, to a surface leads to the reduction of surface free energy. The lowest possible γ_{sa} for a surface is achieved by a monolayer of $-\text{CF}_3$ groups on a surface and γ_{sa} for such surface is in the range of 6-10 mJ/m² [7, 8]. Generally, addition of the materials which contain C-F bonds to a surface reduces its surface free energy, γ_{sa} . For instance, grafting a surface with a monolayer of perfluorodecyltrichlorosilane (FTDS) reduced γ_{sa} and m value of -0.17 is achieved in this

case [1]. As another example for implementing this approach, Irajizad and coworkers [2, 9, 10] used the concept of magnetic liquid surfaces and introduced magnetic slippery surfaces (MAGSS) in which a selective ferrofluid is introduced on the surface to tune $(\gamma_{SW} - \gamma_{SI})$. On such surface, a liquid-liquid interface is formed by a volumetric magnetic force. These MAGSS show low value of m , -0.95, which results in the value of 0.98 for $f(m, x)$. This condition is pretty close to homogeneous ice nucleation limit, i.e. $f(m, x) = 1$. Thus, manipulating $f(m, x)$ through the modification of surface structure and surface free energy results in an increase in energy barrier of ice nucleation and, as a result, reduction of ice nucleation temperature [5]. The role of $f(m, x)$ in ice nucleation is illustrated in Figure I-5. In the experiment shown in this figure, different surfaces are coated on a cold tube with a temperature of -30°C . The tube is exposed to water droplets and due to high value of ΔG^* , i.e. high $f(m, x)$, MAGSS showed lowest ice nucleation among other surfaces.

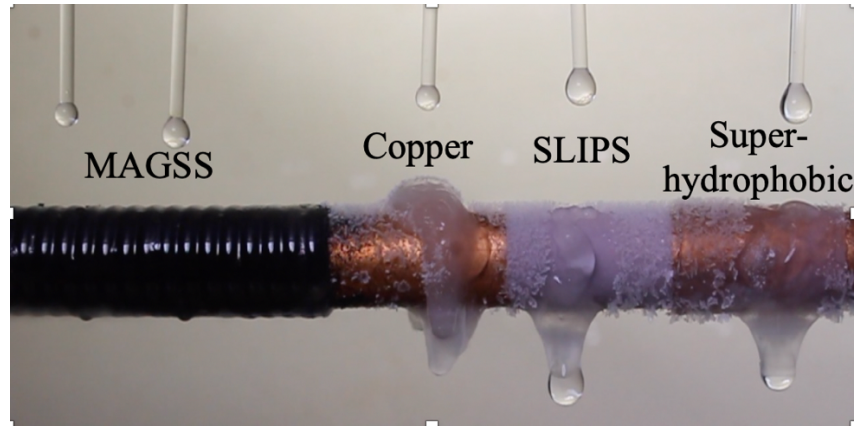


Figure I-5: Different coatings are exposed to water droplets which shows the role of $f(m, x)$ in ice nucleation[5].

Ice nucleation rate, $J(T)$, which is reciprocal of ice nucleation delay time, τ_{av} , is another metric of ice nucleation. τ_{av} is defined as the average time required for a supercooled droplet, in equilibrium with its surrounding environment, to nucleate ice phase. In order to measure τ_{av} , icephobic coating should be initially placed in a cold chamber. Chamber temperature is set to sub-zero temperature and after reaching equilibrium, a water droplet is placed on the coating. At a given temperature, the time required for ice nucleation to occur is recorded and the average time during a set of more than 10 experiments is reported as τ_{av} . Nucleation rate is defined as [3, 11, 12]

$$J(T) = \frac{1}{\tau_{av}} = K \exp\left(-\frac{\Delta G^*}{k_B T}\right), \quad (11)$$

where k_B is Boltzmann constant and K is kinetic constant which is defined as [11]

$$K = Z\beta N, \quad (12)$$

in which N denotes number of atomic nucleation sites per unit volume, β denotes the rate of addition of atoms or molecules to the critical nucleus and Z denotes Zeldovich non-equilibrium factor.

Ice nucleation delay time is an important metric in ice nucleation and depends on ΔG^* , as is shown in Eq. (11), which can be tuned by modification of surface roughness and surface free energy. The other approach to increase τ_{av} is to increase hydrophobicity of surfaces. In fact, surfaces with higher water contact angle show higher ice nucleation delay times. Basically, by increasing hydrophobicity, m value is decreased [13]. Many studies conducted on hydrophobic and superhydrophobic surfaces indicate that τ_{av} value for such surfaces, especially for superhydrophobic surfaces, is high. For example, Tourkine et

al.[14] grafted fluorinated thiols on a rough copper surface. By doing so, they made a superhydrophobic surface with increased ice nucleation delay time [14]. As another example, Alizadeh et al. [15] developed a superhydrophobic surface by grafting tridecafluoro-1,1,2,2-tetrahydrooctyl-trichlorosilane on a nanostructured silicone surface. By doing so, they boosted ice nucleation delay time [15].

We can rewrite $J(T)$ in terms of chemical potential, μ , as

$$J(T) = K \exp\left(\frac{-8\pi\gamma_{lw}^3}{3k_b T (\rho\Delta\mu)^2}\right), \quad (13)$$

where ρ is the molar density of liquid and $\Delta\mu$ is the chemical potential difference between ice and liquid phase. $\Delta\mu$ depends on temperature and pressure of the system which can be defined in an isothermal condition as

$$\Delta\mu(T, P) = \Delta\mu(T, P_{atm}) + (P_L - P_{atm})(v_w - v_i), \quad (14)$$

in which v_w is specific volume of liquid and v_i is specific volume of ice. P_{atm} is atmospheric pressure and P_L is the liquid pressure which is obtained by Laplace equation (Eq. (15)). Note that this equation is valid down to few nm scale [16-18].

$$P_L - P_{atm} = \frac{2\gamma_{Lv}}{r}, \quad (15)$$

where γ_{Lv} denotes liquid-vapor surface tension and r is the average radius of curvature. In fact, the pressure can have either positive or negative effect on ice nucleation. If the $(v_w - v_i)$ term, which is the slope of solid-liquid phase change line, is positive, pressure increases ice nucleation rate and if the slope is negative, e.g. for water, pressure reduces ice nucleation rate.

The second term on the R.H.S in Eq. (14) is negligible in micro-scale due to high radius of curvature, i.e. the differential between atmospheric and liquid pressure is close to zero (see Eq. (15)). In contrast, the second term is significant in nano-scale, due to the low radius of curvature. For example, the limit of ice nucleation of water, i.e. negative slope of solid-liquid phase change in macro-scale, -38 to -40°C, shifted to lower temperatures at nano-scale. Thus, nano-confined geometry can suppress ice nucleation [19].

1.3 Ice Growth

Although ice nucleation is governed by the thermodynamics of ice-water-surface system, further ice growth is controlled by heat transfer. As ice nucleation occurs, release of freezing enthalpy leads to the temperature increase at water-ice interface. In fact, heat transfer at water-ice interface controls ice growth rate. Here, in order to obtain a theory of ice growth, it is assumed that water-ice interface is flat and the curvature at this interface is ignored. Considering this assumption, Gibbs-Thompson undercooling effect becomes negligible. Gibbs-Thomson undercooling effect is the effect of ice-water interface curvature on the temperature of freezing front. This effect causes the temperature of freezing front to be different from equilibrium melting temperature [20, 21]. We consider that the temperature of freezing front stays at equilibrium temperature of T_f . In case one considers the undercooling effect (ΔT), the equilibrium temperature at water-ice interface should be replaced by $T_f - \Delta T$. Also, airflow around the droplet is a parameter that should be taken into account. To consider airflow effect, two extreme cases of ice growth are defined. The first one is a droplet in an environment without airflow and the second one is a droplet in an environment with airflow surrounding the droplet.

1.3.1. Scenario I: Droplet in an environment without airflow

In this scenario, tip singularity formation is a common phenomenon that occurs during ice growth. In this phenomenon, when a droplet is placed on a cold plate, it freezes and turns to an ice drop with a pointy tip (Figure I-6). Tip singularity formation is mainly due to the water expansion after freezing and is governed by the quasi-steady heat transfer at the later stages of ice formation. Marín et al. [21] stated that the freezing front is convex at earlier stages of ice growth and at the final stages it becomes concave. They also reported that the freezing front is almost perpendicular to the ice-air interface, i.e. $\gamma = \phi + \theta \approx 90^\circ$ (see Figure I-6), due to the fact that latent heat cannot transfer across the solid-air interface due to low thermal conductivity of air. The shape of solid-liquid front is obtained through the assumption of constant front temperature at the equilibrium melting temperature, T_f , i.e. neglecting Gibbs-Thomson effect.

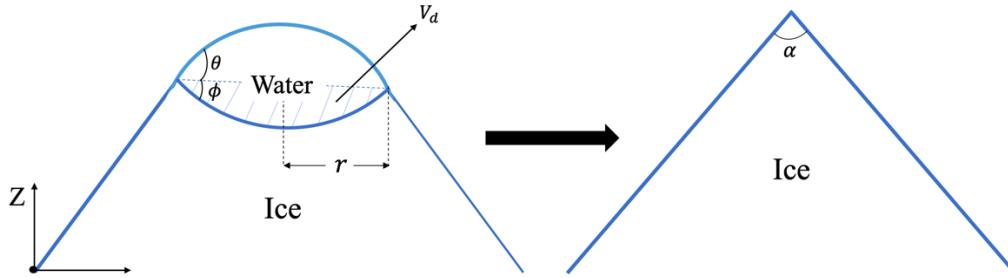


Figure I-6: Geometry of droplet at later stages of ice formation and after complete ice formation [21].

For obtaining geometric theory for tip formation, the first step is to write mass conservation with respect to z , as temporal dynamics is not significant, as

$$\frac{d}{dz}(V_l + \nu V_s) = 0, \quad (16)$$

where V_l and V_s denote liquid and solid volumes, respectively, ν is density ratio, and z is height of trijunction (Figure I-6).

The liquid at the top of freezing front is divided into two parts. The upper part is like a spherical cap with angle of θ and the lower part has a volume of V_d . Thus,

$$V_l = r^3 f(\theta) + V_d \quad (17)$$

$$\text{and } V_s = -V_d + \int_0^z \pi r(z')^2 dz'. \quad (18)$$

Considering the geometries of upper and lower parts of the liquid, one finds

$$f(\theta) = \frac{\pi}{3} \left(\frac{2-3\cos\theta+\cos^3\theta}{\sin^3\theta} \right) \quad (19)$$

$$\text{and } V_d = r^3 f(\phi) = r^3 f(\gamma - \theta). \quad (20)$$

Based on Eqs. (16–20) and the fact that $\tan\theta = -\frac{dz}{dr}$, $r(z)$ can be obtained and a sharp tip is formed when $r \rightarrow 0$. Thus, at this singularity point, one can find θ as

$$f(\gamma - \theta) + f(\theta) = \nu \left[f(\gamma - \theta) + \frac{\pi}{3} \tan\theta \right]. \quad (21)$$

Eq. (21) can give volumes of liquid part before and after freezing. If this equation is multiplied by r^3 , the left side gives the volume of liquid. Also, the right side gives the volume of this liquid when it is frozen where expansion factor is considered. According to Eq. (21), we have $\alpha = \pi - 2\theta$ regardless of ν value and as mentioned before $\gamma \approx 90^\circ$. Therefore, from Eq. (21), a constant value of $\alpha = 131^\circ$ for the tip angle is obtained which is in a great harmony with the experimental results [21].

Now, we determine the growth rate of ice in scenario one (Figure I-7). In this case, as the thermal conductivity of air is low, convective heat transfer is low and the generated

enthalpy of phase-change is transferred through the ice by thermal conduction mechanism and subsequently, through the substrate, $\vec{q}^s$. Isothermal condition is assumed for the liquid at the ice-water interface and heat flux through the liquid, $\vec{q}^l$, is negligible.

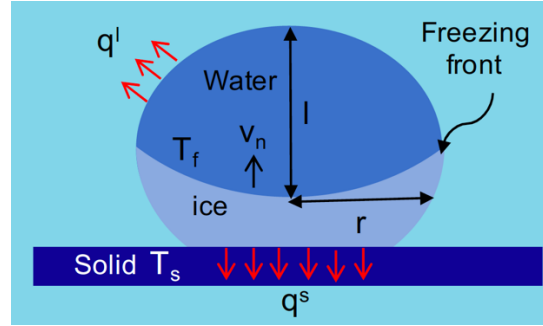


Figure I-7: Ice growth on a sub-zero substrate when the droplet is in an environment without airflow. In this case, ice growth is controlled mainly by heat transfer through the substrate [5].

$\vec{v}_n$, the velocity of freezing front is defined as

$$v_n \sim -\frac{dl}{dt} = -\frac{dr}{dt} \frac{(1-\cos \theta)}{\sin \theta}, \quad (22)$$

where l denotes temporal height and r denotes the radius of freezing front. The heat transfer away from the interface to the substrate, $\vec{q}$, is obtained through the energy balance at the interface for a quasi-steady process as

$$\vec{q} = \rho_i \vec{v}_n H_m, \quad (23)$$

where ρ_i is the density of ice and H_m is the enthalpy of ice formation. Also, using heat conduction equation, $\vec{q}$ is obtained as

$$\vec{q} = \frac{-\delta T}{\left(\frac{l_0-l}{k_i} + \frac{l_m}{k_m}\right)}, \quad (24)$$

where δT denotes the temperature difference between the substrate and ice-water interface ($T_s - T_f$), l_0 denotes initial height of droplet, l_m denotes the thickness of substrate, k_i denotes thermal conductivity of ice and k_m denotes thermal conductivity of substrate. From equations 22, 23 and 24 one finds

$$\frac{-\delta T}{(\frac{l_0-l}{k_i} + \frac{l_m}{k_m})} = \rho_i \left(-\frac{dl}{dt} \right) H_m. \quad (25)$$

From Eq. (25) the height (l) or radius (r) of droplet as a function of time, t , can be obtained in two different conditions. The first one is for the condition where thermal conductivity of substrate is high or thickness of the coating is low. Thus, $l_m/k_m \ll l_0/k_i$ and Eq. (25) can be written as

$$l = l_0 - \sqrt{\frac{-2 k_i \delta T}{\rho_i H_m}} t. \quad (26)$$

The second condition is when the thermal conductivity of coating is low or the thickness of coating is high. In this case, $l_m/k_m \gg l_0/k_i$ and Eq. (27) is obtained as

$$l = l_0 + \frac{k_m \delta T}{\rho_i H_m l_m} t. \quad (27)$$

The important assumption in the aforementioned analysis is quasi-steady heat transfer. In quasi-steady heat transfer it is assumed that time-scale for ice growth, $\frac{r}{v_n}$, is more than thermal diffusion, $\frac{r^2}{D_i}$ in which D_i is thermal diffusivity of the ice. This assumption is correct in the case of a water droplet. For example, for a water droplet with 1mm diameter, the time-scale for growth is around 10 s and time-scale for diffusion is around 1s.

In order to validate the model developed for ice growth rate (Eqs. 26 and 27),

Irajizad et al. [5] collected some experimental data on ice growth rate on different substrates. e.g. PDMS¹ and glass. Furthermore, the reported ice growth rate in [22] is included in this comparison. They plotted collected data in Figure I-8 along with ice growth rate obtained from the theoretical model (Eqs. 26 and 27).

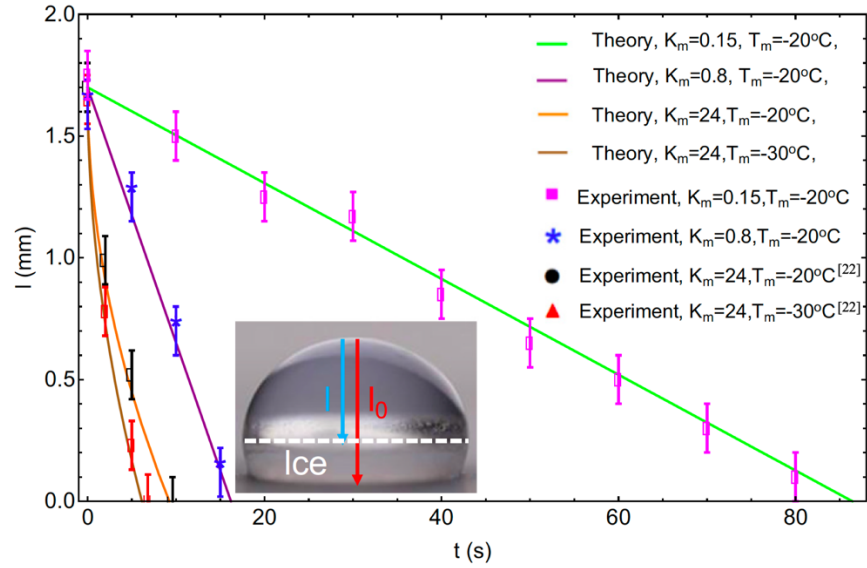


Figure I-8: The experimental data for ice growth rate are compared to theoretical model obtained from Eq. (26) and Eq. (27) [5].

As shown in Figure I-8, the predicted model obtained by heat transfer analysis matches experimental data well [5]. As an example, freezing times of a water droplet on stainless-steel at -20°C and -30°C are 9.6 and 7 s, respectively, which are obtained from the experiment [23]. The freezing times obtained from predicted model are 10 and 6 s for -20°C and -30°C , respectively, which are in a great harmony with the experimental data. In order to obtain isotherms in the ice, the heat equation should be solved in the ice domain ($\nabla^2 T = 0$). The boundary conditions in this case are that ice-water interface temperature is

¹ Polydimethylsiloxane

constant and ice-icephobic substrate interface temperature is prescribed.

1.3.2. Scenario II: Droplet in an environment with external airflow

Second scenario occurs when there is airflow around the water droplet in which convective heat transfer becomes significant (Figure I-9). In this case, instead of solid-liquid interface, ice nucleation occurs at liquid-vapor interface, as convective heat transfer reduces temperature at the surface [24]. Figure I-9 shows ice growth pattern for the droplet exposed to an environment with airflow.

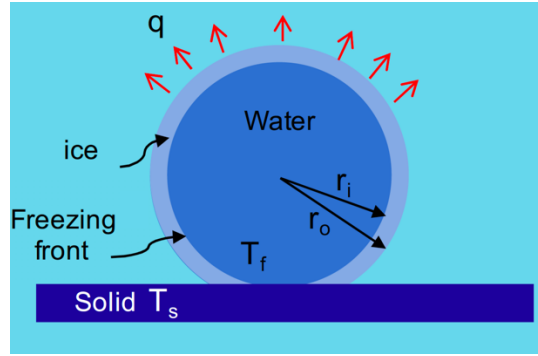


Figure I-9: Ice growth on a sub-zero substrate when the droplet is in an environment with external airflow. In this case, ice growth is controlled mainly by convective heat transfer through airflow [5].

