

Fast and Accurate Determination of Phase Transition Temperature in Computer Simulation

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The generalized canonical ensemble (GCE) simulations are performed in water/ice coexisting systems to obtain its phase transition temperature. For the first time, the equilibrium at water/ice coexisting state can be studied in an individual simulation. This equilibrium, no longer a stochastic process, leads to a remarkable increase in both efficiency and accuracy of determining melting points. In this study, TIP4P/2005, TIP4P/ICE, mW water model are applied to build Ice Ih/water two-phase systems, then equilibrated at distinct areas in energy surface. States such as bulk water, ice and water/ice coexisting have been evolved, and their corresponding temperature are gained at the same time. The result of phase transition temperature is in excellent agreement with previous studies, is 253K, 272K, and 274K, respectively. Results from small systems show subtle accuracy lost. These features make GCE approach determining phase transition temperature robust, easy to use, and particularly good at working on computationally expensive systems.

INTRODUCTION

The transition between different molecular structures induce significant changes in physical properties. However, these changes are not yet well understood in many transitions, their mechanism at the molecular level remains largely unknown. exp1: The transition between the ferromagnetic and paramagnetic phases of magnetic materials at the Curie point. exp2: transition into superconductive state. exp3: Hydrogen bonding between individual water molecules yields a disordered three-dimensional hydrogen-bond network whose rugged and complex global potential energy surface permits a large number of possible network configurations, [1] making water freezing one of the most intriguing phase transition system. These issues call forth more comprehensive knowledge of phase transition, especially the details in phases-coexisting systems (PCS). Studying PCS by performing direct canonical or isothermal-isobaric (NPT) ensemble is well performed worldwide and generally accepted, however the efficiency of this approach is largely determined by the nucleation energy barrier of PCS. Sampling critical states is hard since surface tension increased system energy leads to a less probability of being occupied. Besides, studying thermodynamics by sampling in non-equilibrium systems is controversial.

Estimating transitional temperature is of absolute importance in describing PCS. The technique of direct coexistence is a first choice, studies have been carried out by simulating PCS in a temperature range, order parameters such as density are used to monitor the transition process. Transitional temperature is thus determined as the spinodal temperature of order parameter. However, evolution of states at critical temperature is stochastic, accuracy of this approach depends on not only sensitivity of order parameter and the temperature interval in simulations, the sample volume matters as well. Another

method is proposed by fitting the temperature dependence of free energy for both two phase, the intersection stands for the transitional temperature. This method shows better precision, but estimating free energy of systems is not convenient and takes extra work.

In this work, we aim to provide a simple method of high-precision and efficiency for determining the phase transition temperature in PCS. To achieve such goal, GCE has been implemented successfully in ice Ih/water PCS with mW, TIP4P-2005 and TIP4P-ICE water models. GCE can sufficiently visit the phase-coexistence regions and its energy distribution can be Gaussian-like. Thus the stochastic nature of phase transition can be largely get rid of, making one single simulation enough to estimate phase transition temperature. Besides the enhanced sampling in GCE expanded sample volume insure considerable precision of estimation.

This work is organized as follows: Sec. II describes the models and methodology used in this work. Section III presents the results for phase-coexistence region for different water potential models. The papers ends with a final discussion and the conclusions of this work.

MODELS AND METHODS

A. Water models

In Table I the geometry and the potential parameters of several popular potential models for water are presented. All these models have two common features: a Lennard-Jones (LJ) center is located on the oxygen atom and positive charges are situated on the hydrogen atoms.

For detecting whether the rearrangement of IW or the ionic charge of substrate itself controls water freezing, we prepare the ice-lattice-like but polarized IW in absence of (AgI-like) solid substrates, and check the water freezing

on a few (usually 4 \sim 6) ice-like polarized IW layers. The polarized IW has the same ice lattice but gradually varied hydrogen polarity ξ from 0 (the ice Ih) to 1 (the ice XI) [? ? ? ? ?]. As shown in Figure S4 of Supplementary, the freezing of supercooled water is also found to become more difficult as increasing the hydrogen polarity of the ice-like polarized polarize in absence of AgI-like solid substrates. At 265 K, water freezes on the ice-like polarized IW layers with $\xi = 0.11$, but does not form an ice cluster at $\xi = 0.23$ during 20 ns regular MD simulations. At 255 K, results are similar, water freezes at $\xi = 0.23$, but not at $\xi = 0.63$ within 50 ns.

