Effect of oscillatory shear on the fluid–solid phase transition of supercooled water

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Abstract

The present study aims at the methodological improvement of the electrofreezing of supercooled water by applying oscillatory shear along with a homogeneous electric field in non-equilibrium molecular dynamics simulations of simple water models such as TIP4P and SPC/E. The application of a planar Couette flow field accounts for a moderate speedup in the phase transition. Since the system goes through a nonergodic glassy state in the course of the process, it is not surprising that a macroscopic manifestation of the Lyapunov instability inherent in the equations of motion is observed. The formation of a conjectured high-density ice polymorph (ice XII) has been studied in terms of the applied electric and oscillatory flow fields. The threshold value of the electric field for the crystallization has been determined. The method of applying the oscillatory flow field was also investigated in detail. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

Water is of abiding scientific interest since it is nature’s most important solvent in biological and chemical processes, yet the origins of its remarkable properties are far from understood. The availability of powerful computers and simple but accurate models for water makes it increasingly feasible to perform molecular simulation of liquid water over time scales which are large, relative to its intrinsic translational and rotational relaxation times. Such long simulations are necessary if one wishes to study complex many-body phenomena in water, such as phase transitions.

Because of their application to biological systems and to chemistry at ambient conditions, essentially all intermolecular potential models for water (such as the TIP4P [1] and the SPC/E [2]

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model which are the subjects of this study) have been developed by fitting to experimental data at or around room temperatures. The models are thus very successful in reproducing many water properties at ambient conditions but have only recently been applied at significantly lower [3–7] or higher [8–12] temperatures. The freezing of water in MD simulation has always been a great challenge, but due to its difficulties little progress was made until quite recently [3–7]. The first simulation of ice crystal growth was reported by Báez and Clancy [4], where ice grew on a liquid–solid interface. This was a high-density polymorph, called by the authors ice B, which had not been observed before either in simulation or experimentally. The first direct simulation of the freezing of a bulk sample of water (or, for that matter, any molecular fluid) was reported recently by Svishchev and Kusalik [5,6]. These authors demonstrated that the application of a static electric field to supercooled water samples markedly facilitated the transformation of water to ice. Because of the applied field, highly polarized cubic ice I (Ic) was formed instead of the most common hexagonal ice I (Ih). Shortly thereafter Svishchev and Kusalik found a previously unknown polymorph of ice (which they denoted ice XII) using the same process [7]. This high-density ice is similar to the ice B of Ref. [4]. This open quartz-like structure filled the simulation cell over a period of 1000 ps. The latter can be regarded as a slow transformation computationally when compared to the formation of cubic ice I in a similar-sized simulation cell at lower pressure but higher temperature in about 200 ps [5,6]. The applied electric field \( \sim 0.5 \text{ V} \text{ Å}^{-1} \) was very strong indeed, but it is comparable to that experienced by water molecules within molecular distances of each other \(^1\) or the surfaces of biopolymers [13] and within the cracks of amino acid crystals [14].

The crucial step in the formation of these crystals is the complete breakup of liquid water’s hydrogen bonding network. In the electrofreezing process the sample will be completely polarized when the original hydrogen-bonded network is distorted and/or broken up sufficiently for the molecules to align with the applied field. We recently reported [15] a possible improvement of this electrofreezing method. We applied oscillatory shear in concert with the homogeneous electric field. The new method showed remarkable speedup in the formation of ice XII from a supercooled sample under high pressures and facilitated the formation of cubic ice I under ambient pressures [15]. As we were carrying out more simulations after our preliminary results, several questions arose. In the following, we will report these and the answers based on the more detailed data acquired in the course of this study.

2. Simulation details

In this paper, we shall only be considering the formation of the new high-density crystal, ice XII [7]. In our constant volume simulations we set the density to 1.17 g cm\(^{-3}\). The preparation of the supercooled samples was as follows. We began with a liquid configuration that was equilibrated for 300 ps at 298 K, then cooled to 230 K and equilibrated for another 300 ps. In our simulations, we used 256 particles in a cubic cell applying the usual periodic boundary conditions. The dependence of electrofreezing on ensemble, system size and shape has already been studied previously [5–7].

