



A statistical study of heterogeneous nucleation of ice by molecular dynamics



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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 .

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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 through 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:

$$\ln(N_t/N_0) = -jt \quad (1)$$

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

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homogeneous case is also applicable to heterogeneous nucleation, but with larger j values.

On the other hand, most studies found in the of molecular dynamics (MD) simulation literature, addressing heterogeneous nucleation, have assessed the structure of materials which promote ice nucleation. There are studies of the electric-field-induced phase transition of water, based on the idea that the local electric field at the surface of various materials can play an important role in promoting the crystallization of liquid water [5,20]. In other reports, the behavior of liquid water molecules which were incorporated on a surface of platinum solid was analyzed by studying different interaction potentials between water and platinum molecules and different structures of the solid lattice. Recently, Reinhardt and Doye [21] have performed Monte Carlo simulations of the heterogeneous nucleation of ice on a range of generic surfaces with a monatomic model of water. These authors showed that good lattice matching between the solid surface and ice, as well as a strong water-solid interaction, was very important to promote the heterogeneous nucleation. Despite the different types of work found in the literature, as far as we know, there are no statistical studies describing heterogeneous nucleation with MD simulations.

Following the arguments above, we conducted a set of simulations of MD in systems composed of liquid water and an insoluble crystalline nucleus, and we calculated nucleation rates using Eq. (1). Due to the fact that the most effective ice-nucleating structures are those similar to hexagonal ice (I_h) [2,6,21,22], nuclei were given identical structural and molecular characteristics as those of pure ice. These particles are artificially maintained by applying and external force (position restraints) and therefore they are not particles of ice. Namely, if we suddenly increase the temperature above the melting temperature these particles will remain in solution maintaining their structure and not melt. It can be argued that our IN are the best possible ones since they perfectly match the target structure to grow. In spite that we are considering these particular ice-like particles, the study corresponds to heterogeneous nucleation. A statistical analysis was performed by repeating the simulations with different initial conditions of positions and velocities of the molecules for each system of liquid water and nuclei. Through these simulations, we have first evaluated the qualitative behavior of the nucleation rate in composite systems with different IN sizes at constant temperature. Also, from the rate values obtained we were able to estimate the minimum nucleus size needed for heterogeneous nucleation to occur in our simulated systems: supercooled water of 768 molecules, in simulations of 200 ns long, with periodic boundary conditions and with an IN structure matching that of I_h .

2. Simulations

2.1. Computational details

Molecular dynamics simulations were carried out using the Gromacs simulation package, v.4.5.5 [23,24]. Water molecules were described using the TIP5P-Ew model [25]. In previous simulations [26,27], we had found that this model performs very well in supercooled water conditions, mainly because its architecture presents two sites representing the lone pairs of the water, which contribute to more effectively form the hydrogen bonds.

All simulations were performed in a simulation box with full periodic boundary conditions and at constant molecular number, temperature and pressure (NTP). The working temperature was 250 K, corresponding to the maximum of the isobaric heat capacity estimated for TIP5P-Ew [27]. For some authors [28–30], this maximum indicates the lower limit of the supercooled regime: they

argue that, at this temperature, the probability of nucleation should be the highest possible.

In order to observe ice nucleation in reasonable computer times, we had to work in the best possible scenario, which is at the lowest temperature of the supercooled regime and with the best IN architecture to promote the ice nucleation. Since the nucleation efficiency increases for particles that have a lattice structure similar to ice, we perform our study using IN having exactly the structure of ice maintained by a position restraint algorithm.

A leapfrog algorithm was used for the integration of the dynamical equations, with a time-step of 0.001 ps. A spherical cut-off at 0.9 nm was imposed for the Lennard–Jones and short-range electrostatic interactions. For long-range electrostatic interactions we included corrections using the PME approach. The temperature and pressure of the system were controlled using a Nosé–Hoover thermostat and a Parrinello–Rahman barostat, respectively. Thermostat and barostat time constants were of 0.5 ps and the compressibility was uniform and equal to $4.5 \times 10^5 \text{ bar}^{-1}$.