Similarly, to case I, one can use energy balance at phase-changing interface to obtain ice growth rate. The enthalpy released from freezing makes a heat flux at ice-water interface which is carried out with airflow. Thus,

$$\vec{q}_{conv} = \bar{h}_{conv}(T_s - T_\infty), \quad (28)$$

where $\bar{h}_{conv}$ is convective heat transfer coefficient. In this case, the Nusselt number, written as a function of diameter which is representative dimension (Nu_D), by which one can

obtain convective heat transfer coefficient, is written as Eq. (29) [25]. Note that there is no evaporation on the droplet surface, since ice is formed around the droplet.

$$\overline{Nu_D} = \frac{D \bar{h}_{conv}}{k} = 2 + \left(0.4 Re_D^{\frac{1}{2}} + 0.06 Re_D^{\frac{2}{3}} \right) Pr^{0.4} \left(\frac{\mu}{\mu_s} \right)^{1/4}, \quad (29)$$

where Re_D is Reynolds number for external airflow, Pr is Prandtl's number and μ is dynamic viscosity. Note that Prandtl's number for air at -20°C is 0.75. Considering ice growth, a quasi-steady process, by energy balance at water-ice interface Eq. (23) can be obtained in this case as well. Due to the radial ice growth, the velocity of freezing front is written as Eq. (30)

$$\vec{v}_n = - \frac{dr_i}{dt}. \quad (30)$$

According to energy balance Eq. (31) could be obtained as

$$\vec{q} A_i = \vec{q}_{conv} A_o, \quad (31)$$

where A_i is ice-water interface area and A_o is ice-air interface area. By substituting Eq. (23) and (30) in Eq. (31), the Eq. (32) is obtained as

$$\left(\rho_i \frac{-dr_i}{dt} H_m \right) A_i = \bar{h}_{conv} (T_{r=r_o} - T_\infty) A_o. \quad (32)$$

Now, we can find an equation for ice growth rate. Through solution of heat equation in spherical coordinates, we have

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial T}{\partial r} \right) = 0 \Rightarrow r^2 \frac{\partial T}{\partial r} = C_1 \Rightarrow \frac{\partial T}{\partial r} = \frac{C_1}{r} \quad (33)$$

$$\text{and } T = -\frac{C_1}{r} + C_2. \quad (34)$$

$T(r = r_i) = T_f$ and $T(r = r_0) = T_s$ are ice-water and ice-air interface temperatures, respectively. The boundary conditions are written as

$$@ r = r_i: T = T_f$$

$$\text{and } @ r = r_0: h(T_s - T_\infty) = -k_i \left. \frac{\partial T}{\partial r} \right|_{r=r_0}.$$

By applying boundary conditions on Eq. (34), we have:

$$T_f = -\frac{C_1}{r_i} + C_2,$$

$$h \left(-\frac{C_1}{r_0} + C_2 - T_\infty \right) = -k_i \left(\frac{C_1}{r_0^2} \right),$$

$$C_1 = (T_\infty - T_f) \left(\frac{k_i}{hr_0^2} - \frac{1}{r_0} + \frac{1}{r_i} \right)^{-1},$$

$$\text{and } C_2 = T_\infty - \frac{k_i}{h} \left(\frac{C_1}{r_0^2} \right) + \frac{C_1}{r_0}.$$

We define

$$\theta_f = T_f - T_\infty.$$

Thus,

$$C_1 = -\theta_f \left(\frac{k_i}{hr_0^2} - \frac{1}{r_0} + \frac{1}{r_i} \right)^{-1} \quad (35)$$

$$\text{and } C_2 = T_\infty + \theta_f \left[1 - \left(\frac{k_i r_i}{hr_0^2} - \frac{r_i}{r_0} + 1 \right)^{-1} \right]. \quad (36)$$

The surface temperature is as

$$T_s = -\frac{C_1}{r_0} + C_2,$$

where $r^* = \frac{r_i}{r_0}$ and $\theta_s = T_s - T_\infty$. By substitution of C_1 and C_2 , the following equation for

θ_s is obtained as

$$\theta_s = \frac{\theta_f}{r_0 \left(\frac{k_i}{hr_0^2} \frac{1}{r_0} + \frac{1}{r_i} \right)} + \theta_f \left[1 - \left(\frac{k_i r^*}{hr_0} - r^* + 1 \right)^{-1} \right].$$

Thus, $\frac{\theta_s}{\theta_f}$ is written as

$$\frac{\theta_s}{\theta_f} = \frac{k_i r^*}{k_i \left(r^* - \frac{hr_0}{k_i} r^* + \frac{hr_0}{k_i} \right)}.$$

And $\frac{\theta_s}{\theta_f}$ may be simplified to

$$\frac{\theta_s}{\theta_f} = \frac{r^*}{r^* + B_i(1 - r^*)}, \quad (39)$$

where Biot number is defined as

$$B_i = \frac{hr_0}{k_i},$$

$$\vec{q} = hA_0(T_s - T_\infty) = \rho_i H_m A_i \left(-\frac{dr_i}{dt} \right) \quad (38)$$

$$\text{and } h\theta_s = \rho_i H_m \left(-\frac{dr_i}{dt} \right) r^{*2}.$$

By substitution of θ_s from Eq. (37) in Eq. (39) one has

$$h\theta_f \left(\frac{r^*}{r^* + B_i(1 - r^*)} \right) = \rho_i H_m \left(-r_0 \frac{dr^*}{dt} \right) r^{*2}.$$

By simplification of this equation, one finds

$$-\frac{h\theta_f}{r_0\rho_i H_m}(dt) = (r^* + B_i(1 - r^*))r^* dr^*.$$

Through integration of both sides we have

$$\int -\frac{h\theta_f}{r_0\rho_i H_m} dt = \int (r^* + B_i(1 - r^*))r^* dr^*$$

$$\text{and } -\frac{h\theta_f}{r_0\rho_i H_m} t = \frac{r^{*3}}{3} + B_i \left(\frac{r^{*2}}{2} - \frac{r^{*3}}{3} \right) + C.$$

Also, we have the initial condition for ice growth as

$$t(r^* = 1) = 0.$$

Thus,

$$t = -\frac{r_0\rho_i H_m}{6h\theta_f} (2(1 - B_i)r^{*3} + 3B_i r^{*2} - B_i - 2). \quad (40)$$

Through Eq. (40), the radius of ice as a function of time, i.e. ice growth rate, in high air flow condition is obtained. Irajizad et al. [5] plotted Eq. (40) for different air velocities and temperatures. As shown in Figure I-10, the initial rate of ice growth is low. However, the rate of ice growth increases as the ice growth proceeds.

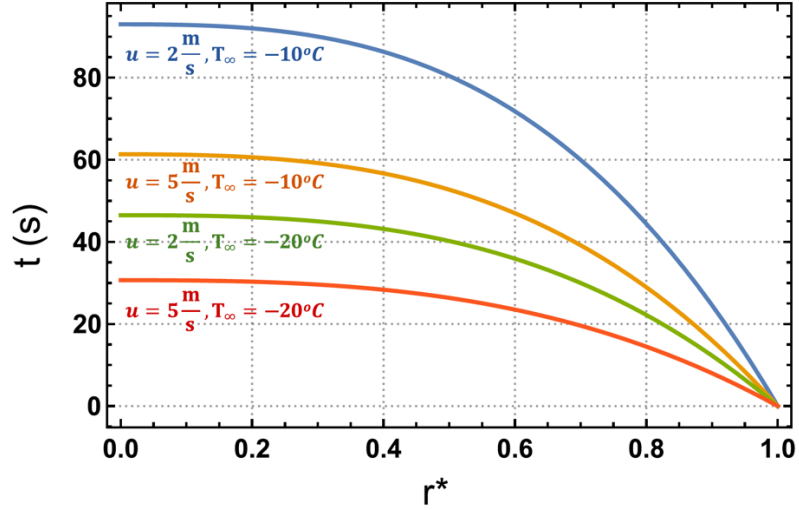


Figure I-10: The plot of Eq. (40) which shows ice growth rate in an environment with external airflow for different environment temperatures and airflow speeds [5].

A critical factor in ice growth in airflow is humidity. For example, in the presence of airflow, at humidity of 30-75%, ice nucleation occurs at liquid-vapor interface which is called homogeneous nucleation, while at humidity close to 100%, heterogeneous ice nucleation which is ice nucleation at solid-liquid interface occurs [24]. This phenomenon can be justified by evaporation rate. Evaporation rate is higher at lower humidity. Therefore, at lower humidity high rate of evaporation cools down the liquid-vapor interface leading to ice nucleation at this interface. On the other hand, once evaporation rate is low in high humidity, ice nucleation occurs at solid-liquid interface. Note that humidity also affects ice growth in the environments with airflow. Airflow with higher amount of humidity has higher amount of heat transfer through convection mechanism. In other words, humidity affects convective heat transfer coefficient, $\bar{h}_{conv}$.

1.4. Ice Bridging Phenomenon

The theories discussed so far are for a single droplet without interference from other droplets. However, in reality, droplets can affect each other's nucleation and cause ice bridging phenomenon. Ice bridging is a phenomenon in which suppression of vapor pressure due to freezing of droplets occurs. This creates a water-vapor gradient between ice and neighboring supercooled droplets. This water-vapor gradient leads to formation of an ice bridge between the frozen droplet and the neighboring supercooled droplet [26, 27]. In fact, the ice bridging between frozen droplet and liquid droplet depends on the length competition between liquid droplet diameter, D , and straight-line distance from liquid droplet to the frozen droplet, L , or ice-to-liquid droplet separation. Chen et al. [26] defined bridging parameter, S , as

$$S = \frac{L}{D}. \quad (41)$$

Smaller S leads to higher possibility of bridging. For example, Chen et al. [26] studied two droplets with the same diameter ($D_1 = D_2 = 28 \mu m$) placed in different distances from a frozen droplet ($L_1 = 9 \mu m, L_2 = 53 \mu m$) as shown in Figure I-11. They demonstrated that droplet (1) with smaller separation length, i.e. $S_1 < 1$, was frozen after 12 s. In contrast, droplet (2) with larger separation length, i.e. $S_2 > 1$, did not form an ice bridge and disappeared after 34 s [26].

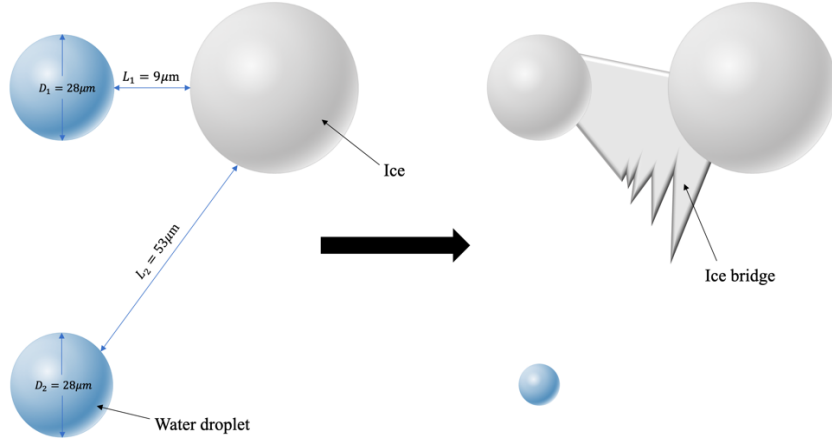


Figure I-11: Ice bridging phenomenon for two similar liquid droplets with different ice-to-liquid droplet separation lengths [26].

As mentioned, ice bridge forms due to freezing of the vapor which is harvested from the liquid droplet. This vapor is transported due to vapor pressure gradient between ice droplet and neighboring supercooled liquid droplet, even if they have different radii. Thus, vapor pressure around the ice droplet should be lower than the vapor pressure around the liquid droplet to have source-sink behavior and form an ice bridge. In fact, the ice bridge forms when the mass of liquid droplet, m_l , is at least equal to the mass of complete ice bridge, m_{bridge} . Otherwise, the entire liquid droplet will evaporate and the formed ice bridge is not connected to the liquid droplet to freeze it. Thus, we will consider the case where $m_l \geq m_{bridge}$. In this case, ice bridge length, L , reaches its maximum value, L_{max} , which is the distance between the edge of the frozen droplet and center of liquid droplet. Here, we assume that the frozen and the liquid droplets are identical and the mass of liquid droplet and ice bridge scales as

$$m_l \sim \rho_l d^3 \quad (42)$$

$$\text{and } m_{bridge} \sim \rho_i L_{max} d^2, \quad (43)$$

where d denotes initial diameter of liquid droplet, and ρ_l and ρ_i are densities of liquid and ice, respectively. From Eq. (42) and Eq. (43), one finds that in order for a complete ice bridge to form, $L_{max} < d$ should be satisfied, because m_l should be higher than m_{bridge} . Otherwise, ice bridge cannot connect to the liquid droplet and a complete ice bridge does not form. In Eqs. (42) and (43), it is assumed that the droplets are almost spherical. Thus, this scaling is good for hydrophobic and superhydrophobic surface on which contact angle is high and the droplet shape is close to a sphere.

Mass flow rate for the evaporation of a liquid droplet is defined by the following equation if it is assumed that droplet temperature is approximately equal to the substrate temperature, as

$$\dot{m}_{l,e} \sim J_{l,e} A_{\parallel} \sim \frac{D}{\bar{R} T_w} \frac{P_{s,l} - P_{n,i}}{\delta} A_{\parallel}, \quad (44)$$

where $J_{l,e}$ denotes mass flux of the vapor evaporating from liquid droplet, $P_{s,l}$ denotes saturation pressure of the liquid droplet, $P_{n,i}$ denotes vapor pressure near the surface of ice droplet and growing ice bridge, T_w is the substrate temperature, D denotes diffusivity of water vapor into the air, $\bar{R}$ is the gas constant of water vapor (461.5 J/kg.K), δ is edge-to-edge separation of droplets, and $A_{\parallel}$ is in-plane area of liquid droplet. Also, mass flow rate for the vapor which forms ice bridge is defined as

$$\dot{m}_{i,c} \sim \rho_i v_b A_{\parallel}, \quad (45)$$

where v_b is in-plane growth rate of the ice bridge and $A_{\parallel}$ is in-plane area of frozen droplet.

By mass conservation, $\dot{m}_{l,e} = \dot{m}_{i,c}$, and the assumption of identical droplets, one finds

$$v_b \sim \frac{D}{\rho_i \bar{R} T_w} \frac{P_{s,l} - P_{n,i}}{\delta}. \quad (46)$$

From this equation it is understood that ice bridge growth rate is independent of atmospheric pressure, P_∞ . However, high values of P_∞ leads to the reduction in the evaporation rate of liquid droplet. Although the diameter of liquid droplet changes over time, the majority of vapor evaporated from the liquid droplet deposits somewhere close to the main base of ice bridge growth, due to the assumption $L_{max} < d$. Thus, pressure gradient can be assumed to be constant during the ice bridge formation. Thus, from Eq. (46), v_b can be assumed to be constant during ice bridge formation.

The length of ice bridge as a function of time can be obtained from $v_b = \frac{dx}{dt}$ with boundary conditions of $x(0) = 0$ and $x(\tau) = L$, where τ is the time for ice bridge connection to the liquid droplet. The final length of ice bridge varies between δ and L_{max} for $L_{max} \ll d$ and $L_{max} \sim d$, respectively [27].

1.5. Contributions

In this chapter, fundamentals of ice formation on an icephobic substrate are discussed. Ice formation is divided into two steps: ice nucleation and ice growth. As a droplet is placed on a sub-zero surface, after ice nucleation delay time, the ice nucleolus forms by a process governed by thermodynamics of ice-water-surface system. Gibbs energy barrier is the parameter that determines ice nucleation temperature (Eq. 1), and depends on surface factor which can be tuned through manipulating surface geometry and surface free energy. Surface factor is obtained as a function of surface geometry and surface free energy for both convex and concave surfaces (Eqs. 7 and 9). Nucleation rate is defined for a droplet

on the surface as a function of temperature and Gibbs energy barrier (Eq. 11). The second step in ice formation on a surface is ice growth. This step which is controlled by heat transfer is studied in two different cases. The first case is when there is no airflow around the droplet and the second one is in the presence of a highly convective external air flow. Theoretical models are developed for both these cases through energy and mass balance equations. In the first case, heat transfer mostly occurs through the solid substrate and the ice grows from solid-liquid interface. Ice growth rate is determined for different conductivities and thicknesses of substrates (Eq. 26 and 27). In the second case, heat transfer mostly occurs through convection and the ice growth originates at air-liquid interface by the rate given in Eq. (40). Ice bridging is a phenomenon where an ice bridge is formed between a frozen droplet and its adjacent liquid droplet which leads to the freezing of the liquid droplet. The ice bridge growth rate is governed by vapor pressure gradient between a frozen and a liquid droplet where they show source-sink behavior for the vapor, Eq. (46).

1.6. Outcomes

Book Chapter

- A. Hakimian, S. Nazifi, H. Ghasemi; “Physics of ice nucleation and growth on a surface,” in “Ice Adhesion: Mechanism, Measurement, and Mitigation” edited by K. L. Mittal and Chang-Hwan Choi, Wiley, 2020.
- A. Hakimian, S. Nazifi, H. Ghasemi; “Durability Assessment of Icephobic Coatings,” in “Ice Adhesion: Mechanism, Measurement, and Mitigation” edited by K. L. Mittal and Chang-Hwan Choi, Wiley, 2020.
- A. Hakimian, S. Nazifi, H. Ghasemi; “Metrology of Ice Adhesion,” in “Ice Adhesion: Mechanism, Measurement, and Mitigation” edited by K. L. Mittal and Chang-Hwan Choi, Wiley, 2020.

Journals

- A. Hakimian, M. Mohebinia, M. Nazari, A. Davoodabadi, S. Nazifi, Z. Huang, J. Bao, H. Ghasemi; “Freezing of Few Nanometers Water Droplets,” *Nature Communications* 12, 6973 (2021).

1.7. Organization

The remainder of this dissertation is organized as follows. Chapter 2 reviews the freezing of water nanodroplets in nanoscale. In Chapter 3, we presented metrologies exist for the measurement of ice adhesion on a surface and we proposed a standard methodology to assess ice adhesion strength on a surface. The proposed metric is compared to other existing metrics. We discuss conclusions and highlight future research directions in Chapter 4.

CHAPTER 2

II. FREEZING OF FEW NANOMETER WATER DROPLETS

1.3.Introduction

Climate fluctuations, global radiative properties and microphysical processes in clouds are strong functions of water nucleation mechanism and distribution of ice particles. Ice particles formed by various mechanisms in different shapes have critical roles in hydrological fluxes and the climate [28,29]. Ice nucleation in the atmosphere could occur either on particles (heterogeneous) or in a liquid droplet (or a dilute solution droplet) surrounded by a vapor environment (homogenous). The required number of water molecules to form crystalline ice from liquid phase is determined to be 275 through IR excitation-modulated photoionization spectroscopy (~ 2 nm droplet) [30]. Homogenous nucleation of nanoscopic liquid water droplets is explored through hypersonic expansion and the freezing temperature is demonstrated [31,32] to occur in “no man’s land” [33]. Also, computational approaches [34-36] thorough large-scale MD simulation have highlighted the suppression of ice nucleation in nanodroplets.

On the other hand, heterogeneous ice nucleation occurs in the atmosphere, a wide range of species (e.g. extracellular matrix in wood frogs [37] Antarctic fishes [38,39]) and technological embodiments (e.g. aviation [40] and infrastructures, including transportation systems, power systems, and energy systems [41-43]) and causes outstanding financial burden [44]. Nanoscopic anti-icing surfaces developed to address the icing challenge aim to tune the water-ice transformation at few nm scales. These include nanostructured surfaces [45-47], slippery liquid infused porous surfaces (SLIPS) [48,49],

magnetic slippery surfaces (MAGSS) [50] and even anti-frosting [51-55] surfaces. Furthermore, confinement effects could drastically affect the phase-change phenomenon in membrane [56], porous material [57-60], nanochannels [61,62] and carbon nanotubes [63,64]. However, direct probing of water-ice phase transformation in few nm scales in heterogeneous environments has been challenging: nanoscopic water droplets could evaporate or grow by condensation extremely fast (i.e. Order of 10^{-35} s) [65]. Hence, the study of nanodroplets in confinements is needed to accurately probe their phase transformation.

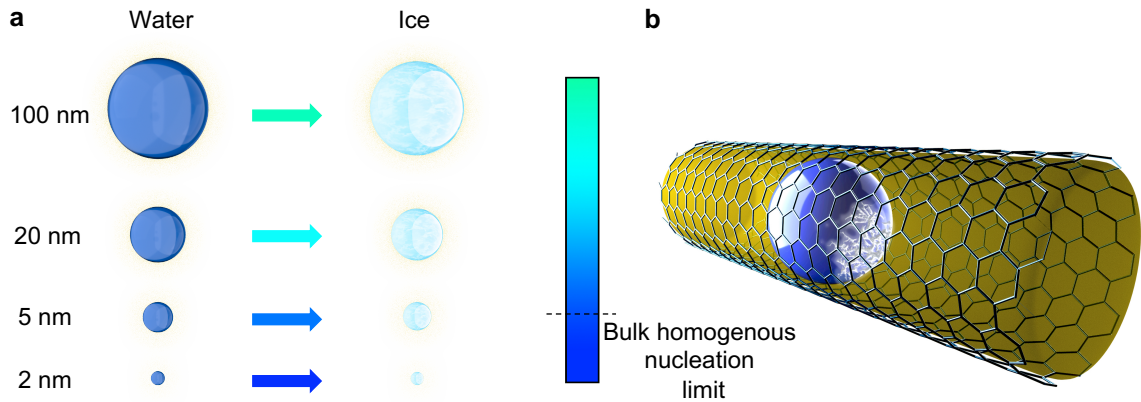


Figure II-1: (a) The length dependence of water-ice transformation in heterogeneous mode. (b) Schematic of a nanodroplet formed in confined geometry and surrounded by an oil environment where ice nucleation occurs at the oil-water interface.

Here, we report water-ice phase transformation in confined geometries down to 2 nm in diameter, Figure II-1a. It is shown that despite being heterogeneous, ice nucleation in 2 nm length scale breaks the limit of homogeneous bulk nucleation. We form water nanodroplets with diameters ranging from 150 nm to 2 nm in membrane pores surrounded by an oil environment, Figure II-1b. The high interfacial curvature of these nanodroplets leads to large positive pressures in these droplets (up to 500 bar). Through two independent

electrical resistance metrology and FTIR spectroscopy, the ice nucleation temperature in these nanodroplets is probed. The phase transformation temperature of nanodroplets has a length dependence and this dependence becomes more pronounced at the sub-10 nm scale. The ice phase formed within nanodroplets as small as 2 nm in diameter is I_h (hexagonal). At few nm scales, the soft curved interface of oil-water plays a critical role in the suppression of ice nucleation and the characteristics of this interface is entirely different than those of concave stiff solid-water interfaces.

