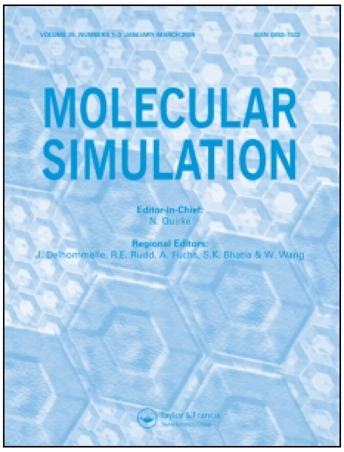

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Studies of ice melting using molecular dynamics

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Studies of ice melting using molecular dynamics

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In this paper, the melting of ice 1h is studied using molecular dynamics (MD). Common potential functions employed in the MD simulations include SPC/E, TIP4P, TIP5P, TIP4/ice and TIP5P/E. We first conducted melting of ice bulks and then studied the melting speed of the ice/water interface during ice melting. It is found that various potentials result in similar ice-melting phenomena. The result is compared with the analytical solution for phase change problem. We also studied size effects and temperature gradient effects on ice melting.

Keywords: ice 1h; potential; melting; molecular dynamics

1. Introduction

Water is one of the most important chemical substances in nature. It is essential for the survival of living creatures. It covers 71% of the Earth's surface and has the second highest specific heat capacity of any known chemical compound, as well as a high heat of vaporisation. These two unusual properties make water play a determining role in Earth's climate [1]. Moreover, water is very interesting in other aspects. For example, in addition to water in liquid form, water can exist in gas form and in 13 distinct solid crystalline forms.

Because of these unique features, a lot of research has been done to understand water properties over the last 40 years. In the early stages of computer simulation of water [2,3], researchers mainly focused on observing physical phenomena in one phase, liquid water or ice. The first computer simulation of water was performed by Barker and Watts [4]. They used the Monte Carlo method to calculate water structure and properties at room temperature. The simulation of ice was first conducted by Rahman and Stillinger [5,6]. They computed the dipole correlations and Kirkwood correlation factor of ice 1c and ice 1h. With the development of molecular dynamics (MD) theory and computer techniques, research groups have employed MD simulations of water/ice to study the dynamics of the two-phase interface over the last two decades. Karim and Haymet [7–10] and other groups [11–18] did much work on simulating the interface between water and ice 1h. These simulations mainly concerned the dynamics of ice, water, or both, or intended to obtain the melting temperature of ice. Moreover, the dynamics of ice melting, especially the melting speed, is also important to understand ice/water property. To study the dynamics of ice melting, the melting speed is important. However, not many published research articles about the study of melting speed, especially by computational simulations can be found.

To elucidate physical phenomena at the nanoscale via MD simulation, the key issue is to choose proper potential functions. Many different potential models for water molecules have already been proposed. Guillot [19] summarised those models in 2002. He pointed out that SPC, SPC/E, TIP3P, TIP4P and TIP5P were the most commonly used potential models in the past years. A common criterion to choose a proper potential model is the ability to reproduce the properties of real water by computer simulations. Unfortunately, for a long time, the reproduction of water properties at ambient condition (298 K, 1 bar) was the only concern when performing simulations using these common potential models. However, the accuracy was not satisfying when the conditions were other than ambient. In order to reproduce thermodynamics and structural properties of water not just at ambient conditions, TIP4P-Ew, TIP4P/2005, TIP4P/ice and TIP5P/E have been proposed and used in recent years. Vega et al. [20] used these models to obtain the melting temperature with Gibbs–Duhem methodology and obtained reasonable results.

Among the study of dynamics of the ice/water interface, melting speed or crystallisation speed are some of the key parameters in the phenomenon of phase change. After obtaining them, the MD simulation can then be coupled with microscale and macroscale simulation to form a whole scale simulation of material melting or formation. The purpose of this paper in performing MD is to estimate the melting speed of ice 1h using the common potentials of SPC/E, TIP4P, TIP5P, TIP4/ice and TIP5P/E.

