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Nucleation of Crystalline Phases of Water in Homogeneous and Inhomogeneous Environments

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Abstract

We employ two-body and three-body bond-orientational order-parameters, in conjunction with non-Boltzmann sampling to calculate the free energy barrier to nucleation of crystalline phases of water. We find that, as the coupling between the successive peaks of the direct correlation function increases, the free energy barrier to nucleation decreases. On this basis we explain the important parameters that govern the nucleation rate involving crystalline phases of water in different homogeneous and inhomogeneous environments, giving a “unified picture” of ice nucleation in water.

Nucleation of crystalline phases of water are encountered in several scientific disciplines: (i) Homogeneous and heterogeneous nucleation of ice are the mechanisms by which ice microcrystals form in the clouds [1]; (ii) In the direct injection of liquid CO₂ into the ocean (a proposed scheme for the mitigation of green house gas emissions [2]), one encounters the nucleation of clathrate hydrate (a crystalline solid that includes CO₂ molecules in cages formed by water molecules); (iii) Antarctic fish and certain species of beetles inhibit nucleation of intracellular ice with the aid of antifreeze proteins [3]. Although the phase transition from water to ice has recently been observed under different conditions in computer simulation studies [4-7], the process of nucleation is best described by an ensemble of molecular dynamics trajectories (or Monte Carlo paths) connecting the stable regions of the free energy landscape rather than a single trajectory. Consequently, the intermediate states are characterizable by unifying patterns (structural or energetic) that are common to these paths. In a statistical sense, identifying the dynamical variables to quantify the patterns and averaging over the different molecular configurations characterized by the dynamical variables can yield valuable insight into the free energy landscape relevant to the nucleation process. These dynamical variables, also referred to as order parameters, are quantities that can classify the symmetries associated with the crystalline ice phase and distinguish them from the disordered liquid water phase.

Recently, we described a detailed study of nucleation of clathrate hydrates, where we derived the relevant order parameters of crystalline phases involving water, and presented a methodology to compute the free energy barrier to nucleation by employing the order parameters [3]. In this Letter, we apply our methodology to study several systems involving

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the nucleation of crystalline phases of water in different homogeneous and inhomogeneous environments. We then present a unifying picture of the nucleation of ice by deriving a relationship between the structure of the fluid (quantified in terms of the order parameters) and free energy barrier to nucleate the crystalline phase (formation of the critical nucleus) within the fluid.

Using the TIP4P potential for water [8], the Harris and Yung potential for CO₂ [9], and the 10-4-3 Steele potential for a graphite slit-pore (see, e.g., Ref. [10]), we studied several systems (see Table I): water in the bulk, a water-CO₂ mixture at $x_{\text{CO}_2} = 0.14$ that corresponds to a region of the water-CO₂ liquid-liquid interface, water in the presence of an electric field of strength $\vec{E} = 1 \text{ V} / \text{\AA}$, and water in a graphite slit-pore of width 9.4 \AA, that can accommodate a bilayer of adsorbed water molecules. In each of these cases we used NPT Monte Carlo simulations, except for water in the pore where we used grand canonical Monte Carlo simulations. The simulations were performed for large systems consisting of 1000–3000 molecules, with the explicit use of Ewald summation to treat long-range electrostatic interactions. For details see Ref. [2].

In order to compute the free energy barrier to nucleation of the crystalline phase for each of the systems in Table I, we chose to perform umbrella sampling over bond-orientational order parameters [2] defined in terms of average geometrical distribution of nearest-neighbor bonds. Nearest neighbors were identified as those molecules less than a cutoff distance of $r_{nn} = 3.47 \text{ \AA}$ [corresponding to the first minimum in the pair correlation function, $g(r)$] from a given molecule. The bond-orientational order parameters, Q_i 's and W_i 's introduced by Steinhardt *et al.* [11] are based on the expansion of the pair correlation function $g(\vec{r})$ in spherical coordinates, and hence are indicative of the rotational symmetry of the system. The Steinhardt order parameters are calculated by averaging over the nearest-neighbor bonds, implying that they are nearest-neighbor order parameters (Φ_{NN}). For waterlike fluids, which assume perfect tetrahedral coordination in the crystalline phase, the tetrahedral order parameter ζ introduced by Chau and Hardwick [12,13] measures the degree of tetrahedral coordination in water molecules. Unlike Steinhardt order parameters, which are nearest-neighbor order parameters, the tetrahedral order parameter ζ , being a three-body order parameter, serves as an effective next-nearest neighbor order parameter (Φ_{NNN}). The relevant order parameters [2, 14] to describe the nucleation of the crystalline phase for each of the systems in Table I are enumerated in Table II.

