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Ice nucleation in water droplets on glass surfaces: From micro- to macro-scale

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ABSTRACT

Ice nucleation encountered in engineering systems is often induced by solid/water interfaces. When classical nucleation theory is used to analyze ice nucleation in such systems, the uniformity of interfaces that contribute to ice nucleation must be carefully considered, because classical nucleation theory cannot be directly applied to non-uniform interfaces. In this study, to discuss the uniformity of ice nucleating activity of solid/water interfaces, ice nucleation in water droplets prepared on glass surfaces was investigated for various droplet sizes from micrometer to sub-millimeter. When the interfacial area between water and the glass surface was smaller than 1×10^{-10} m^2, the ice nucleation temperature showed scatter of about 2 °C, suggesting uniformity of the interface. However, when the interfacial area was larger than 1×10^{-8} m^2, the ice nucleation temperature showed large scatter, suggesting the ice nucleating activity was no longer uniform.

Nucléation de glace en gouttelettes d'eau sur des surfaces vitrées : de l'échelle micro à macro

Mots clés : Glace ; Nucléation ; Gouttelettes ; Surface de verre ; Théorie classique de la nucléation

1. Introduction

Ice nucleation in a supercooled water droplet is classified into two categories depending on where an ice crystal first nucleates: volume-induced nucleation, in which ice forms from an arbitrary point in the interior of the droplet without any contribution from interfaces, and surface-induced nucleation, in which ice forms from interfaces between water and environmental phases (Wood and Walton, 1970; Taborek, 1985; Tabazadeh et al., 2002; Duft and Leisner, 2004; Kuhn et al., 2011). This classification can be applied not only to ice but also to other crystals (Kaneko et al., 1999; Carvalho and Dalnoki-Veress, 2010).

Volume-induced nucleation is generally regarded as homogeneous nucleation, which is often observed in cloud

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Nomenclature

A	interfacial area (m^2)
d	diameter of droplet (m)
F	fraction of droplets satisfying $T_f > T_{cr}$
f	fraction of unfrozen droplets
J	nucleation rate (s^{-1})
J_C	nucleation rate per unit length ($m^{-1}\ s^{-1}$)
J_S	nucleation rate per unit surface area ($m^{-2}\ s^{-1}$)
J_V	nucleation rate per unit volume ($m^{-3}\ s^{-1}$)
L	length of triple contact line (m)
N	density of active nucleating site (m^{-2})
n	number of droplets
T	temperature (°C or K)
T_{cr}	theoretical freezing temperature at $f = 0.99$ (°C)
T_f	nucleation temperature (°C)
V	volume of droplets (m^3)
ΔT	degree of supercooling (K)
Δt	time step (s)
τ	function of T (K^{-5})

formation process (Peter et al., 2006; Kuhn et al., 2011; Murray et al., 2012), and its nucleation rate is proportional to the droplet volume. For surface-induced nucleation in water droplets, several types of interface can contribute to ice nucleation: gas/liquid interfaces for droplets in the atmosphere (Tabazadeh et al., 2002; Kay et al., 2003; Duft and Leisner, 2004; Kuhn et al., 2011), liquid/liquid interfaces for droplets in water-in-oil (W/O) emulsions (Wood and Walton, 1970; Taborek, 1985; Tabazadeh et al., 2002; Inada et al., 2011), and liquid/solid interfaces and gas/liquid/solid (or liquid/liquid/solid) triple contact lines for droplets attached to solid surfaces (Carvalho and Dalnoki-Veress, 2010; Gurganus et al., 2011; Inada et al., 2011; Alizadeh et al., 2012; Li et al., 2012). In addition, in a general sense, surface-induced nucleation can include ice nucleation from the surfaces of solid particles suspended in water droplets (Shaw et al., 2005; Zobrist et al., 2008; Inada et al., 2012), which is referred to "immersion freezing" in the terminology of cloud physics (Vali, 1985). The rate of surface-induced nucleation is proportional to the surface area of the interfaces or to the length of the triple contact lines.

Surface-induced nucleation, as well as volume-induced nucleation, is often investigated based on classical nucleation theory, which assumes a stochastic (time-dependent) process that depends on random fluctuations of water clusters (Wood and Walton, 1970; Seeley and Seidler, 2001; Tabazadeh et al., 2002). Although some assumptions of classical nucleation theory have been questioned when applied to ice nucleation in the melt phase (Rasmussen, 1982; Huang and Bartell, 1995; Seeley and Seidler, 2001; Zobrist et al., 2003; Murray et al., 2012), numerous examples demonstrate the usefulness of classical nucleation theory for qualitative understanding of surface-induced ice nucleation in the melt (Tabazadeh et al., 2002; Kuhn et al., 2011; Inada et al., 2011; Alizadeh et al., 2012; Li et al., 2012). However, in order to apply classical nucleation theory directly to surface-induced nucleation, a reproducible uniform ice nucleating activity of the interface that contributes to ice nucleation must be guaranteed (Vali, 2008). If not, somewhat complicated models that consider the non-uniformity of the interface should be applied (Niedermeier et al., 2011; Broadley et al., 2012; Ervens and Feingold, 2012). Therefore, when investigating surface-induced nucleation based on classical nucleation theory, the uniformity of interfaces that contribute to ice nucleation must be carefully considered.

Ice formation encountered in engineering systems in the field of refrigeration and air conditioning is commonly induced by certain interfaces, such as frost formation on fin surfaces of heat exchangers (Jhee et al., 2002; Xia et al., 2006) and freezing of aqueous coolant or water flowing in pipes (Hirata and Ishihara, 1985; Inaba et al., 1994; Wang et al., 2012). In most cases in such systems, the interfaces that contribute to ice nucleation have non-uniform ice nucleating activities due to the large scale of these interfaces and also to the uncontrolled environment. Furthermore, such ice nucleating activities often change gradually over several weeks (Okawa et al., 2002). On the contrary, in laboratory studies, to develop novel technologies related to ice formation or ice prevention, fundamental phenomena of ice nucleation are often investigated by intentionally using micro-scale interfaces that have a reproducible uniform ice nucleating activity (Inada et al., 2011; Li et al., 2012). Therefore, to develop practical technologies in the field of refrigeration and air conditioning, attention should be paid to the difference in the uniformity of ice nucleating activity between micro- and macro-scale interfaces.

In this study, we investigated ice nucleation in supercooled water droplets on glass surfaces for various droplet sizes from micrometer to sub-millimeter. Based on the experimental results, we discuss the critical scale at which the ice nucleating activity of the interface can no longer be regarded as uniform, namely, at which classical nucleation theory can no longer be applied directly.

2. Materials and methods

2.1. *Materials*

Two types of water were used in this study: purified deionized water from which foreign particles larger than 220 nm were removed (Millipore, Elix-UV-3 and Academic-A10) and tap water without any filtration (collected from the public water supply for Tsukuba, Japan, in April 2013). Here, W/O emulsions were prepared by using *n*-heptane (Wako Pure Chemical Industries, spectrochemical analysis grade) as a continuous phase and sorbitan tristearate (Sigma, SPAN 65) as an emulsifier. Commercial cover glasses (Matsunami Glass Industries, boron-silicate glass, 18-mm diameter, 0.12- to 0.17-mm thickness) were used for ice nucleation experiments, without further treatment.

2.2. *Water droplets*

Three different types of samples were prepared on the cover glass surfaces for ice nucleation experiments: water droplets in W/O emulsions (Sample 1: Fig. 1a), a single water droplet