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The reason we choose melting, not freezing, is that the latter needs a very long time for simulation via MD. The difficulty lies with the fact that hydrogen bonding between individual water molecules yields a disordered 3D hydrogen-bond network whose rugged and complex global potential energy surface permits a large number of possible network configurations. As a result, it is very challenging to reproduce the freezing of 'real' water into a solid with a unique crystalline structure. For pure and spatially unconfined water, however, MD simulations of freezing are severely hampered by the large number of possible network configurations that exist [21]. Matsumoto et al. have shown the nucleation of ice from only 512 water molecules after several months of simulation within a supercomputer.

In this paper, the water potential models and methodology are described in Section 2. In Section 3, we present the simulation results for ice melting and also study the possible size effect. The comparison with analytical solution for phase change problem and the conclusion is given in Section 4.

2. Potential models and methodology

2.1 Water potential models

We use SPC/E, TIP4P and TIP5P, as well as TIP4/ice and TIP5P/E, potential models to conduct numerical simulations in this paper. All of those potentials are in the form of the intermolecular pair potential, which has two contributions, a Lennard–Jones, u_{LJ}, and an electrostatic interaction, u_{elec}. The expression for the potential function of water is

$$U = u_{\mathrm{LJ}} + u_{\mathrm{elec}} = 4\varepsilon\left[\left(\frac{\sigma}{r_{\mathrm{oo}}}\right)^{12} - \left(\frac{\sigma}{r_{\mathrm{oo}}}\right)^{6}\right] + \frac{e^2}{4\pi\varepsilon_0}\sum_{a,b}\frac{q_a q_b}{r_{ab}}, \tag{1}$$

where σ and ε are Lennard-Jones parameters, r_{oo} is the distance between the oxygen sites of two water molecules, e is the proton charge, ε_0 is the permittivity of vacuum, a and b stand for the charged sites of molecules i and j. So, the electrostatic interaction is between the two charged sites on two water molecules. The potential parameters for these water molecular models are listed in Table 1.

The geometry of SPC/E is the same as that of SPC, which has three interaction sites corresponding to the three atoms of the water molecule, but the partial charges on the H and O atoms are increased slightly in the SPC/E model. It adds an average polarisation correction to the potential energy function. Consequently, the SPC/E model results in better density and diffusion constants than the SPC model.

In the TIP models, differences arise from the location of the negative charge. In the TIP3P model, the negative charge is located on the oxygen atom. The TIP4P model places the negative charge on a dummy atom placed near the oxygen along the bisector of the H—O—H angle. This improves the electrostatic distribution around the water molecule. The first model to use this approach was the Bernal–Fowler [22] model published in 1933, which may also be the earliest water model. A new version of TIP4P is TIP4P/ice [23]. This greatly improves the melting properties and can be used to study equilibrium state. The TIP5P model places the negative charge on dummy atoms representing the lone pairs of the oxygen atom, with a tetrahedral-like geometry. By reoptimising the two Lennard-Jones parameters of the TIP5P model, the modified version of TIP5P/E is constructed. This model is accurate over a range of temperatures and pressures, and it would work better than TIP5P when using Ewald sums [24].

Table 1. Potential parameters of water models.

Model	σ (Å)	ε (kJ mol^{-1})	q_{H} (e)	q_{M} (e)	ε_0
SPC/E	3.166	0.650	+0.4238	−0.8476	71
TIP4P	3.15365	0.6480	+0.5200	−1.0400	53
TIP5P	3.12000	0.6694	+0.2410	−0.2410	81.5
TIP4P/ice	3.1668	0.8822	+0.5897	−1.1794	62.9
TIP5P/E	3.097	0.7448	+0.2410	−0.2410	92

Notes: The meaning of each symbol can be found in [19] and [24]. σ and ε are Lennard-Jones parameters; q_{H} and q_{M} are the charges on the hydrogen and M sites, respectively; ε_0 is the permittivity of vacuum.