2.2. Preparation of systems

We used a method somewhat similar to that of Yokoyama and Hagiwara [7] to prepare our simulated systems. These consisted of 768 water molecules. The ice nucleus (IN_M) was constituted by M molecules and the rest were placed in liquid state. The positions of the molecules of IN_M were partially restricted with the simulation technique named position restraints (harmonic potential of force constant equal to $1000 \text{ kJ mol}^{-1} \text{ nm}^{-2}$). This technique was very effective in maintaining molecules locally confined, without preventing realistic thermal agitation, so the nucleus remained solid throughout the total time of the simulation. The introduction of the position restraints changes the energy of the system with respect to what it would have without applying these external forces. This is precisely the intended effect in order to artificially keep the IN with their ice structure.

The initial configurations were prepared following these steps:

- A system of 768 molecules with ice structure was simulated at constant temperature of 250 K at constant pressure of 1 bar during 10 ns. The simulation box dimensions were such that ice bulk was correctly reproduced with periodic boundary conditions. The three Bernal–Fowler rules were satisfied in all hydrogen bonds. The final volume of the box was equal to $xyz = 2.636 \times 3.043 \times 2.959 \text{ nm}^3$. Ice basal plane was perpendicular to the z axis and the secondary and primary prismatic planes were perpendicular to the x and y axes respectively.
- Six ice nuclei of different amount of molecules ($M = 48, 56, 64, 72, 80$ and 90) were selected from the final state of the previous simulation to constitute the IN_M with their positions restrained. These nuclei were parallelepipeds with flat faces parallel to box simulation planes (see Figure 1).
- At constant volume, these six systems were shaken at the constant temperature of 400 K during a sufficiently long time (10 ns), so that the not-restricted ice was completely melted.
- For each system constituted by a particular IN_M , we randomly extracted fourteen states (called replicas) from the trajectory of the last 2 ns of the previous simulations. These 14 replicas had different molecular coordinates and were used as initial configurations to perform the simulations of nucleation. The molecular velocities for each replica were randomly generated using a Maxwell–Boltzmann distribution with $T = 250 \text{ K}$. We have ensured the greatest mismatch between replicas, choosing states not closer than 100 ps.

All replicas of all systems were simulated at 250 K and 1 bar until the complete freezing of the system occurred or until the simulation

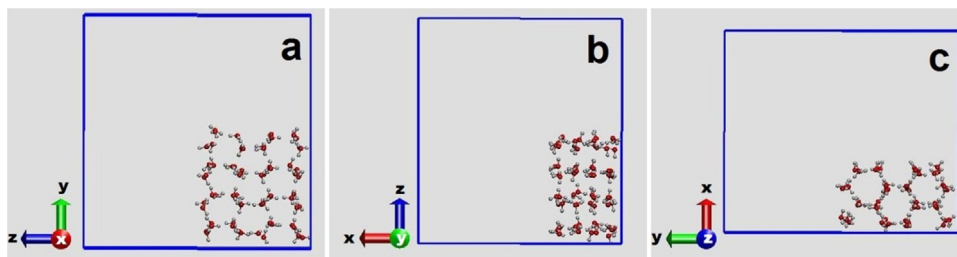


Figure 1. Ice nucleus for the case $M=64$, seen from the two prismatic planes in the x and y directions (a and b respectively) and the basal plane in the z direction (c). Red and white circles represent oxygen and hydrogen atoms respectively (unrestricted molecules not shown). The blue rectangle limits the simulation box. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this Letter.)

time reached 200 ns. The total number of simulations in our study was 84, each one taking approximately four days to run with our computational capability.

3. Results

By the end of the simulation all replicas with 64, 72, 80 and 90-molecule nuclei were frozen. The whole of the system freezes in a short lapse (as compared to the total simulation time) and the time when freezing begins, that is, the time of nucleation, is different for replicas of different nucleus sizes, and even for different replicas of the same nucleus size. It was possible to monitor the number of unfrozen replicas (N_t) for each nucleus size as a function of time, and this we were able to calculate the N_t/N_0 ($N_0 = 14$) quotient and estimate the nucleation rate for each type of nucleus (j_M), calculating the linear fitting slope of Eq. (1). For the system with the 56-molecules nucleus there was nucleation only for one replica, while no nucleation event was seen for the IN_{48} case.

