Electrofreezing of Liquid Water: A Microscopic Perspective

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Abstract: Using molecular dynamics simulations performed with the TIP4P and SPC/E pair potentials we examine the process of field-induced crystallization (electrofreezing) of supercooled liquid water. In the presence of an electric field the transformation of a liquid into a crystalline solid is observed for a narrow range of density and temperature on a time scale of a few hundred picoseconds. The resulting crystal has the structure of polar cubic ice **I**. TIP4P water appears to be more susceptible to nucleation than SPC/E water. For a field of 0.5 V/Å TIP4P water undergoes crystallization at densities between 0.94 and 0.96 g/cm^3 at a temperature of 250 K. Intermediate structures emerging during the electrofeeezing of water closely resemble a low-density amorphous ice. We observe formation of a high-density amorphous component at densities above those favoring the crystallization of the cubic ice. Application of an electric field to low-density water samples (0.90−0.92 g/cm^3 for TIP4P water at 250 K) produces low-density amorphous ices. Constant density conditions were found to be more favorable than constant pressure conditions for producing polar ice crystals.

1. Introduction

The crystallization of liquid water plays a fundamental role in many natural and technological processes. Over many years an enormous number of phenomenological observations of water freezing under a variety of conditions have been accumulated.[1,2] It is now well-documented that a geometric match between the microscopic structure of a substrate surface and the ice structure can help to facilitate ice nucleation at the surfaces of various materials.[2,3] However, reports have persisted of another important mechanism with which nature controls the freezing of water. The (electric) field-induced crystallization, or electrofreezing, of supercooled liquid water has been put forward to explain many intriguing observations.[4−7] It has been argued that local electric fields have the ability to induce the crystallization of liquid water at surfaces which can be distinctly different from those of ice. As a recent and insightful example, Gavish et al.[4] have carried out a careful study of ice nucleation on the hydrophobic faces of single amino acid crystals that have no structural match with ice. They observed a dependence of the freezing point of water upon the chirality of the molecules in the amino acid crystals and concluded that the critical nucleation events were being influenced by large electric fields within cracks on the substrate surface. This supposition that electric fields can affect the dynamics of freezing was not universally accepted. Wilen[8] offered a thermophysical explanation for the observed behavior which predicts a lowering of the equilibrium freezing temperature. Another recent study[9] focusing upon cyclic tropospheric responses to solar variations has suggested that global weather and climate changes can be related to solar activity via a process involving the electrofreezing of supercooled water droplets in the Earth's atmosphere. However, despite the phenomenological evidence provided by these studies for the nucleation-promoting effect of electric fields, the actual microscopic picture of the electrofreezing of water has remained obscure. This is not surprising since even with the aid of computer simulation it has not been possible, until very recently, to observe directly ice nucleation at the molecular level.

Very recently in a computer simulation study[10] of electric field effects on the phase behavior of low-tempeature TIP4P water, we discovered that at a particular state point an applied homogeneous static electric field can induce crystallization of the supercooled liquid. The resulting polar crystal formed under these applied field conditions had the structure of cubic ice **I**. We point out that, although computer simulations of the crystallization of simple monatomic fluids can now be performed almost routinely,[11] the crystallization of molecular liquids in simulations poses unique difficulties. The glassy states which have universally emerged upon slow reduction of the temperature have effectively prevented the detection of a spontaneous nucleation of a molecular heterophase within the time scale of a typical simulation. For water, a highly polar substance, the application of an electric field in a computer simulation appears to facilitate the nucleation of polar ice $\mathbf{I}_c$ from the metastable liquid, thereby providing a unique opportunity to study directly the process of electrofreezing of water at the molecular level.

Following our earlier exploratory work[10] we have performed a series of extensive molecular dynamics (MD) simulations of low-temperature water subject to applied electric fields. We have examined the TIP4P[12] and SPC/E[13] models for water; both have been shown to describe reasonably successfully the properties of the real liquid and various amorphous and crystalline ices (in the works of Haymet and co-workers,[14]

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Stanley and co-workers,[15] Tse and Klein,[16] Ji and Pettit[17]). Our main purpose in this study was to determine the specific conditions of temperature and density which favor field-induced crystallization of supercooled water, as described by these models, and to provide insights into the microscopic structural transformations occurring at different stages of field-induced ice nucleation.

