Published in final edited form as:

J Am Chem Soc. 2003 June 25; 125(25): 7743–7747. doi:10.1021/ja0211252.

Nucleation of Hexagonal Ice (I_h) in Liquid Water

Ravi Radhakrishnan, Bernhardt L. Trout

Contribution from the Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, Massachusetts 02139

Abstract

The process by which supercooled fluids form stable, crystalline solids has been found to be elusive both experimentally and via computer simulations. This is because this process, generally called nucleation, is statistical in nature and because the set of intermediate states, generally called the critical nucleus, is very short-lived. Thus, there are very large uncertainties in even the limited experimental data that exist, and computer simulations that have been performed can yield descriptive information at best. Here we present a detailed and quantitatively accurate observation of the most important nucleation process, the freezing of liquid water at ambient conditions. We have accomplished this by using a method based on choosing a suitable set of order parameters to characterize the crystallinity of the system and a non-Boltzmann sampling Monte Carlo approach to obtain a statistical average of the properties of the system during its transition from liquid to ice (I_h). We have characterized the order of the system statistically at intermediate states between liquid water and ice I_h and in so doing described the nucleation process.

1. Introduction

The familiar process of nucleation of ice from supercooled water is encountered in several scientific and technologically relevant processes. The formation of ice microcrystals in clouds via nucleation is a phenomenon that has a large impact in governing global climatic changes.¹ The key to the survival of Antarctic fish and certain species of beetles through harsh winters is their ability to inhibit nucleation of intracellular ice with the aid of antifreeze proteins.^{2,3} At the other end of the spectrum, certain protein assemblies called ice-nucleation agents are believed to be responsible for catalyzing ice nucleation, a phenomenon which is exploited by certain bacteria to derive nutrients from their host plants.^{4,5} Controlling the formation and propagation of intracellular ice is an issue that is gaining prominence because of the increasing need for cryopreservation of natural and biosynthetic tissues.⁶ Several experimental studies on ice nucleation focused on measuring the rate of nuclei formation under nearly homogeneous conditions.^{7,8} Characterization of the structural attributes of the intermediate states in the ice-nucleation process has not been attempted in experimental studies, owing to the very short lifetimes of the intermediate states. On the other hand, the phase transformation of water to ice has recently been observed under different conditions in computer simulations studies.⁹⁻¹² These studies each yielded a single molecular dynamics trajectory, connecting the metastable water phase to the stable “ice”

phase. The process of nucleation, however, should be described by an ensemble of molecular dynamics trajectories 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 molecular dynamics trajectories. In a statistical sense, identifying dynamical variables to quantify the patterns and averaging over the different molecular configurations that have the same values of the dynamical variables can yield important information relating the evolution of the patterns to the free energy landscape relevant to the nucleation process.¹³ 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. In addition, the order parameters depend on the nature of intermolecular forces in water. Consequently, their choice will be impacted by the hydrogen-bond-forming character of water molecules. The information on the free energy landscape is useful in quantifying the rate of nucleation, while the evolution of the order parameters along the path of nucleation is useful in identifying the structural changes in the arrangement of molecules leading to the formation of the patterns and relating them to the free energy landscape. In this article, we adopt such an approach.

2. Simulation Methods

Molecular Simulation and Free Energy.

Monte Carlo (MC) simulations were performed on a system of TIP4P water molecules¹⁴ at constant temperature (180 K) and pressure (0.1 MPa) in a hexagonal cell (cell geometry: $a = b < c, \alpha = \beta = 90^\circ, \gamma = 120^\circ$) constrained to have a ratio of $c/a = 1.2281$. Periodic boundary conditions were applied in all three directions, and the method of Ewald summation was used to account for the long-range electrostatic interactions due to the partial charges of water. Typical production runs involved averaging the properties over a billion MC configurations. The simulations were done by performing two-dimensional umbrella sampling on the bond orientational order parameters Q_6 and ζ , while monitoring the order parameters Q_4 and W_4 .^{15,16} These order parameters are defined on the basis of the geometrical distribution of nearest-neighbor bonds. Nearest neighbors were identified as those molecules that were less than a cutoff distance of $r_{nn} = 3.47 \text{ \AA}$ (corresponding to the first minimum in the pair correlation function, $g(r)$, which defines the first coordination shell) away from a given molecule. For a definition of the order parameters Q_i and W_i , see Steinhardt et al.,¹⁵ and for the order parameter ζ , see Chau and Hardwick.¹⁶ Motivated by the work of Frenkel and co-workers,^{17,18} a histogram of the multidimensional probability distribution function $P[Q_4, Q_6, W_4, \zeta]$ was computed during the simulation runs by collecting statistics of the number of occurrences of particular values of the order parameters Q_4 , Q_6 , W_4 , and ζ .¹⁹ The Gibbs free energy is calculated by performing a numerical integration of the probability distribution function given by

$$\exp(-\beta G) = \int dQ_4 \int dQ_6 \int dW_4 \int d\zeta P[Q_4, Q_6, W_4, \zeta] \quad (1)$$