1.4.Methods

1.4.1. Confined nanodroplets

The nanomembranes are acquired from InRedox Co and are cleaned with IPA and Plasma cleaner. The membrane was secured between the two reservoirs as shown in Figure II-2.

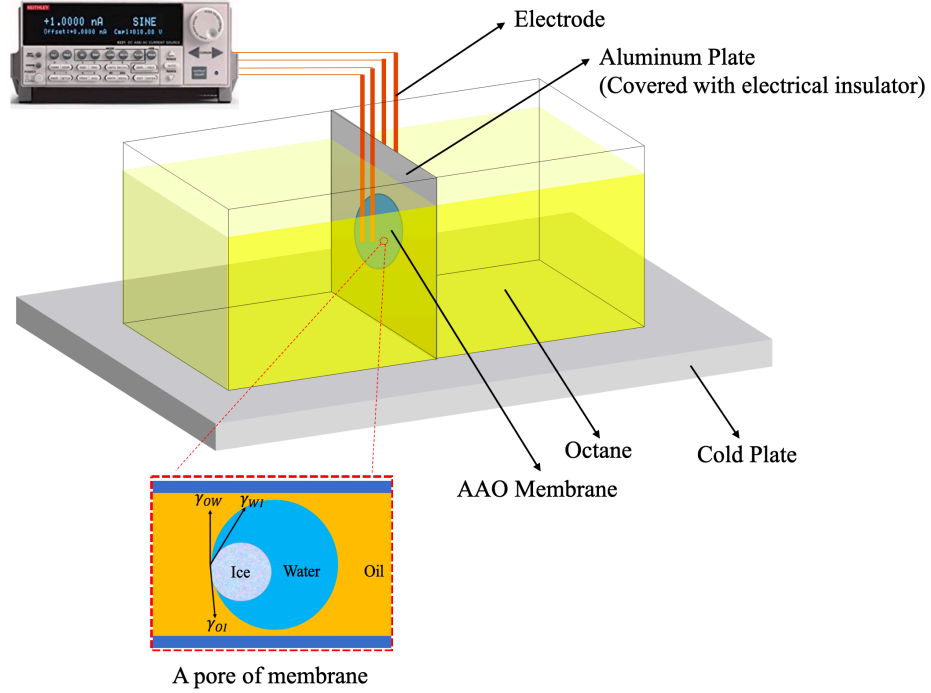


Figure II-2: The schematic of the experimental setup for electrical resistance metrology. The I-V curve across the pores is measured at a given temperature to probe the onset of water-ice phase change, TN.

One side of the membrane was wetted with water and allowed for capillary force to drive the water into the pores. To ensure complete wetting of nanopores, the setup is placed in a sonicator for 5 mins. Once the other side of the membrane is wet, it indicates filling of the nanomembrane with water. We let the extra water on both sides of the membrane to evaporates for 30 mins. Due to wetting characteristics of water, water droplet adopts high negative pressure in the pore [62,79]. In the next step, both reservoirs were filled with octane to confine the water droplet in the nanopores. Octane wets the membrane faces and flows inside the pores. The final configuration of the nanodroplet in the pores is shown in Figure II-1. We examined the existence of water nanodroplets in the pores through electrical resistance measurements shown in Figure II-3.

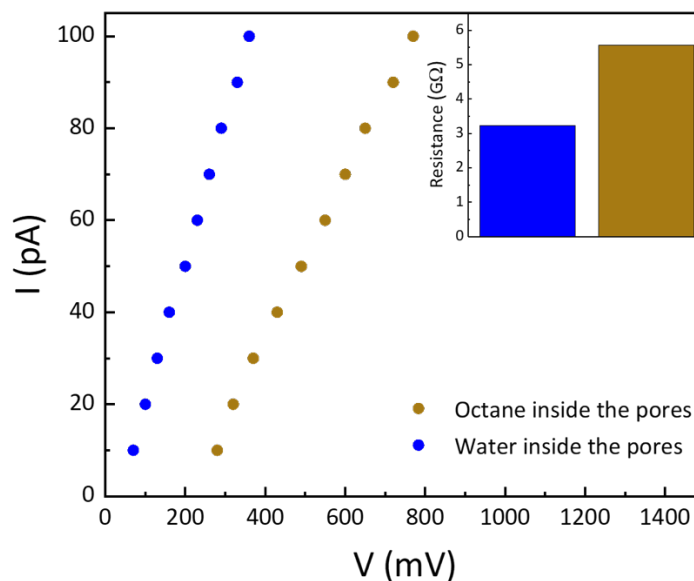


Figure II-3: Comparison between I-V curves obtained for the cases of pores of filled octane and the cases of pores with water nanodroplets inside. These experiments are conducted on the same setup and at the same ambient temperature (23 °C).

The geometry and dimension of pores in the nanomembranes are probed with scanning probe microscopy (SPM) as shown in Figure II-4. The 5 and 2 nm membranes are made of two layers, the active layer with a small pore dimension and the supporting layer with pore dimensions of 150-200 nm. For 2 nm membranes, the pores have a size distribution of 2-4 nm.

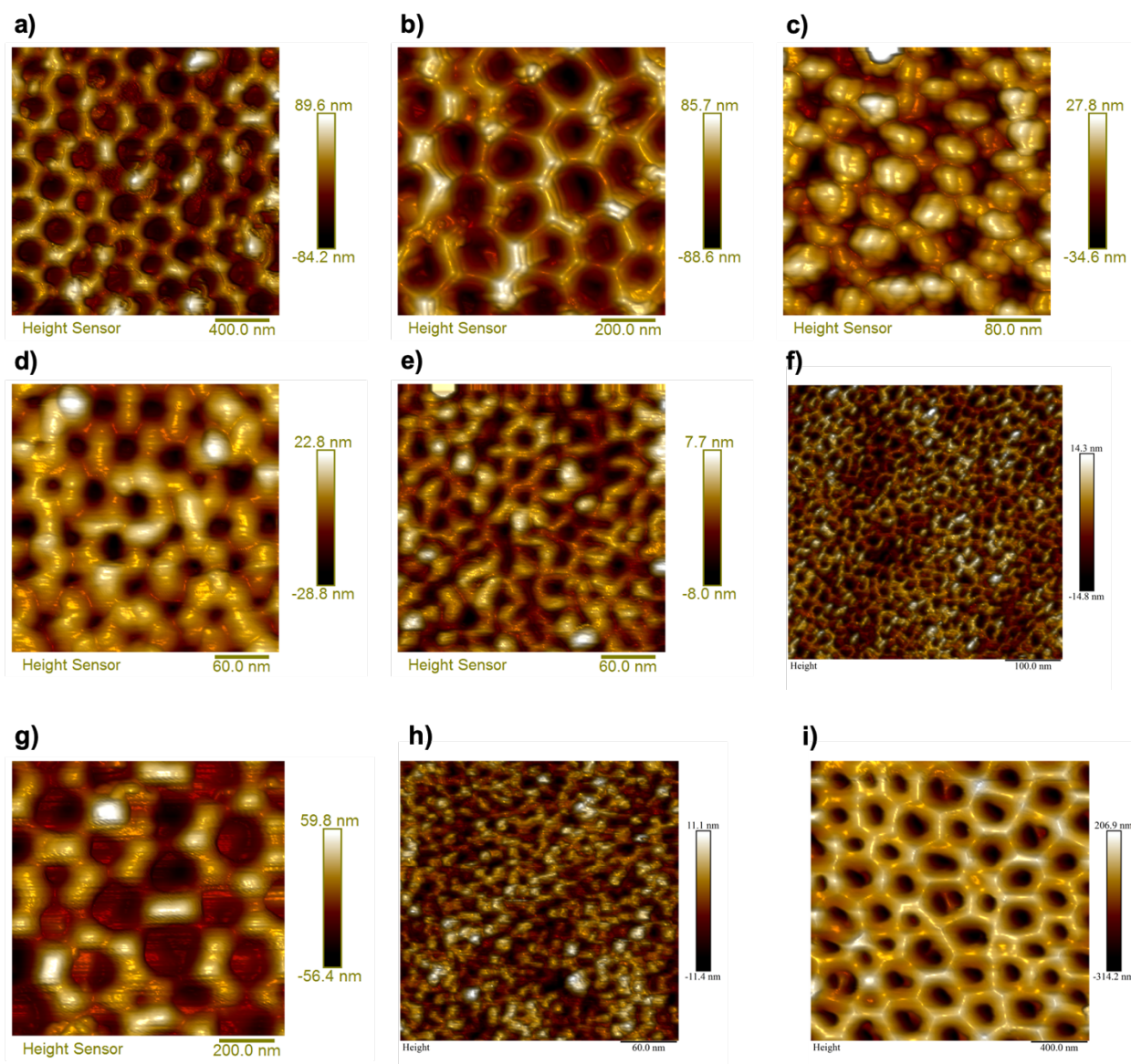


Figure II-4: Surface morphology of AAO membranes. (a) 150 nm (b) 80 nm (c) 40 nm (d) 20 nm (e) 10 nm (f) 5 nm (active layer) (g) 5 nm (support layer) (h) 2 nm (active layer) (i) 2 nm (support layer).

Furthermore, the cross-section of these nanomembranes is shown schematically in Figure II-5.

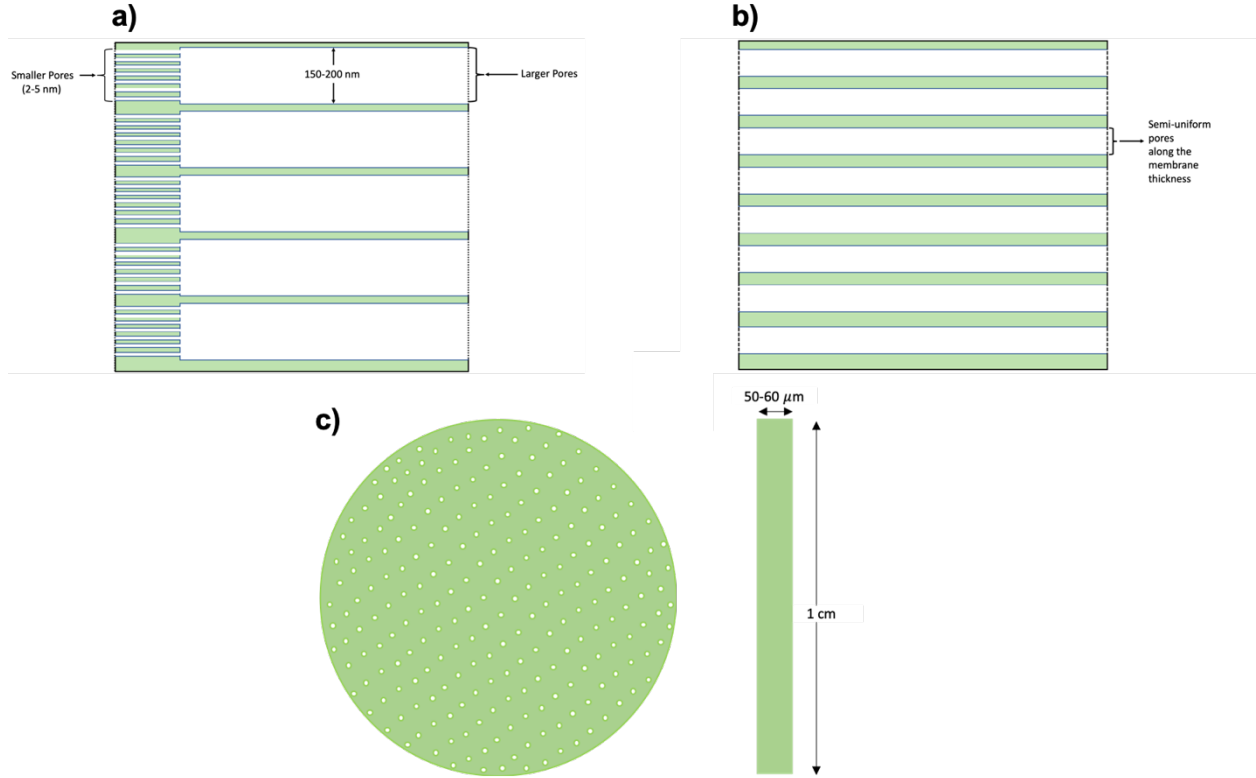


Figure II-5: Schematic of AAO membranes used in this research. These membranes are either (a) Anisotropic or (b) Isotropic. 2 and 5 nm AAO membranes are anisotropic and the rest of the membranes are isotropic.

1.4.1.1. The existence of water nanodroplets in the pores and volume effect

The electrical conductance across nanopores of 80 nm is measured through the four-probe method. If the pores are fully filled with octane, the electrical resistance is approximately 5.5 GΩ, while the introduction of nanodroplets in these pores drops the

resistance to approximately 3 G Ω . Note that the existence of any blocked air bubble in the pore would result in the insulating characteristics of these pores.

We performed quartz crystal microbalance (QCM) measurement on the membranes before and after filling with water to determine the volume and length of water nanodroplets inside the pores. A piece of membrane was mounted on a gold chip before and after filling with water. This chip was placed in an electrochemical quartz crystal microbalance (Gamry's eQCM 10M). The weight of water inside the pores was measured based on the changes in the resonant frequency of the oscillating quartz crystal before and after filling with water. We also compared the measurements with the theoretical values calculated from the membrane properties provided by the vendor. The results are tabulated in Table 1. The volume of water within the pores is 0.817 $\mu\text{L cm}^{-2}$ for 20 nm pores, 0.511 $\mu\text{L cm}^{-2}$ for 10 nm pores, and 1.312 $\mu\text{L cm}^{-2}$ for 5 nm pores.

Table 1: Volume of liquid in the pores measured by QCM metrology

Pore Diameter (<i>nm</i>)	Pore Density ($\frac{1}{\text{cm}^2}$)	Thickness of membrane (μm)	Theoretical weight of water inside the pores ($\frac{\mu\text{g}}{\text{cm}^2}$)	Fs (MHz)		Weight of water inside the pores ($\frac{\mu\text{g}}{\text{cm}^2}$)
				Empty membrane	Filled membrane	
20	5×10^{10}	50	785	10.0036792	10.00349456	816.99
10	1.6×10^{11}	50	628	10.0036887	10.00357321	511.02

Table1 (continued)

Active layer: 5	Active layer: 9×10^{11}	Active layer: 3				
Support layer: 150	Support layer: 1.5×10^9	Support layer: 60	1616.12	10.0036916	10.00339504	1312.21

To clarify the droplet volume effect, we should note that the droplets in these pores are elongated ellipsoid droplets with a smaller diameter in the range of few nm while the other diameter in tens of micrometer. The approximate volume of isolated water droplet in the pores are given in the table below:

Table 2: Volume of water inside each single pore of membranes with different pore diameter

Pore Diameter (nm)	Volume of water inside each pore (pL)
150	8.83×10^{-4}
80	2.51×10^{-4}
40	6.28×10^{-5}
20	1.57×10^{-5}
10	3.92×10^{-6}
5	1.17×10^{-7}
2-4	4.24×10^{-8}

We compared the volume of these droplets with the volume of water droplets reported by Li *et al.* [32], Figure II-6. As shown, for water droplets higher than 6.1 nm, the ice nucleation rate is similar to bulk water. The volume of 6.1 nm droplet is 9.5×10^{-10} pL. All

of the droplets studied in this work have volumes at least 2 orders of magnitude higher than this limit. Thus, the volume effect on ice nucleation rate is insignificant in this study.

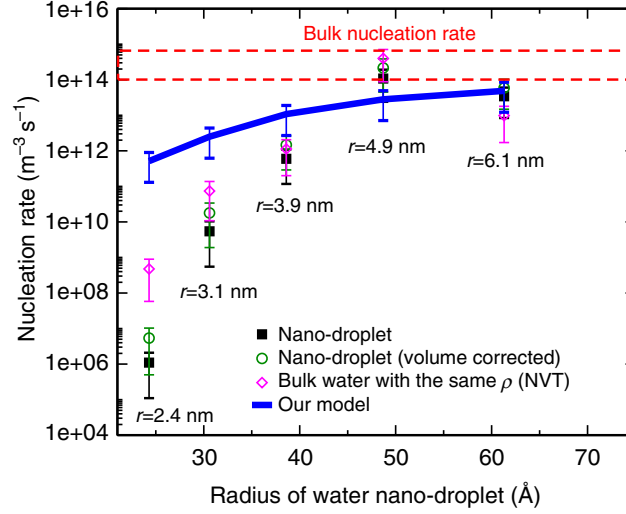


Figure II-6: Size dependence of ice nucleation rates in the mW water droplets at 230 K [32].

1.4.2. Selection of surrounding fluid of the nanodroplets

The included pressure inside the nanodroplets (P_{Nd}) is determined through the Laplace equation written as, $P_{Nd} - P_{atm} = \gamma_{ow} (C_1 + C_2)$, where P_{atm} denotes the atmospheric pressure equal to oil pressure, γ_{ow} is the interfacial tension of the oil-water interface, and C_1 and C_2 are the principal curvatures of the water-oil interface¹. Based on the volume of water in the pores, we expect the water nanodroplets are formed in the shape of elongated droplets in the pores. As the thickness of membranes is much larger than the diameter of pores (i.e. 50-60 μm thickness compared to the 2-150 nm pore diameter), the value of C_2 becomes negligible compared to C_1 . Here, we considered that the value of C_1 is approximately inverse of the radius of pores.

Table 3: Induced pressures for confined nanodroplets for different potential surrounding fluid

Size(nm)	P (bar)					
	Dichloromethane	Carbon tetrachloride	Hexane	Heptane	Octane	Decane
100	5.77	9.18	10.40	10.58	10.71	9.18
80	7.18	11.43	12.95	13.18	13.33	11.43
50	11.43	18.18	20.60	20.96	21.21	18.18
20	28.41	45.18	51.20	52.10	52.71	45.18
10	56.71	90.18	102.20	104.00	105.21	90.18
5	113.31	180.18	204.20	207.80	210.21	180.18
2	283.11	450.18	510.20	519.20	525.21	450.18

Regarding the effect of Span80 on interfacial tension, it should be noted that HLB (Hydrophilic–lipophilic balance) value for span 80 is 4.3 which means that span 80 is oil soluble and water-insoluble. Furthermore, we used pendant drop method to access the role of Span80 concentration on octane-water interfacial tension. In these experiments, a water droplet is introduced in an octane medium with different concentrations of Span80 as shown below. The Bond number (Bo) is defined as

$$Bo = \frac{\Delta\rho \, g \, R_0^2}{\gamma_{ow}}, \quad (47)$$

where $\Delta\rho$ denotes the density difference between water and octane, g is the gravitational acceleration and R_0 is the radius of curvature at the drop apex, Figure II-7. The differential form of Young-Laplace equation in terms of arc length (s) is written as

$$\frac{d\phi}{d\bar{s}} = 2 - Bo \, \bar{z} - \frac{\sin \phi}{\bar{r}}, \quad (48)$$

$$\frac{d\bar{r}}{d\bar{s}} = \cos \phi \quad (49)$$

$$\text{and } \frac{d\bar{z}}{d\bar{s}} = \sin \phi, \quad (50)$$

where the bar indicates dimensionless values scaled by R_0 . The boundary conditions are

$$@ s = 0: \bar{r} = 0; \bar{z} = 0; \phi = 0.$$

The input to this system of equations is Bo or specifically γ_{ow} .



Figure II-7: Schematic of pendant drop experiments

Once this value is given, one can solve this system of equations numerically. We determined numerically the shape of the droplet for a range of surface tension values and compared the calculated droplet shape with the one measured, Figure II-8. For each considered value of surface tension, we determined the coefficient of determination (R^2) between the calculated shape and measured shape. The surface tension with the highest value of R^2 provides gives us γ_{ow} through pendant droplet method, Table 4. As a control experiment, we compared the measured interfacial tension for octane-water with the reported value in the literature which shows less than 5% error.