\(^1\) A.A. Chialvo, personal communication. A. Chialvo calculated the spherical average of the local electric field induced by the water molecules in SPC/E water at room temperature, with \( \rho = 1.17 \text{ g cm}^{-3} \). In the first coordination shell this is around 0.1 V Å\(^{-1}\).
shearing, the SLLOD algorithm [16] has been used along with the Lees–Edwards periodic boundary conditions. The TIP4P and SPC/E rigid, point charge water models were used as the intermolecular potential models (for a description of the models, see Refs. [1,2], respectively). The long range electrostatic interactions were handled by using the reaction field method [17]. The equations of motion were integrated by a fourth-order Gear predictor–corrector method with a timestep of 0.001 ps. The motion of the molecular sites was implemented using the Evans–Murad quaternion algorithm [18] and the temperature kept constant by using a Gaussian thermostat [16]. The constant electric field was applied in the $z$-axis direction in the laboratory frame.

The idea behind the modification of the electrofreezing was that another form of external field may facilitate the break-up of the hydrogen-bonded network. The action of the field should result in perturbation of the molecular positions and possible reorientation of the hydrogen bonds to facilitate the molecules exploring phase space and locating the minimum energy configuration associated with the solid state. We applied an oscillatory planar Couette flow in our molecular dynamics simulations (as described in Ref. [15]), with strain rates $\gamma_{\alpha\beta} = \partial v_\alpha / \partial \beta(\alpha, \beta \in \{x, y, z\}$ and $\alpha \neq \beta$) varying from $-\gamma_{\alpha\beta,0}$ to $\gamma_{\alpha\beta,0}$ given by

$$\gamma_{\alpha\beta} = \gamma_{\alpha\beta,0}\cos(\omega t). \tag{1}$$

We found [15] that oscillatory shear alone could not induce crystallization from supercooled water samples, but a combination of oscillatory shear and electrofreezing proved to be much more effective than electrofreezing alone.

3. Results and discussion

First we shall discuss the way in which oscillatory shear was implemented in the simulations. Starting from a supercooled sample, the oscillatory shear and the electric field were turned on at the beginning for a certain period of time, usually 100–200 ps. (No explicit dependence on the length of this period has been found. We chose this interval to be 100 ps in all the calculations reported in this paper, unless otherwise stated.) Then, the shear field was turned off, with the electric field remaining on. The reason for this is that once the crystal is formed, it can be broken up by the constant motion due to the applied shear. Thus, the application of shear can be thought of as providing help to the system to break up the hydrogen-bonding network and converge to the energetically favorable crystal state, and hence should be applied for a limited time. This is the general recipe of the method; we shall now concentrate on the first period when the shear field is applied.

We have previously shown [15] that the continuous application of the oscillatory shear in the conventional $x$-direction ($\gamma_{xy,0} = 1.0$) did not have any effect on the speed of the crystallization. (We used unity for the maximum reduced shear rate, corresponding to $6 \times 10^{11}$ Hz in real units, throughout our simulations, unless otherwise stated.) We deployed several variations of this method to achieve one showing significant speedup in the freezing process. In Fig. 1, we plotted the configurational energy averaged over four runs started from different initial conditions vs. time of the three different methods deployed (top curves). The first curve (dotted line) denotes the simulations where shearing acted in the $z$-axis (direction of the electric field) instead of the $x$-axis direction with maximum strain rates $\gamma_{z,0}$ equal to unity. The second one (dashed line) corresponds to the results where the orientation of the shear was varying every 1 ps (corresponding to one period of oscillation...
Fig. 1. The configurational energy (in kJ/mol) is plotted against time (in ps) in the top part of the figure for the electrofreezing process averaged over runs from four different starting configurations of TIP4P molecules. The dotted line shows the results when the shear acted only in the $z$-axis direction, $\dot{\gamma}_{z,0} = 1.0$. The dashed line represents data from runs with $\dot{\gamma}_{a,0} = 1.0$, where $\alpha$ and $\beta$ changed after each cycle of shear (1 ps) to use all the Cartesian coordinate axes ($x, y, z$). The full line refers to a method similar to the second, but there was a 3-ps long relaxation period between the shear cycles in different directions. The two curves with the lower energy show the configurational energy in kJ/mol of SPC$^E$ molecules plotted against time. The dashed line represents data from runs with $\dot{\gamma}_{a,0} = 1.0$, and the full line refers to the data where no oscillatory shear was applied. ($\rho = 1.17$ g cm$^{-3}$, $T = 230$ K).