The error bars associated with the calculated values of the Gibbs free energy were estimated by performing five different umbrella sampling simulations in an order parameter window 0.0 Q_6 0.09 and assuming that the standard deviation is the same for all windows.

Transition Path Sampling.

The commitment probability distribution, P_B , where B is the hexagonal ice phase, was computed with the help of 400 short molecular dynamics trajectories. The concept of commitment probability distribution was first introduced by Du et al. and further elucidated by Bolhuis and co-workers.^{20,21} Every point in configuration space has a commitment probability. For transitions from a stable state A to a stable state B, the commitment probability P_B is the probability that short trajectories initiated from that configuration with randomly chosen initial momenta will reach state B. As shown by Du et al.,²¹ the transition-state surface for the transition between A and B consists of configurations for which $P_B = P_A \approx 1/2$. Fifty configurations were randomly chosen from the transition-state ensemble, i.e., configurations with $Q_4 = 0.12$, $Q_6 = 0.165$, $W_4 = 0.14$, and $\zeta = 0.83$. For each of the configurations, eight molecular dynamics trajectories for 10 ps were initiated, each with a different initial velocity distribution, randomly chosen from a Gaussian distribution with a second moment proportional to $T^{1/2}$.

3. Results and Discussion

In Figure 1 is shown a series of representative snapshots from our simulations for a model system of water molecules along the path of nucleation. The evolution of order is strikingly apparent as the system traverses from being liquid water to being hexagonal ice. The degree of order is quantified using the order parameters based on the geometrical distribution of bonds connecting pairs of water molecules that are nearest neighbors. The corresponding change in the average internal energy and Gibbs free energy along the path of nucleation is provided in Figure 2. The Gibbs free energy profile clearly shows the metastable water phase and the thermodynamically stable ice phase at 180 K. In a molecular dynamics trajectory, Matsumoto et al.⁹ observed that the initiation of the nucleation event occurs via the formation of a six-membered-ring configuration. Such a configuration is typical of snapshots from configurations with order parameter values $Q_4 = 0.09$, $Q_6 = 0.11$, $W_4 = 0.11$, and $\zeta = 0.80$, as depicted in the inset of Figure 1b. However, the formation of hexagonal ringed structures occurs prior to the transition-state region, as evident from the free energy profile in Figure 2. The evolution of the ordered “nucleus” is observed to occur for configurations with higher values of the order parameters, eventually transforming the whole system into the hexagonal ice phase.

The transition state is identified as an ensemble of configurations that contribute to the saddle region of the Gibbs free energy surface, which is historically referred to as the critical nucleus. The nature of the transition state is such that, in a local region of space, the water molecules are ordered in an arrangement whose symmetry can be characterized using the order parameters Q_4 , Q_6 , W_4 , and ζ . The number of water molecules that participate in the ordered environment is tracked using the distribution of molecular clusters existing in different ordered states, as shown in Figure 3. The statistics of the degree of ordering within

each molecular cluster for five states, including the transition state e, show the evolution of local order in molecular clusters. Note that we do see an identifiable nucleus that has a structure like that of hexagonal ice. Such an observation is what one would expect from the classical nucleation theory.²² However, the ordered structure, referred to as the “nucleus”, is dynamic in character. In particular, the number of molecules constituting the critical nucleus (identified as clusters with $Q_4 \approx 0.20$, $Q_6 \approx 0.25$, $\zeta \approx 0.9$) fluctuates between 210 and 260. This observation is contrary to the mean-field character of the classical nucleation theory,²² although in a qualitative sense, the snapshots suggest an embedded “crystalline nucleus” within the liquid phase. The differences in the statistical distribution of order within the molecular clusters in a, b, d, e, and f in Figure 3 indicate that the number of molecular clusters that assume ice-like symmetry (quantified by order parameters Q_4 , Q_6 , ζ) steadily increases along the path of nucleation.