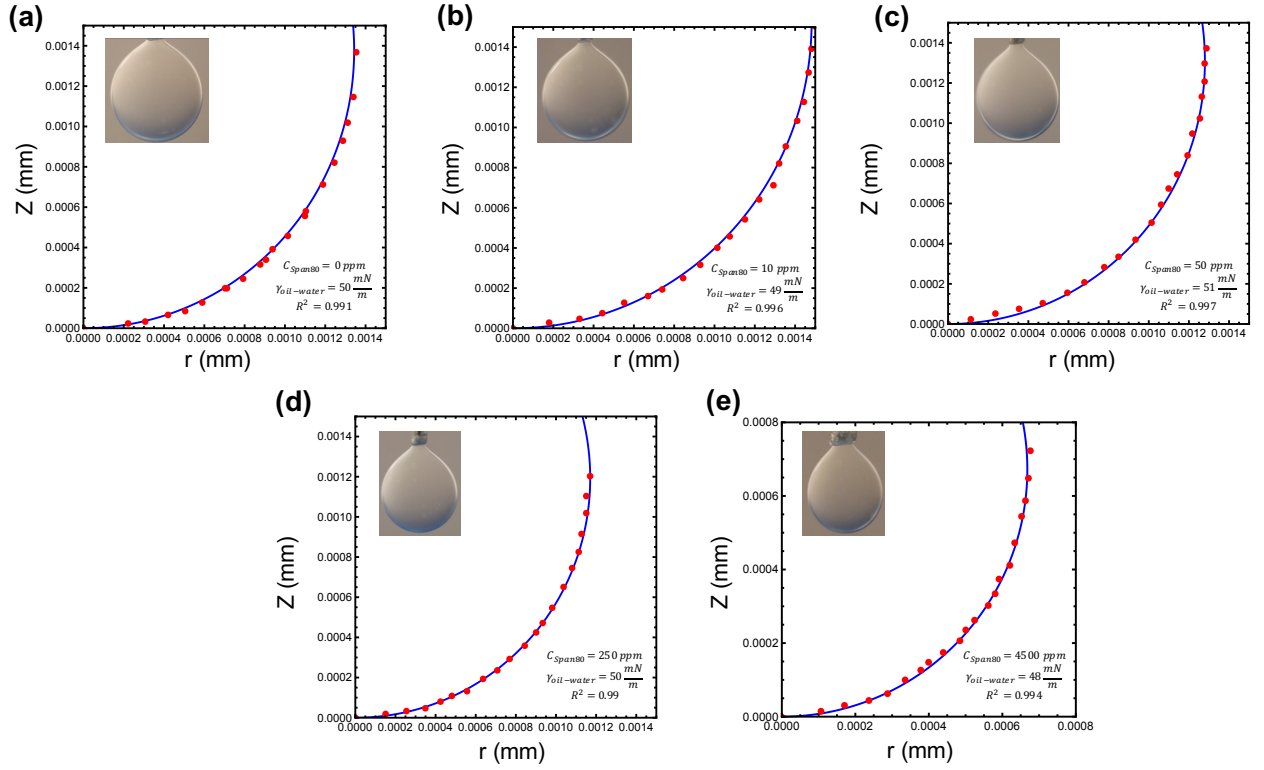


Figure II-8: The measured shape of water droplet suspended in octane are compared with the calculated shape to determine the surface tension of octane-water interface as a function of Span80 concentration.

Table 4: Surface tension of oil-water interface as a function of Span80 concentration

Concentration of Span 80	γ_{ow} in literature (mNm^{-1})	Measured γ_{ow} (mNm^{-1})
0 ppm	51	50
10 ppm		49
50 ppm		51
250 ppm		50
4500 ppm		48

1.4.3. Electrical resistance metrology

Electrical resistance experiments were performed using a setup shown in Figure II-2. In this setup, an aluminum plate with a hole in the middle was acquired and AAO membranes were mounted on top of the hole. The aluminum plate provides an isothermal condition in the membrane. The plate surface except the membrane area was coated with an insulator material to avoid any electrical shortcut through the plate. This plate was placed between two reservoirs and two electrodes placed on each side of the membrane such that the distances between electrodes were equal and the electrodes were as close as possible to the membrane to reduce oil resistance. The electrodes were connected to a high-resolution source meter (Keithley 2602B) to generate I-V curves at different temperatures. The I-V curves were produced in different temperatures using a Labview code. The setup was cooled down using TEC coolers connected to a power supply.

The schematic of the experimental setup is shown in Figure II-2. In this metrology, the nanomembrane was placed between two reservoirs separated by a heat conducting wall. We measured the temperature of two reservoirs during the experiments to ensure isothermal conditions. The coordinates of the electrodes are fixed. Once the water nanodroplets are formed inside the pores, the temperature of the system in a quasi-static manner is reduced and the I-V curves across the pores are probed.

A 4-point probe consists of four electrical probes in a line, with equal spacing between each of the probes. Based on this method, a high impedance current source is used to supply current through the outer two probes; a voltmeter measures the voltage across the inner two probes (See Figure II-9). Due to the high impedance of voltmeter, no current flows through inner electrodes. In this case, the voltage drop is measured between two inner electrodes

where wire resistances (R_{w2} and R_{w3}) and contact resistances (R_{c2} and R_{c3}) do not contribute in voltage measurement and it is just the resistance of sample (R_{s2}) which leads to the voltage drop (ΔV).

We explored one polarity where we applied current and measured the voltage. In fact, what is important here are non-linearities in the resistance and by this method, we can observe those nonlinearities and jump in the resistance due to solid-liquid phase change. Based on the 4-point probing method, the voltage is measured between two inner electrodes and these two electrodes are pretty close to the membrane, almost attached to the membrane. As a result, almost all of the voltage drop here comes from the membrane and the liquid inside the membrane and the changes observed in the resistance are due to the characteristic changes in the liquid inside the membrane. The liquid phase contains water and octane. Octane conductivity is due to the existence of a tiny amount of Span80 and conductivity of water is due to the sodium and chloride ions. Addition of sodium and chloride ions increases the conductivity of water due to ion conductivity. The most important feature is that, as water freezes, ions cannot move, and this increases ice resistance compared to water by more than three orders of magnitude. On the other hand, when there is no ion inside the water, the resistance of ice and water is in the same order of magnitude. It should be noted that these ions are not soluble in octane, as octane is completely non-polar, and after adding NaCl to octane it precipitates and octane resistivity, which is in order of Giga ohm (GW), does not change. Thus, sodium and chloride ions cannot be responsible for the charge transport inside the octane. Also, HLB (Hydrophilic–lipophilic balance) value for span 80 is 4.3 which means that span 80 is oil soluble and

water-insoluble. We took two independent approaches to show that the electrical resistance of water and ice could differ by more than three orders of magnitude.

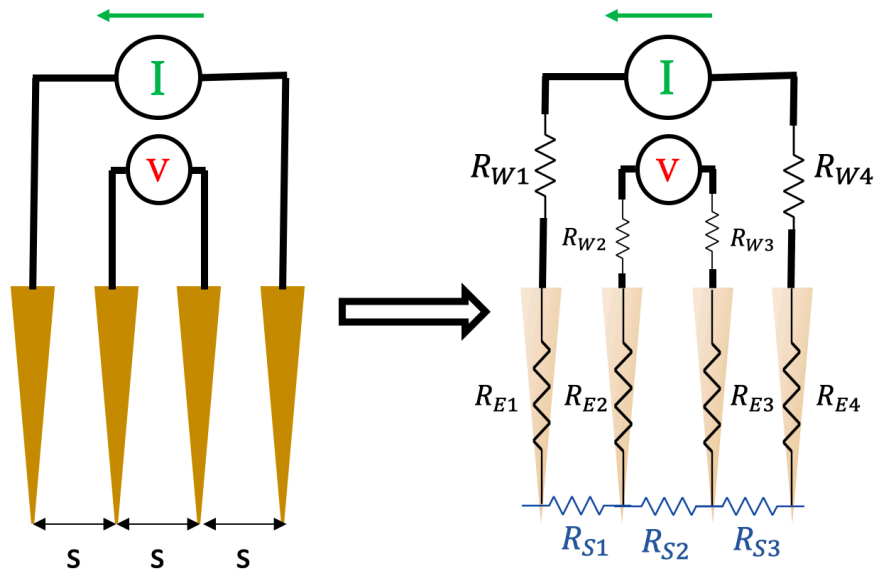


Figure II-9: 4-point probing method concept

1.4.3.1.Approach 1

As mobility of ions in ice approaches zero, the resistance of ice is close to its pure ice value as reported as 107 ohm.m. (C. Jaccard, Mechanism of the electrical conductivity in ice, Annals of the New York Academy of Sciences, 125, 390-400, 1965). The electrical resistivity of water with 50 ppm of salt is reported ~ 100 ohm.m (Steve Felber, Water Fundamentals Handbook, DRI-STEEM, 2017). This suggests that there are five orders of magnitude difference between resistance of water solution and pure ice. Please note that the membrane is made of many pores surrounded by water/octane and calculation of total resistance of the system will have high uncertainty.

1.4.3.2. Approach 2

In the second approach, we measured the electrical resistance of water solution and ice filled in a plastic tube with inner diameter of 1 mm as shown in Figure II-10. The tube was filled with water solution with 50 ppm NaCl and four-probe electrodes were attached to the tube. The specific electrical resistivity of the water is measured at 1 °C as 395 ohm.m. The temperature of the system is dropped to -10 °C allowing to ice form in the tube. The specific electrical resistivity of ice was measured as 2093333 ohm.m. That is, the specific resistivity of ice is ~5000 times higher than that of water solution.

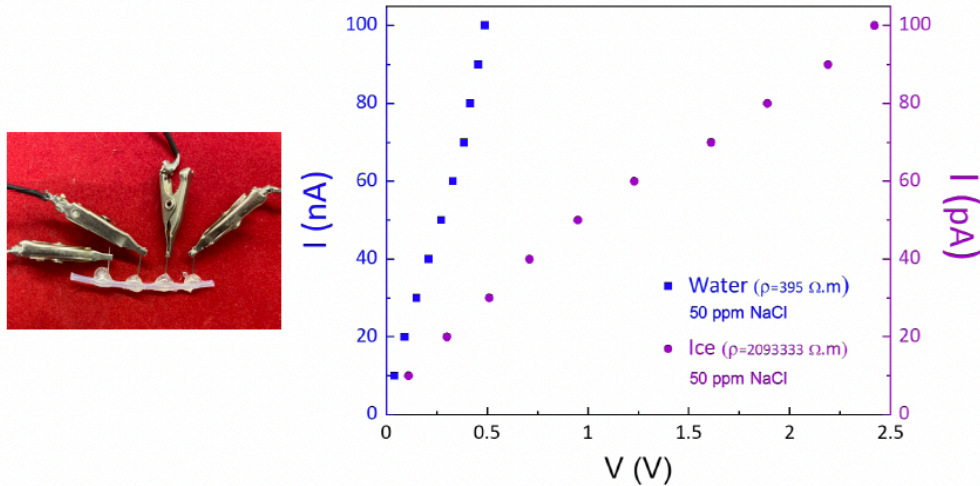


Figure II-10: The specific electrical resistivity of water solution and corresponding ice phase were measured in a plastic tube with inner diameter if 1mm.

1.4.4. FTIR metrology

The membrane was placed in water and sonicated for 5 minutes. Then it was removed from water and we let the extra water on both sides of the membrane evaporates. A thin layer of octane is injected on the membrane in a parallel direction with the surface of the membrane to wash any water that may exist on the surface. This membrane was sandwiched between two glass coverslips and placed under Thermo Scientific Nicolet iS50 FT-IR on a Zinc Selenide window to acquire FTIR spectra as a function of temperature.

The FTIR experimental setups are shown below. We used peltier coolers to control the sample temperature. In Attenuated Total Reflectance (ATR) mode, once the sample was placed on the FTIR stage, the peltier coolers were placed on a part of the membrane covered by a coverslip. For probing the sample temperature, a thermocouple was attached to the edge of the membrane. Because the membrane is placed between coolers, FTIR stage and coverslip, the vapor condensation from the surrounding environment is minimal. Furthermore, to prevent any possible frost formation, nitrogen gas was purged in the setup continuously. In the transmission mode, the membrane was sandwiched between coverslips and mounted on a stand and the light passed through the sample. C-H peaks from oil are subtracted using background and the resolution of the instrument is 4 cm^{-1} .

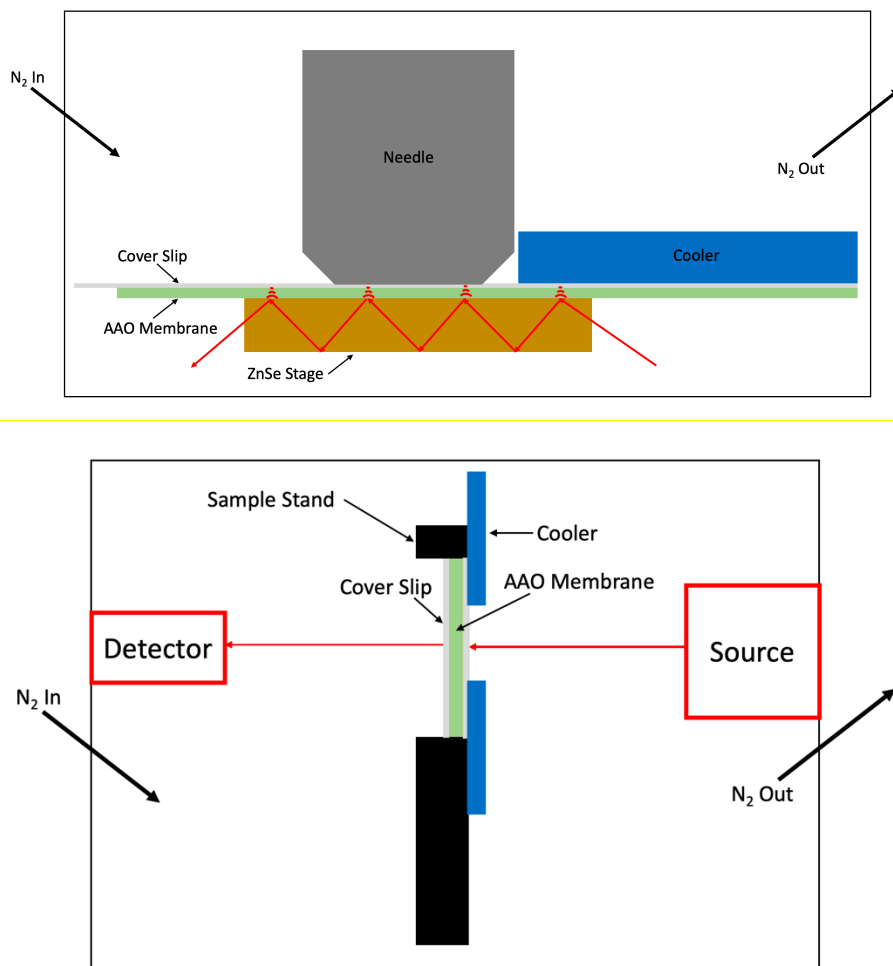


Figure II-11: Schematic of FTIR analysis setup that is used.

1.5. Results

1.5.1. Ice Nucleation Temperature Measured by Electrical Resistance Method

The water nanodroplets are formed inside pores of Anodized Aluminum Oxide (AAO) membranes. A range of AAO membranes with pore diameters of 150 nm to 2 nm and thickness of 50-60 μm are acquired. For all membranes, the pore diameters are highly uniform, but for 2 nm membrane, pore dimensions have a distribution of 2-4 nm. In

exception of 5 and 2 nm membranes, the pores are extended uniformly along the thickness of the membrane and are called isotropic. 5 and 2 nm membranes are anisotropic and made of two layers with different pore dimensions: small pores are extended from one side to approximately 10% of thickness of the membrane (active layer) and the remainder of the membrane is made of pores with dimension of 150 nm (supporting layer). The procedure for formation of nanodroplets in these nanopores is discussed in **2.2.1**. These nanodroplets are surrounded by an oil environment forming an oil-water interface. The criteria for selection of the oil were (1) to wet the pore wall and (2) to maximize water-oil interfacial tension. Octane was selected as the most appropriate oil to form nanodroplets in the pores after various choices of the oil were compared as discussed in 2.2.2. To ensure the presence of water nanodroplets in the pores, electrical resistances across the porous membrane were compared for cases of pores filled with octane and pores with confined water nanodroplets surrounded by octane. For the case that the pores are completely filled by octane, the electrical resistance is almost 5.5 G Ω . By introduction of water inside the pores, the electrical resistance is reduced to almost 3 G Ω . Also, the existence of water inside the pores is confirmed with FTIR that will be discussed in the following. Once the existence of nanodroplets in the pores was confirmed, we studied the water-ice phase change of these nanodroplets through two independent metrologies. Note that ice nucleation in these pores takes place heterogeneously, that is nucleation initiates from the oil-water interface due to the lower energy barrier required compared to that for homogenous nucleation. Also, solid-liquid phase change temperature of octane is -57 °C, well below the temperatures considered in this study. Once, the entire system including water droplet and surrounding environment is cooled down in a quasi-equilibrium condition, the ice formation is

characterized by median ice nucleation temperature (T_N) [43]. As the electrical conductance of water and ice are different up to three orders of magnitude [66] (depending on ion concentration), water-ice phase change in nanodroplets should manifest itself in the electrical conductance metric. Thus, we used electrical conductance metrology across the pores with the four-probe method [67] (that minimizes the effect of parasitic resistances) to investigate phase transformation temperature in water nanodroplets. 50 ppm of NaCl was added to de-ionized water to enhance the electrical conductance contrast between water and ice phases. This concentration of salt does not have any measurable effect on phase change temperature [68]. Also, 250 ppm of Span80 (nonionic surfactant, Sigma Aldrich) was added to the octane to enhance its electrical conductance. This surfactant did not show any significant effect on oil-water interfacial tension. The experimental setup and the methodology is presented in 2.2.3. For a given pore dimension, in a quasi-steady process, we gradually decreased the temperature of the system (0.3 °C/min) and measured the current-voltage (I-V) curves at each selected temperature, as shown in Figure II-12. As shown, for a representative membrane of 150 nm, as the system temperature decreases, the resistance across the pore increases linearly indicating the effect of temperature on the electrical resistivity of the liquid in the pore. However, between -9 °C and -11°C, we detected a high, nonlinear shift in resistivity and a jump in electrical resistance. As the conductance of ice and water are significantly different, this jump is an indication of water-ice phase transformation inside the pores. We continued these measurements to lower temperatures and no additional jump was detected at lower temperatures. This metrology was conducted on confined nanodroplets in membranes with pores of 80, 40, 20 and 10 nm and for all these pores, the jump in electrical resistance was observed but at different

temperatures indicating the size dependence of T_N of nanodroplets. The results are presented in Figure II-13. As discussed, for membranes with pore dimensions of 5 and 2 nm, in addition to small pores, there are larger pores in the supporting layer with the dimension of 150-200 nm. As we conducted the phase transformation studies on these pores, we observed two jumps, one at higher temperatures (~ -8 °C) was associated with larger pore dimension and the one at lower temperatures was attributed to phase change within smaller pores. The electrical resistivity results for different pore dimensions along with observed jumps are depicted in Figure II-12e. The size dependence of T_N for nanodroplets of 10 nm and below becomes more pronounced. Interestingly, despite being heterogeneous nucleation, we observed that water-ice phase transformation at pore dimension of 2 nm occurs at lower temperatures (-41 °C) than that for *homogenous bulk nucleation*, (~ -38 °C) [69,70]. That is, for few nm water droplets ice formation could be suppressed to extremely low temperatures. We continued these studies with another independent approach to re-measure T_N and acquire an understanding on the type of ice phase formed by these nanodroplets.

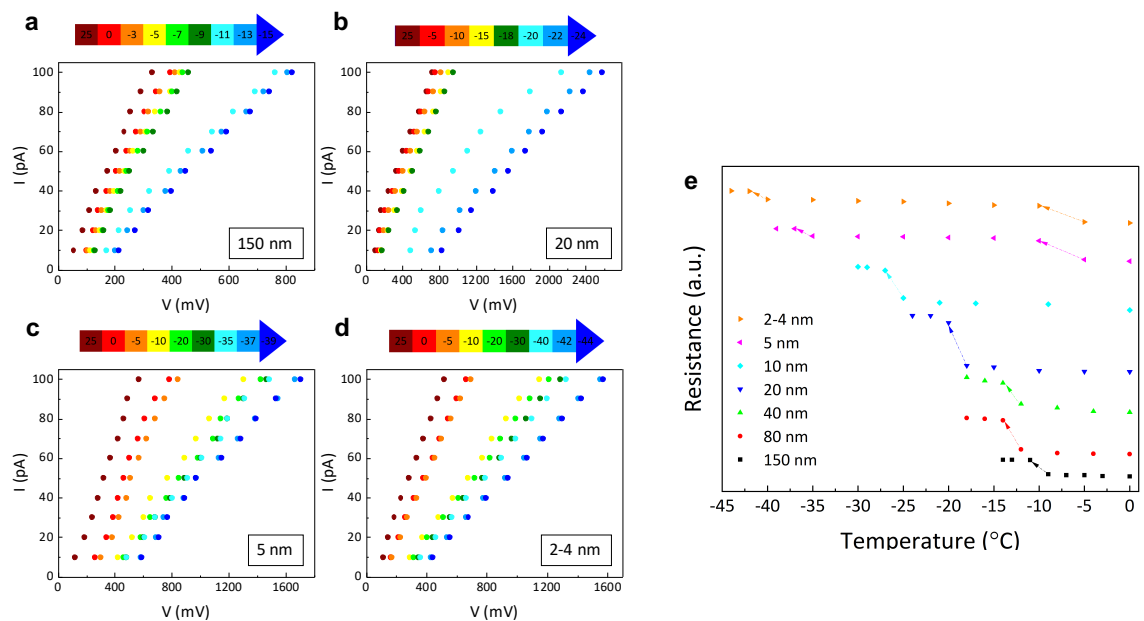


Figure II-12: Electrical resistance metrology. I-V curves were measured across the nanopores confining nanodroplets (a) Nanodroplets of ~ 150 nm (b) 20 nm (c) 5 nm (d) 2 nm (e) The normalized resistance jumps.