The remainder of this paper is organized as follows. In Section 2 we outline the computational procedure and in Section 3 we present our results. Finally, we offer some concluding remarks in Section 4.

2. Simulation Details

In this article we report results from applied-field molecular dynamics simulations of low-temperature water performed with the TIP4P[12] and SPC/E[13] pair potentials. In order to facilitate the nucleation events in these simulations we employed boundary conditions which support the diamond-type packing of cubic ice **I**, the most favorable "in-field" crystalline polymorph in our model systems. We chose to work with 256- and 64-particle samples, respectively, in truncated octahedral and cubic simulation cells. It is clear from symmetry considerations that both truncated octahedral and cubic samples with $N = {}^1/_2(4n^3)$ and $8(n^3)$, respectively, where $n = 1, 2, 3, ...$, will accommodate an ice $\mathbf{I}_c$ lattice in periodic boundary conditions. We remark that the boundary conditions employed in our simulations would not support ice $\mathbf{I}_h$. However, the large interaction term between our applied fields and the total dipole moment of the systems strongly favor the nucleation of the cubic isomorph of ice **I** as only it can be 100% polarized (fully proton ordered).

In our simulations the Ewald summation technique[18] was used to evaluate the long-range electrostatic interactions. Our implementation of the Ewald method can be found elsewhere.[19] Both constant pressure (Nose barostat[18]) and constant density conditions were explored. A fourth-order Gear algorithm[18] with a time step of 1.25 fs was used to integrate our Gaussian isokinetic equations of motion[20] in which the rotational degrees of freedom were represented using quaternions. The homogeneous static electric field was always applied along the laboratory *Z*-axis.

3. Results and Discussion

(a) Constant Density Simulations. We focus first upon the density dependences in the field-induced transformations of low-temperature TIP4P water. Several bulk samples of supercooled liquid TIP4P water at 250 K and at constant densities ranging from 0.9 to 1.00 g/cm^3 were prepared by cooling (within 50 ps) well-equilibrated liquid configurations at 298 K. Following a further equilibration of 200 ps, these supercooled liquid configurations were subjected to a homogeneous static electric field of 0.5 V/Å and various physical properties sensitive to phase composition were monitored. Our earlier exploratory work (see ref 10) had indicated that the threshold value of the field strength which would induce TIP4P water at 250 K to undergo a liquid-to-solid transition lies between 0.1 and 0.5 V/Å. These field strengths are significantly smaller than the average local electric fields within condensed phases of water (which range around 1.5−2.0 V/Å) and are comparable with the fields suggested to exist within the cracks of the amino acid crystals studied in ref 4.

