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Molecular Simulation

Publication details, including instructions for authors and subscription information:

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To cite this Article Bryk, Taras and Haymet, A. D. J.(2004) 'The Ice/Water Interface: Density-Temperature Phase Diagram for the SPC/E Model of Liquid Water', *Molecular Simulation*, 30: 2, 131 – 135

To link to this Article: DOI: 10.1080/0892702031000152172

URL: <http://dx.doi.org/10.1080/0892702031000152172>

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The Ice/Water Interface: Density–Temperature Phase Diagram for the SPC/E Model of Liquid Water

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(Received October 2002; In final form January 2003)

The density–temperature diagram for SPC/E water at one bar pressure is studied with correct treatment of long-range potentials. The density maximum was obtained at temperature 240 K. The melting temperature for ice I_h is estimated to be 225 ± 5 K from the simulations of ice/water coexistence. A local order parameter for ice/water interface is discussed.

Keywords: Phase diagram; Melting temperature; Water; Ice

INTRODUCTION

Here we study the coexistence of ice I_h and water using the SPC/E model of water molecules [1] as part of an exploration of the structural and dynamical properties of ice/water interfaces and estimation of the melting temperature of the SPC/E ice I_h . We also present the density-temperature diagram for the water in SPC/E model. It is a difficult task to prepare an ice-water interface [2] for simulations in the NVT ensemble without knowing the proper density of water for the desired temperature. However, we were not able to find in the literature a correct constant pressure, density–temperature phase diagram with full treatment of Coulombic interactions. In simulations of 360 water molecules at the pressure of one bar, the SPC/E potentials have been used, first with a cutoff radius of 9 Å [3], and then by smooth truncation using a switching function between 6 and 9 Å [4]. Although no other difference was reported in these two studies, the density-temperature diagrams are distinctly different. The density maxima in

the constant pressure ρ – T plane were reported to be at 235 K with $\rho = 1.0265 \text{ gcm}^{-3}$ [3] and 255 K with $\rho = 1.0082 \text{ gcm}^{-3}$ [4]. In preparation for our ice/water interface studies [2], we have performed time-consuming simulations of a large system at different temperatures and one bar pressure with explicit treatment of long-range Coulomb potentials via Ewald summation.

There exist several approaches of theoretical estimation of the melting point for any given system: the free energy method involving the thermodynamic integration technique [5]; an approach based on grand-canonical Monte Carlo simulations [6]; more approximate studies of finite sized clusters and the melting temperature dependence on the cluster size [7]; and direct simulations of solid–liquid coexistence by the molecular dynamics method [8]. The last method is becoming more and more popular because the increasing power of computers allows the study of realistic systems consisting of up to a hundred thousand particles. The two-phase coexistence approach has been applied successfully in studies of the melting temperature in Lennard–Jones systems [9,10], silicon [11], aluminum [12] and iron [13,14]. It was found [12] that the coexistence method and free energy approach result in different melting temperatures, with a lower value obtained from direct simulations of two-phase coexistence. Recently, Alfè *et al.*, [14] investigated the drawbacks inherent to both methods and focused on *ab initio* corrections to them.

The melting temperatures obtained from all the theoretical approaches are very sensitive to

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the choice of the model for interatomic potentials and their cut-off radius. Therefore, the correct treatment of long-range Coulomb interaction by Ewald summation for the case of ice/water simulations will be a sufficient advantage over the ice melting temperature estimation by the free energy approach with truncated long-range potentials, reported in [4]. Recently Arbuckle and Clancy [15] studied the effect of Ewald sum on the free energy of SPC/E water. They used a rather small system of 360 molecules to obtain the density-temperature phase diagram at the one bar pressure. The melting temperature of proton-disordered ice I_h was estimated in that free energy study to be 279 ± 5 K [15].

In this study we aimed to obtain the density-temperature phase diagram for a large system of 1728 SPC/E water molecules with Ewald summation for long-range Coulomb interaction and rather large cut-off radius for Lennard–Jones pair interactions. The same precision of Ewald summation and cut-off radii of short-range interactions were used for simulations of two-phase coexistence between ice I_h and water with 1920 molecules having the purpose to estimate the melting point by the coexistence method.

The remaining paper is organized as follows: in the next section we give details of the bulk water and two-phase simulation; in the third section the results for density-temperature phase diagram of SPC/E water is discussed together with results on the stability of ice/water interface, and our conclusions have collected in the fourth section.