The water-ice phase transformation for different size nanodroplets is shown in Figure II-13. The non-linear shift in resistance across the pores indicates the phase change temperature (T_N).

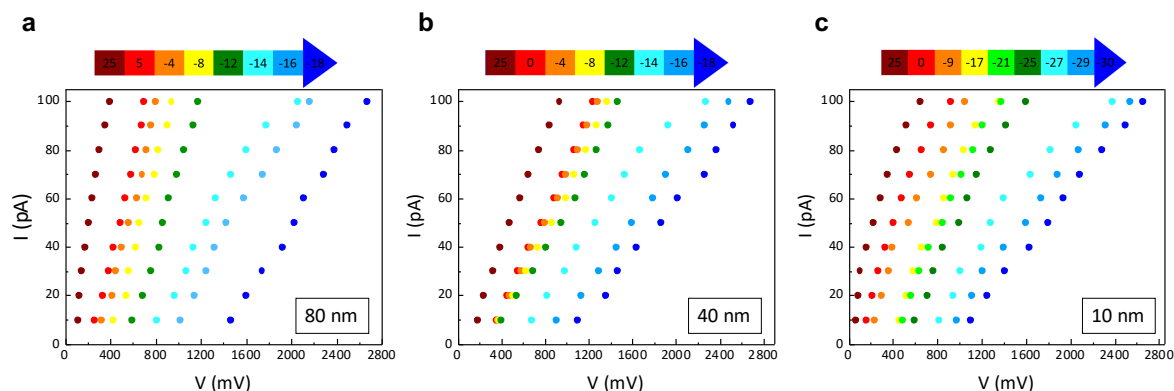


Figure II-13: I-V curve across nanopores measured as a function of temperature for water nanodroplets in the pores of membranes in the sizes of (a) 80 nm (b) 40 nm and (c) 10 nm.

We measured temperature-dependent I-V curves for octane-only filled membranes for 80 nm membrane and results are shown in Figure II-14. From this figure, we cannot observe any non-linearity down to -14°C . However, we observed non-linearity in resistance in water-filled 80 nm membranes around -12°C . This proves that non-linearities in resistance are not because of the octane.

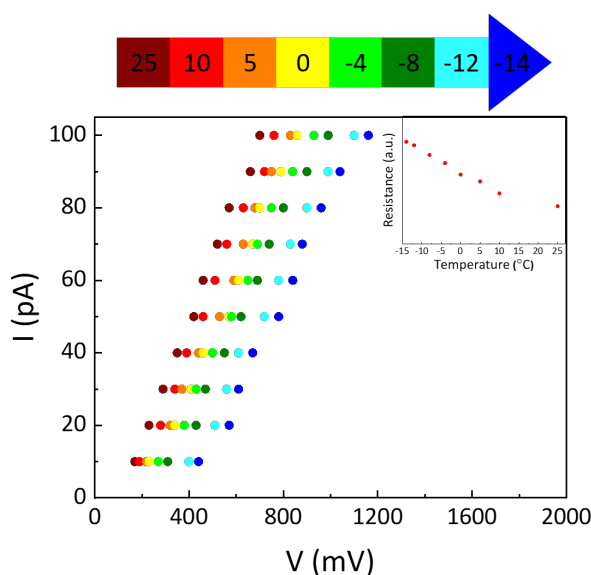


Figure II-14: I-V curves measured across the membrane when there is no water inside the pores in the membrane with pore diameter of 80 nm. There is no nonlinear jump in electrical resistance down to -14°C .

1.5.2. Ice Nucleation Temperature Measured by FTIR

In the second metrology, once the nanodroplets are formed in the pores, we probed FTIR spectrum of these droplets as a function of temperature. Figure II-15a shows FTIR spectroscopy of nanodroplets confined in 150 nm pores and indicates water OH stretch peak at 3300 cm^{-1} . However, once the temperature of the system drops to $-11\text{ }^{\circ}\text{C}$, the OH stretch peak becomes narrower and shifts to lower wavenumbers due to the stronger and less heterogeneous hydrogen bonding networks [71,72]. This narrowing and peak shift indicate water-ice phase transformation. We continued these experiments for other pore dimensions of 80, 40, 20 and 10 nm as shown in Figure II-16. Similar to the previous metrology, we found size dependence of water-ice transformation temperature in these nanodroplets. As we have two pore dimensions in 5 and 2 nm membranes, ice OH stretch peak in smaller pores would be overshadowed by ice OH peaks in larger pores. To address this challenge, we only wetted one side of the membrane and at the same time, we introduced octane from the other side of the membrane to limit the water nanodroplets in the small pore. The results are shown in Figure II-15c and II-15d for 5 and 2 nm pores and shows the OH stretch peak shift at much lower temperatures than large pores. This is in harmony with the findings of the electrical resistance metrology. There is more insight into this metrology compared to the first metrology. We found that the OH stretch bond in these few nm nanodroplets is similar to the larger nanodroplets and indicates that the ice phase formed in these small nanodroplets is I_h phase. The size dependence of water-ice phase transformation of nanodroplets measured through two metrologies are compared in Figure II-15e. The results from both metrologies are in close agreement and indicate a sharp dependence of transformation temperature for droplets smaller than 10 nm. We should

emphasize that the observed size dependence of ice nucleation is not caused by the volume of water in the pores. The volume of water inside the pores was measured using quartz crystal microbalance (QCM) analysis and the results are tabulated in Table 1 which shows that the membranes are substantially filled with water and the volume of liquid in all pore dimensions are in the same order.

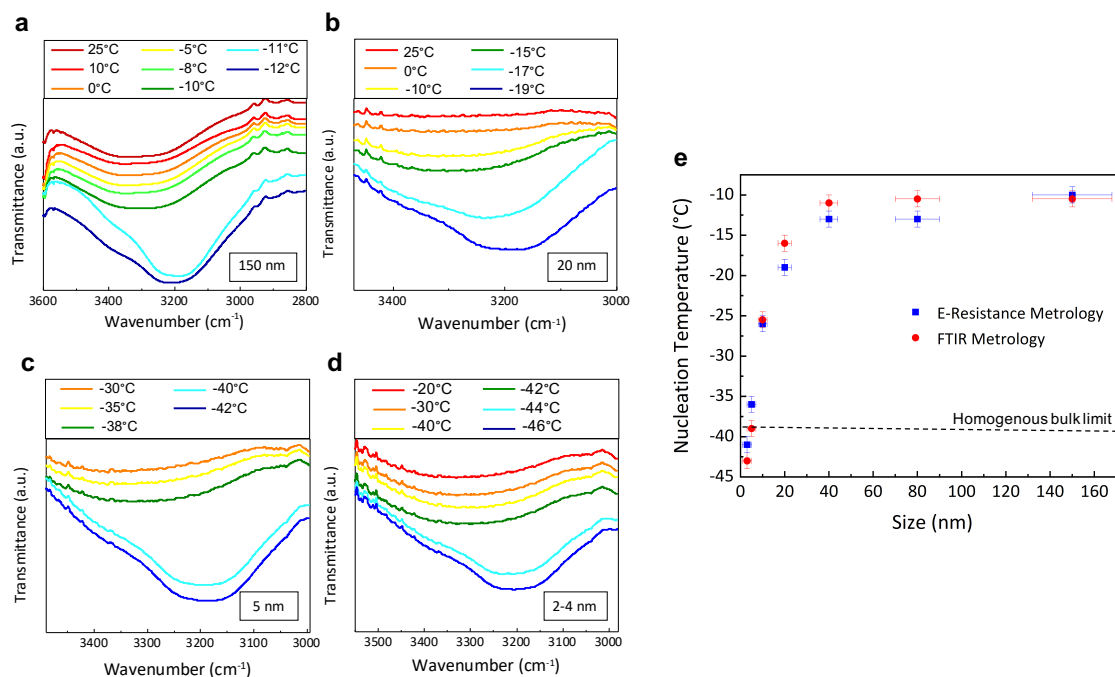


Figure II-15: FTIR metrology(a)150 nm (b) 20 nm (c) 5 nm (d) 2 nm (e) The nucleation temperature of nanodroplets measured through two independent metrologies is shown as a function of length scale.

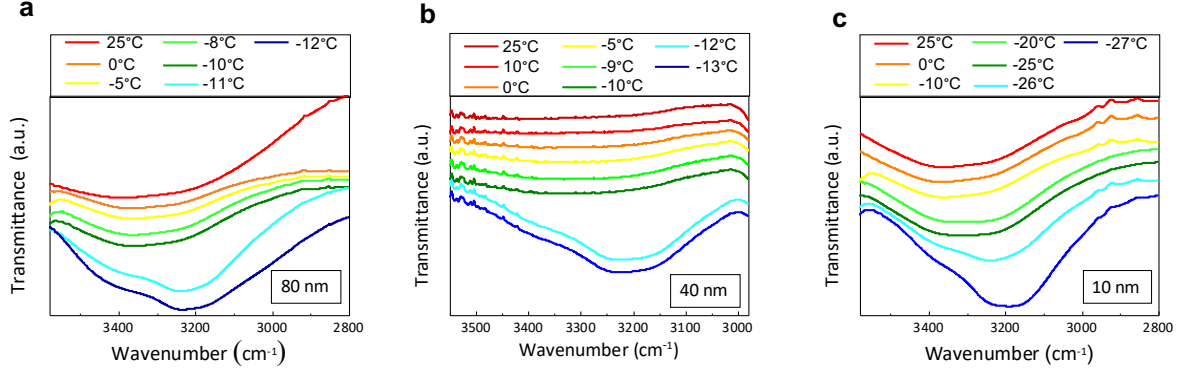


Figure II-16: FTIR metrology of nano-confined water droplets in the pores of the membrane with diameters of (a) 80 nm (b) 40 nm and (c) 10 nm encapsulated by octane. The temperature of the system is reduced in a quasi-static approach.

1.5.3. The Effect of Surface Factor and Chemical Potential Difference on Ice

Nucleation

To understand the length-scale dependence of heterogenous phase transformation, we explored the role of length-scale on Gibbs energy barrier of water-ice phase change.

The Gibbs energy barrier for heterogenous nucleation (ΔG^*) is written as [43,73]

$$\Delta G^* = \frac{16\pi\gamma_{IW}^3}{3(\rho\Delta\mu)^2} f(m, x), \quad (51)$$

where γ_{IW} denotes interfacial tension between water and ice, ρ is the density of water, $\Delta\mu$ is the chemical potential difference between ice and water phases, and $f(m, x)$ is the surface function which depends on interfacial energies, m , and interface geometry, x . The length-scale plays a role in ρ , $f(m, x)$ and $\Delta\mu$. For the nanodroplets which experience high pressure, the liquid density varies by $\sim 1.5\%$ [34]. As the nanodroplets are encapsulated by oil, the interface for heterogeneous ice nucleation (oil-water) is concave. The expression

of surface function is given in 2.4 and is plotted as a function of length scale for both -10 and -41 °C in Figure II-17. By considering the role of curvature, $f(m, x)$ function drops sharply for few nm droplets leading to drop of ΔG^* and consequently higher ice nucleation temperature for few nm water droplets. Also, through MD modeling, it has been shown that on solid concave interfaces, ice nucleation rate dramatically increases due to geometry effect on ΔG^* [74]. Surprisingly, this is contradictory with the experimental findings above and points to a missing understanding here. As the oil-water interface is soft, Figure II-18, once an ice nucleolus forms at this interface, the complete interfacial force balance needs to account for the unbalanced force of $\gamma_{IW} \sin \theta$ which leads to deformation of interface forming ripples at the oil-water interface [75]. In the case of stiff solid surfaces, this unbalanced force could be neglected due to the high modulus of solid surfaces. Thus, upon ice nucleation at the oil-water interface, the ripples form at the periphery of the water droplet and adjust the local curvatures of the interface. That is, the oil-water interface forms combined convex and concave interfaces. Ice nucleation occurs at both concave and convex coordinates. As the measured ice nucleation temperature is the average transformation temperature for the entire droplet, we may approximate zero curvature and determine $f(m, x)$ only as a function of m . Also, it should be noted that the effect of pore walls (to act as active sites) is negligible on ice nucleation here. Since the oil used in this study (Octane) possesses a lower surface tension (21.6 mN/m) compared to water (72 mN/m), it is a safe assumption is that the inner surfaces of the pores are preferably wetted by the oil phase. Hence, water must be encompassed by the oil phase and should not have contact with pore walls and potential active sites. Moreover, while the $P\Delta v$ (P is pressure difference at the oil-water interface and Δv is the specific volume difference between water

and ice) term showed a significant effect on ice nucleation, the surface factor did not, which suggests that pore walls do not play a role in nucleation here. This would have not been the case should water-wall interface was available for ice nucleation. Even if one considers that some pores have defects or water has contact with the pore wall, one observes the changes in both electrical resistance and FTIR spectrum when most of the pores are frozen. In other words, freezing of few pores does not show measurable changes in the results and significant changes occur when the majority of pores are frozen.

Theoretical analysis shows that if water has contact with pore walls and they act as nucleation sites, the effect of the surface factor becomes significant. To further demonstrate this fact, we filled membranes with water without addition of oil, where water has contact with pores walls and nucleation starts from the wall active sites. In this case, we performed FTIR analysis on membranes with different pore dimensions to find T_N as a function of size and results are shown in below. It is observed that in this case, T_N is higher even than the bulk nucleation temperature. For example, for a pore dimension of 2 nm filled just with water, through FTIR measurement, we have shown that ice forms at the temperature of ~ 0 °C. However, for the same pore dimension with the oil-water interface involved, ice forms at -42 °C. This is attributed to the effect of pore wall active sites.

1.6.Heterogeneous Nucleation of Nanodroplets

Gibbs energy barrier for heterogeneous ice nucleation is written as [16,50]

$$\Delta G^* = \frac{16\pi\gamma_{IW}^3}{3(\rho\Delta\mu)^2} f(m, x), \quad (52)$$

where γ_{IW} denotes interfacial tension between water and ice, $\Delta\mu$ is the chemical potential difference between ice and water phases and $f(m, x)$ denotes the surface function. Surface function depends on interfacial tensions, m , and surface geometry, x , defined as

$$m = \frac{\gamma_{OW} - \gamma_{OI}}{\gamma_{IW}} = \cos \theta, \quad (53)$$

where γ_{OW} is oil-water interfacial tension, γ_{OI} is oil-ice interfacial tension, γ_{IW} is ice-water interfacial tension and θ is the ice embryo contact angle with the oil-ice interface. x depends on interfacial geometry and is written as

$$x = \frac{R}{r_c}, \quad (54)$$

where r_c is the critical nucleolus radius and R is the radius of curvature of the oil-water interface. r_c is written as [16,73]

$$r_c = \frac{2\gamma_{IW}}{\Delta G_v} \quad (55)$$

$$\text{and } \Delta G_v = \Delta H_v \frac{T_m - T}{T_m}, \quad (56)$$

where ΔG_v denotes the free energy difference per unit volume between water and ice, ΔH_v denotes enthalpy of phase change per unit volume, T_m is the melting temperature of ice, and T is the temperature of the system. Also, ice-water interfacial tension is estimated as [16]

$$\gamma_{IW} = 23.24 \left(\frac{T}{235.8} \right)^{0.35}. \quad (57)$$

Table 5: Critical nucleolus radius as a function of temperature

Temperature (°C)	r_c (nm)
-10	4.21
-15	2.92
-20	2.23
-25	1.80
-30	1.50
-35	1.29
-40	1.13
-45	1.00
-50	0.89

The surface function, $f(m, x)$, for a concave surface is written as [45]

$$f(m, x) = \frac{1}{2} \left\{ 1 - \left(\frac{1+mx}{g_c} \right)^3 - x^3 \left[2 - 3 \left(\frac{x+m}{g_c} \right) + \left(\frac{x+m}{g_c} \right)^3 \right] + 3mx^2 \left(\frac{x+m}{g_c} - 1 \right) \right\} \quad (58)$$

$$\text{and } g_c = (1 + x^2 + 2mx)^{1/2}. \quad (59)$$

If one considers the effect of oil-water interface geometry, x , upon decreasing pore diameter, we observe a decrease in $f(m, x)$ and as a result a reduction in ΔG^* , as shown in Figure II-17 for two different temperatures.

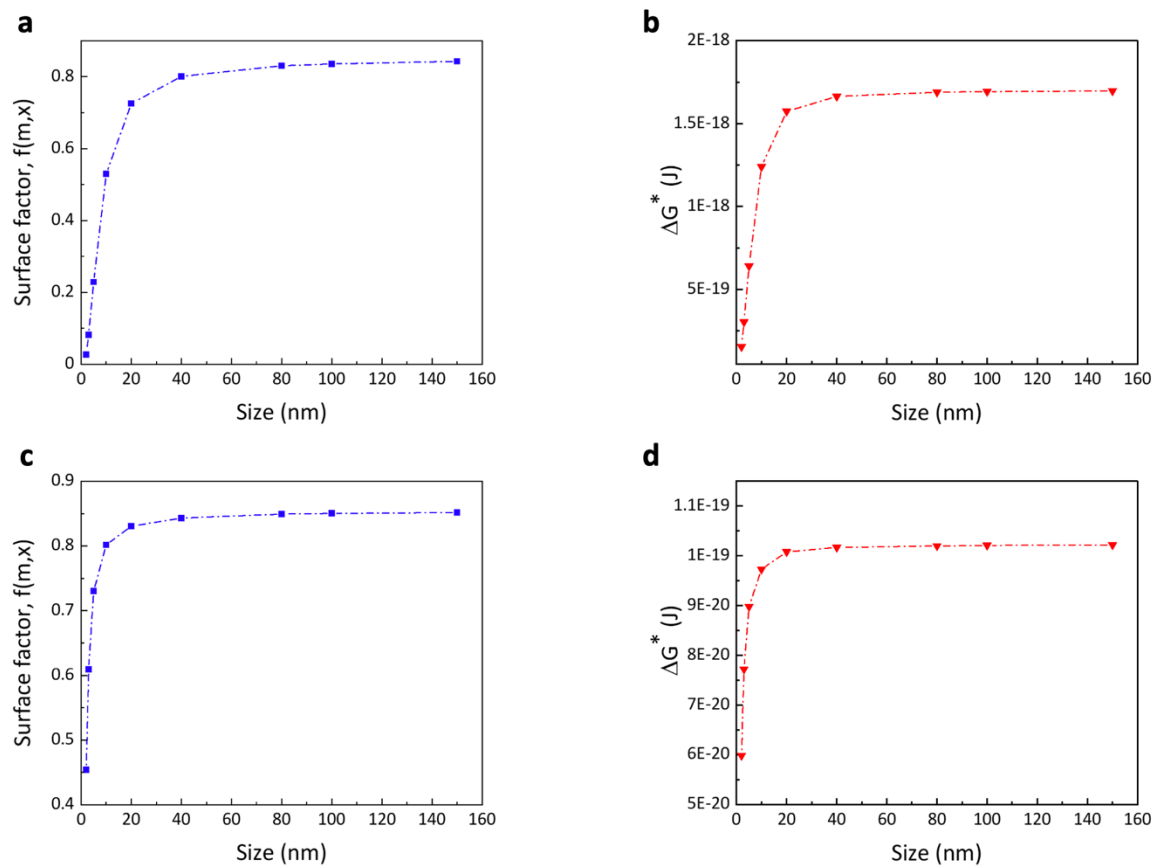


Figure II-17: (a) The role of x on $f(m,x)$ (b) ΔG^* as a function of length scale by considering the effect of interface geometry at $T=-10^\circ\text{C}$. (c) The role of x on $f(m,x)$ (d) ΔG^* as a function of length scale by considering the effect of interface geometry at $T=-41^\circ\text{C}$.