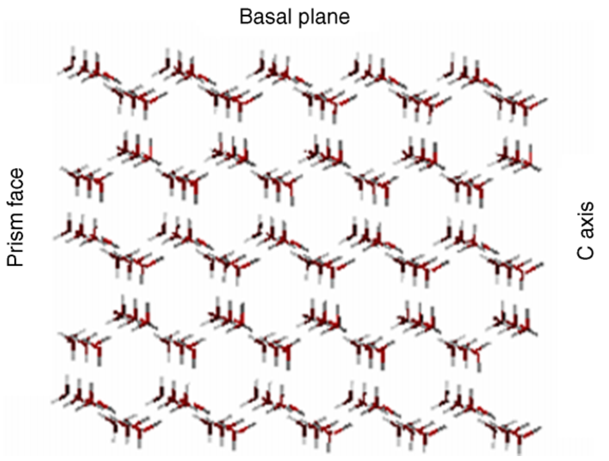

Figure 1. The molecular structure of ice 1h.

Water has many solid phases. Being one of its crystalline phases, ice 1h (hexagonal ice), shown in Figure 1, is the form of all natural snow and ice on Earth. Ice 1h crystals form hexagonal plates and columns where the top and bottom faces are basal planes {0 0 0 1}, and the six equivalent side faces are called the prism faces {1 0 − 1 0}. Secondary prism faces {1 1 − 2 0} may be formed down the planes formed by the sides of the chair structures. Ice 1h shows anomalous reduction in thermal conductivity with increasing pressure similar to ice 1c and low-density amorphous ice, but different from most

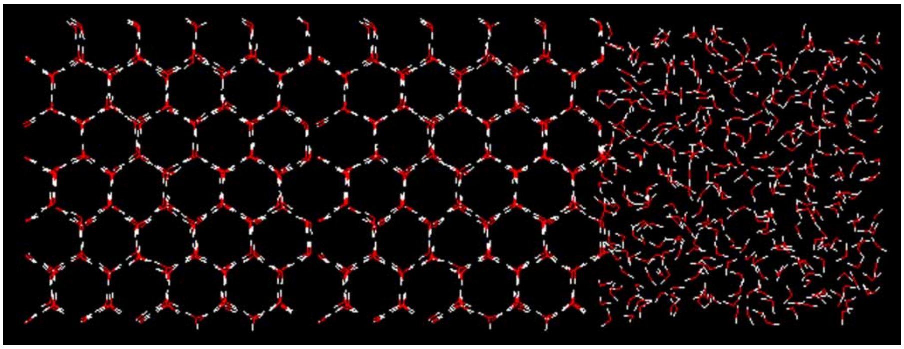

Figure 2. Configuration of contacting ice and water.

crystals. The molecular structure of ice 1h has been widely used for MD simulations by researchers to study the properties and melting temperatures of ice. In this paper, we also use ice 1h to conduct simulations.

2.2 Methodology

Based on classical MD theory, the equations of motion can be written as follows if there is not any external force:

$$m_i \ddot{\mathbf{r}}_i = -\nabla_i U(\mathbf{r}), \tag{2}$$

where U is the total potential of the simulated system as expressed in Equation (1), m_i is the mass of atom i and r_i represents its location.

In this paper, we conduct simulations in two different basic configurations. The first configuration contains only ice 1h. We want to use this to simulate the melting of ice bulks. We use the algorithm from Fernández et al. [25] to generate the ice bulk model. Periodic boundary conditions are employed on all three directions. We first ran a short MD to minimise energy in order to get a proper ice structure. It is called relaxation. During relaxation, the temperature is maintained at 30 K lower than the melting temperature. Then, we conduct NPT MD simulations under 1 atmosphere at 30 K higher than the melting temperature [20,26]. The time step used in simulations is 2 fs and the total simulation time is 200 ps.

We also study the movement of the water/ice interface during the ice melting. The simulation model contains both ice and liquid water contacting with each other as shown in Figure 2. Periodic boundary conditions are employed except on the axial direction. Along the axial direction, both ends are subject to thermostats. During the simulation, the left boundary of ice is maintained at a low temperature T_i, which is lower than the melting temperature, while the right boundary of water is maintained at a high temperature T_0, which is higher than the melting temperature. Consequently, the simulated system is subject to a temperature gradient. After relaxation of the simulated model, we conduct the NPT MD simulation under 1 atmosphere. The time step used in the simulations was 2 fs. The typical length of the simulations was about 200 ps. We determine the melting speed by observing the ice/water interface front movement.