It is difficult (if not impossible) to directly simulate water freezing on IW with larger ξ due to the requirement of too long MD time. Recently, Sanz *et al.* [?] developed an efficient indirect MD method to study the homogeneous ice nucleation of bulk water. They detected the corresponding supercooled temperature of a preset spheric ice nucleus instead of directly detecting the critical nucleus at a temperature. The main difficulty to expand the method in freezing on substrate surfaces is that the shape and structure of critical ice nucleus, such as the contact angle and crystalline surface of nucleus on substrates, are unknown. Here, we present a subtle simulation scheme to gradually adjust the shape and size of preset ice nucleus on substrates for approaching to a critical one, then get the corresponding supercooled temperature: (1) we generate a sphere-cap (or other shapes, such as spheric) hexagonal ice (I_h) nucleus and locate it on the surface then immerse them in supercooled water as the initial conformation. We also guess a few neighboring supercooled temperatures around a central temperature; (2) we simulate from the initial conformation a segment of time, *e.g.*, 10 ns, at each set temperatures; (3) we choose one from these trajectories where the shape of ice nucleus was most obviously adjusted (but not completely melting out or growing up). The final conformation of chosen trajectory is set as new initial conformation, and the corresponding temperature is as the new central temperature. We reset a few new simulation temperatures around the central temperature by supposing the ice nucleus will grow or melt (with or without shape adjustment) at these temperatures, respectively. (4) We repeat the step (2) and (3) a few times, until the ice nucleus less correlates with the preset one at beginning, and its shape do not change obviously any more. Thus we get a critical ice nucleus on substrate, and we can get two neighbouring temperatures where the ice nucleus grows and shrinks, respectively. The medium value approximately gives the corresponding temperature of the critical nucleus. Figure 3 illustrates the whole simulation scheme on the ice-like IW with $\xi = 0.234$. The ice nucleus is sufficiently adjusted to change its shape and its size (initial 2000 to final 2350 molecules) after 6×10 ns simulations. Then we simulate the final 10 ns trajectories at a few temperatures and find the ice nucleus shrinks at 259 K

but growing at 258 K, thus we get the middle temperature $T = 258.5$ K where the ice nucleus is in critical.

We apply the method on the ice-like polarized IW with various ξ to get the critical ice nuclei and the corresponding temperatures T . By extracting the outlines of the final ice nuclei from the average density of ice nuclei $\rho = 0.5\rho_I$, we find that all the critical ice nuclei are approximately sphere-cap, as the expectation of the classic nucleation theory (CNT), except small deviation in the first layers in small and large ξ cases, see Figure 4. Here ρ_I is the density of bulk ice, about 0.906 g/cm^3 in this model. From the simulations, we have the size N_c , radius R , the (apparent) contact angle θ of the sphere-cap critical nucleus, the corresponding (supercooled) temperature and the free energy barrier ΔG of nucleation, shown in Table II. We estimate the free energy barriers from the CNT, $\Delta G = f(\theta) \frac{4\pi\gamma}{3(\kappa\Delta T)^2}$. Here $f(\theta) = \frac{1}{4}(2 + \cos\theta)(1 - \cos\theta)^2$ is the shape factor of spherical cap.

In Figure 5, we find that the reverse of radius R of critical nucleus is proportional to the corresponding supercooled temperature, $1/R \approx \kappa\Delta T$, with $\kappa \approx 0.03 \text{ nm}^{-1}\text{K}^{-1}$. The result is in good agreement with the expectation of CNT, and $\kappa = \frac{\rho_I\alpha}{2\gamma} \approx 0.02 \text{ nm}^{-1}\text{K}^{-1}$. Here $\alpha = \frac{|\Delta\mu|}{\Delta T}$ about $0.0043 \text{ kcal/mol/K}$ [?], the ice-water surface tension $\gamma \approx 26 \text{ mN/m}$, and $\Delta\mu$ is the chemical potential difference between ice and water.