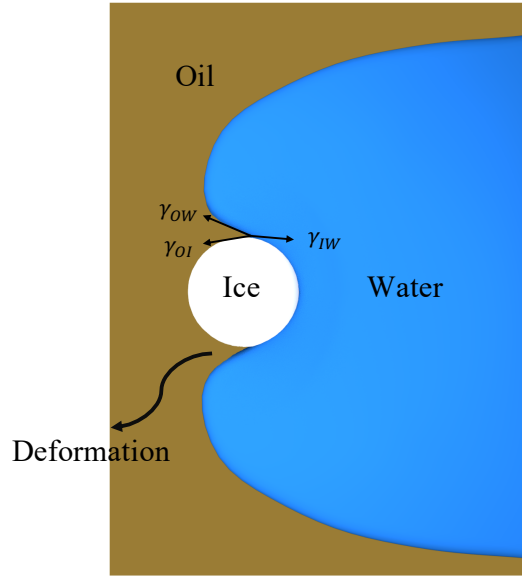


Figure II-18: Deformation of oil-water interface as ice nucleates at the interface. The deformation is caused by unbalanced $\gamma_{IW} \sin \theta$ force leading to local convex and concave coordinate (ripples) at the oil-water interface.

Here, we have distinguished heterogeneous and homogeneous modes of nucleation through Gibbs energy barrier (ΔG^*) analysis. If the nucleation in these pores were homogenous, we should not observe any effect of confinement size on the nucleation temperature. For example, for the case of pure water in the confinement, the nucleation temperature varies from -7 to 0 °C.

To further confirm this, we performed another set of experiments with membrane with pore dimension of 10 nm where we switched the encapsulating Octane phase with PDMS/Octane mixture to provide different modulus at the water-PDMS/Octane interface as shown in Table 6. In these experiments, we filled the membranes with water and encapsulated them with different ratios of sylgard and octane mixture (i.e. ratio of base to crosslinker). We performed FTIR analysis and the results are shown in Figure II-19. The results show that as the modulus of interface increases, due to the effect of surface factor

on Gibbs energy barrier, ice nucleation temperature increases. This is another proof that the ice nucleation is heterogenous and not within the bulk of the liquid. This additional experiment also confirms that the soft octane-water interface leads to suppression of freezing to extremely low temperatures.

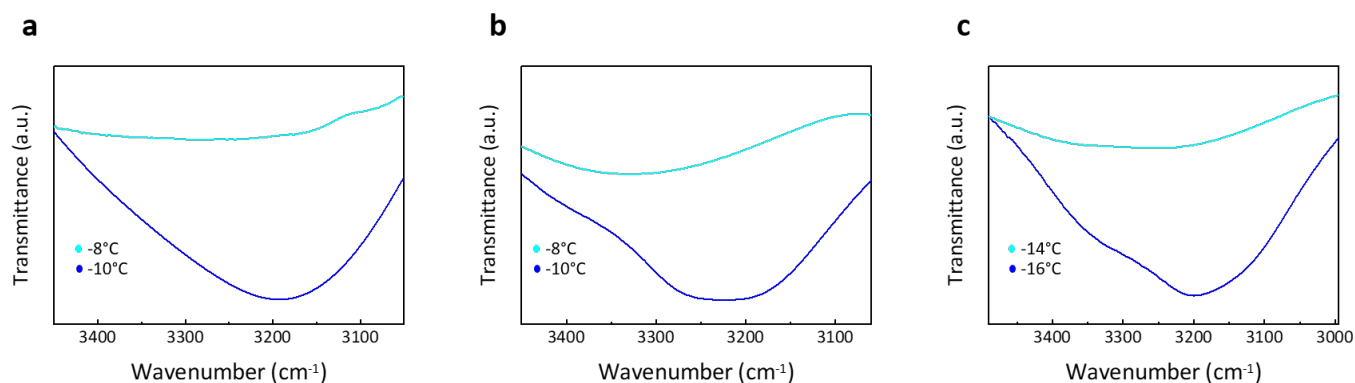


Figure II-19: FTIR spectrum of nanodroplets in membrane with pore diameter of 10 nm surrounded by PDMS/Octane with different moduli (different ratio of prepolymer to curing agent) (a) 10:1 (b) 30:1 and (c) 60:1

Table 6: Nucleation temperature of water nano-droplet confined in 10 nm nanopores and encapsulated with PDMS/Octane with different moduli.

Octane: Base: Crosslinker (weight ratio)	Young modulus (kPa)	TN (°C)
50: 10: 1	1300	-9
150: 30: 1	120	-9
300: 60: 1	3	-15
Just Octane	0	-26

1.7. Length-scale Dependence of Chemical Potential, Surface Factor and Ice Nucleation Rate

The length-scale dependence of chemical potential manifests itself in the form of pressure and is written as [43,76]

$$\Delta\mu_{Nd}(T, P) = \Delta\mu_b(T, P_{atm}) + (P_{Nd} - P_{atm})(v_w - v_i), \quad (60)$$

in which $\Delta\mu_{Nd}(T, P)$ and $\Delta\mu_b(T, P_{atm})$ are the chemical potential difference between ice and water for a nanodroplet and bulk water, respectively, $(P_{Nd} - P_{atm})$ is pressure difference at the oil-water interface, and v_w and v_i are specific volumes of water and ice, respectively. We plotted the dependence of $\Delta\mu$ as a function of length-scale of nanodroplets in Figure II-20a. As shown, the chemical potential difference drops sharply for few nm droplets due to high Laplace pressure. Having these dependencies, the Gibbs energy barrier for heterogeneous ice nucleation of nanodroplets is shown in Figure II-20b. As shown, in nanodroplets with dimensions of less than 10 nm, the Gibbs energy barrier is increased. Given the Gibbs energy barrier, we determined the theoretical ice nucleation temperature of nanodroplets based on the classical nucleation theory (CNT) [73], and plotted in Figure II-20c. We considered the same nucleation rate at T_N for all the nanodroplets in these calculations. In addition, the average measured T_N by two metrologies is included here. As shown, there is a good agreement between the measurement and predictions by CNT. The ratio of ice nucleation in nanodroplets compared to bulk value is written as [34]

$$\frac{R_{Nd}}{R_b} = \exp \left[-\frac{16\pi \gamma_{Iw}^3 f(m)}{3k_B T \rho^2} \left(\frac{1}{(\Delta\mu_b + p\Delta v)^2} - \frac{1}{\Delta\mu_b^2} \right) \right]. \quad (61)$$

This ratio as a function of length-scale is shown in Figure II-20d. At length scales smaller than 10 nm, the ice nucleation rate drops drastically compared to that in the bulk phase suggesting the suppression of ice formation in these nanodroplets.

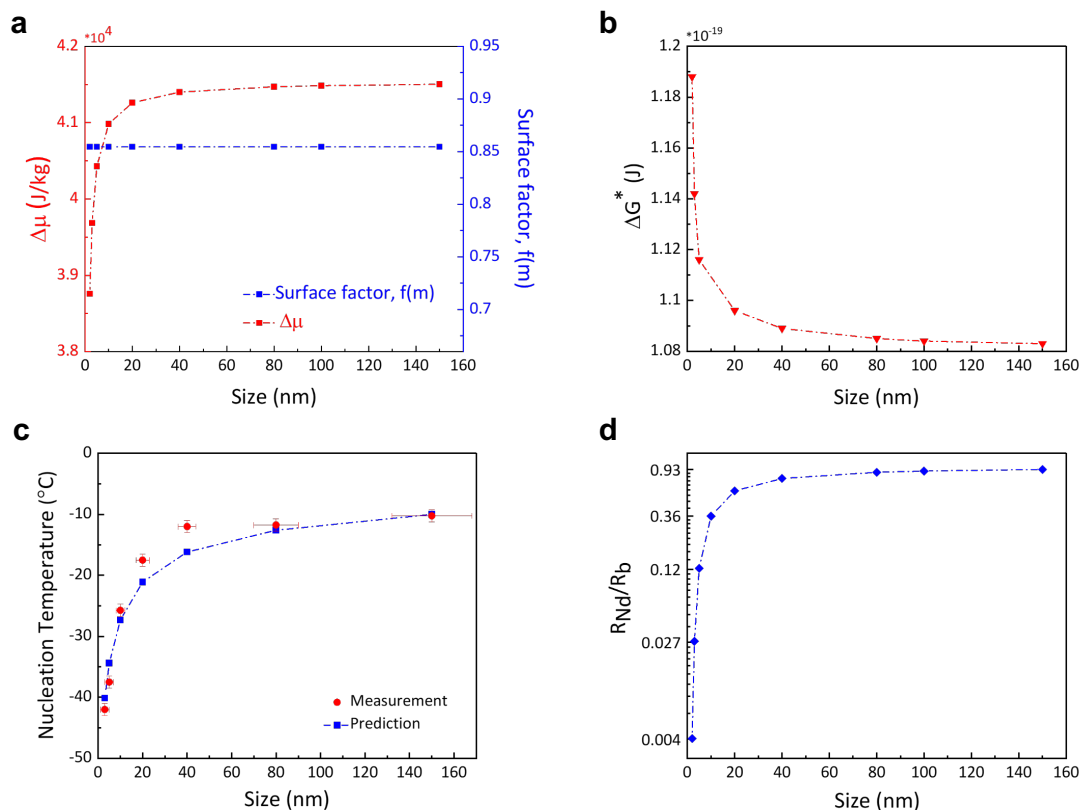


Figure II-20: (a) $\Delta\mu$ as a function of length scale (b) ΔG^* as a function of nanodroplets diameters. (c) Predicted T_N by CNT and averaged measured T_N (d) Normalized ice nucleation rate of nanodroplets with respect to bulk water at $T=-41^{\circ}\text{C}$.

1.8. Effect of pores wall active sites on ice nucleation

We conducted ice formation experiments in pores just filled with water and no oil through FTIR metrology with different pore sizes. The results are shown in Figure II-21. As shown, ice nucleation temperature increases as the size decreases. In this case, the water has contact with the inner surface of the pores and the pore's walls act as nucleation sites.

Ice nucleation temperature as a function of pore dimension is shown in Figure II-22. Note that this is completely in contrast to the case that the oil-water interface exists in which ice nucleation temperature drops at lower pore dimensions.

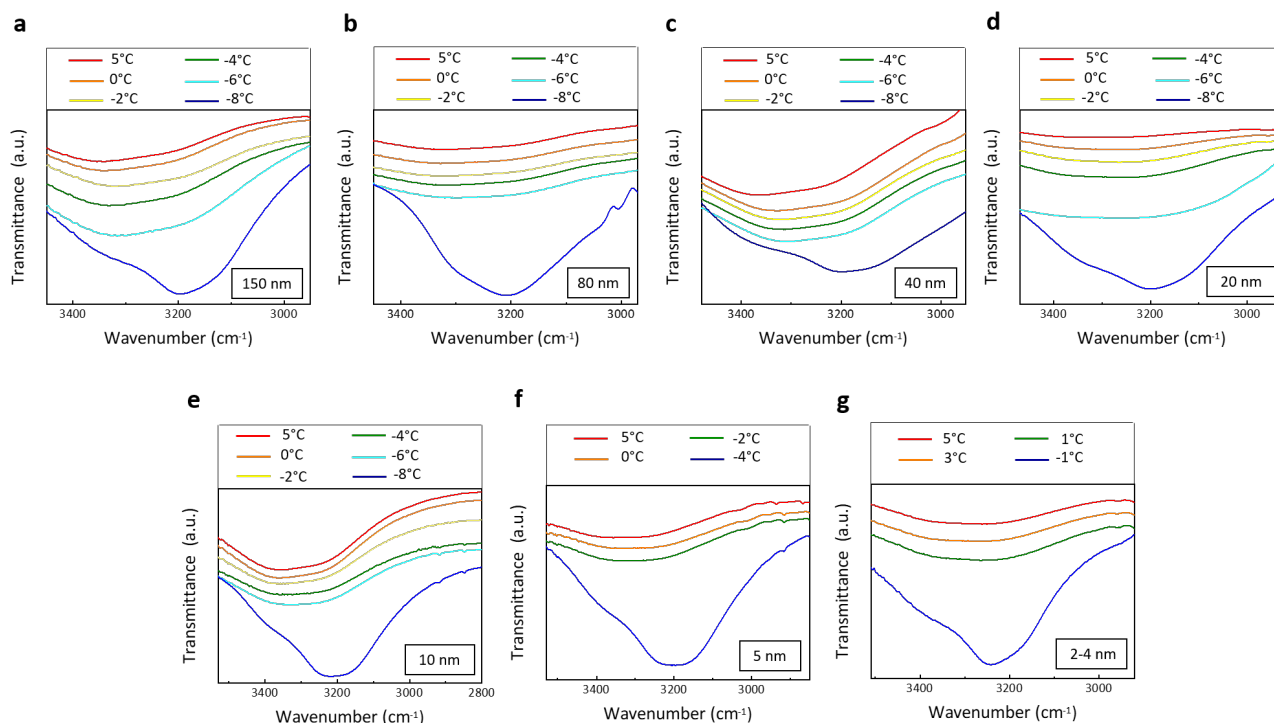


Figure II-21: FTIR spectrum of nanodroplets in various pore dimensions when pores are filled with water without addition of oil around them. (a) 150 nm (b) 80 nm (c) 40 nm (d) 20 nm (e) 10 nm (f) 5 nm (g) 2 nm.

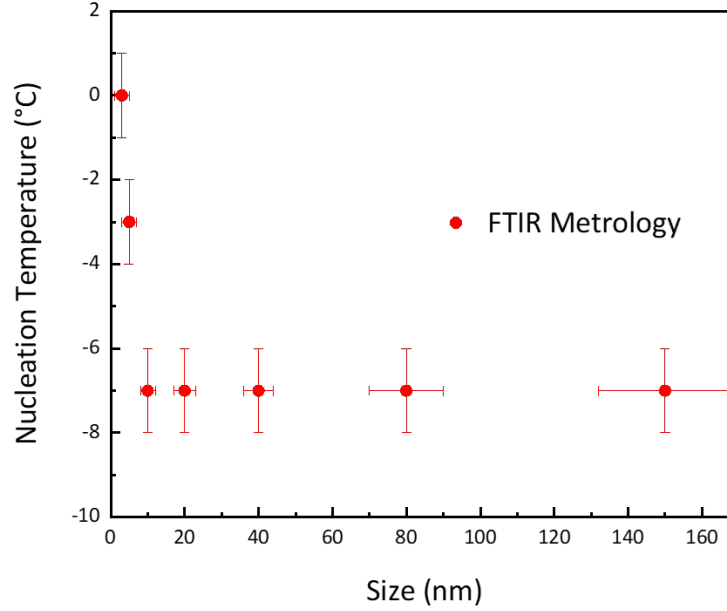


Figure II-22: The nucleation temperature of water droplets, when the membrane is filled with water without addition of oil, measured through FTIR metrology is shown as a function of length scale.

The observed nucleation temperature could be explained through the thermodynamics of ice nucleation. In this case, nanodroplets experience negative pressure inside the pores due to the curvature of the water meniscus. Surface factor, $f(m, x)$, and chemical potential difference, $\Delta\mu$, are calculated for this scenario as a function of pore dimension and are plotted in Figure II-23a. As shown, as the size decreases, the surface factor decreases as well, primarily due to the concave interface of pore walls. In addition, the negative Laplace pressure in the nanodroplet decreases, which in turn leads to an increase in the chemical potential difference. The decrease in $f(m, x)$ and the increase in $\Delta\mu$ both lead to drops in the Gibbs energy barrier for ice nucleation, Figure II-23b.

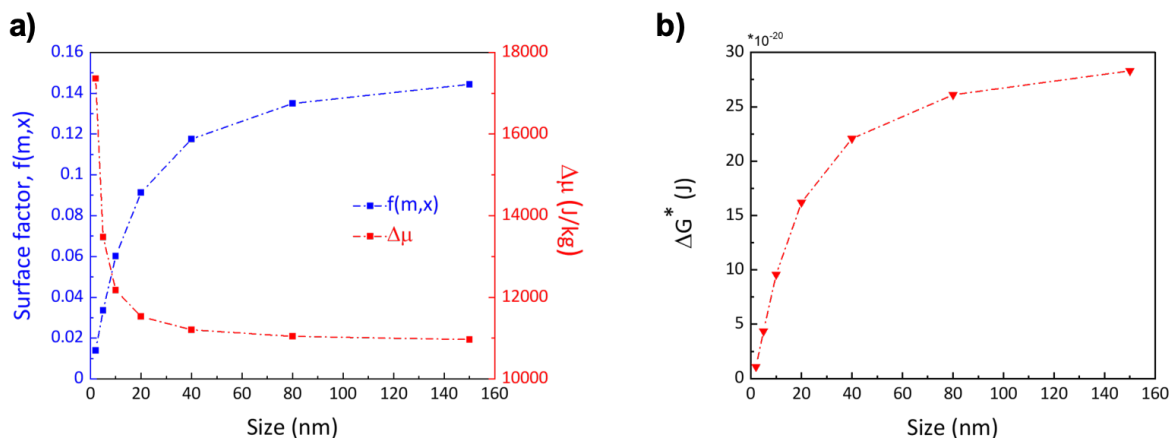


Figure II-23: (a) The role of interfacial curvature on surface function and chemical potential difference when pores are filled with water without addition of the oil. (b) ΔG^* for water-ice phase change of nanodroplets as a function of the diameter.

We assume that oil wets the surface and water is encompassed by oil, as the oil has lower surface tension than water and the system is stable when the oil wets the pore walls. Thus, water does not have contact with pore walls and active sites. Also, even if we consider that some pores have defects or water has contact with the pore wall and freeze in higher temperatures, we can observe the changes in both electrical resistance and FTIR method, when most of the pores are frozen. In other words, freeing of few pores does not show significant changes in results and significant changes occur when the majority of pores are frozen.

To further demonstrate that pore walls (with their potential active nucleation sites) are not involved in ice nucleation, we calculated surface factor, $f(m,x)$, and chemical potential difference, $\Delta\mu$, for a *hypothetical* case where water contained inside the pores is surrounded by the oil at the ends, but oil does not wet the interior pore walls. Therefore, water is in direct contact with the walls within the pores. In this case, due to the curvature of the oil-water interface, there is a positive pressure build-up inside the water. The surface

factor for the inner concave surface of pore walls is also known, thus Gibbs free energy can be obtained. As shown in Figure II-24a, upon decreasing the size, f and $\Delta\mu$ both decrease and the effect of f is more significant. Thus, ΔG^* must decrease (Figure II-24b) for smaller sizes which is in contrast with our experimental observations; hence this scenario fails i.e., the walls are wetted with the oil.

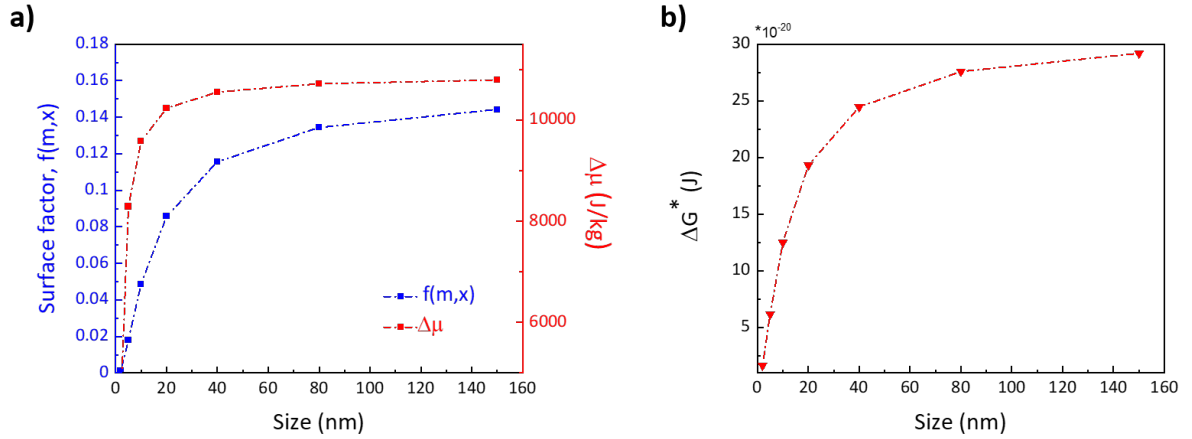


Figure II-24: (a) The role of interfacial curvature on $f(m,x)$ and $\Delta\mu$ when pores are filled with water and the assumption that oil does not wet the pore wall. (b) ΔG^* as a function of diameter of nanodroplets.

Due to the fact that ice nucleates inside the water not oil, the oil is a concave substrate for ice nucleation as shown in Figure II-25. Also, for a concave interface, ΔG^* decreases as the size of droplet decreases. (i.e. $f(m,x)$ becomes smaller for smaller droplets).