The probability distribution function $P[\Phi_1, \Phi_2, \dots]$, where the Φ_i 's are the order parameters, is calculated during a simulation run by collecting statistics of the number of occurrences of particular values of $\Phi_1, \Phi_2, \dots$ (as a multi-dimensional histogram) during the course of the NPT simulations. The Landau free energy $\Lambda[\Phi_1, \Phi_2, \dots]$ is defined as

$$\Lambda[\Phi_1, \Phi_2, \dots] = -k_B T \ln(P[\Phi_1, \Phi_2, \dots]) + \text{constant}. \quad (1)$$

The Gibbs free energy, $G = -k_B T \ln(Q_{NPT})$, is then related to the Landau free energy by the integral,

$$\exp(-\beta G) = \Pi_i \left\{ \int d\Phi_i \right\} \exp(-\beta \Lambda[\Phi_1, \Phi_2, \dots]). \quad (2)$$

To calculate the Gibbs free energy of a particular phase A , the limits of integration in Eq. (2) are from the minimum value of the set $\{\Phi_i\}$ to the maximum value of the set $\{\Phi_i\}$, that characterize the phase A . Further details on the implementation of the Landau free energy method are provided in Ref. [2].

The free energy barrier to nucleation for each of the systems described in Table I, was computed using the order parameters described in Table II, and the methodology outlined above. Our results are summarized in Table II. As an example, in Fig. 1 we show the projection of the Landau free energy surface (also known as potential of mean force) along the order parameter coordinate Q_6 for system 4 in Table I, for water in an external $\vec{E}$ field. In this case, the stable crystalline phase is the proton ordered cubic ice I_c . The free energy surface along with the three snapshots, clearly depict the two minima corresponding to liquid water and cubic ice phases and the maximum corresponding to the formation of the critical nucleus; the free energy barrier to nucleation was calculated using Eq. (2) to be $25k_B T$. Similar potential of mean force calculations were performed for other systems in Table I. For the case of the water-CO₂ mixture (system 5 in Table I), the Landau free energy calculations similar to Fig. 1 (not shown in this Letter), showed the stable crystalline phase to be structure I CO₂ clathrate hydrate, with a free energy barrier to nucleation of $55k_B T$ [2], while in the case of bulk water (systems 6–8 in Table I), the Landau free energy calculations showed a transition into hexagonal ice I_h [14]. Similar calculations for a bilayer of water confined in a hydrophobic slit-pore (systems 1 and 2 in Table I), showed the stable crystalline phase to be a cubic ice phase at higher activity, and an ice structure with distorted hexagons at lower activity [15] (the latter transition was also observed by Koga *et al.* [5]). The computed free energy barrier to nucleation (βG) for each system is provided in Table II.

A unifying picture of ice nucleation in an arbitrary environment emerges if we consider our results in the light of density functional theory (DFT). Ramakrishnan and Yussouff derived the grand free energy functional of an inhomogeneous hypernetted chain (HNC) fluid about the isotropic phase, $\Delta\Omega = \Omega[\rho(\vec{r})] - \Omega[\rho]$, in terms of spatially varying density, $\rho(\vec{r})$ [17],

$$\frac{\Delta\Omega}{k_B T} = \sum_{i=1} \frac{\xi_i^2}{2c_i} - (1 - c_o) \times \left[\eta + \frac{\eta^2}{2} \right], \quad (3)$$

where the $c_i = c_{\vec{k}_i}$ and $c_o = c_{\vec{k}} = 0$ are the Fourier coefficients of the fluid phase direct correlation function $c(\vec{r})$, ρ_o is the density of the fluid, and $\eta = (\bar{\rho}^{\text{crystal}} - \rho_o) / \rho_o$ is the fractional change in density on freezing. ξ_j 's are coefficients of the density expansion (defined such that they are independent of system size) for the density modes at the reciprocal lattice (RL) positions $\vec{k}_j$,

$$\rho(\vec{r}) = \rho_o(1 + \eta) + \rho_o \sum_j \frac{\xi_j}{c_j} \exp(i\vec{k}_j \cdot \vec{r}). \quad (4)$$

In DFT, the ξ_j 's and η are varied to look for functions that yield $\Omega = 0$. The first term in Eq. (3) is the free energy penalty (FP) incurred by creating the density modulations of magnitude proportional to ξ_j in the isotropic phase (and therefore is related to the free energy barrier to nucleation), while the second term is the free energy advantage (equal to $-V P$) due to the density modulation causing an increase in the overall density, also called “density condensation.” The positive term (FP) decreases with increasing values of c_j i.e., with decreasing temperature, as the liquid becomes more correlated. Therefore, it is physical to associate the positive term (FP) in Eq. (3) with the free energy barrier to nucleation.