SIMULATION METHOD

We have simulated bulk SPC/E water in the range 200–298 K using the DL_POLY package [17], for a collection of 1728 rigid molecules with periodic boundary conditions. The time step was chosen to be 1.5 fs. An isotropic *NPT* ensemble was used to keep the pressure at the level of one bar with thermostat and barostat relaxation times of 0.05 ps and 1.0 ps, respectively. Equilibration runs were performed for each temperature and took from 10 ps for 298 K to 400 ps at 200 K. The production runs were performed up to 600 ps in order to get the acceptable convergence of the average density.

The long-range Coulomb interaction was taken into account using 3D Ewald summation, and short-range Lennard–Jones part of intermolecular potential was cut off at $r_{\text{cut}} = 10$ Å. The Ewald convergence parameter was $\alpha = 0.284$ Å⁻¹ and the highest reciprocal lattice numbers were $|n_x| = |n_y| = |n_z| = 10$.

For two-phase ice/water simulations we used a system of 1920 SPC/E molecules in a rectangular

box. We used the same cut-off radius for short-range part of potentials as for bulk water. To keep the same precision for Ewald summation the Ewald convergence parameter α was identical to the value used for bulk water, but the highest reciprocal lattice numbers were $|n_x| = |n_y| = 8$ and $|n_z| = 18$. Production runs were performed for ice/water interfaces over 1.2 ns. All the details of ice/water simulations for basal and prism interfaces can be found elsewhere [2].

RESULTS AND DISCUSSION

Density–Temperature Phase Diagram for SPC/E Water

The density-temperature phase diagram at the pressure of 1 bar obtained in this study is shown in Fig. 1, together with two different data sets reported earlier by Baez and Clancy [3,4]. The famous density maximum of water is found for this model at 240 K with $\rho = 1.01163$ g cm⁻³ (Table I). It is instructive to follow the equilibrium density dependence together with the three-molecule angle distribution function shown in Fig. 2. The decrease of the equilibrium density for temperatures $T < 240$ K is connected with the increase of tetrahedral configurations with four nearest neighbors (see Table II) and an average three-molecule angle of 109.47°.

A disagreement exists between our density-temperature phase diagram with the one reported by Arbuckle and Clancy [15], where the density maximum occurs at the temperature of 260 K. This can be attributed to different precision in Ewald summation as well as different cut-off radius of short-range potentials. For comparison with our precision, Arbuckle and Clancy used the switching function between 6 Å and 9 Å to cut-off smoothly Lennard–Jones potentials, and the highest

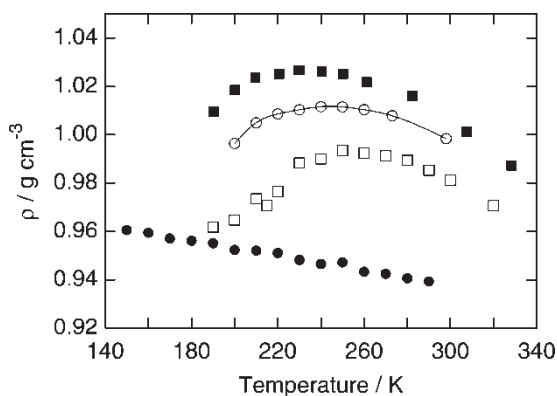


FIGURE 1 The density–temperature phase diagram for SPC/E water: open circles connected by spline line—this study, filled and open boxes—results for SPC/E model with truncated long-range interaction reported in Refs. [3] and [4], respectively. Filled circles represent ice I_h phase diagram reported in Refs. [16].

TABLE I Equilibrium density of SPC/E water at the pressure of 1 bar

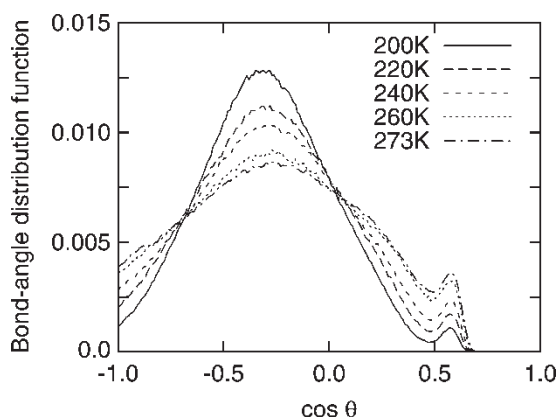
T (K)	ρ (g cm $^{-3}$)
200	0.99640 ± 0.0008
210	1.00495 ± 0.0020
220	1.00860 ± 0.0003
230	1.01032 ± 0.0003
240	1.01163 ± 0.0007
250	1.01148 ± 0.0002
260	1.01038 ± 0.0012
273	1.00783 ± 0.0006
298	0.99842 ± 0.0002

reciprocal lattice numbers in the Ewald sum were $|n_x| = |n_y| = |n_z| = 5$.