Whether we are able to properly characterize the Gibbs free energy landscape in terms of a few order parameters is determined by computing the distribution of the commitment probabilities, P_B , for the configurations belonging to the ensemble of the observed transition state. If our choice of the order parameters describes the system well, then P_B is narrow and peaked near $P_B = 1/2$.^{20,21} The distributions of commitment probabilities at three different temperatures are given in Figure 4; note that the freezing temperature of TIP4P water is 240 ± 15 K.²³ At $T = 180$ K, the distribution of P_B is clearly unimodal, peaked around $P_B = 1/2$, validating that the chosen set of order parameters truly characterizes the Gibbs free energy surface. We note that all of the four order parameters (Q_4 , Q_6 , W_4 , ζ) had to be included in the calculation of commitment probabilities in order to obtain a unimodal distribution in Figure 4; hence, the order parameter space to describe the ice-nucleation process must include the complete set (Q_4 , Q_6 , W_4 , ζ). The commitment probability distribution for the same transition-state ensemble was calculated at two other (lower) temperatures, and the shifting of the peaks in the distribution of P_B toward $P_B = 1$ is consistent with the qualitative features of classical nucleation theory, in that decreasing temperature leads to a decrease in the size of the critical nucleus (for a given fluid, this is certainly the case in classical nucleation theory).

The Gibbs free energy landscape of the ice-nucleation process can be understood in terms of the order parameters that we have identified. The Steinhardt order parameters Q_4 , Q_6 , and W_4 , being nearest-neighbor order parameters, characterize the evolution of the ice-like density modulations, which qualitatively correspond to the correct ordering at the nearest-neighbor distances (umbrella sampling within the space of Q_4 , Q_6 , and W_4 failed to induce ice-like structuring in the $g(r)$ function beyond the first peak). However, the formation of the “nucleus” in liquid water is incomplete without the evolution of higher order modes in the density²⁴ that are responsible for ordering beyond nearest-neighbor distances (as reflected by the evolution of the second peak in $g(r)$). The addition of the tetrahedral order parameter ζ to the set Q_4 , Q_6 , and W_4 in the umbrella sampling scheme effectively induces the correct density modulations beyond nearest-neighbor distances.

In the case of simple fluids such as argon that undergo volume condensation on freezing, only density modes corresponding to the nearest-neighbor ordering contribute to the free energy compensation.²⁵ Consequently, the free energy surface of crystal nucleation in

simple fluids can be described by an order parameter space spanned by just the Steinhardt order parameters Q_6 and W_4 .^{17,18} In contrast, for the case of water, the formation of ice leads to an expansion in density; therefore, the free energy penalty incurred by the creation of density modes is compensated not by volume condensation, but by an increased degree of hydrogen bonding that is related to a perfect tetrahedral alignment. The synergy of the tetrahedral order parameter ζ and the Steinhardt order parameters Q_4 , Q_6 , and W_4 affects the structure beyond nearest-neighbor distances, suggesting that the effects of local tetrahedrality propagate beyond a central molecule's nearest-neighbor shell, thereby playing a crucial part in the ice-nucleation process. This is an essential difference between crystal nucleation in water and that in other simple fluids. For this very reason, the Gibbs free energy barrier to crystal nucleation in water is much higher than the corresponding value in the case of simple fluids.²⁴ For example, the Gibbs free energy barrier to nucleation of a Lennard-Jones fluid ($\sigma = 3.81 \text{ \AA}$, $\epsilon/k_B T = 148 \text{ K}$) at a temperature $k_B T/\epsilon = 0.6$ is $20 k_B T$.²⁴

In conclusion, we have presented a stochastic picture of nucleation in which we have statistically characterized the disordered, ordered, and intermediate states associated with the freezing of water in terms of a few order parameters. Nucleation is described via a minimum free energy path in order parameter space, along which the molecular configurations assume spatially inhomogeneous order parameter profiles that evolve in the direction of increasing order. The inhomogeneous order parameter profiles correspond to a locally ordered region that has a solid-like structure. However, the statistical characterization in terms of the distribution of order parameters in molecular clusters revealed large fluctuations in the number of molecules constituting the “nucleus”. This contrasts with the classical, mean-field view of a “nucleus”.²² The effect of external potentials and foreign surfaces on the mechanism of ice nucleation is reported as a separate study.²⁴ The order parameter approach has a wide scope of applicability in quantifying the effect of local fluid structure on the free energy landscape and has the potential to be gainfully employed in aqueous inhomogeneous systems including biological systems.

Acknowledgment.

This work was partially funded by a grant from the Singapore—MIT alliance.

