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A statistical study of heterogeneous nucleation of ice by molecular dynamics

Aleida J. Bermúdez di Lorenzo [a], Marcelo A. Carignano [b], Rodolfo G. Pereyra [a,c,*]

[a] Facultad de Matemática, Astronomía y Física, Universidad Nacional de Córdoba, X5000HUA Córdoba, Argentina
[b] Qatar Environment and Energy Research Institute, P.O. Box 5825, Doha, Qatar
[c] IFEG-CONICET, X5016LAE Córdoba, Argentina

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ABSTRACT

We studied the stochastic nature of heterogeneous nucleation of supercooled liquid water by molecular dynamics simulations. The systems were composed of 768 molecules; M of them had their positions restricted forming a solid nucleus (IN_M) for $M = 48$, 56, 64, 72, 80 and 90 molecules, and the rest were arranged in liquid state. By using a statistical analysis, we determined the nucleation rate (j_M) for systems formed with IN_{64}, IN_{72}, IN_{80} and IN_{90}. These results are coherent with the stochastic hypothesis for heterogeneous nucleation and show a direct relationship between M and j_M.

1. Introduction

Ice nucleation in supercooled liquid water is of great interest in various contexts associated to the climate of our planet, for example: formation of ice particles in natural clouds [1,2]. This process is responsible for everyday events such as the initiation of frost on plants and is the object of investigations in several specific fields of science, e.g., the cellular cryobiology [3].

The initiation of the solid phase of water is caused by the presence of insoluble solid particles, known as ice nuclei (*IN*), in the liquid medium. This type of nucleation, called heterogeneous nucleation, is naturally produced in a greater extent than the homogeneous one. Heterogeneous ice nucleation is a natural phenomenon still under discussion, and many studies are focused on evaluating the ability of certain types of particles to nucleate ice [4–7]. Thus, it is very useful and important to understand the process that is triggered by *IN* in supercooled liquid water.

From the viewpoint of classical theory of formation of critical ice embryos, heterogeneous nucleation requires lower activation energy than the homogeneous case. That is, ice embryos are more likely to generate on a solid surface than within a liquid volume. This point is easily understood observing the value of the minimum work required to create critical size ice embryos by heterogeneous nucleation (W_{het}), as compared to the corresponding values for the homogeneous case (W_{hom}). The relation is: $W_{het} = W_{hom} f$ [8], where f is known as *catalytic power factor* and satisfies $0 \leq f \leq 1$, which quantifies the ability of *IN* to produce heterogeneous nucleation. The value of f depends on the contact angle between the *IN* and ice embryo and in turn this angle is linked to the chemical composition, size, surface area, morphology and crystallographic structure of the *IN* [9].

A measure of the nucleation activity is the probability, per unit time, that an embryo, under certain circumstances, will reach the critical size. This probability is commonly defined as extensive nucleation rate (j), and can be calculated trough theoretical formulae as well as from experimental data. In this regard, Pruppacher and Klett [10] and Vali [11] reported equations for calculating rates for homogeneous and heterogeneous nucleation.

Moreover, nucleation rates have been experimentally determined, measuring the time that supercooled water droplets take to freeze under controlled conditions [12–16]. In their work, Baumgärtel and Zimmermann [17] present a statistical study of freezing of droplets, taking nucleation time as a random variable. These authors showed that for the case of homogeneous nucleation, the number of droplets not frozen at time t (N_t) and the initial number of drops (N_0) are related by a Poisson distribution:

$$\ln(N_t/N_0) = -jt \tag{1}$$

In the case of heterogeneous nucleation, Pruppacher and Klett [10] indicated that *IN* increase the efficiency of the nucleation process but do not alter its stochastic nature (stochastic assumption [11,14,18,19]). Under these conditions, Eq. (1), which describes the

* Corresponding author at: Facultad de Matemática, Astronomía y Física, Universidad Nacional de Córdoba, X5000HUA Córdoba, Argentina.
E-mail address: pereyra@famaf.unc.edu.ar (R.G. Pereyra).

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