3. Results

3.1 Melting of ice bulks

We first simulate ice bulk, which contains 360 molecules and has a size of 2.24 × 2.33 × 2.19 nm^3. SPC/E model is employed first. Figure 3 illustrates the change in the number of hydrogen bonds during the simulation. Some hydrogen bonds will be broken during ice melting. We can clearly find that ice starts to melt around time 40 ps and totally melt around time 70 ps. Figure 4 shows the evolutions of the simulated ice bulk at different times: 0, 40, 50 and 70 ps, respectively. When the ice starts melting, a slight disruption in the lattice first occurs inside the ice

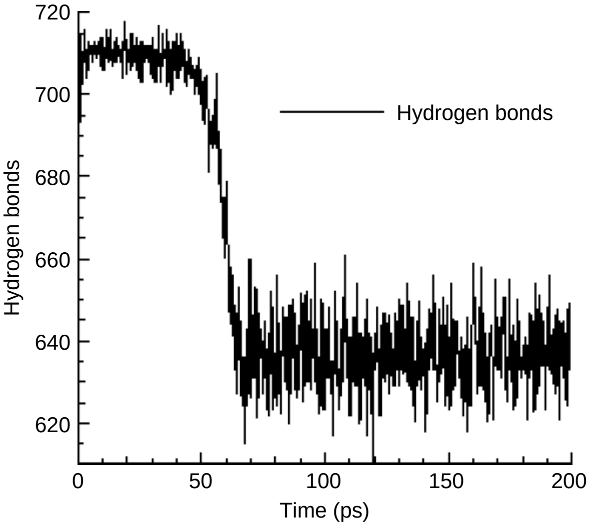

Figure 3. Number of hydrogen bonds with time.