Ice/Water Interfaces: Stability of the Density Profiles

In Fig. 3, the mass–density profiles $\rho(z)$ are shown at different time windows of the MD run for three temperatures in the range 220–240 K for the basal ice/water interface. At the temperature of 240 K one can see obvious change in the density profile at different time windows due to melting. At 230 K slow melting still takes place, while at 220 K one can observe a sharpening of the peaks in the density profiles. In [2] the density profiles were studied with the step of 2.5 K in temperature between 220 and 230 K, that allowed an estimation of the temperature of the stable coexistence for SPC/E ice and water to be 225 K, which we believe is the melting temperature. This differs from the results of Baez and Clancy [4] for SPC/E water with truncated long-range potentials, which showed at 240 K either growth of the ice B structure on the ice B/water interface, or oscillatory shifts of the ice II/water interface around its mean position.

Our simulations of two-phase ice/water coexistence for SPC/E model result in the melting temperature which is approximately 50 K below

FIGURE 2 Molecular angle distribution function $P(\cos \theta)$ at five temperatures and one bar pressure.TABLE II Fraction of nearest H $_2$ O molecules within a sphere of radius $r_c = 3.3$ Å in the SPC/E water at different temperatures and one bar pressure

Number of neighbors	200 K	220 K	240 K	260 K	273 K
2	0.00	0.01	0.01	0.02	0.01
3	0.07	0.09	0.12	0.13	0.13
4	0.85	0.75	0.66	0.55	0.52
5	0.08	0.14	0.19	0.25	0.27
6	0.00	0.01	0.02	0.05	0.06
7	0.00	0.00	0.00	0.00	0.01

the estimated value of 279 K from the free energy study of Arbuckle and Clancy [15]. A similar tendency was pointed out by Morris [12], when the melting point from two-phase coexistence simulations for aluminium was lower than the value from free-energy calculations. To date the origin of the discrepancy in melting point estimation between direct two-phase simulations and free-energy

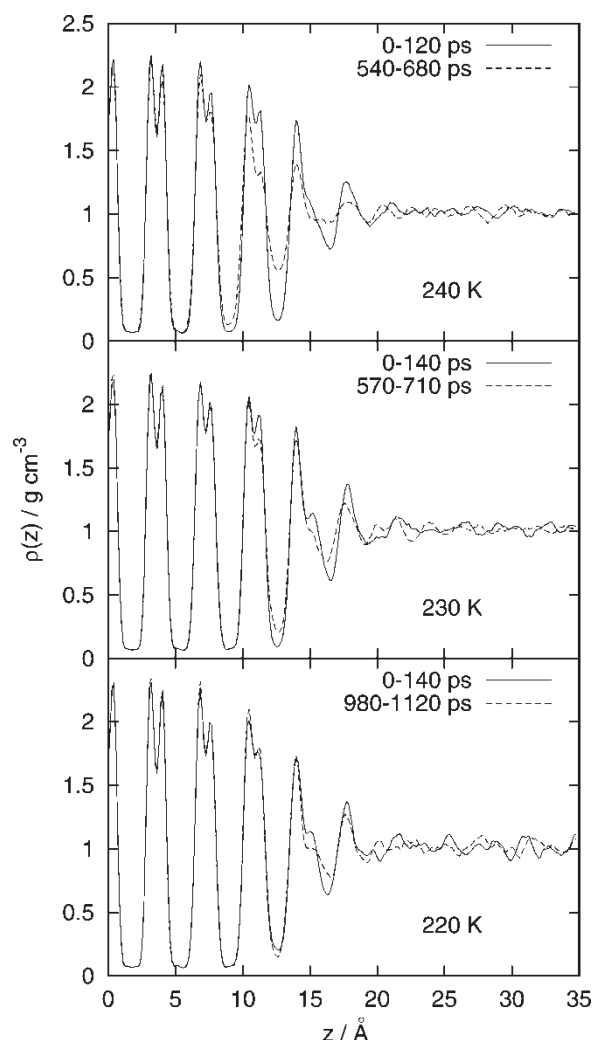


FIGURE 3 Mass–density profiles for basal ice/water interface at the temperatures 240, 230 and 220 K estimated during two different time windows of MD simulations.

methods is not known. On the other hand, the melting temperature of 225 ± 5 K obtained in this study with SPC/E model is in closer agreement with the results of free-energy study of melting temperature using TIP4P model [18], where the value of 238 ± 7 K was obtained. Also, the *ab initio* Car-Parrinello dynamics study of ice surface disordering [19] indicated that the melting temperature of I_h ice is between 190 and 230 K, which is in quite good agreement with our result.