In order to monitor the nucleation process, we first had considered the potential energy (E_p) as a function of simulation time (t). Figure 2a, for example, shows the behavior of $E_p(t)$ for a particular replica of the system with IN_{64} . The graph indicates that there were three states in the freezing process: the black zone ($0 \text{ ns} < t < 125 \text{ ns}$) of relatively constant E_p (only showing the noise due to molecular motions generated by thermal agitation), where the liquid water portion of the system did not suffer any change; the blue zone ($125 \text{ ns} < t < 140 \text{ ns}$) where E_p decreased in a relatively short simulation time, corresponds to the post-nucleation growing process; and the violet zone ($140 \text{ ns} < t < 200 \text{ ns}$) where E_p came back to a constant value, lower, on average, to that of the black zone, reflecting the complete formation of the ice phase.

In Figure 2a, it is possible to see that the nucleation process was triggered at approximately 125 ns. However, due to the high noise that was observed in E_p , we decided to use another parameter to determine the nucleation time (t_N) more precisely. This time-dependent parameter, denoted n_i , was the quantity of molecules with its oxygen atom nearly stationary for the rest of the simulation. In practical terms, for each time t we calculated the average position of the oxygen atom from t to 200 ns. The molecule is considered in ice state if its oxygen never departs more than 0.1 nm in any of the three Cartesian directions from its average center during the remaining of the trajectory. The choice of 0.1 nm is rather arbitrary and the result of practical tests. The fact that the curves n_i vs. t and E_p vs. t display essentially the same nucleation time is further proof of the correctness of our definition. In more simple terms, n_i quantified the number of molecules of the solid region of the system. In Figure 2b, the graph of n_i vs. t for the same case described in Figure 2a is shown. The noise level of n_i was noticeably lower than E_p , so we could determine t_N with better precision.

In Figure 3 we show $\ln(N_t/14)$ vs. t_N for systems with IN_{64} (black dots), IN_{72} (red dots), IN_{80} (green dots), IN_{90} (blue dots). All data in Figure 3 are detailed in Table 1. In order to prove if data

follow a Poisson-like distribution like as Eq. (1), we have done a statistical analysis with chi-square test [31]. Considering an error of hypothesis rejection of 5% we have concluded that data behavior is given by Eq. (1) for the four cases of nucleus sizes. Straight lines showed in Figure 3 correspond to the linear fit described by Eq. (1). As shown in the figure, the dispersion of the data, which can be attributed to the low number of replicas, is more pronounced for the 64 and 72-molecule nuclei. However, the slopes of the straight lines (j_M) yielded values with reasonable behavior as functions of M , i.e., in a decreasing manner. The nucleation rate values for each nucleus size are presented in Table 2. Also in Table 2 the linear correlation coefficients are presented.

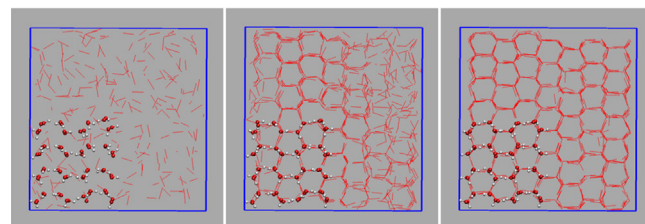
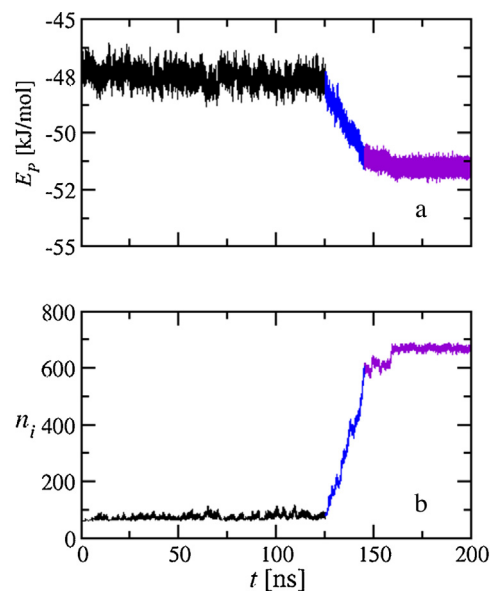