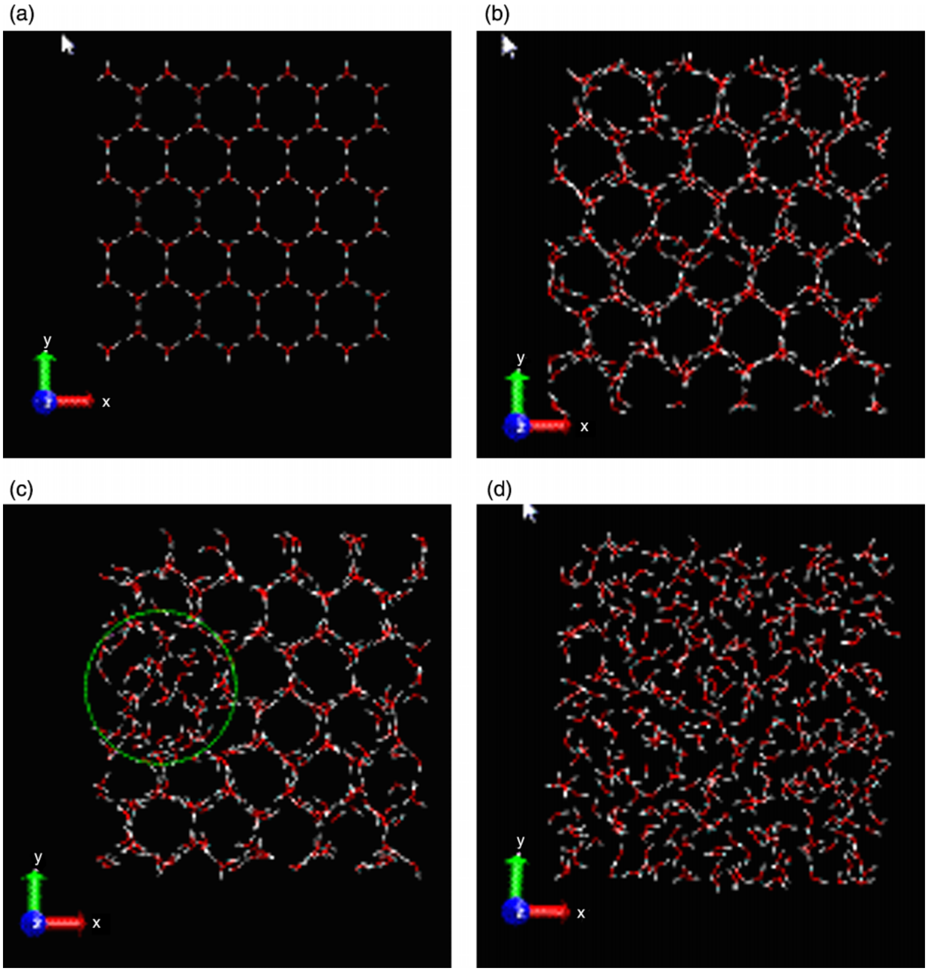

Figure 4. The ice crystal at different times: (a) 0, (b) 40, (c) 50 and (d) 70 ps.

crystal. Such a disruption then expands along the plane, which is perpendicular to the lattice as shown in the circle area in Figure 4(c). After that, melting occurs in the plane and expands rapidly over the whole system.

Table 2 lists the melting times of different water models. We can find that the melting times of the simulated ice bulk for various potential models are close, except that the melting time is slightly longer if the model with higher melting temperature is employed. It should be noted that the temperature maintained in the MD simulation is the melting temperature as described in Section 2.

In order to check the possible size effect, we conduct simulations with various sizes of ice bulks via expanding the simulation model in all of the three dimensions. The volume of ice bulk in the previous simulation is 11.40 nm^3. Here, we study the ice bulks with the following volumes: 22.27, 38.48 and 91.20 nm^3. Since various potential models result in similar melting time, only the SPC/E potential is used here. During the simulations, we calculated the melting time as well as the average melting speed in units of nm^3/ps.

Table 2. Melting time of different water models.

Model	Melting temperature (K)	Melting time (ps)
SPC/E	213	30.00
TIP4P	230	32.00
TIP4P/ice	269	34.00
TIP5P/E	271	35.00
TIP5P	273	35.00

Table 3 compares the melting times and speeds for various sizes of ice bulks. It can be seen that the melting time is longer for the ice bulk with larger size. However, we also found that the average melting speed is not the same for various sizes of ice bulks. The larger ice bulk, the higher

Table 3. Melting time of different simulation boxes.

Ice bulks' volumes (nm^3)	Melting time (ps)	Melting speed (nm^3/ps)
11.4	35	0.326
22.27	40	0.557
38.48	45	0.855
91.20	50	1.824

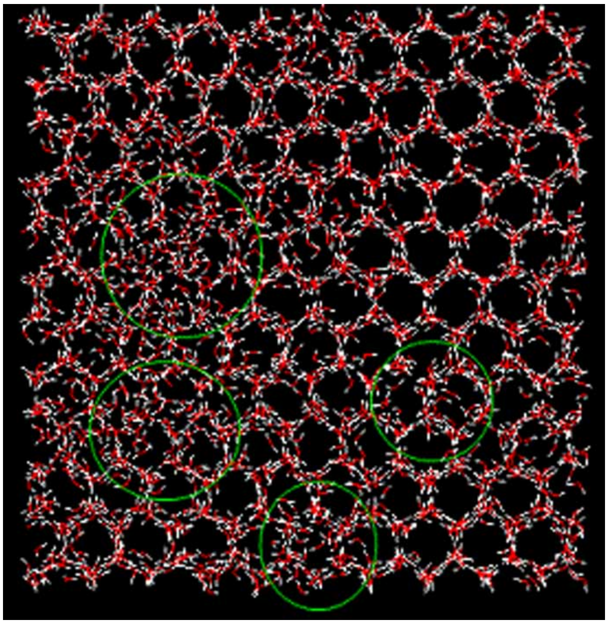

Figure 5. Disruptions in a large ice crystal (colour online).

average melting speed. The reason is that, in the MD simulation, the atoms are coupled with an external energy bath. The melting time depends on how fast these atoms absorb thermal energies from the bath. So, for a large-sized ice bulk, the number of atoms coupled to the external bath is also larger, and thus absorbing more energy into the system per unit time. Also, in a large-sized ice bulk, more disruptions (areas in green circle in Figure 5) occur at the same time, so the melting happens at many locations simultaneously in the crystal, and therefore the total melting speed increases.