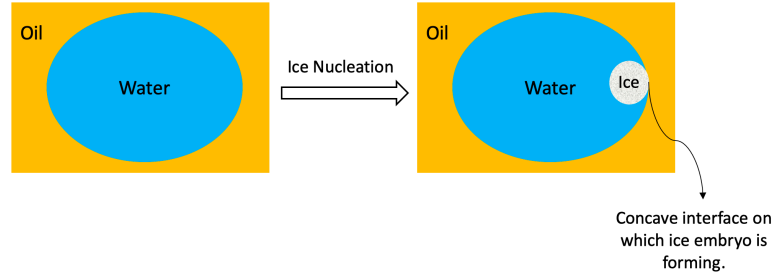


Figure II-25: Schematic of water nano droplet encapsulated in oil and the formation of ice embryo inside water.

1.9.Theoretical ice nucleation temperature of nanodroplets based on the classical nucleation theory (CNT)

Ice nucleation rate which is a function of Gibbs energy barrier is defined in Eq. (62) [16], as

$$R(T) = \frac{1}{\tau_{av}} = K \exp\left(-\frac{\Delta G^*}{k_B T}\right), \quad (62)$$

where τ_{av} is ice nucleation delay time and K is a kinetic constant and defined as [16]

$$K = Z\beta N, \quad (63)$$

where Z is Zeldovich non-equilibrium factor, β is the rate of addition of atoms or molecules to the critical nucleus and N is the number of atomic nucleation sites per unit volume. By substituting Eq. (52) in Eq. (62), we have

$$R = K \exp\left(-\frac{16\pi\gamma_{IW}^3 f(m)}{3k_B T (\rho\Delta\mu)^2}\right). \quad (64)$$

Also, $\Delta\mu$ for a nanodroplet can be expressed as

$$\Delta\mu_{Nd} = \Delta\mu_b + p\Delta v. \quad (65)$$

By substituting Eq. (60) in Eq. (64), we can write the ice nucleation rate of nanodroplets with respect to bulk water as

$$\frac{R_{Nd}}{R_b} = \exp \left[-\frac{16\pi \gamma_{lw}^3 f(m)}{3k_B T \rho^2} \left(\frac{1}{(\Delta\mu_b + p\Delta v)^2} - \frac{1}{\Delta\mu_b^2} \right) \right]. \quad (66)$$

$\Delta\mu_b$ can be estimated as [16]

$$\Delta\mu_b = \frac{\Delta H(T_m - T)}{T_m}, \quad (67)$$

where $\Delta H = 271000 \frac{J}{kg}$ is the specific enthalpy of freezing. By substituting Eqs. (65) and (67) into Eq. (66), we get to

$$\alpha = T^{0.05} \left[\frac{1}{(998(T_m - T) + P\Delta v)^2} - \frac{1}{(998(T_m - T))^2} \right], \quad (68)$$

where α is a constant and is written as

$$\alpha = -\frac{7.5 \cdot 10^7 * k_B * \rho^2 * \ln\left(\frac{R_{Nd}}{R_b}\right) * f(m)}{16\pi}. \quad (69)$$

We calculated α by replacing Laplace pressure and the experimental T_N obtained for 150 nm nanodroplets in Eq. (69). Then, this α was used to calculate T_N for the other sizes.

Note that we considered at the nucleation temperature of each nanodroplet, the rate of nucleation is the same.

Furthermore, the ratio $\left(\frac{R_{Nd}}{R_b}\right)$ is plotted as a function of size at $T = -41^\circ\text{C}$ in Figure

II-20d in the main text and $T = -10^\circ\text{C}$ in Figure II-26.

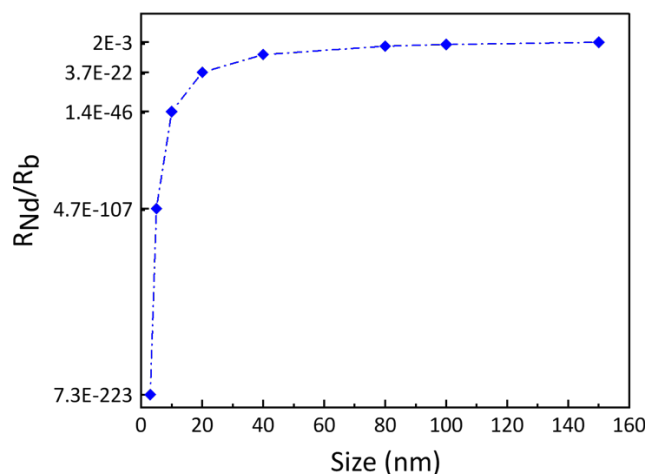


Figure II-26: The normalized ice nucleation rate of nanodroplets with respect to bulk water is shown as a function of length scale at $T = -10^\circ\text{C}$.

1.10. Discussion

We probed the ice nucleation of nanodroplets down to 2 nm scale and found that interfacial deformation at soft interfaces and high pressure could significantly suppress ice nucleation rate and delay ice nucleation to temperatures even lower than homogenous bulk nucleation temperature [77-79]. The pressures induced in these nanodroplets are up to ~500 bar and the only stable phases of ice in this pressure range based on the phase-equilibrium data are Ih (hexagonal) and Ic (cubic). However, it has been shown that ice formed by freezing of supercooled water forms stacking default ice, ice Isd, with a high degree of cubicity that anneals to stable hexagonal ice on the time scale of hours and this transition is subject to the kinetics of recrystallization [80-83]. It has been discussed that nanoconfined water could show narrowing of OH peaks due to no free OH groups that are in the bulk phase. We did not observe this effect possibly due to the elongated ellipsoidal

shape of nanodroplets here. The analysis of the finding through CNT suggests that the pressure in these nanodroplets is the governing factor in the suppression of ice nucleation and agreement between the finding and the CNT predictions support the dominant role of pressure. It has been discussed that ice nucleation in water clusters containing 275 water molecules occurs at temperatures in the range of $-183 \sim -158$ °C [30], and some simulations have shown that ice nucleation in nanodroplets with diameter of 2 nm can be suppressed down to -123 °C. If we consider the case of homogenous nucleation and assume the value of $f(m, x)$ equal to 1, the value of Gibbs energy barrier could be increased by $\sim 17\%$ meaning that ice nucleation temperature (Figure II-20b and II-20c) could be dropped by a few degrees. However, the more salient effect comes from the role of pressure in a spherical droplet. If one develops a hypothetical case of 2 nm spherical droplets in the air, the pressure in the droplets could be increased by approximately two times compared to the studied nanodroplets here. That is, based on the decreased nucleation rate, and extrapolation of the above findings, the solid-ice temperature could drop to -60 °C, which is still far from the predictions of -123 °C. It has been suggested that for nanoconfined water droplets in order of 1 nm, there are significant broken O-H bond [77] leading to an exotic state and for 2-3 nm confined droplets, ice-like nanocluster of water is formed [78] that could affect the solid-liquid phase change characteristics. Furthermore, the phase change transition could be completely non-monotonic [64]. The nature of OH group in few nm droplets and the finite number of molecules may be a key to address this difference. The findings provide an understanding of various natural phenomena and provide a route for the design of superior anti-icing biomimetics or smooth liquid-infused surfaces [48-50].

1.11. Conclusion

Water-ice transformation of droplets even a few nanometers in size can affect nature, impacting climate, clouds and survival mechanisms of animals in cold environments. Ice can also affect infrastructure, crippling transportation networks, causing power outages and energy shortages, and damaging the economy. Experimental probing of freezing temperatures of a few nanometer water droplets has been an unresolved challenge. We have been able to probe freezing of water droplets from the micron scale down to the two-nanometer scale. Until now, researchers believed that all water would freeze when exposed to temperatures between 0 to -38 °C. But we found that if a water droplet is in contact with a soft interface, freezing temperature could be significantly lower than it is on hard surfaces. A few-nanometer water droplet could avoid freezing down to -44 °C if it is in contact with a soft interface. Anti-icing surfaces play a critical role when the temperature drops, yet the development of high-performance anti-icing surfaces has remained elusive. These findings provide new insights, the scientists said, into water-ice transformation phenomena that will improve the design of anti-icing systems for infrastructure, transportation networks, power generation systems and even cryopreservation.

CHAPTER 3

III. METROLOGY OF ICE ADHESION

3.1. Introduction

As an icephobic coating is developed, it is crucial to examine icephobic properties including ice adhesion strength on the coating. There are several approaches used in the literature for ice adhesion measurements. Among these approaches, pushing test method, shear test method, centrifugal force method, and tensile force method are widely-used approaches. These approaches can be implemented in different setups with various geometries and dimensions. The diversity in ice adhesion measurement methods makes the comparison of reported data difficult and even for the same coating materials different ice adhesion strengths are reported in the literature. Thus, this diversity highlights the importance of introducing a standard approach by which reproducible data can be obtained in different laboratories.

In this chapter, we explain the theory of ice adhesion on a surface and derive an equation for the calculation of ice adhesion on the surface of an elastomer. Although this formula is obtained for an elastomer, it can be generalized for the other types of coatings. After that, different approaches which are used for ice adhesion measurement in the literature are discussed. At the end of this chapter, a standard method is fostered which is obtained through mechanics of ice adhesion on a surface. This standard approach leads to the unification of ice adhesion values obtained from different laboratories with the same metrics.

3.2. Theory of ice adhesion on a surface

As ice is formed on a surface, it can form van der Waal's force, electrostatic forces or hydrogen-bonding forces with the surface [84,85]. Elastomers are introduced as the materials which have low ice adhesion and are widely used in the coatings for icephobic applications [86]. When a rigid ice is formed on an elastomer surface, a threshold force on ice is required to remove it. If the force, F , is applied at the plane of ice-surface, detachment does not occur. On the other hand, if the force is applied at a plane higher than the interface, it induces an external torque on the ice which generates a normal stress at the interface. As this stress reaches to a critical stress, ice is detached from the surface. The applied torque, τ , can be obtained by the formula as

$$\tau = F \cdot l = a \int \sigma_n x dx, \quad (70)$$

where l is distance between coordinate of applied force from the interface, a denotes the dimension of ice, σ_n is normal stress at the interface, and x is horizontal axis. The applied force for detachment of ice from the surface can be obtained as

$$F = a^2 \sigma_s, \quad (71)$$

where σ_s is the adhesion stress of the interface (i.e. $\sigma_s \sim \frac{a}{l} \sigma_n$). As it mentioned before, the force should not be applied to the interface plane [87]

$$\sigma_s \neq 0: l \rightarrow 0 \Rightarrow \sigma_n \rightarrow 0.$$

Considering the equation of continuity, elastic energy of an elastomer can be obtained by

$$U \sim Gh \delta^2 \left[\frac{\lambda}{h^2} + \frac{1}{\lambda} \right]^2, \quad (72)$$

where G denotes shear modulus of the elastomer, h is the characteristic length, δ is the amplitude of perturbation of the elastomer and λ is the wavelength of the elastic waves at the interface. The normal stress at the interface of elastomer can be obtained by derivative of Eq. 72 with respect to δ as

$$\sigma_n \sim \frac{G\delta}{h}. \quad (73)$$

Total energy of elastomer-ice system per unit width can be obtained by the summation of elastic energy of elastomer and the surface energy as

$$U = \left(\int_0^a \int_0^{\delta^*} \sigma_n d\delta dx \right) - W_a a, \quad (74)$$

where W_a denotes the work of adhesion and δ^* is the maximum displacement at the interface which is a result of elastic instability. In fact, it is elastic instability which is the responsible for the ice detachment from the surface. Critical stress can be obtained through the setting derivative of total energy with respect to crack length to zero. Thus, using normal stress definition, the work of adhesion is obtained as

$$W_a \sim \frac{G\delta^*}{h}. \quad (75)$$

Then adhesion stress at the ice-icephobic coating interface for a uniform elastomer is expressed as

$$\sigma_s \sim \left(\frac{a}{l} \right) \sqrt{\frac{W_a G}{h}}. \quad (76)$$

This equation is obtained with assumption of $\delta^* \sim a$. This assumption is valid for an elastomer which has linear correlation of vertical displacement with respect to a . According to Eq. 76, in order to reduce ice adhesion, G and W_a should be reduced. G is a more feasible tuning parameter as it can be tuned by several orders of magnitude which will have significant effect on the reduction of ice adhesion. For example, by adding oil into the chains of an elastomer which has shear modulus around 1 GPa, gel will be formed which has shear modulus around 1kPa resulting in significant reduction in ice adhesion. However, the range of change in W_a is limited. As an example, fluorinating surface of a coating is an approach to decrease W_a . Irajizad et al. collected ice adhesion data on different elastomers and plotted these ice adhesion values as a function of $\sqrt{\frac{W_a G}{h}}$ (Figure III-1) [88].

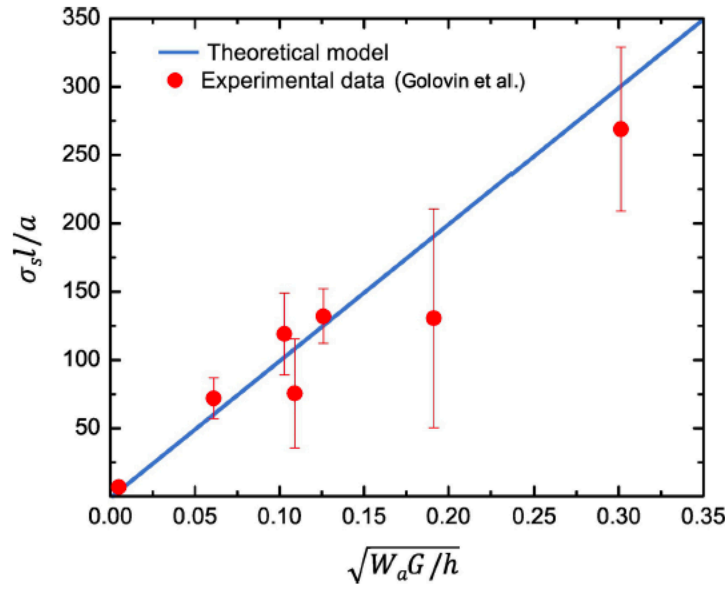


Figure III-1: The reported values of ice adhesion according to Eq. 76 [88]

According to the Eq. 76, theoretical model for this curve is the bisector of curve, and as it is clear in this curve, experimental data are in a good agreement with the theoretical model. a and l are the parameters that depend on the setup of ice adhesion measurement and its geometry. The inconsistency in the reported values of ice adhesion for same materials in the literature is caused by inconsistency in geometrical parameters of implemented setups [89-91]. This endorses significance of introducing a standard approach for ice adhesion measurement.

3.3. Centrifugal force method

In this method, icephobic coating is coated at end of a rotating beam as shown in Figure III-2. Ice can be formed on the icephobic coating through placing water inside a mold, e.g. cuvette column, and cooling down it to freeze, or through rain of sub-cooled droplets. The beam starts rotating and induces shear force to the interface between ice and coating. As the rotating speed increases, the induced shear force increases until the ice is detached from the icephobic coating. Ice adhesion strength is defined as the centrifugal force divided by cross-sectional area of detached ice at the moment on which the ice is detached from the icephobic coating. In order to record the moment of detachment, ice separation from the surface is detected by detectors, e.g. piezoelectric cells.

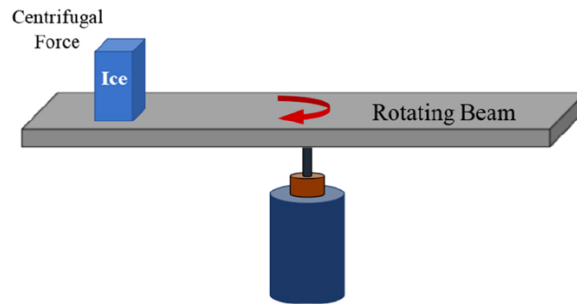


Figure III-2: Schematic of centrifugal force method for ice adhesion measurement [88]

The vibrations in the beam during the movement can make errors in the measurement. These vibrations are mostly due to the imbalance in the beam. In the method introduced by Anti-icing Materials International Laboratory (AMIL), a counter-weight can be provided on the other side of beam to decrease such vibrations (Figure III-3) [92].

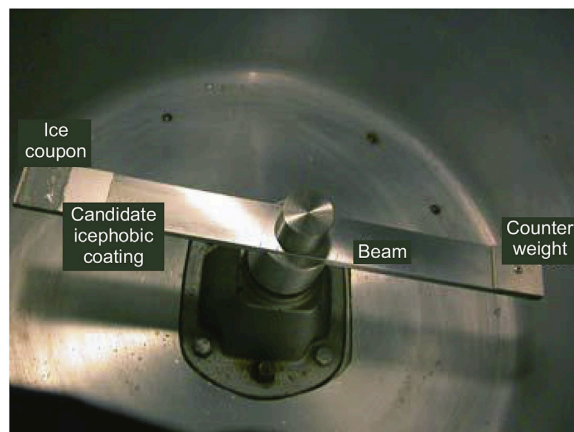


Figure III-3. Experimental setup for ice adhesion measurement using centrifugal method with counter weight [93]

With assumption that shear distribution is uniform in the ice-icephobic substrate, shear strength of ice can be expressed as

$$\tau = \frac{F}{A}. \quad (77)$$

However, stress at the ice-icephobic substrate is complex and shear stress exists mostly on the edges of the samples and dominant stress on the other parts of sample are peel stresses. In order to consider this complex, nonuniform stress Adhesion Reduction Factor (AFR) is taken into the account. AFR is defined as the adhesion strength of a baseline material, usually aluminum in centrifugal force method, divided by the adhesion strength of ice to the icephobic coating in the centrifugal force method. This method needs detailed finite element analysis to give quantitative results for the adhesion of ice to the substrate, while without these analyses, it is just a comparison to the baseline material. Sample preparation and ice formation on a substrate is reported in two formats. In the first one, the rotating beam is coated with icephobic coating and the ice is formed on the coating using a mold, e.g. column cuvette, to freeze water [94]. The second way is preparing samples batch off the setup and then fasten the sample on the beam. This method has the benefit of simulating real conditions of ice formation. For example, sample preparation can be conducted in a wind tunnel to make ice as it forms on an airplane. Also, the repeatability of measurements can be assessed in batch off method [92]. However, in these cases, formation of ice in another location and transfer of it to the setup may induce mechanical and thermal stresses on the ice and dissipate frozen stresses, which has significant effects on ice adhesion strength, in the interface. Also, these stresses lead to changes in the ice, e.g. cracking, that alters ice adhesion strength. These stresses are complex and considering them in the ice adhesion measurement is a difficult task.

Centrifugal force method has some other drawbacks. The first one is that stress-strain curves for centrifugal force method are not developed which make it difficult to

analyze results in detail. In addition, it is hard to find the relationship between the strain rate and adhesion strength. Second, the sample is not well-preserved in centrifugal force method making it impossible to go through the sheared interface. Third, ice geometry in centrifugal force method differs near the edges of samples leading to variable stress concentrations. However, this variation is small and centrifugal force method has shown acceptable reproducibility. The last drawback of centrifugal force method is that the vibrations and aerodynamic loadings exist in the experimental setup may cause error in ice adhesion measurement. However, as it is mentioned before using a counter weight obviate vibration problems [92].

There is another method in this category called calculated centrifuge adhesion test (CCAT). In this method, the adhesion and tensile strength are calculated according to the distance of pieces of ice from the rotator. While this method obviates in situ issues arisen with CAT method and decreases edge usage, it has some problems. The rotating speed increases as the distance from the center of rotator increases. Thus, ice gathered differs over the length of rotator. In addition, this method does not give accurate information regarding the characteristics of impacted ice [95,96]

Table 7 summarizes the standard ice adhesion measurement parameters for some icephobic coatings which are obtained by centrifugal force method [88].

Table 7: Ice adhesion on various icephobic surfaces measured by centrifugal force method

Sample	Physics	τ_{ice} [kPa]	Refrence
100/0 PDMS/Silicone Oil	PDMS Coating	62	[97-99]
85/15 PDMS/Silicone Oil		77	
70/30 PDMS/Silicone Oil		41	
55/45 PDMS/Silicone Oil		33	
50/50 PDMS/Silicone Oil		34	
Bare Steel		617	
Silicone functionalized steel		127	
Nano-micro structured hydrophilic Zn-surface		816	
Silicone functionalized-Zn surface	Superhydrophobic coating	98	
Etched Al/ODTMS		90	
TiO ₂ -Zonyl (Spin coated)		175	
TiO ₂ -Zonyl (Sprayed)		370	

3.4. Peak Force Method

The second method which is widely used for ice adhesion measurement is peak force method. In this method, the coated substrate is located on a cold plate. A mold, e.g. cuvette column, is located on the coating and filled with water to form ice. After ice formation, an increasing force, which can be pushing or pulling, is applied to the test column to detach the ice column from the icephobic coating. The maximum recorded force by a force meter, which is at the moment of ice detachment from the surface, is divided

over ice-substrate interface cross-sectional area to convert it to ice adhesion strength [90]. This method is illustrated in Figure III-4.

