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In a previous paper[1] we report the calculated melting temperature of the proton-disordered hexagonal ice I_h using a four-site water model, the TIP4P (Ref. 2) and a five-site model, the TIP5P.[3] In that work, we used a free-energy method. For the TIP4P model, the calculated melting temperature at 1 bar is $T_m = 229 \pm 9$ K, whereas for the TIP5P model, $T_m = 268 \pm 6$ K. For both models, the long-ranged interactions were truncated at 17 Å. Interestingly, these values of T_m are very close to $T_m = 232 \pm 5$ K and $T_m = 273.9$ K reported by Sanz *et al.*[4] and Vega *et al.*[5] who used a slightly different free-energy method along with Ewald summation technique, although both the TIP4P and TIP5P models were originally developed for use with a truncated Coulomb interaction.

The purpose of this paper is twofold: (1) to compute the melting temperature (T_m) of ice I_h with both TIP4P and TIP5P models by using the two-phase coexistence method and to compare with previously obtained T_m; (2) to compute the T_m using recently improved TIP4P and TIP5P models, namely, the TIP4P-Ew (Ref. 6) and TIP5P-Ew (Ref. 7) models. Both models are developed specifically for use with Ewald techniques. The TIP4P-Ew model, in particular, has shown substantial improvement over the original TIP4P model as it can reproduce the density maximum at about 274 K, very close to 277 K of the real water. The original TIP5P model can reproduce the measured T_m. It will be of interest to see whether the improved TIP5P-Ew model can still hold the same level of prediction as far as the T_m is concerned.

We followed the simulation procedure reported in a previous paper[8] to prepare equilibrated coexisting solid and liquid systems. First, a pure solid phase with a given lattice structure is equilibrated via molecular-dynamics (MD) simulation using the isobaric-isothermal (*NPT*) ensemble. The Nose–Andersen method[9] is used to control the temperature T and pressure P. The initial temperature of the solid was selected not too far below the T_m at the ambient pressure $P = 1$ bar. The liquid phase can be obtained through melting the solid phase at a high temperature using the *NVT* ensemble, where the volume V of the simulation cell is set identical to the cell volume in the final step of the simulation of the solid phase. The liquid phase is then cooled to the temperature T, the same as the initial temperature set for the solid phase, and

is equilibrated. Next, the well-equilibrated solid and liquid phases were put into contact at a particular solid surface. Because the merging of the two phases may generate a large interfacial contact stress in the direction normal to the solid-liquid interface, the entire two-phase system will undergo another brief preparation run in the *NPT* ensemble prior to the production run.

For the production run, we chose the *NPH* ensemble (i.e., constant pressure, particle number, and enthalpy ensemble).[10,11] The *NPH* ensemble is more convenient (compared to the *NVE* ensemble) since we only calculate one point on the phase diagram, namely, the T_m at $P = 1$ bar. Another advantage of the *NPH*-ensemble approach over the *NVE* approach is that the stress-anisotropy problem is never an issue[8] since three principal components of the stress tensor can be adjusted to match the given pressure. As with the *NVE* approach, however, the system size has to be sufficiently large to avoid the system transforming completely into one phase during the production run. Here, we used the Andersen method to control the pressure of the system.[12]

In the preparation of the simulation system, an initial configuration of the proton-disordered ice was constructed to meet the conditions such that the Bernal–Fowler rule is satisfied and that the entire ice has zero total dipole moment.[13] We then equilibrated the solid and liquid subsystems separately following the procedure given above. Next, the equilibrated ice and liquid water subsystems were brought into contact at the (001) surface of ice. The total number of water molecules in the two-phase system is $N = 12\,288$. The dimension of the system is about $53.9 \times 62.3 \times 115.6$ Å^3. Here, a simple switching function was used to smoothly shift the pairwise potential function to zero from $r = 7$ to 9 Å. The standard quaternion technique[12] was employed to calculate the angular momentum and the torque. The predictor-corrector algorithm was applied to solve the equations of motion, for which the MD time step of 1.0 fs was chosen.