3.2 *Melting speed of the ice/water interface*

To study the melting speed of the ice/water interface, we first consider the simulated model having a size of $6.71 \times 2.33 \times 2.19\,\mathrm{nm}^3$. It contains 720 molecules in ice and 360 molecules in water. The left end of ice is subject to 253 K, while the right end of water is subject to 283 K. The simulated model is then subject to the temperature gradient of 13.5 K/nm. The TIP5P potential model is first employed in MD simulations. The movement of the ice/water interface is shown in Figure 6.

From Figure 6, we can observe the melting interface moving from right to left. The melting process is similar to bulk ice melting. When the ice starts melting, one or more slight disruptions in the lattice first occur inside the ice crystal but close to the initial ice/water interface, and then expand rapidly from right to left. Although the melting front is not a perfect plane surface, we can still identify it as shown in Figure 6 to calculate the melting speed of the ice/water interface as shown in Figure 7. It can be seen that the melting speed decreases with time. We also employed other potential models to conduct a similar MD simulation. It can be seen that the melting speed is independent of the potential models as shown in Figure 7.

This is little surprising since the melting temperature of each potential model has a big difference. We analyse whether the configuration of our simulation plays an important role here. Since the ice crystal is contacting with water and subjected to a temperature gradient, the melting time depends on the size of the simulation configuration, the temperature applied on both sides and the subjected temperature gradient. The potential function of each potential model only results in little difference in the melting speed.

To study the size effect on the melting speed of the ice/water interface, we increase only the length of the simulated model since the sides are subject to a periodic boundary condition as described in Section 2. Because moving speeds of the water/ice interface are very similar for different potentials, we mainly employ the TIP5P model here. We first keep the same temperature gradient as in the previous simulation, 13.5 K/nm. Therefore, the temperature to which the left end of ice is subject will be decreased based on the length elongated. Figure 8 illustrates that there is no size effect on the melting speed of the ice/water interface if the temperature gradient remains the same. With the further study of the ice/water interface melting speed, the melting speed will decrease with time and finally approach a constant. Based on the simulated data, the melting speed of the ice/water interface can be predicted as

$$v = \frac{a}{\sqrt{t}}, \tag{3}$$

where a is a constant, its unit being $\mathrm{m/s}^{0.5}$, and it is 2.6×10^{-5} in this case.

We also studied the effect of the temperature gradient on the melting speed of the ice/water interface. The simulated model is the same as the initial one with a length of 6.71 nm. We changed the temperatures of the thermostats on the two ends of the simulated model so that the model is subject to various temperature gradients as follows: 13.5, 27.0, 40.5 and 54.0 K/nm. Figure 9 illustrates that the melting speed increases as the temperature gradient increases. Consequently, the constant a in Equation (3) is related to the temperature gradient.

4. Conclusion

For an ideal 1D ice to water transition, the analytical solution has already been obtained for the classical phase change problem [27–31]. By solving the thermal diffusion equation both in the solid and liquid phase, one can obtain the melting interface position of the analytical solution as