Figure 2. Potential energy (a) and number of molecules in 'ice state' (b), both versus time simulation at 250 K for one of the replicas of the system with IN_{64} . Regions of different colors are explained in the text. The intersection between black zone and blue zone indicates the nucleation time t_N . The three snapshots above are representative of each colored zone (left, central and right snapshot correspond to black, blue and violet zone, respectively). The red and white circles represent oxygen and hydrogen atoms of the IN respectively and the red segments are the hydrogen bonds of liquid water. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this Letter.)

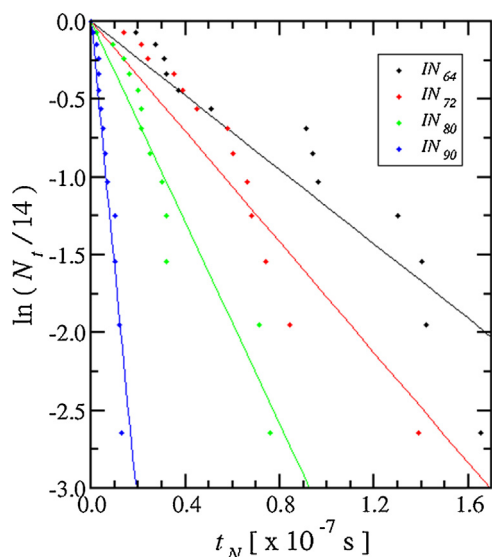


Figure 3. $\ln(N_t/14)$ as function of t_N for systems with IN of 64 (black), 72 (red), 80 (green) and 90 (blue) molecules. The numerical data are in Table 1. The straight lines represent the corresponding linear fits of slope values presented in Table 2. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this Letter.)

Table 1
Number of unfrozen replicas (N_t) and nucleation time (t_N) obtained in the simulations.

N_t	$\ln(N_t/14)$	$t_N \pm 0.01 \times 10^{-7}$ s			
		IN_{64}	IN_{72}	IN_{80}	IN_{90}
14	0.00	0.00	0.00	0.00	0.00
13	-0.07	0.19	0.14	0.02	0.01
12	-0.15	0.27	0.21	0.09	0.02
11	-0.24	0.31	0.24	0.14	0.03
10	-0.34	0.32	0.35	0.16	0.03
9	-0.44	0.37	0.39	0.20	0.03
8	-0.56	0.51	0.45	0.21	0.04
7	-0.69	0.91	0.58	0.21	0.05
6	-0.85	0.94	0.60	0.25	0.06
5	-1.03	0.96	0.66	0.30	0.07
4	-1.25	1.30	0.68	0.32	0.10
3	-1.54	1.40	0.74	0.32	0.10
2	-1.95	1.42	0.84	0.71	0.12
1	-2.64	1.65	1.39	0.76	0.13

Figure 4 displays the j_M vs. M graph for the four cases. Based on the analyses of these results and our observation of the simulation behaviors, we expected that if the number of molecules of the nucleus diminished sufficiently, the nucleation rate would reach zero for some value of M_{min} . In fact we have observed that for $M=48$ there is no nucleation within our 200 ns limit. Therefore, extrapolating the data to $j_M=0$ will provide an estimation of the minimum number of molecules for a nucleus that can initiate nucleation in our systems. The roughly linear relation showed by the three lower values of M is extended to obtain an estimation of that result in $M_{min} = 56$. This value is consistent with the fact that

Table 2
Nucleation rates (j_N) for linear fit of $\ln(N_t/14)$ vs. t_N function from Figure 3. In third column the respective linear correlation coefficients (r) are presented.