Of the shear, since $\omega$ in Eq. (1) was set to $2\pi$ ps$^{-1}$; $x$-, followed by $y$-, followed by the $z$-direction. The third curve (full line) denotes the result of a similar method to the previous one. The only difference is that a relaxation period of 3 ps is inserted between each shearing cycle. This third method is clearly the best among them, attaining the ice XII crystal energy plateau at around 450 ps, whereas the others fail to reach the plateau until 600 ps. (It should be noted that the crystal contains defects, so turning the field off would result in melting of the crystal. Defects can be eliminated (and the crystal conserved) by cooling it even further [5].) In our calculations, the third method has been used unless stated otherwise. We investigated the dependence on $\omega$ and found no effect of $\omega$ on the results for $\omega$ between 0.2 and 10 ps$^{-1}$.

Most of our calculations have been done using the TIP4P potential, but for the sake of consistency the SPC/E model has also been evaluated. In the bottom part of Fig. 1 the configurational energy of
the SPC/E sample has been plotted against the time throughout the electrofreezing process with (dashed line) and without (full line) oscillatory shear. The crystallization is very fast compared to the TIP4P model, and the effect of the shear is significant. In Fig. 2, a snapshot of the simulation box is presented at the end of the electrofreezing process. For clarity only the O–H bonds are drawn. Note that the crystal is fully proton-ordered. This is a natural consequence of the electric field. Even at ambient pressure, the simulations preferred the (fully proton-ordered) cubic isomorph of ice I to the hexagonal [5,6]. It should also be noted that the cubic simulation cell is not commensurate with the conjectured ice XII lattice in Ref. [7]. This means that a perfect lattice cannot be expected in our simulations. The characteristic features of the ice XII lattice can be identified in the snapshot. However, the unit cell itself cannot be found since a very similar structure commensurate with the cubic cell has emerged. The number of lattice defects is relatively low. The crystalline order can also be seen in Fig. 3, where the oxygen–oxygen pair correlation function, \( g_{oo}(r) \), of our sample at the beginning and at the end of the electrofreezing process can be seen.

Svishchev and Kusalik [5,6] suggested values between 0.1 and 0.5 V Å\(^{-1}\) for the magnitude of the electric field. We tested this range (0.1 to 1.0 V Å\(^{-1}\)) in our systems and found that the threshold value for the electrofreezing process to take place is 0.5 V Å\(^{-1}\) (see Fig. 4).

As we were acquiring more results after the initial ones [15], we recognized that the crystallization times depended rather strongly on the starting configuration of the supercooled liquid, as did the speedups by the oscillatory shear, which varied from 0% to an order of magnitude. Moreover, as we employed different computer architectures (namely, IBM RS6000 390 and SGI MIPS R10000 Indigo 2), the outcome significantly differed even for the same starting configuration. In Fig. 5, we plotted the polarization rate defined as the average of the cosines of the angles formed by the dipole
The oxygen–oxygen pair correlation function $g_{OO}(r)$ as a function of the O–O distance $r$ (in Angstroms) for the SPC/E model water. The $g_{OO}(r)$ of the sample just before turning on the electric field (full line) is shown along with that of the sample after 600 ps of electrofreezing with oscillatory shear applied (dashed line). ($\rho = 1.17$ g cm$^{-3}$, $T = 230$ K).