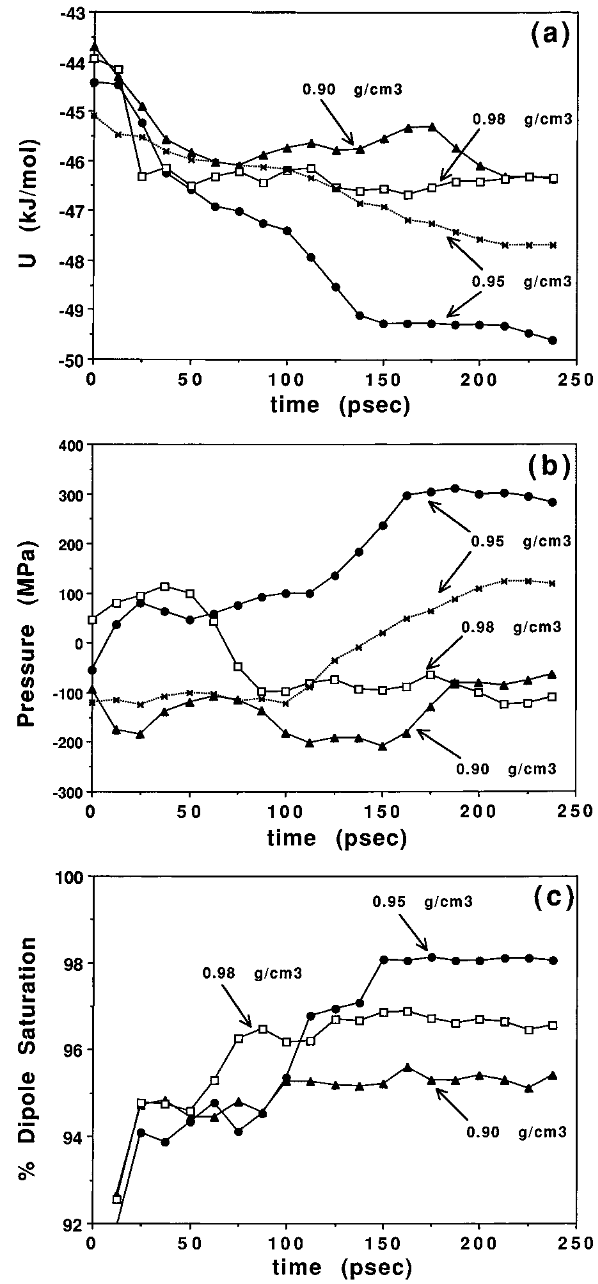

Figure 1. The time dependence for (a) the configurational energy, (b) the pressure, and (c) the percent dipole saturation in TIP4P water samples with different densities subjected to an electric field. Each point represents a block average taken over 12.5 ps. All data are at a temperature of 250 K for a field of 0.5 V/Å. The values at $t = 0$ represent field-off conditions. The triangels, the open squares, and the circles connected with solid lines are the results obtained with a cubic simulation cell containing 64 molecules, while the crosses connected with dotted lines are the results obtained with a truncated octahedral simulation cell containing 256 molecules.

Figures 1−4 demonstrate the apparent sensitivity of the electrofreezing process to the density. Figures 1a−c display respectively the total configurational energy, the pressure, and the percent dipole saturation of several water samples as a function of time. The percent dipole saturation is defined as $(100\% \cdot M)/(N \cdot \mu)$, where M is the total dipole moment of a sample, N is the number of particles, and μ is the dipole moment of the water molecules. In Figure 1 $t = 0$ corresponds to the moment when the field was applied. Typical results for low-, intermediate-, and high-density samples, $\rho = 0.90$, 0.95, and 0.98 g/cm^3, respectively, are shown. Figures 2, 3, and 4 display