The cosine of contact angle is found to be linearly related to ξ in the whole range $0 < \xi < 1$, as shown in Figure 5. From the Young's equation, we have

$$\frac{\Delta\gamma(\xi)}{\gamma} \approx 0.66 - 1.7\xi. \quad (1)$$

Here $\Delta\gamma(\xi) = \gamma_{\text{water},IW}(\xi) - \gamma_{\text{ice},IW}(\xi)$, the difference of the water-IW and the ice-IW surface tensions. Considering the fact that the IW with $\xi = 0$ is similar to the normal hexagonal ice, we have $\gamma_{\text{ice},IW}(\xi) = \gamma(\delta_1 + k_1\xi + \dots)$, while $\gamma_{\text{water},IW}(\xi) = \gamma(1 - \delta_2 + k_2\xi + \dots)$. Here both δ_1 and δ_2 are small positive values, and $k_1 > k_2 > 0$, since liquid water is more flexible than ice nucleus to rearrange its conformations on IW. Therefore, we have, $\delta_1 + \delta_2 \approx 0.34$, and $k_1 - k_2 = 1.7$. The higher order dependence of surface tensions on ξ seems very small (or cancel each other) even while ξ is approached to unity, where the completely polarized IW distorts the lattice of both itself and the growing ice nucleus to avoid dangling hydrogen bonds.

As summary, we show that the matching between the structure of interfacial water (IW) and the ice, involving both the ice-like oxygen lattice order and the hydrogen direction disorder, corresponds to the capability of substrates on the heterogeneous ice nucleation, only the lattice matching of substrates with ice may be not sufficient to aid ice nucleation. The result is helpful to finding and designing anti-/aid- freezing materials for application.

TABLE I. The critical ice nuclei on the ice-like IW with different hydrogen polarity ξ . The unit of radius R is the interlayer distance of ice, about 3.7Å, (the error of R is about 0.1 in the unit); free energy ΔG in kcal/mol.

ξ	θ	$f(\theta)$	R	N_c	T (K)	ΔT	ΔG
0.187	72	0.28	10.0	1950	262 \pm 1	10	50
0.234	78	0.35	8.8	2350	258 \pm 1	14	32
0.400	90	0.5	7.7	1750	257 \pm 1	15	40
0.800	134	0.94	6.1	2300	252 \pm 1	20	42

TABLE II. Parameters of water model.

Model	$d_{oh}(\text{\AA})$	H-O-H	$\sigma(\text{\AA})$	$\epsilon/k(K)$	$q_H(e)$	$T_m(K)$
TIP4P-2005	0.9572	104.52	3.3589	93.20	0.5564	252.1
TIP4P-ICE	0.9572	104.52	3.1668	106.1	0.5897	272.2
mW	-	-	-	-	-	274.6

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fig1.png

FIG. 1. The growing of ice cluster upon the AgI-like substrates with different q is shown. $T = 260$ K. Inset: the ice-like first layer of interfacial water under constraint. Ag: white sphere; I: purple sphere.

- [1] M. Matsumoto, S. Saito, and I. Ohmine, Nature **416**, 409 (2002).