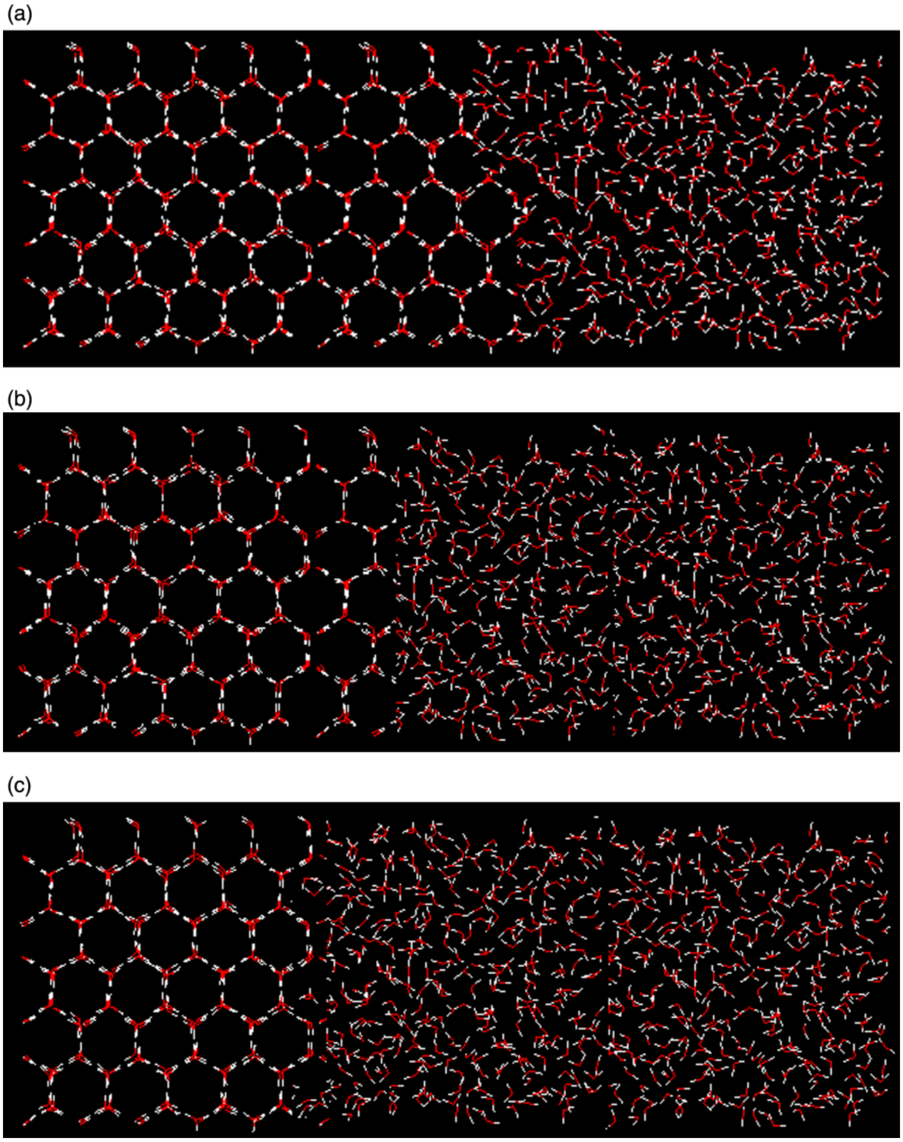

Figure 6. Melting interface at different times: (a) 10, (b) 40 and (c) 60 ps.

follows:

$$\delta(t) = 2\lambda(\alpha_l t)^{1/2} = 0.0262t^{1/2}, \tag{4}$$

where $\delta(t)$ is the melting interface position, λ is a constant which is determined by solid and liquid temperatures and α_l is the diffusive coefficient of the liquid. Here, we assume that the water is at the temperature of 283 K while the ice is at the temperature of 253 K.

Taking the first derivative of the melting interface position with respect to time, we can obtain the analytical melting speed as follows:

$$v(t) = \frac{\mathrm{d}(2\lambda(\alpha_l t)^{1/2})}{\mathrm{d}t} = \frac{a}{\sqrt{t}}. \tag{5}$$

Here, the constant a is equal to 13.1×10^{-5} m/s$^{0.5}$. It is easy to find that the analytical solution is much larger than the MD simulation results. The reason for such a large difference between the MD result and analytical solution is that the conventional analytical solution is obtained on the macroscale heat transfer theory which describes macroscopic behaviour averaged over many grains. Therefore, in macroscopic length scale, many places in the ice crystal may start melting at the same time, similar to what we observed for large-sized ice bulk in Section 3, thus, the melting speed of the analytical solution is relatively large.