Owing to the exponential decay of correlations [peaks of $\alpha(k)$, viz., c_1, c_2, c_3 , etc., decay with increasing k] in the fluid phase, the spontaneous creation of a higher order density mode by thermal fluctuation is accompanied by a large free energy penalty, FP, that cannot be effectively compensated by the gain in free energy (via “density condensation”) associated with the higher order modes; consequently, Ω can be described using density modes corresponding to the only the first and second set of RL vectors [17], and coefficients ξ_j 's corresponding to the higher modes remain zero even in the crystal phase. Specifically, for the case of a fluid in which only the first two modes contribute significantly to lowering of Ω (it will be shown later that this is the case for water), the free energy barrier to nucleation, $\Omega^{\text{nuc}}/k_B T$, is given by,

$$\frac{\Omega^{\text{nuc}}}{k_B T} \sim \frac{c_2(\xi_1^{\text{crystal}})^2 + c_1(\xi_2^{\text{crystal}})^2}{2c_1c_2}. \quad (5)$$

A spontaneous thermal fluctuation ($d\Omega$) of $O(k_B T)$ has the effect of inducing density modulations ($d\xi_i^2$) in a fluid whose magnitude is inversely proportional to the corresponding c_i . Consequently, within DFT, since the ξ_j 's are the only order parameters describing the free energy surface, the coupling between the order parameters can be described within linear response as $\xi_1^2 / \xi_2^2 = c_1 / c_2$. This leads to two limits for the barrier to nucleation (Ω^{nuc}), depending on the value of the parameter χ_2 defined as $c_2 c_1^{\text{crystal}} / c_2^{\text{crystal}} c_1$. We call χ_2 the coupling parameter as it includes the coupling between density modes in describing nucleation. The condition for supercooling of a liquid is given by $c_1 \approx c_1^{\text{crystal}}$ (as shown by Ramakrishnan [17] this is the basis for the Hansen-Verlet criterion); with these conditions, and in the limit $\chi_2 \ll 1$, the free energy barrier to nucleation Ω^{nuc} scales as $1/\chi_2$. In the limit $\chi_2 \rightarrow 1$, Ω^{nuc} decreases (to within $k_B T$, hence this is the spinodal limit) linearly with an increase in χ_2 . In both scenarios the coupling parameter $\chi_2 < 1$, and the free energy barrier to nucleation decreases with an increase in the value of the coupling parameter.

During the course of the simulation, the pair correlation function was calculated, from which $s(k)$ and hence $\alpha(k) = 1 - 1/s(k)$ was calculated. The coupling parameters corresponding to

the second and third density modes, χ_2 and χ_3 (defined analogously to χ_2) were estimated for each system in Table I, the values of χ_2 are provided in Table II. The values of χ_3 were either indeterminate because $c_3^{\text{crystal}}, c_3^{\text{liquid}} \rightarrow 0$ (for all systems except systems 3, 5), or ≈ 1 (for systems 3, 5), which implies third and higher order modes are not important for the systems we have considered. We also note that for all the systems in Table I, the coupling parameter $\chi_2 < 1$. Thus, as anticipated, the free energy barrier to nucleation decreases with an increase in the value of the coupling parameter χ_2 (see Fig. 2).