For both TIP4P and TIP5P systems, we run two independent simulations with different initial temperatures. For the TIP4P system, two initial temperatures $T = 225$ and 235 K were chosen, guided by previous simulations with free-energy method.[1] For the TIP5P system, two initial temperatures $T = 265$ and 275 K were chosen, again guided by previous simulations. Figures 1(a) and 1(b) display the
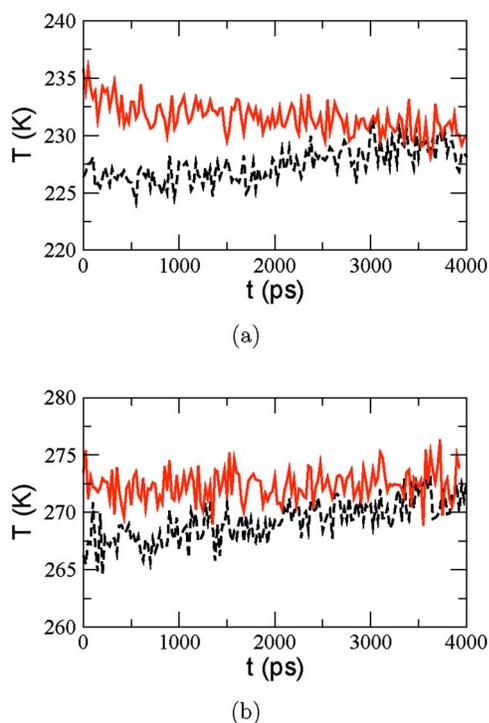
FIG. 1. (Color online) The two-phase coexistence simulation in the *NPH* ensemble for (a) TIP4P and (b) TIP5P ice I_h systems at $P=1$ bar. (a) For the TIP4P system, two initial coexisting ice-water systems are prepared, one with $T=225$ K and another 235 K. (b) For the TIP5P system, the two initial systems prepared have initial temperatures $T=265$ and 275 K, respectively.

instantaneous kinetic temperature T versus the MD time t for the TIP4P and TIP5P systems, respectively. One can see that the kinetic temperature of the two systems (having different initial temperature) gradually converges to nearly the same (averaged) value at $t \sim 3500$ ps. We then used the next 500 ps to compute the T_m. For the TIP4P ice, the calculated $T_m = 229.3 \pm 1.0$ K, while for the TIP5P ice, $T_m = 272.2 \pm 0.6$ K. These values of T_m are in very good agreement with $T_m = 229 \pm 9$ K and $T_m = 268 \pm 6$ K calculated based on the free-energy method for the TIP4P and TIP5P ice, respectively.[1] Interestingly, these values are also very close to $T_m = 232 \pm 5$ K and $T_m = 273.9$ K calculated based on a different free-energy method and using the Ewald technique for long-range interactions.[5] These results suggest that T_m of the TIP4P and TIP5P ice are not very sensitive to the inclusion of Ewald summation.

To compute the T_m with the improved TIP4P-Ew and TIP5P-Ew models, we used identical system size ($N = 12\,288$) and followed the same simulation procedure as for the TIP4P and TIP5P models. The Ewald summation was carried out by means of smooth-particle-mesh-Ewald technique which is implemented in the parallel version of the DL_POLY_2 MD program.[14] Since we had no *priori* information on their values of T_m, except only the location of the density of maximum (close to 274 K), we first examined five initial temperatures within 240–280 K with 10-K interval, for each model. We monitored the evolution of the system temperature, typically for about 200 ps for the five independent simulations, from which we determined that the proper temperature range to locate the T_m is from 250 to 260 K, for
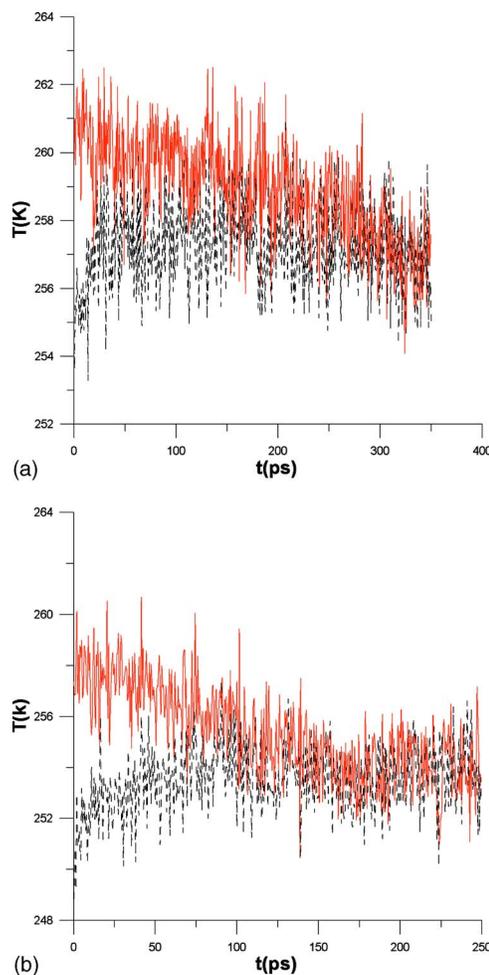