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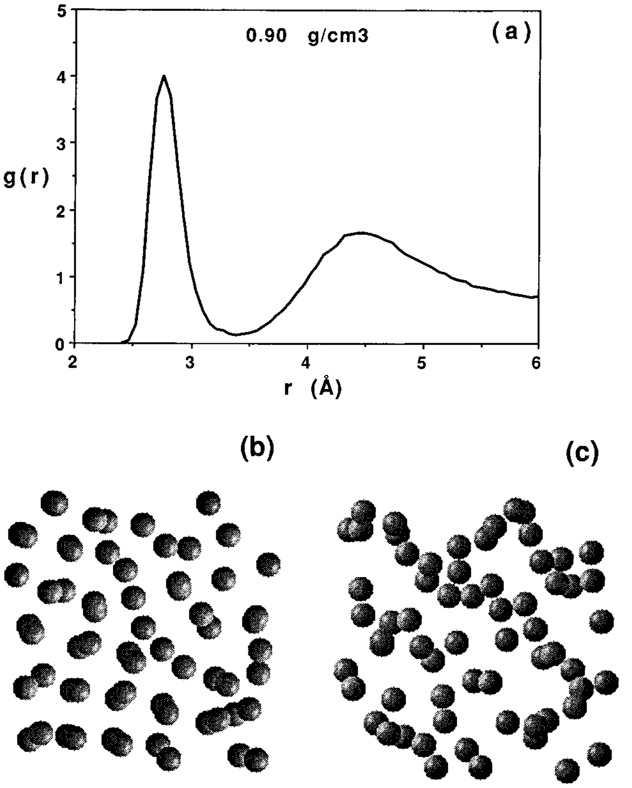
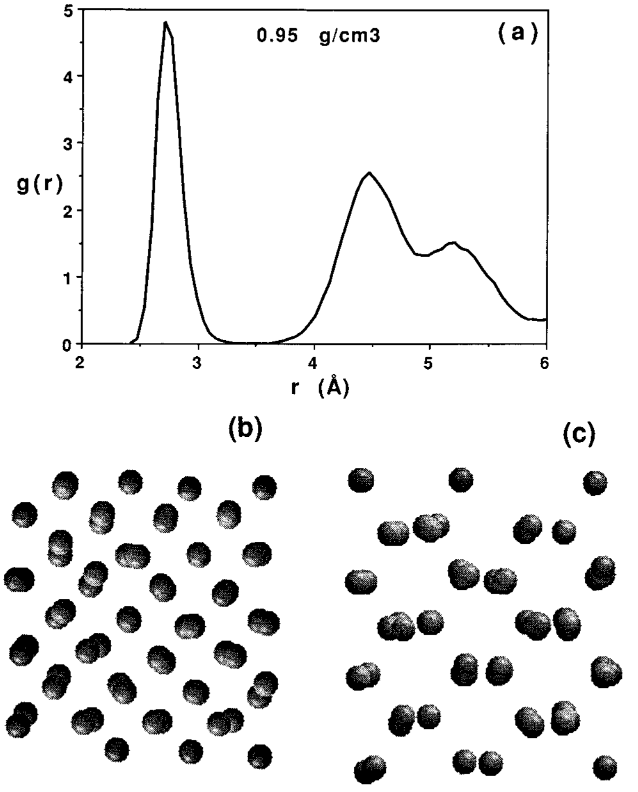


Figure 2. The structure in the amorphous solid formed from supercooled TIP4P water at a density of 0.9 g/cm^3 under a field of 0.5 V/Å. The oxygen−oxygen radial distribution function is shown in (a), while the final molecular configuration as viewed from two different directions is displayed in (b) and (c). The gray spheres represent the oxygen atoms of the water molecules. In (b) the applied field is acting along the normal to the plane of the figure; in (c) the applied field lies in the plane of the figure. The data were obtained at 250 K with a cubic simulation cell containing 64 molecules.



(001) (101)

Figure 3. The structure in polar ice **I**$_c$ formed from supercooled TIP4P water at a density of 0.95 g/cm^3 under a field of 0.5 V/Å. (a) and (b) are as in Figure 2. The projection in (c) is chosen to demonstrate the crystallographic plane (101) of the diamond-type packing of cubic ice.

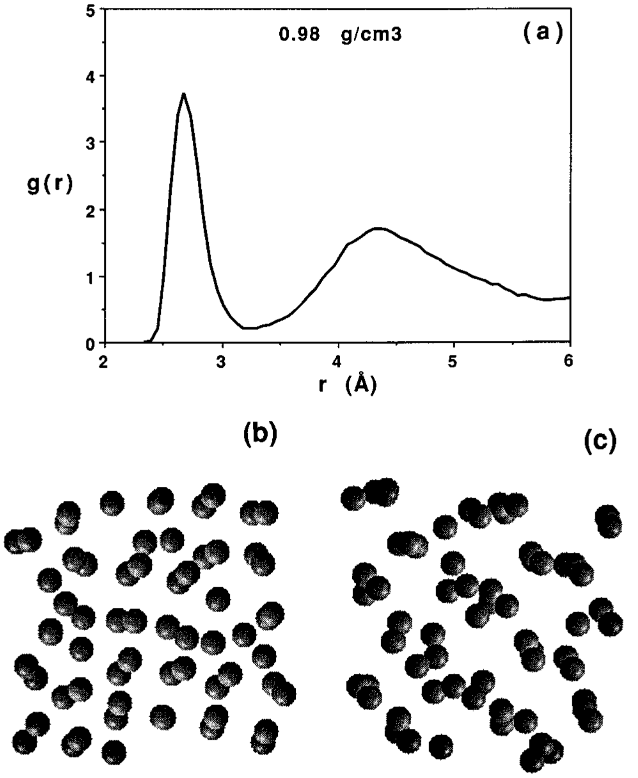


Figure 4. The structure in the amorphous solid formed from supercooled TIP4P water at a density of 0.98 g/cm^3 under a field of 0.5 V/Å. (a), (b), and (c) are as in Figure 2.