The following unifying picture emerges from the correlation in Fig. 2. In crystalline phases predominantly consisting of water molecules, the lattice structure is that of an expanded crystal, i.e., the density condensation occurs not due to increase in overall density (the $-V/P$ term), but because of the lowering of potential energy due to increase in the degree of hydrogen bonding. As a reflection of this fact, in the crystalline phase, the water molecules are always perfectly tetrahedrally coordinated (the three-body order parameter, $\zeta \approx 1$). This necessity of the next-nearest neighbor order parameter (ζ) implies that the second density mode (in addition to the first) clearly contributes to lowering Ω and dominates the nucleation behavior [18]. However, in an arbitrary environment, the barrier to nucleation of the crystalline phase of water not only depends on how the external potentials (such as presence of a field, surface, or solute) are able to induce a change in c_i^{liquid} , but also how the external potentials affect the coupling between the first and second density modes. The following conclusions can therefore be drawn from our simulation results (see Fig. 2). (i) For water in the bulk, $\chi_2 \ll 1$, and nucleation of hexagonal ice occurs via a thermal fluctuation that induces local density modulations corresponding to first as well as second density modes. Because of this reason, we explicitly needed to use the NNN order parameter ζ , in addition to NN Steinhardt order parameters in the simulations [18]. Accordingly, the free energy barrier to nucleation is high. (ii) For the case of water confined in a hydrophobic pore and water in the presence of an external electric field, the external potential induces a strong coupling between the density modes describing the water structure ($\chi_2 \approx 1$). As a result, the barrier to nucleation is lower when compared to that of unperturbed water, and the scaling of Ω^{nuc} approaches the spinodal limit. This fact also serves to explain why heterogeneous nucleation of ice typically always has a lower free energy barrier to nucleation, and is in some cases spontaneous. (iii) For the case of a water- CO_2 mixture, the presence of the guest molecules does not perturb the water structure significantly (χ_2 is only slightly more than that in bulk water). The free energy barrier to nucleation is comparable with that of bulk water [19]. (iv) As an example, we considered the effect of the insect antifreeze protein 1EZG [20] on the nucleation of ice; we performed a molecular dynamics simulation of the protein interacting in an aqueous environment (6000 water molecules) using the CHARMM simulation package [21]. During the course of the 1 ns simulation run, we calculated the pair correlation function $g(r)$ of water in a volume of $(9 \text{ \AA})^3$ adjacent to the protein, from which we calculated the coupling parameter $\chi_2 = 0.12$. By an extrapolation of the correlation in Fig. 2, it is clear that the reduction of χ_2 increases the barrier to nucleation (open symbol in Fig. 2), hence reducing the rate of nucleation.

The correlation between the free energy barrier to nucleation and the coupling parameter in Fig. 2 can in principle be verified experimentally via a combination of experiments

measuring nucleation rates and scattering experiments. We note that the asymptotic behavior of the correlation in Fig. 2, up to a scaling factor, is independent of the details of the intermolecular potentials; therefore, it represents a global behavior for the class of fluids satisfying Eq. (5). We have verified the consistency of the above order parameter method in the case of nucleation of hexagonal ice, by ensuring that the transition state ensemble obtained by our choice of the order parameters indeed possesses the attributes of a true transition state ensemble [14,22].

Acknowledgments

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FIG. 1.

Potential of mean force, $\beta\Lambda^{(1)}[Q_6]$, for water in an electric field, $\vec{E} = 1 \text{ V} / \text{\AA}$, at 200 K and 1 MPa, showing the transformation from liquid water to cubic ice. The snapshots indicate the positions of the oxygen atoms along with the distribution of hydrogen bonds and correspond to the three extrema of the free energy surface.

FIG. 2.

The free energy barrier to nucleation vs the coupling parameter χ_2 . The filled symbols are the calculated values for systems in Table I, the error bars correspond to the size of the symbols [14]. The solid line is a fit to the computed values and defines the correlation between ΔG and χ_2 . The form of the equation for the fit $[A(1 - \chi_2^2) / \chi_2]$ was chosen to behave asymptotically as $1/\chi_2$ in the limit $\chi_2 \rightarrow 0$ and $1 - \chi_2$ in the limit $\chi_2 \rightarrow 1$.

TABLE I.

Water in different environments.

	System	State condition
1	Water in a pore	180 K, μ at $P = 10$ MPa
2	Water in a pore	180 K, μ at $P = 1$ MPa
3	LJ in bulk	$k_B T \epsilon = 0.6$, $P \sigma^3 / \epsilon = 0.0008$
4	Water in $\vec{E}$ field	200 K, 1 MPa, $\vec{E} = 1 \text{ V} / \text{\AA}$
5	Water-CO ₂ mixture	220 K, 4 MPa, $x_{\text{CO}_2} = 0.14$
6	Water in bulk	140 K, 0.1 MPa
7	Water in bulk	160 K, 0.1 MPa
8	Water in bulk	180 K, 0.1 MPa

TABLE II.

Coupling parameters in different systems.

	Phase	χ_2	Φ_{NN}	Φ_{NNN}	β	G
1	Ice I_c [15]	0.9	Q_6, Q_4	...	5	
2	Ice a [15]	0.88	Q_6, Q_4	...	7	
3	FCC [10]	0.65	Q_6, W_4	...	20	
4	Ice I_c	0.61	Q_6, Q_4	...	25	
5	Clathrate [2]	0.39	$W_4^{gg}, \zeta_1^{gg}, \zeta_2^{gg}$ [16]	ζ	55	
6	Ice I_h [14]	0.37	Q_6, Q_4, W_4	ζ	54	
7	Ice I_h [14]	0.34	Q_6, Q_4, W_4	ζ	58	
8	Ice I_h [14]	0.31	Q_6, Q_4, W_4	ζ	63	

^aIce with distorted hexagons as found in Ref. [5] I_c = cubic ice, I_h = hexagonal ice.