N	$j_N \times 10^7$ s ⁻¹	r
64	1.2 ± 0.4	-0.88
72	1.8 ± 0.5	-0.90
80	3.2 ± 0.9	-0.89
90	16 ± 5	-0.90

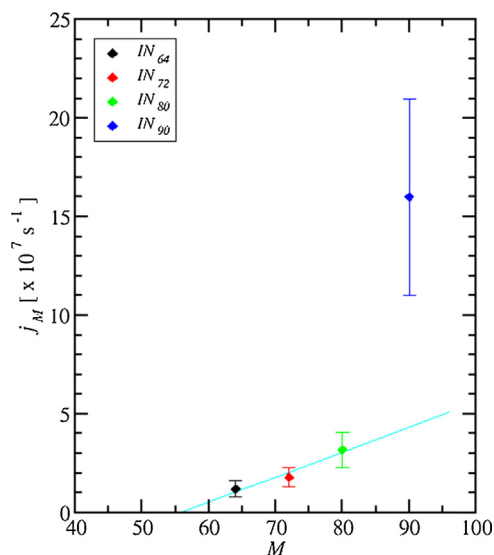


Figure 4. The j_M vs. M graph for IN_{64} , IN_{72} , IN_{80} and IN_{90} systems (with the same colors of Figure 3). The light-blue line corresponds to the linear fit of the three first data. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this Letter.)

we could observe only one event of nucleation in the IN_{56} case and no event for the IN_{48} case, in both cases out of 14 trials runs.

4. Discussion and conclusions

Figure 3 shows that our results describe the stochastic nature of heterogeneous nucleation of supercooled water quite well. These findings are consistent with the *stochastic hypothesis* [10,32], which states that at constant temperature the heterogeneous ice nucleation event is a time dependent event with fixed probability of occurrence. This probability value is dependent on the ice nucleus characteristics. Several experimental observations support this point of view and in a recent study by Niedermeier et al. [19], the authors set out a theoretical model for the process of heterogeneous nucleation, and concluded that it is produced by a stochastic process when the IN present in the water drop have similar surface properties.

Furthermore, there is also the *singular hypothesis* [10,11,33–35], which assumes that ice embryos are formed at a specific temperature T_s on ‘active’ sites on IN surface. According to this hypothesis, when water droplets are cooled up to T_s , the ice nucleation will be initiated instantly over the active sites of the IN , that is, the nucleation process is not random and is not time dependent. If the temperature is kept constant and the environmental conditions are the same, no new nucleation events appear [36–38].

Our numerical study is the first to perform a statistical analysis of heterogeneous nucleation at an atomic level, and we consider that these results can be used to support the stochastic hypothesis and to refute the singular hypothesis, taking of course the limitations of our study into account. In Figure 4 we could see that insofar as IN_M increases, j_M does also, which is the expected behavior due to fact that the nucleation process is most likely to occur when the liquid has a particle to provide it with a larger contact surface. Our ice nuclei were the most suitable to promote nucleation; since they were made with the same molecules that of liquid and they had ice structure, so the estimation of the minimum nucleus is the lowest possible with this technique.

Among the experimental studies that have directly measured the size of the critical heterogeneous nucleus, we can mention Liu et al. [39] These researchers, using a method to determine crystallization temperatures of microemulsions composed of a certain

type of IN , found that the smallest ice embryo that forms on the surface of the nucleating particle consisted of 70 water molecules, at a temperature lower than that reported here (-32.3°C).

Finally, we believe appropriate to list other MD studies which would be useful to carry out in order to improve and expand the results of present work: simulations with systems of much larger sizes to avoid possible edge effects caused by the periodic boundary conditions and approach the infinite dilution limit (indeed, we observed longer nucleation times for simulation boxes with eight times the volume of the ones reported here); more replicas for better representation of Eq. (1); different temperatures values to study the behavior of the nucleation rate as a function of temperature, and different substances for the nuclei, for example, silver iodide (AgI), platinum (Pt), desert dust, to weigh their efficiencies as nucleating agents comparing the values of j under similar thermodynamic conditions.

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