the structures of the solids formed 250 ps after the electric field was applied.

At both low-density ($\rho = 0.90-0.92$ g/cm^3) and high-density ($\rho = 0.98-1.00$ g/cm^3) we failed to observe crystallization of our water samples upon application of an electric field of 0.5 V/Å. Radial distribution functions for the oxygen atoms and representative molecular configurations (see Figure 2 and Figure 4) indicate that the resulting solid phases in these samples are amorphous. In order to test the dependence of the resulting phase composition upon the applied field strength several simulations were carried out with a field of 1.0 V/Å and the physical picture remained unchanged. We found that in our high-density water samples the pressure usually decreases between 50 and 80 ps after application of the field, eventually attaining values comparable with those maintained in our low-density samples. We have carried out extensive animation of molecular configurations generated in these simulations. These detailed microscopic visualizations confirm that a characteristic structural ordering, apparent as layering (e.g. see Figures 2c and 4c), begins to develop in these water samples at about 50−80 ps after application of the field.

The field-induced crystallization of liquid TIP4P water was found to take place within a small range of densities, from 0.94 to 0.96 g/cm^3 at $T = 250$ K, on a time scale of a few hundred picoseconds. The time dependences in the pressure and the energy obtained from our 64- and 256-particle samples with the density of 0.95 g/cm^3 are shown in Figure 1. Upon application of the electric field these supercooled liquids appear to transform rapidly, within 50−80 ps, into amorphous-like (layered) materials. After approximately 120 ps the pressure in these water samples increases markedly indicating a change of phase. At the same time their microscopic structures begin to demonstrate the features of a regular crystalline solid. At 160−200 ps after the application of the field the pressure curves plateau (see Figure 1b) marking the point beyond which we can say a new crystalline phase exists. The polar ice crystal that emerges at this stage still possesses numerous lattice defects and will melt if the electric field is removed. Melting of this imperfect ice crystal in the absence of applied field can be avoided by quenching it to a temperature of 200 K. In the continued presence of the field, lattice defects tend to disappear, usually after a further 100−200 ps, and the resulting crystal is stable at $T = 250$ K in the absence of the field. Thus, the electric field has successfully induced the homogeneous nucleation of a stable crystalline solid from the metastable liquid. As we might expect the resulting crystalline samples attain a substantially lower energy and a higher degree of the dipole saturation than any amorphous configurations (see Figures 1a and 1c) at the same temperature.

Figure 3 displays the structure of a polar crystal formed from supercooled liquid TIP4P water at 250 K under an applied field of 0.5 V/Å. This structure can be unambiguously identified as cubic ice **I**.[10,21] Although hexagonal ice is the predominant crystalline form of water encountered on the Earth, the crystallization of liquid water into cubic ice can be observed under natural conditions. It has been argued that small droplets of water in the upper atmosphere often freeze into cubic ice.[22−24] In the laboratory cubic ice has been obtained by freezing liquid water in porous materials,[25] by vapor-deposition,[21] by warming amorphous and high-pressure crystalline ices,[21,26] and by freezing very large clusters of water in supersonic flows.[27] Upon heating or applied pressure cubic ice irreversibly converts into hexagonal ice; the microscopic mechanism of such conversion is not known. Under the highly polarized conditions imposed in our computer experiments with classical models of water (our water samples are typically 95−98% polarized) we would expect proton-ordered cubic ice **I** to be the preferred crystalline form.[28] For our cubic ice crystals formed under the field of 0.5 V/Å the smallest interplanar separation is approximately 1.7 Å. As noted recently by Xia and Berkowitz,[29] water layers next to the surface of charged Pt walls are also separated by a distance of 1.7 Å which has led them to conclude that these layers tend to acquire a cubic ice structure.