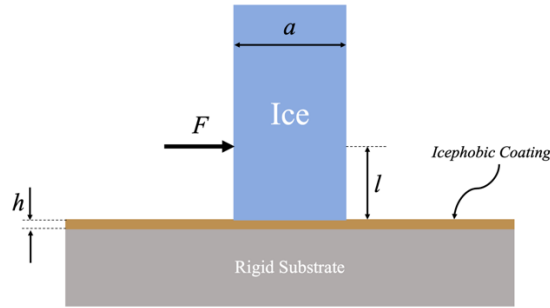


Figure III-4: Schematic of peak force method for ice adhesion measurement [88]

The types of mold and applied force in this method are diverse. For example, the mold can be circular or square. However, the square one is preferred to the circular one, since it minimizes possibility of twisting of mold during applying the force [100]. Also, the method of applying force is diverse. For instance, it can be a needle pushing ice mold (Figure III-5) [101-103], a string pulling the mold [100], or a washer on a cylinder and so on [104-107].

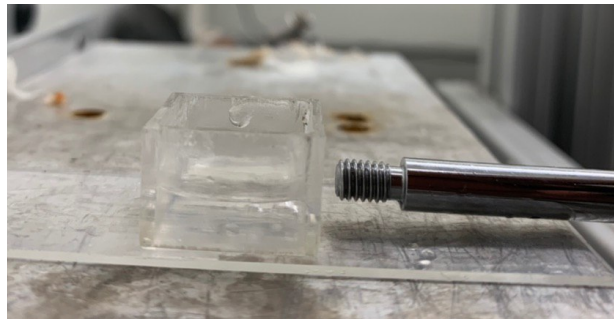


Figure III-5: Experimental setup for ice adhesion measurement using pushing method on a cubic cuvette

A drawback of peak force method is that the applied force cannot impact the ice directly. In addition, finite element analysis is needed to be applied on the geometries of tests to correct the obtained data. Two ways are introduced to apply force: in the first one, force is applied to the samples individually. In this case, in addition to force transducer, a motion stage can be used to control the velocity of needle or probe [90]. In the second method, the force is applied to all of the samples at the same time and an average of results is reported as adhesion strength. However, this method has a major drawback. As the sample with weakest ice adhesion to the surface is separated, suddenly an increase in the applied force to the other samples occurs which make them more susceptible to separate from the surface [92,107].

Also, it is possible to use this method for the impact ice as studied by many researches. Although it is more difficult than non-impact ice. For example, ice can be formed on an airfoil [108] or on a cylinder and disk [109,110]. Then, the substrate is transferred to the push method experimental setup to assess ice adhesion. Then the ice adhesion measurement can be done by placing, for example, the airfoil into a mold and pushing the ice through the mold [92].

There are some other pushing methods which are used in the literature. For instance, one of these approaches is two cylinders method. There are some openings on the outer cylinder through which ice can be formed on the inner cylinder. After ice formation, the outer cylinder rotates and impose shear force on the ice until ice is removed from the surface. However, in pushing the impacted ice comparison is difficult, since various geometries are implemented [92].

Table 8 summarizes the standard ice adhesion measurement parameters for some icephobic coatings which are obtained by peak force method [88].

Table 8: Ice adhesion on various icephobic surfaces measured by pushing method on cuvette.

Sample	Physics	τ_{ice} [kPa]	References
Bare Steel		698 ± 112	[90,111]
PMMA		463 ± 65	
PC		400 ± 83	
PBMA		384 ± 52	
PDMS (Sylgard 184)		291 ± 44	
PEMA		510 ± 101	
95/5 PEMA/ fluorodecyl POSS	Superhydrophobic Coating	278 ± 93	
70/30 PEMA/ fluorodecyl POSS		166 ± 44	
Tecnoflon		389 ± 63	
95/5 Tecnoflon/fluorodecyl POSS	Superhydrophobic Coating	328 ± 97	
70/30 Tecnoflon/fluorodecyl POSS		205 ± 40	
fluorodecyl POSS		250 ± 54	
Bare Steel		1021	[112]
Bare Si		1131	
pDVB on Si		852	
pPFD on Si		284	
BL (10nm) on Si	Linker-Free Grafting	183	
BL (40nm) on Si		247	
BL (10nm) on Steel		152	
BL (40nm) on Steel		199	
Pure and Smooth PDMS Film (SF)	Photothermal Icephobic Film	750	[113]
Porous Film (PF)		2380	
Fluorinated Porous Film (FF)		100	
PDMS resin	Syneresis Liquid Layer	74.1	[114]
AR20		3.1	
AR20+TSF437		0.4	
SLWL Surface	Self-lubricating Water Layer	67 ± 8	[115]

Table 8 (continued)

HA-D	Aqueous Lubricating Layer	77.6	[116]
PU-0	Aqueous Lubricating Layer	253	[117]
PU-3		92	
PU-6		39	
PU-9		27	
Superhydrophobic Surface	Smooth & Structured Surfaces/ Lubricants	50-100	[118]
Solid-Gel Coating with perfluorinated polyether		75	
SLIPS		15	
Lubricant-Infused Surfaces		10-100	
PDMS Mixed with Silicone Oil		1.7	
Aluminum (Al)	Liquid-Infused Nanostructures	1070 $\pm$ 210	[119]
K100-Al		1145 $\pm$ 310	
K100-F13-Al		515 $\pm$ 130	
F13-Ppy-Al		845 $\pm$ 52	
K100-F13-Ppy-Al (SLIPS-Al)		15.6 $\pm$ 3.6	
S-FNM-K103	Lubricant- infused Electrospray	55	[120]
S-NM-K103		55	
S-M-K103		55	
S-F-K103		55	

There is another method in this category called shear test method. Shear test are categorized, according to the geometry, into rotational shear tests [121], 0° cone tests [122] and lap shear test [123,124].

In the rotational shear test a cylindrical or annular setup is used. In the cylindrical form, the cylinder is placed on a massive plate that has walls and forms lip around the cylinder. Ice is formed in the gap between walls and cylinder. Then, torque is applied through a torsion rod to the cylinder. The cylinder is coated with icephobic coating and ice adhesion on the base-plate is high. Stresses on the edges of cylinder are complex. Thus, in

order to obviate this problem an annular setup is used in which the base-plate is substituted with another specimen which makes an annular interface that gives higher value of ice adhesion strength [125].

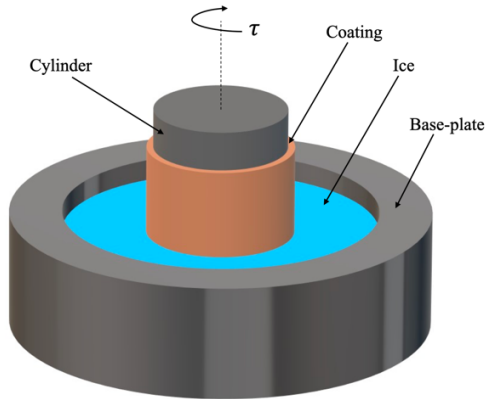


Figure III-6: Rotational shear test method

Lap shear tests are the second and most widely-used type of shear test that have advantageous of low stress concentration [126]. In this methods, two flat plates, one of which is coated with icephobic coating, confines ice between themselves. A pushing force is applied to the coated surface which to remove ice from the coating. Various formats of lap test are reported in the literature, e.g. single and double-lap shear method. In double-lap shear method, the icephobic material is coated on both sides of the substrate, and ice is formed in the gaps between coating and substrate according to Figure III-7 [127].

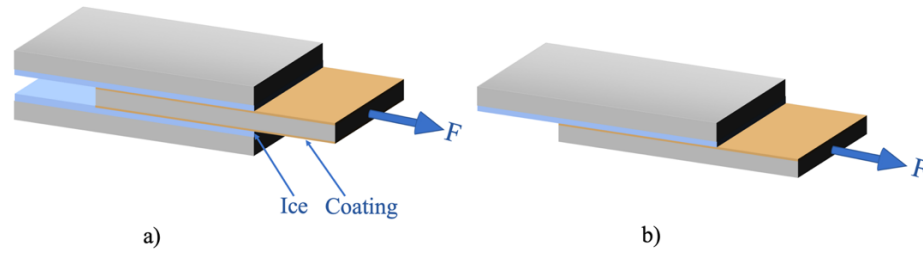


Figure III-7: Schematic of shear stress method for ice adhesion measurement

0° cone test is a special form of shear test. In this test, instead of two flat plates, an annulus and a cylinder are used. The gap between the rod and hollow cylinder is filled with water to form ice adhering to both surfaces, and the ice adhesion is measured by pushing the inner cylinder out along the common axis with the annulus immobilized [128].

Different loading methods used by the similar geometries produce different stress concentrations leading to different ice adhesion measurement. Table 9 summarizes the standard ice adhesion measurement parameters for some icephobic coatings obtained by shear stress methods [88].

Table 9: Ice adhesion on various icephobic surfaces measured by shear test method

Sample	Physics	τ_{Ice} [kPa]	References
Sylgard 184 (SG 184) 10:1		264	[128]
SG 184 1:1	Interfacial Slippage	14	
SG 184 10:1 + 25% 100-cP Silicone Oil		35	
SG 184 10:1 + 25% PMHS		10	
1:9 SG 527:184 + 25% 100-cP Silicone Oil		14	
Perfluoropolyether (PFPE)		238	
PFPE + 25% Krytox 100	Interfacial Slippage	31	

VytaFlex40 + 20% Vegetable Oil		10.5	
VytaFlex40 + 15% Cod Liver		27	
VytaFlex40 + 10% 100-cP SO		41	
VytaFlex40 + 15% Safflower Oil		4	
VytaFlex40 + 20% Cod Liver		97	

3.5. Tensile Force Methods

The other kind of ice adhesion measurement is tensile force method in which tension plays the central role in the ice adhesion measurement, as shown in Figure III-8. The setup in this method includes two concentric cylinders between which a gap exists. Cylinder is selected from the material which have high ice adhesion, usually aluminum. The inner surface of outer cylinder is coated with the icephobic coating and outer surface of inner cylinder remains intact. The gap between two cylinders is filled with water and is cooled down to freeze. After ice formation in the gap between two cylinders, the setup is located on a tensile machine and a pull up force is applied to the inner cylinder which is without coating. Since ice adhesion on the cylinder is high, ice will be removed from the coating on the outer cylinder. At the moment of detachment, the force is recorded and by dividing this force to the area of ice-icephobic coating interface, ice adhesion strength is obtained.

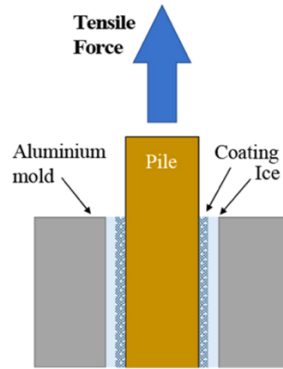


Figure III-8: Schematic of Tensile force method for ice adhesion measurement [88]

In addition to cylindrical geometry, other geometries can be implemented for tensile force method. For example, ice can be formed in the gap between two square blocks. One of the blocks is coated with icephobic coating and the other block is bare. After ice formation, pulling force is applied on the blocks and the ice will be removed from the ice-icephobic coating interface (Figure III-9).

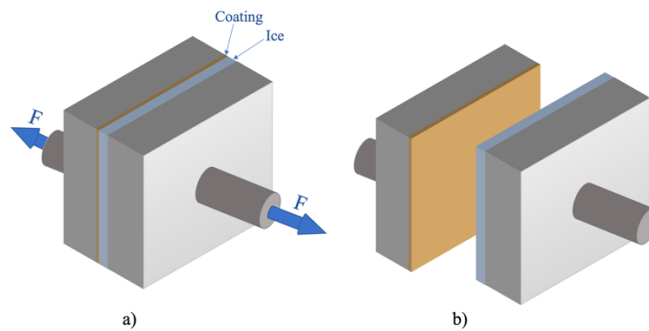


Figure III-9: Experimental setup used for ice adhesion measurement with tensile method
a) before and b) after detachment

3.6. Standard Procedure of Ice Adhesion Measurement

Introducing a standard approach for ice adhesion measurement is important. Lack of such standard method causes the data in the literature not to be comparable to each other. Also, different ice adhesion values are reported for the same materials in the literature. For example, for PDMS, ice adhesion values are reported in the range of 100-800 kPa [89-91]. Irajizad et al. introduced a standard method for the measurement of ice adhesion that can make the data comparable and uniform. Two important factors should be considered in the developed standard approach which are shear rate and geometry of experimental setup, including l , a , and h (Figure III-10). Regarding the shear rate, in order to detach ice from the surface, shear rate should reach to a critical shear rate value on which interface fracture occurs. At the shear rates lower than critical shear rate, ice only slides on the surface and detachment will not occur. Critical shear rate depends on the shear modulus of materials. As the shear modulus increases, critical shear stress decreases [87]. Irajizad et al. stated that for the elastomers with shear modulus in the range of 0.5 MPa-100 MPa and thickness of $300 \pm 20 \mu m$, upper limit for critical shear rate is 0.1 mms^{-1} [88].

The second important factor is the geometry of ice adhesion experimental setup. In the derivation of Eq. 76, some assumptions are considered by which standard parameters can be obtained. The first one is that lubrication approximation of Stock's law is used for the determination of hydrostatic pressure field in the elastomer. In order for this approximation to be valid a and h should satisfy $\frac{a}{h} \gg 1$. Irajizad et al. proposed 15 mm and $300 \mu m$ for the a and h , respectively, to satisfy mentioned condition. The second assumption in the derivation of Eq. 76 is that the vertical displacement of the ice and

horizontal length scale have linear relation. For this assumption to be valid, l and a should satisfy $l/a \ll 1$. Therefore, to satisfy this condition 3 mm for l values is proposed. Although this standard approach and mentioned theories in section 2 is obtained based on the assumption that the material is elastomer, it can be generalized to other materials and coatings. Implementing mentioned standard approach in the ice adhesion measurements, leads to reproducible and comparable data obtained in different laboratories.

Table 10: Parameters for standard ice adhesion measurements [88]

Shear rate	a	h	l
0.1 mms^{-1}	15 mm	$300 \mu\text{m}$	3mm

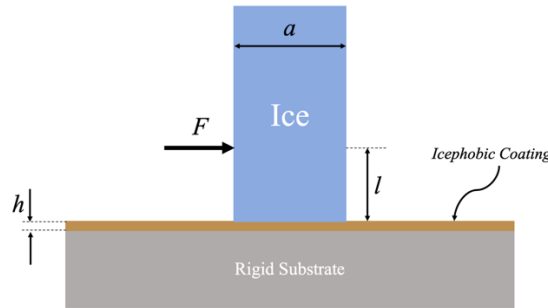


Figure III-10: Schematic of standard setup for ice adhesion measurement [88]

3.7. Conclusion

Ice adhesion measurement method is an important factor in determining the icephobic application of a material. Different methods and approaches used in the literature make the comparison of data impossible. There are several methods used in the literature for ice adhesion measurement among which centrifugal force method, peak force method and

tensile force method are three widely-used methods. In all of these methods a force is applied to remove the ice from the icephobic substrate. This force can be in different forms, e.g. centrifugal force which is created by a rotating beam or a tensile force. Different experimental setups with different geometries are used for each of the mentioned methods in the literature which causes the data obtained from the same methods to be different from each other. In order to unify ice adhesion measurement results from different laboratories a standard method is proposed. In this standard method, peak force method is selected and shear rate as well as geometry of experimental setup are introduced as two important factors in the designing of experimental setup. In addition, standard values for these two factors are introduced.

CHAPTER 4

IV. CONCLUSIONS AND FUTURE WORK

In this dissertation, we focused on the physics of ice nucleation in nanoscale. Understanding of this physics helps us to design icephobic surfaces in a rational way. As the first step, we provided physics of ice nucleation and growth on a surface to identify the basics of how ice embryo starts to form on a surface and its further growth. Fundamental understanding of ice formation on a surface, i.e. heterogeneous formation, is critical to suppress ice accretion on the surfaces. Ice formation on a surface includes two steps of ice nucleation and further ice growth. As water droplet is placed on a sub-zero surface, with a time delay, ice nucleolus form on the surface. Ice nucleation is governed by thermodynamics of ice-water-surface system and it is described by Gibbs energy barrier, ΔG^* , which strongly depends on surface factor, $f(m, x)$. Surface factor is a function of surface geometry, i.e. nano or micro, as well as surface free energy and through manipulating these parameters, ice nucleation can be controlled. After ice nucleation, ice further grows in a process which is controlled through heat transfer. Ice growth could be described by two extreme scenarios. In the first one, ice formation occurs with no airflow around where heat transfer through the substrate determines ice growth rate. In the second scenario, ice growth occurs in an environment with external airflow in which ice growth rate is controlled mainly by convective heat transfer. All of mentioned theories about ice formation on a surface are applicable for a single, isolated droplet. However, in reality existence of many droplets on a surface can interfere with ice nucleation and growth of droplets leading to ice bridging phenomenon which is a result of vapor source-sink

behavior due to the vapor pressure gradient between a frozen droplet and adjacent liquid droplets.

Then we probed the ice nucleation of nanodroplets down to 2 nm scale and found that interfacial deformation at soft interfaces and high pressure could significantly suppress ice nucleation rate and delay ice nucleation to temperatures even lower than homogenous bulk nucleation temperature. It has been discussed that nanoconfined water could show narrowing of OH peaks due to no free OH groups that are in the bulk phase. We did not observe this effect possibly due to the elongated ellipsoidal shape of nanodroplets here. The analysis of the finding through CNT suggests that the pressure in these nanodroplets is the governing factor in the suppression of ice nucleation and agreement between the finding and the CNT predictions support the dominant role of pressure. It has been suggested that for nanoconfined water droplets in order of 1 nm, there are significant broken O-H bond leading to an exotic state and for 2-3 nm confined droplets, ice-like nanocluster of water are formed that could affect the solid-liquid phase change characteristics. Furthermore, the phase change transition could be completely non-monotonic. The nature of OH group in few nm droplets and the finite number of molecules may be a key to address this difference. The findings provide an understanding of various natural phenomena and provide a route for the design of superior anti-icing biomimetics or smooth liquid-infused surfaces. We report direct probing of water-ice transformation down to 2 nm scale and the length-scale dependence of transformation temperature through two independent metrologies. The transformation temperature shows a sharp length dependence in nanodroplets smaller than 10 nm and for 2 nm droplet, this temperature falls below the homogenous bulk nucleation limit. The formed ice phase even down to 2 nm is

Ih (hexagonal). Contrary to nucleation on curved stiff solid surfaces, ice formation on soft interfaces (omnipresent in nature) could deform the interface leading to suppression of ice nucleation. Considering the interfacial deformation, the findings are in good agreement with predictions of classical nucleation theory. This understanding contributes to a greater knowledge of natural phenomena and rational design of anti-icing systems for aviation, wind energy and infrastructures.

At the end, we explain the theory of ice adhesion on a surface and derive an equation for the calculation of ice adhesion on the surface of an elastomer. Although this formula is obtained for an elastomer, it can be generalized for the other types of coatings. After that, different approaches which are used for ice adhesion measurement in the literature are discussed. Also, a standard method is fostered which is obtained through mechanics of ice adhesion on a surface. This standard approach leads to the unification of ice adhesion values obtained from different laboratories with the same metrics.

Regarding the potential applications for such a discovery, there are many applications that can be implemented. Airplanes wings, for instance, may no longer need to be doused in deicing fluids. Instead, they could be covered in a coating with many tiny deformations. Such deformation could, perhaps, be tuned to match whatever weather that an aircraft might face. Similarly, ice accumulation on the blades of wind turbines can reduce power production by as much as 80 percent. Heating elements can curb the problem, but their use is energy intensive. A coating would keep blades free of ice without using additional energy. In fact, one needs curvature at the interface and does not need it for the whole droplet. In other words, if we have high curvature at the interface, we can implement the principles of this research.

Cryopreservation is another area where the ability to go to low temperatures without freezing would be a major advantage. The expansion that comes with the crystallization of water can mean the destruction of any biological elements. The developed droplets in this research were two or three nanometers in diameter, but they up to 50 microns long, so future cryopreservation does not need to be limited to spherical shapes. With the soft nanostructures, long water droplets, and the biology that depends on them, can be brought to -40°C , and kept there without being damaged.

For future work the following extensions of the problems studied is suggested. First of all, to see the role of unconfined geometry on ice nucleation and through the acquired fundamental knowledge, which parameters provide a route to reach exceptional icephobic characteristics at low temperatures. The other thing which is needed to study is ice growth. We need to study the effect of surrounding environment on ice growth rate regime and what is the fundamental role of interface curvature on ice growth rate at nano-scale. Also, the fundamental difference of icing in confined and unconfined geometries is the other topic which is needed to study. At the end, this finding should be implemented in designing icephobic surfaces and how can one break the limit of ice adhesion through localization effect, $g(\varphi_2)$, in composite nano-viscoelastic materials?

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