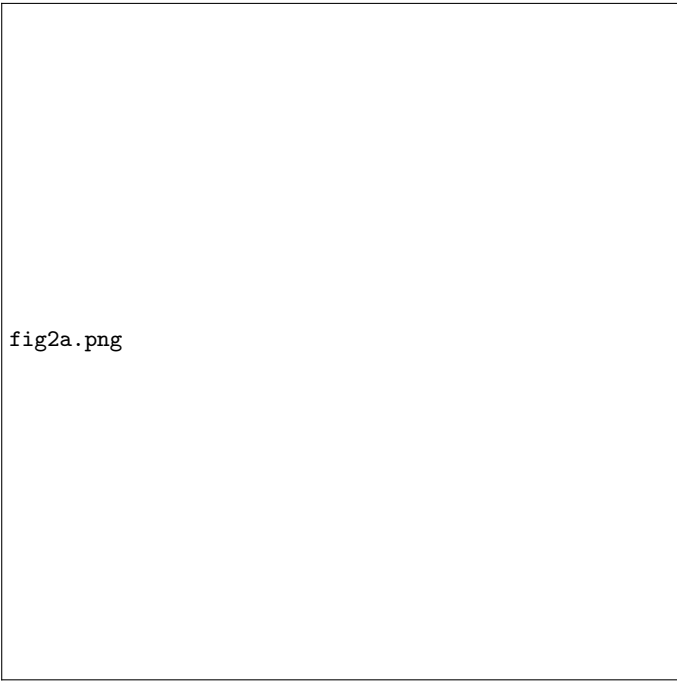


fig2a.png

(a)

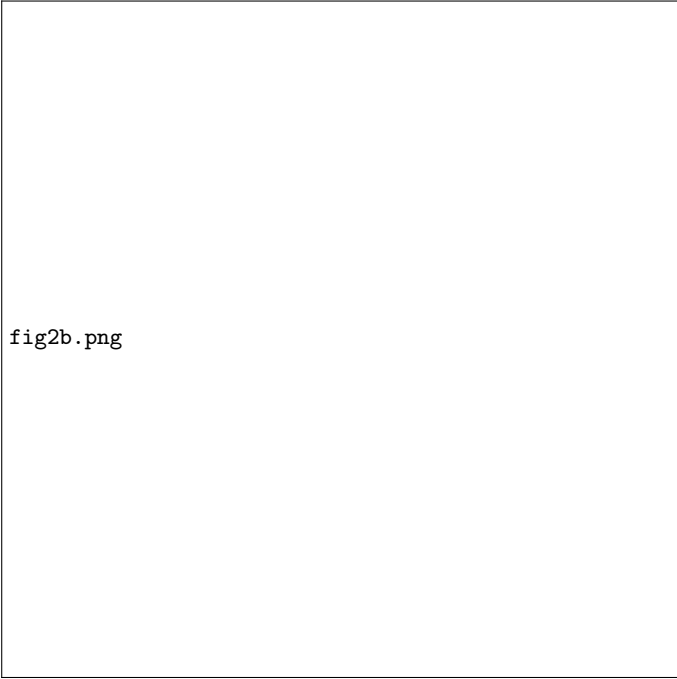


fig2b.png

(b)

FIG. 2. (a) The hydrogen polarity of interfacial water varies as the ionic charge of surface. The side view of water molecules on substrates are shown while $q = 0.6 e$ (bottom-right) and $q = 1.4 e$ (top-left). (b) The approximate phase diagram of frozen temperature and hydrogen polarity of interfacial water. Each point is obtained by a 50 ns standard MD simulations from initial liquid.

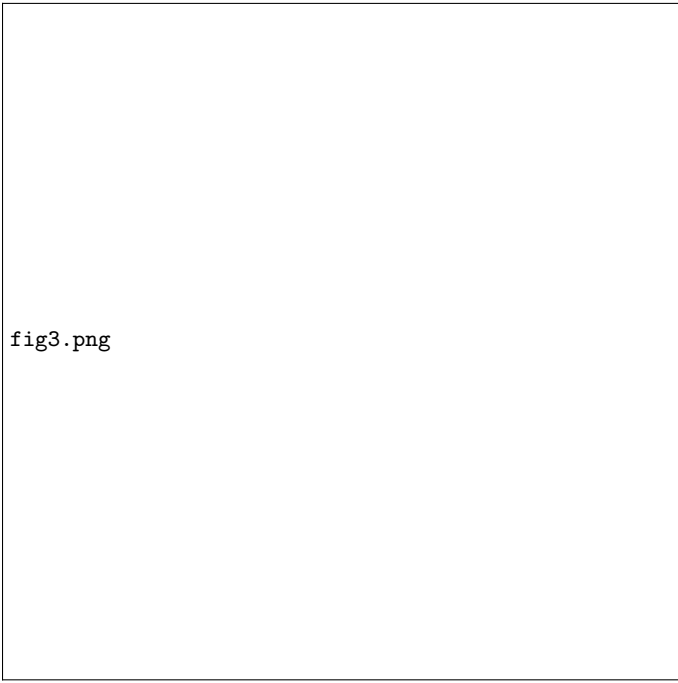


fig3.png

FIG. 3. The time evolution of the size and shape of ice nucleus during the simulations of adjusting critical ice nucleus on the IW with $\xi = 0.234$. The outlines of half ice nucleus at 0, 30 and 60 ns are shown.