Our results reveal a remarkable similarity between the final amorphous structures forming in our low-density water samples ($\rho = 0.90-0.92$ g/cm^3) and the structures appearing at intermediate stages during crystallization in our more dense samples ($\rho = 0.94-0.96$ g/cm^3). Figure 5 displays a typical molecular configuration of an emerging intermediate solid phase for a water sample with the density of 0.95 g/cm^3. This sample consists of stacked molecular layers with numerous planar defects and long-range disorder within the layers. The local structure in this disordered material is characterized by a tetrahedral four-coordinated arrangement of hydrogen-bonded molecules. It does not exhibit the "interstitially" coordinated molecules peculiar to the local structure in liquid water at ambient conditions[30,31] and high-density amorphous ice.[16] An analogous packing pattern characterizes the final structure obtained for the noncrystallizing low-density water samples (see Figure 2). Hence we have identified these solids as low-density amorphous ice.[32−34] We recall[30,31] that the interstitial coordination of H_2O molecules accounts for the elevated pair density in the region of the first minimum in the radial distribution function (RDF) of oxygen atoms for liquid water and high-density amorphous ice at about 3.5 Å; in the spatial distribution function (which represents the spatial analog of the RDF) this "interstitial" coordination appears as local maxima at nontetrahedral positions at separations of about 3.3−3.9 Å. A detailed analysis of the spatial distributions of atoms in the condensed phases of water can be found elsewhere.[10,30,31,35]

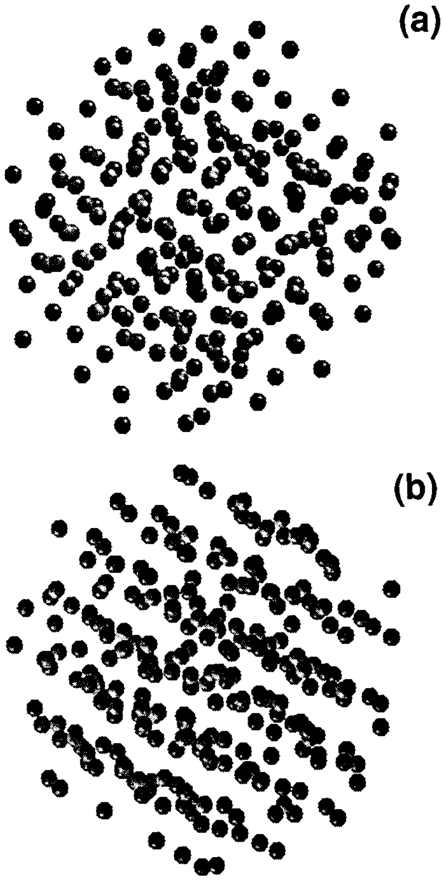


Figure 5. A typical molecular configuration of an intermediate phase. The configuration is of a water sample with a density of 0.95 g/cm^3 at about 110 ps after the field was applied. The gray spheres represent the oxygen atoms of the water molecules. In (a) the applied field is acting along the normal to the plane of the figure. The orientation of the sample in (b) was chosen to demonstrate the peculiar layering pattern as discussed in the text. This configuration was obtained at a temperature of 250 K using a truncated octahedral simulation cell containing 256 molecules.