References

- (1). Baker MB Science 1997, 276, 1072–1078.
- (2). Yeh Y; Feeney RE Chem. Rev 1996, 96, 601–617. [PubMed: 11848766]
- (3). Liou Y-C; Tocilj A; Davies PL; Jia Z Nature 2000, 406, 322–324. [PubMed: 10917536]
- (4). Zachariassen KE; Kristiansen E Cryobiology 2000, 41, 257–279. [PubMed: 11222024]
- (5). Hew CL; Yang DSC Eur. J. Biochem 1992, 203, 33–42. [PubMed: 1730239]
- (6). Acker JP; Elliott JAW; McGann LE Biophys. J 2001, 81, 1389–1397. [PubMed: 11509353]
- (7). Koop T; Luo B; Tsias A; Peter T Nature 2000, 406, 611–614. [PubMed: 10949298]
- (8). Krämer B; Hübner O; Vortish H; Wöste L; Leisner T; Schwell M; Rühl E; Baumgärtel H J. Chem. Phys 1999, 111, 6521–6527.
- (9). Matsumoto M; Saito S; Ohmine I Nature 2002, 416, 409–413. [PubMed: 11919628]
- (10). Koga K; Tanaka H; Zeng XC Nature 2000, 408, 564–567. [PubMed: 11117739]
- (11). Svishchev IM; Kusalik PG Phys. Rev. Lett 1994, 73, 975–978. [PubMed: 10057588]

- (12). Yamada M; Mossa S; Stanley HE; Sciortino F Phys. Rev. Lett 2002, 88, 195701. [PubMed: 12005645]
- (13). Sastry S Nature 2002, 416, 376–377. [PubMed: 11919609]
- (14). Jorgensen WL; Chandrasekhar J; Madura JD J. Chem. Phys 1983, 79, 926–935.
- (15). Steinhardt PJ; Nelson DR; Ronchetti M Phys. Rev. B 1983, 28, 784–805.
- (16). Chau PL; Hardwick AJ Mol. Phys 1998, 93, 511–518. Errington JR; Debenedetti PG Nature 2001, 409, 318–321. [PubMed: 11201735]
- (17). Van Duijneveldt JS; Frenkel D J. Chem. Phys 1992, 96, 4655–4668.
- (18). Lynden-Bell RM; Van Duijneveldt JS; Frenkel D Mol. Phys 1993, 80, 801–814.
- (19). Radhakrishnan R; Trout BL J. Chem. Phys 2002, 117, 1786–1796.
- (20). Bolhuis PG; Dellago C; Chandler D Proc. Natl. Acad. Sci. U.S.A 2000, 97, 5877–5882. [PubMed: 10801977]
- (21). Du R; Pande VS; Grosberg AY; Tanaka T; Shakhnovich ES J. Chem. Phys 1998, 108, 334–350.
- (22). Debenedetti PG Metastable Liquids; Princeton University Press: Princeton, NJ, 1996.
- (23). Gao GT; Zeng XC; Tanaka H J. Chem. Phys 2000, 112, 8534–8538. Karim OA; Haymet ADJ J. Chem. Phys 1988, 89, 6889–6896.
- (24). Radhakrishnan R; Trout BL Phys. Rev. Lett 2003, in press.
- (25). Ramakrishnan TV; Yussouff M Phys. Rev. B 1979, 19, 2775–2794.

Figure 1.

Snapshots along the path of freezing showing the distribution of hydrogen bonds. The snapshots are representative of the ensemble of configurations generated using Monte Carlo simulations (see Simulation Methods). Pictures a—f are at different sets of values of the four order parameters. The inset (dotted square) in picture b shows the formation of a hexagonal ringed structure.

Figure 2.

Average internal energy and Gibbs free energy along the path of nucleation (see Simulation Methods). The points marked a—f correspond to the states having the set of order parameters Q_4 , Q_6 , W_4 , and ζ as described in the figure. The representative snapshots in Figure 1 belong to each of the states a—f, respectively.

Figure 3.

Distribution of order parameters among molecular clusters in five different states corresponding to states a, b, d, e, and f in Figures 1 and 2. Each cluster consists of a central water molecule together with its nearest neighbors. The open histograms correspond to ice-like clusters (identified as clusters with $Q_4 < 0.20$, $Q_6 < 0.25$, and $\zeta > 0.9$), and the filled histograms correspond to water-like clusters. The histograms for states a, b, d, and f are from an average of 10 000 configurations around a single snapshot.

Figure 4. Un-normalized commitment probability distribution functions (see Simulation Methods) corresponding to the transition-state ensemble.