Vectors of the molecules with the electric field ($\langle \cos \theta \rangle$), against time for two different runs. One was obtained by simple (i.e., shear-free) electrofreezing on SGI (dashed line) and the other on the IBM (full line) computer architectures using 64-bit arithmetic. This quantity can trace the crystallization process as can the configurational energy, the hydrostatic pressure, or $g_{OO}(r)$. Extensive testing of the codes on the IBM and SGI, which were identical at the source level, verified that the differences in the results of the two codes could only be attributed to roundoff error. The figure clearly shows that although the result (the crystal) is the same, the path that leads to it is quite different even when the only difference is the way the computers handle roundoffs in the 16th decimal digit! This behavior

The configurational energy (in kJ/mol) plotted against time (in ps) for the electrofreezing process of molecules averaged over runs from four different starting samples. In all runs oscillatory shear (with $q_{\theta} = 1.0$) was applied. The full, dashed, broken and dotted lines refer to simulations where the magnitude of the electric field was 0.1, 0.4, 0.5 and 1.0 V Å$^{-1}$, respectively.
can be explained by the highly nonergodic nature of the glassy supercooled water samples and the Lyapunov instability [19] which is inherent in the equations of motion and causes the exponential divergence of nearby trajectories in phase space. From this graph we can also conclude that in the electrofreezing the liquid hydrogen-bonding network breaks up very fast and the molecules line up with the field’s direction very soon. The formation of the crystal’s hydrogen-bonding network is the (sometimes very) time consuming part of the process.

In Fig. 6, we present the average of the hydrostatic pressures of four processes starting from different initial configurations by applying electric field only (full line) or additional oscillatory shear for the first 100 ps (broken line). The four runs were quite different from each other but the averages show that the oscillatory shear clearly speeds up the freezing: it takes about 450 ps to reach the crystalline state with the help of shear, whereas, without that, it takes about 650 ps to reach the same
pressure. (Note that in water the pressure increases upon freezing at constant volume.) However, the no-shear curve reaches the final value earlier and more smoothly; the variation is higher in the case when the shear is applied.

It should be noted that in identifying the resulting ice structure, we used the nomenclature of Svishchev and Kusalik in Ref. [7]. During revision of this paper, Lobban et al. [20] reported in Nature that they had found experimentally a new ice phase which they also called ice XII. This new ice phase apparently differs from both ice forms found in simulations by Báez and Clancy [4] and by Svishchev and Kusalik [7].

4. Conclusions

When investigating the electrofreezing of high pressure water to ice XII, we have shown that the threshold value for the electric field is between 0.4 and 0.5 V Å⁻¹. We find that oscillatory shear can be applied to the process with success. The SPC/E potential model appeared to be at least as capable of freezing this way as the TIP4P model, enabling us to conclude that the phenomenon is not an artefact of a specific model. The results presented in this paper show that the applied oscillatory shear was successful in producing ice from supercooled water when combined with an applied electric field, but the speedup over the standard electrofreezing is not always as favorable as found earlier [15]. The reason for this is that the glassy, and hence nonergodic, nature of the supercooled initial configurations causes fluctuations in the crystallization speed. In the light of these findings, the simple step of adding oscillatory shear (which comes at essentially no cost computationally) should be considered a useful tool in the simulation of freezing, since it can result in faster crystallization.

5. List of symbols

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\begin{align*}
\gamma & \quad \text{strain rate} \\
\omega & \quad \text{frequency} \\
g_{oo}(r) & \quad \text{oxygen–oxygen pair correlation function} \\
\theta & \quad \text{angle between the dipole vector of the molecules and the z-axis}
\end{align*}
\]

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