The microscopic structure found in our amorphous solids with densities of 0.98−1.00 g/cm^3 features a small fraction of molecules (less than 5%) occupying interstitial positions in the cavities of the local hydrogen-bond network. This observation

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indicates formation of a high-density amorphous component[16] at densities above those favoring the crystallization of cubic ice. An important question to be resolved by future studies is whether electric fields have the ability to induce the nucleation of the proton-ordered high-density crystalline forms of ice.[21]

The influence of temperature upon the crystallization of TIP4P water was examined using 64-particle samples with densities of 0.95 g/cm^3 and an applied field of 0.5 V/Å. Over a time scale of several hundred picoseconds we did not observe crystallization at temperatures higher than 260 K. At $T = 260$ K the regular solid produced by the field always exhibited some disorder, the thermal motion of the water molecules allowing for rapid formation and removal of local lattice defects. Ice crystals obtained from more deeply supercooled water samples (at or below $T = 230$ K) were found to contain defects which the applied field was unable to eliminate over the observation time. One possible explanation for their persistence is that at low temperatures the higher viscosity of the original liquid prevents proper orientation of (and in) the nucleation seeds.

In this work we carried out eight separate 256-particle constant-density simulations using the SPC/E model. Temperatures between 220 and 250 K and densities between 0.95 and 1.00 g/cm^3 were examined. In general, SPC/E water proved to be less susceptible to nucleation than TIP4P water. Supercooled liquid SPC/E water samples did not crystallize within 300 ps after the application of a field of 0.5 V/Å, nor did they give any indication that such a transformation would occur. We observed a sluggish crystallization of our 0.98 g/cm^3 sample at 220 K with a field of 0.7 V/Å; a defective bulk SPC/E ice crystal was formed at this state point only after 350 ps. We remark that this model dependence is consistent with the work of Haymet and co-workers[14] which suggests that SPC water has a lower thermodynamic melting temperature than TIP4P water (200 K vs 240 K). Similarly, it has been noted that the SPC/E model exhibits a lower temperature of maximum density as compared with the TIP4P model (235 K vs 260 K).[15,36]

(b) Constant Pressure Simulations. In these simulations several 64-particle samples of supercooled TIP4P water at 250 K and at constant pressures ranging from −100 to 100 MPa were subjected to an electric field of 0.5 V/Å. Figures 6a−c display respectively the total configurational energy, the pressure, and the percent dipole saturation in these water samples as a function of time, $t = 0$ again corresponding to the instant the field was applied. Typical results obtained at low, intermediate, and high pressures, $P = -100$, 0, and 100 MPa, respectively, are shown.

The field-induced crystallization of liquid TIP4P water at $T = 250$ K was found to take place at pressures between 0 and 50 MPa. The time dependence shown in Figure 6 indicate that this transformation at $P = 0$ MPa proceeds rather smoothly and takes approximately 150−200 ps. In particular, Figure 6b demonstrates that water (unlike most other liquids) expands upon freezing (into ice **I**). The ice crystals nucleating under constant pressure conditions were found to contain more defect than those forming under constant density conditions and usually appear misaligned within a simulation cell. The application of an electric field to our $P = -100$ and 100 MPa samples produced amorphous solids composed of disordered molecular layers, similar to what we obtained in many of our constant density simulations. To test the effect of system size we performed a simulation with a larger 256-particle sample of TIP4P water at $P = 0$ MPa. The resulting solid formed from this supercooled liquid under the field of 0.5 V/Å consisted of at least one misaligned crystalline block of cubic ice.