In addition, when we consider both length scale and time scale, we can find that the melting speed in nanoscale is much faster than that in macroscale. For example, the ice melting speed is 0.8 m/s at 1 ns while it is

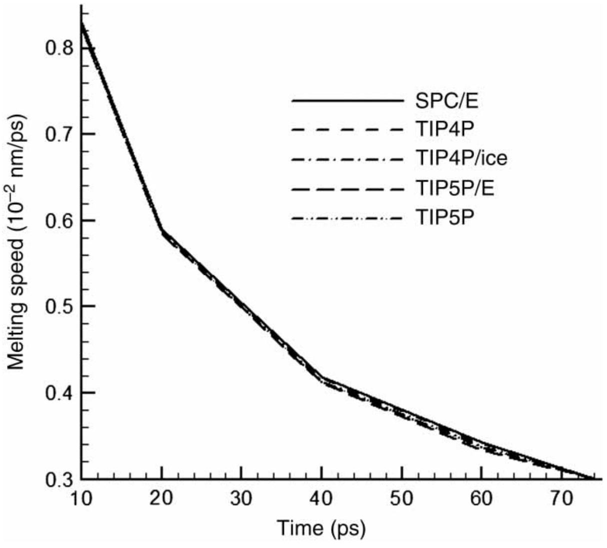

Figure 7. Melting speeds for different potential models.

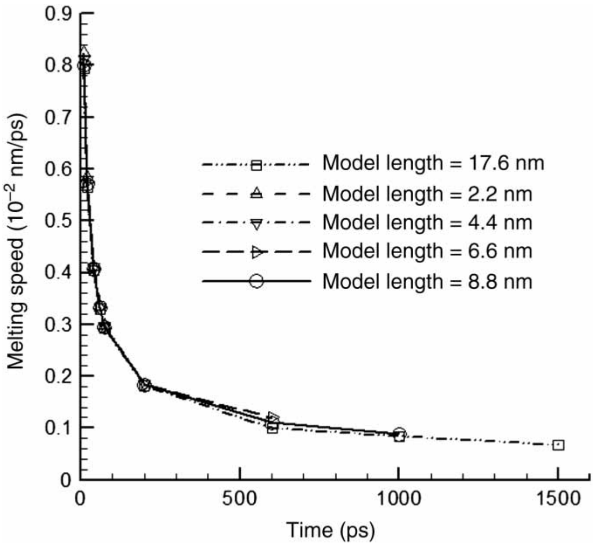

Figure 8. Melting speed for different simulation box lengths of TIP5P.

13.1×10^{-5} m/s at 1 s. The results illustrate that phase change problems are scale dependent.

In this paper, we conducted MD simulations to study melting phenomena of ice at the nanoscale. We studied melting of ice bulks as well as the speed of the ice/water interface during ice melting. Since a number of potential functions of water molecules were proposed in previous research, the following common potential functions were considered in this paper: SPC/E, TIP4P, TIP5P, TIP4/ice and TIP5P/E. We found that various potential functions result in similar phenomena. We also studied size effects on ice melting. We found that the melting time is longer for an ice bulk with larger size but that the average melting speed is also size dependent. There is no size effect on the speed of the ice/water interface during ice melting if the same temperature gradient is applied. Further research shows that such a melting speed depends on the temperature gradient. When compared with macroscale melting speed, we find that the phase change problem is scale dependent.

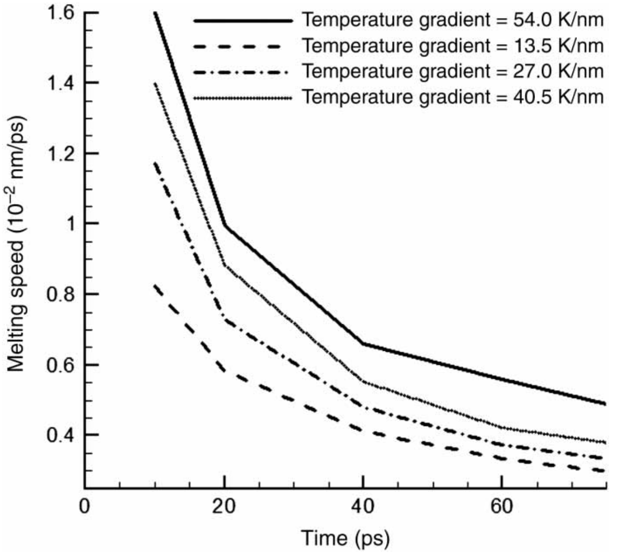

Figure 9. Melting speed of TIP5P with different temperature gradients.

Acknowledgements

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