Local Order Parameters for the Ice/Water Two-phase System

For ice/water interface studies, in contrast to intrinsic order parameters, such as local density and translational order, one can define local order parameters which depend only on the position of a reference molecule. There exist many different local order parameters, some of which are convenient to use in the case of high-symmetry solid phases on one side of the interface, such as fcc or bcc:

$$q_m = \left\langle \frac{1}{N} \sum_{i,j,k} \cos [m\theta_{xy}(i,j,k)] \right\rangle, \quad m = 2, 4, 6,$$

where the Z axis is normal to the interface, and $\theta_{xy}(i,j,k)$ is the projection onto the XY plane of

the angle between nearest three molecules. However, in the case of the ice/water interface we found it better the local order parameter for tetrahedral configurations [20,21]:

$$q_t = \left\langle \frac{1}{N} \sum_{i,j,k} \left[\cos \theta(i,j,k) + \frac{1}{3} \right]^2 \right\rangle.$$

Figure 4 shows the evolution of the tetrahedral order parameter for the basal ice/water interface. In the crystal phase, the molecules reside in an almost ideal tetrahedral environment, and the local order parameter takes the values close to 1. The order parameter $q_t(z)$ changes across the interface and takes the values of ~ 0.45 – 0.55 in the bulk liquid, because there is still a large fraction of tetrahedral configurations in water at 225 K (see Table II). The change in tetrahedral order parameter $q_t(z)$ from 0.9 to 0.6 clearly indicates the position of the interface, and allows us to estimate the width of the basal ice/water interface to be ≈ 11 Å, which is in good agreement with the values of 10.54 and 12.86 Å from translational and window-averaged density order parameters, respectively, reported in [2].

CONCLUSIONS

In this study we investigated by using MD computer simulations the density-temperature phase diagram of SPC/E water at one bar pressure and two-phase ice/water coexistence. The aim of this study was to correct the results reported for SPC/E model with truncated long-range potentials [3,4]. We have obtained the density maximum of $\rho = 1.01163 \text{ g cm}^{-3}$ at the temperature 240 K. The melting temperature estimated from the simulations of ice/water coexistence is 225 ± 5 K. The local order parameter which reflects the change in tetrahedral environment across the interface allowed us to estimate the width of the basal ice/water interface to be ≈ 11 Å.

Acknowledgements

This research was supported by the Texas Advanced Research Program under Grant No. 003652-0303-1999. The calculations were performed on Cray-T3E at Texas Advanced Computing Center under NPACI award. DL_POLY is a package of molecular simulation routines written by W. Smith and T.R. Forester, copyright The Council for the Central Laboratory of the Research Councils, Daresbury Laboratory at Daresbury, Nr. Warrington (1996).

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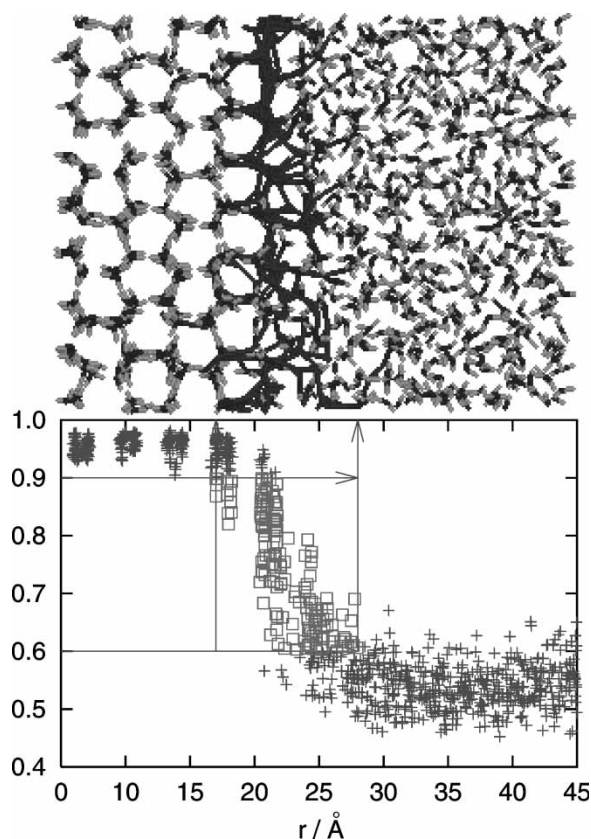


FIGURE 4 Tetrahedral local order parameter $q_t(z)$ for the basal ice/water interface at 225 K. The open boxes indicate the change of local order parameter $q_t(z)$ across the interface.

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