FIG. 2. (Color online) The two-phase coexistence simulation in the *NPH* ensemble for (a) TIP4P-Ew and (b) TIP5P-Ew ice I_h systems at $P=1$ bar. (a) For the TIP4P-Ew system, two initial coexisting ice-water systems are prepared, one with $T=250$ K and another 260 K. (b) For the TIP5P-Ew system, the two independent systems have the initial temperatures $T=250$ and 260 K, respectively.

both models. In Fig. 2(a), we plot the instantaneous kinetic temperature versus MD time for the two independent TIP4P-Ew systems, one with 250 K and the other with 260 K as the initial temperature. Once the temperatures of the two independent systems converged to nearly the same (averaged) value, we view that both systems reach the full equilibration. Then, we used the next 50 ps to evaluate the melting temperature, which is $T_m = 257.0 \pm 1.1$ K. This value is much closer to the measured value (273 K) than the original TIP4P model, namely, another major improvement over the TIP4P model. In Fig. 2(b), we plot the temperature versus MD time for two independent TIP5P-Ew systems. Again, once the two systems reach equilibration, we used additional 50 ps run to calculate the melting temperature, which is $T_m = 253.9 \pm 1.1$ K. This value, however, deviates from the measured value by about 20 K. Clearly, some reparametrization to the TIP5P-Ew model is needed in order to reproduce the measured T_m (as the original TIP5P does).

Finally, we remark that the T_m of the TIP4P-Ew ice has been recently calculated by Vega *et al.*[5] using a free-energy method, which is $T_m = 245.5$ K. This value differs from ours $T_m = 257.7 \pm 1$ K by about 12 K. We note also that a large

discrepancy in T_m has also been seen for the three-site extended simple point-charge (SPC/E) water model:[15] a free-energy calculation predicted $T_m=279\pm5$ K (Ref. 16) whereas a two-phase coexistence simulation predicted $T_m=225\pm5$ K.[17] A more recent free-energy calculation for the SPC/E ice, however, predicted $T_m=215\pm7$ K.[4,5] Although the latter value is much closer to $T_m=225$ K, computed from the two-phase coexistence method, still the relative difference $\Delta T_m/T_m$ amounts to about 5%. It seems that the free-energy calculation tends to give a lower T_m than the two-phase coexistence simulation, especially when the Ewald techniques are employed in the simulation. In summary, the origin of these large discrepancies in T_m for the TIP4P-Ew and SPC/E models requires further investigation.[17]

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[1] Y. Koyama, H. Tanaka, G. Gao, and X. C. Zeng, J. Chem. Phys. **121**, 7926 (2004).

[2] W. L. Jorgensen, J. Chandrasekha, J. D. Madura, R. W. Impey, and M. L. Klein, J. Chem. Phys. **79**, 926 (1983).

[3] M. W. Mahoney and W. L. Jorgensen, J. Chem. Phys. **112**, 8910 (2000).

[4] E. Sanz, C. Vega, J. L. F. Abascal, and L. G. MacDowell, Phys. Rev. Lett. **92**, 255701 (2004).

[5] C. Vega, E. Sanz, and J. L. F. Abascal, J. Chem. Phys. **122**, 14507 (2005).

[6] W. Horn, W. C. Swope, J. W. Pitera, J. C. Madura, T. J. Dick, G. L. Hura, and T. Head-Gordon, J. Chem. Phys. **120**, 9665 (2004).

[7] S. W. Rick, J. Chem. Phys. **120**, 6085 (2004).

[8] S. Yoo, X. C. Zeng, and J. R. Morris, J. Chem. Phys. **120**, 1654 (2004).

[9] D. C. Rapaport, *The Art of Molecular Dynamics Simulations* (Cambridge University Press, Cambridge, 1997).

[10] A. Laio, S. Bernard, G. L. Chiarotti, S. Scandolo, and E. Tosatti, Science **287**, 1027 (2000).

[11] D. Brown and J. H. R. Clarke, Mol. Phys. **51**, 1243 (1984).

[12] M. P. Allen and D. J Tildesley, *Computer Simulation of Liquids* (Oxford University Press, New York, 1987).

[13] J. A. Hayward and J. R. Reimers, J. Chem. Phys. **106**, 1518 (1997).

[14] W. Smith and T. R. Forester, Molecular Simulation Package DL_POLY_2.15, Daresbury Laboratory, Cheshire, UK.

[15] H. J. C. Berendsen, J. R. Grigera, and T. P. Straatsma, J. Phys. Chem. **91**, 6269 (1987).

[16] B. W. Arbuckle and P. Clancy, J. Chem. Phys. **116**, 5090 (2002).

[17] T. Bryk and A. D. J. Haymet, Mol. Simul. **30**, 131 (2004).