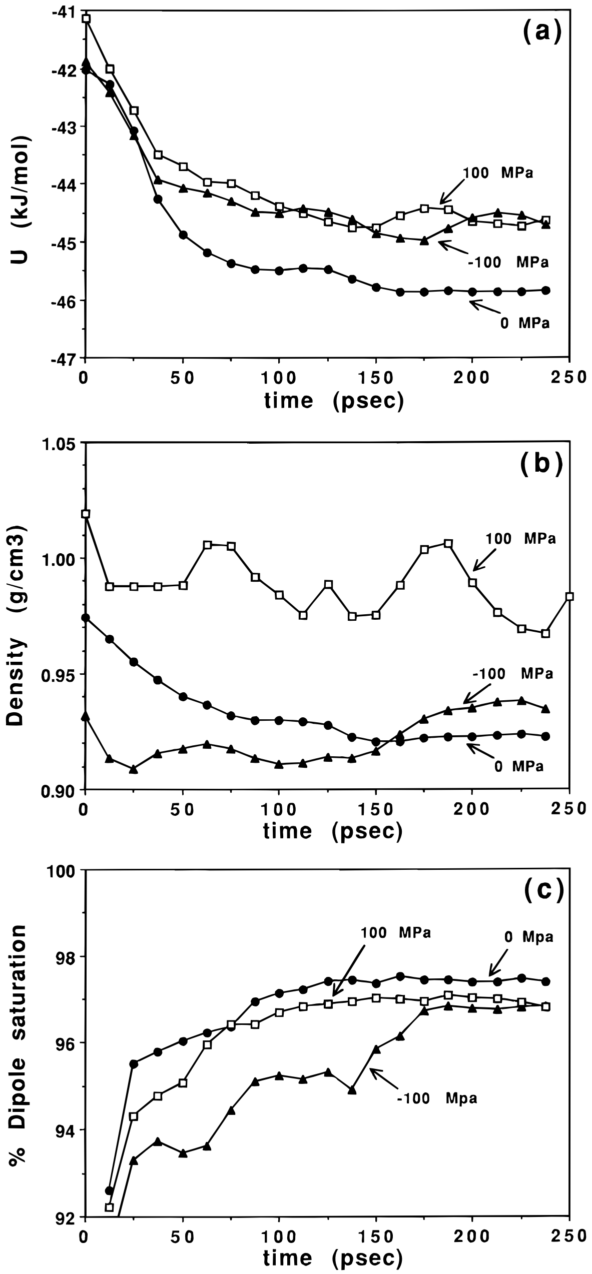

Figure 6. The time dependence for (a) the configurational energy, (b) the density, and (c) the percent dipole saturation in TIP4P water samples at different pressures subjected to an electric field. Each point represents a block average taken over 12.5 ps. All data are at a temperature of 250 K for a field of 0.5 V/Å. The values at $t = 0$ represent field-off conditions. These results were obtained with a cubic simulation cell containing 64 molecules.

4. Concluding Remarks

In this work we have studied the field-induced crystallization (electrofreezing) of supercooled liquid water using MD simulations performed with the TIP4P and SPC/E potentials. In the presence of an electric field a transformation from a liquid to a polar ice **I** crystal was observed for a narrow range of density and temperature on a time scale of a few hundred picoseconds. TIP4P water appeared to be more susceptible to nucleation than SPC/E water, yet even its field of crystallization spans densities of only 0.94 to 0.96 g/cm^3 at a temperature of 250 K. We found that constant density conditions are superior to constant pressure

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conditions for producing "good" ice crystals. An analysis of intermediate structures emerging during the field-induced crystallization of water suggests that they closely resemble a low-density amorphous ice.

The application of an electric field to low-density TIP4P water samples at 250 K with $\rho = 0.90-0.92$ g/cm^3 produces low-density amorphous ices. The local structure in these low-density amorphous solids is characterized by a tetrahedral four-coordinated arrangement of hydrogen-bonded molecules. It does not exhibit the "interstitially" coordinated molecules peculiar to the local structure in liquid water or high-density amorphous ice. The microscopic structure found in our amorphous samples with $\rho = 0.98-1.00$ g/cm^3 features a small fraction of molecules occupying "interstitial" positions indicating formation of a high-density amorphous component at densities above those favoring the crystallization of cubic ice.

The nonequilibrium computer simulation methodology employed in this work can be extended to a variety of polar liquids (such as liquid ammonia, hydrogen halides, etc.); these studies of the microscopic dynamics of crystallization are now underway. From the experimental standpoint it is certainly worth exploring the effects of strong electric fields on the structure of water layers absorbed on electrode surfaces at low temperatures. The freezing of water on the surfaces of polar crystals[4] and in similar ordering environments also merits further investigations. Supersonic flow experiments[37] with charged water clusters is another technique that might be used to examine electric field effects in the freezing of water. One can expect that a combination of such experiments and computer simulations will provide us with a detailed picture of how ice crystals are formed under a variety of conditions and, in general, a better microscopic understanding of crystallization phenomena in molecular systems.

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