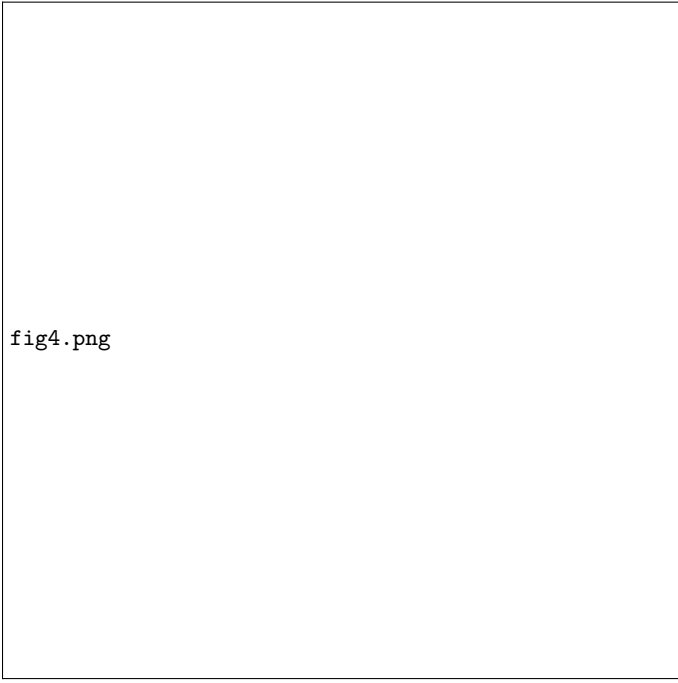


fig4.png

FIG. 4. Top: the obtained critical ice nuclei on the polarized IW surface with $\xi = 0.187, 0.234, 0.4$ and 0.8 in (a), (b), (c) and (d), respectively. All nuclei are sphere-cap, here only show the right half of them due to the symmetry. Bottom: the hydrogen-bond connection between atoms in critical nucleus (red) and that in polarized IW (blue) with $\xi = 0.234$ and 0.8 , respectively.

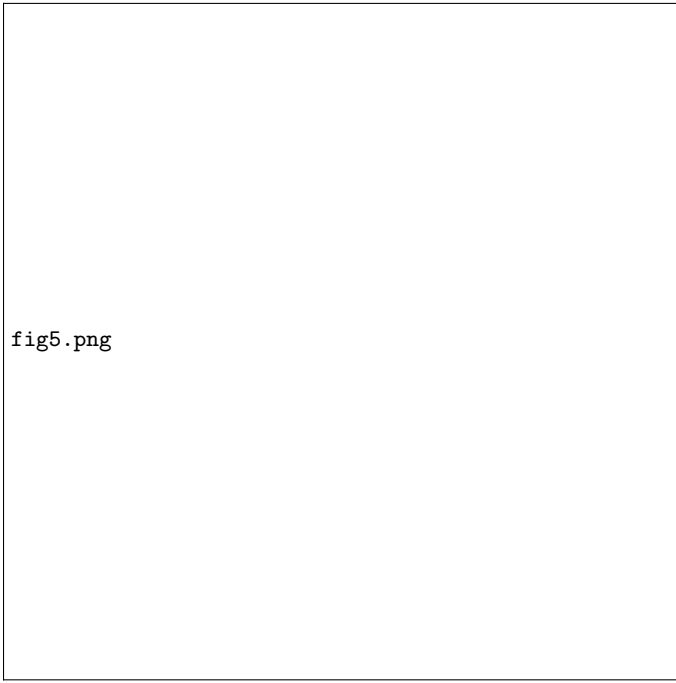


FIG. 5. Left, the reverse radius of ice nuclei versus super-cooling temperatures. The line is fitted based on the classic nucleation theory; right, the relation between contact angles of ice nuclei versus the hydrogen polarity of IW.