Phase diagram of the TIP4P/Ice water model by enhanced sampling simulations

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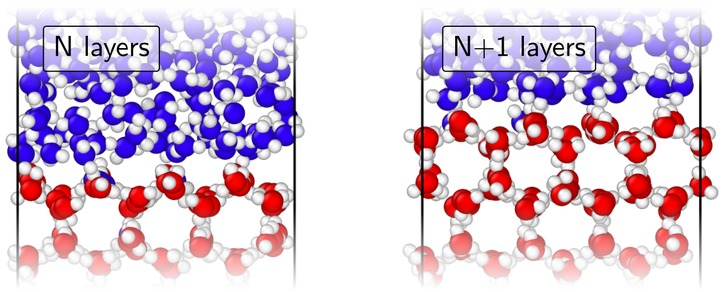
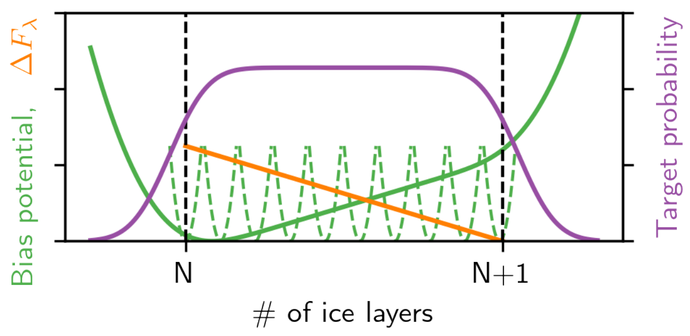
Abstract

We studied the phase diagram for the TIP4P/Ice water model using enhanced sampling molecular dynamics simulations.[1] Our approach is based on the calculation of ice-liquid free energy differences from biased coexistence simulations that sample reversibly the melting and growth of layers of ice. We computed a total of 19 melting points for five different ice polymorphs, which are in excellent agreement with the melting lines obtained from the integration of the Clausius-Clapeyron equation (Panel IIIa). For proton-ordered and fully-proton-disordered ice phases, the results are in very good agreement with previous calculations based on thermodynamic integration. For the partially-proton-disordered ice III, we find a large increase in stability that is in line with previous observations using direct coexistence simulations for the TIP4P/2005 model (Panel IIIb). This issue highlights the robustness of the approach employed here for ice polymorphs with diverse degrees of proton disorder. Our approach is very general and can be applied to the calculation of other complex phase diagrams.

Enhanced coexistence

The goal of enhanced coexistence simulations is to estimate the free energy of forming a layer of ice and use it to estimate the melting temperature. To do so, we run enhanced sampling simulations with the number of ice molecules as a collective variable (Panel I). We count the number of ice molecules by comparing the local environment of each oxygen atom to a set of reference environments specific to each ice polymorph (Panel Ia). From this, we obtain an environment similarity kernel that can distinguish ice from liquid with high accuracy (Panel Ib and Ic).





In principle, any enhanced sampling technique can be used, but in this case, we apply *multiumbrella sampling* illustrated above.[2] As an example, Panel II shows the steps involved in estimating the melting point for ice I_h. First, the formation of ice is sampled reversibly (Panel IIa). Second, free-energy profiles are extracted from the statistics of the time evolution of the collective variable (Panel IIb):

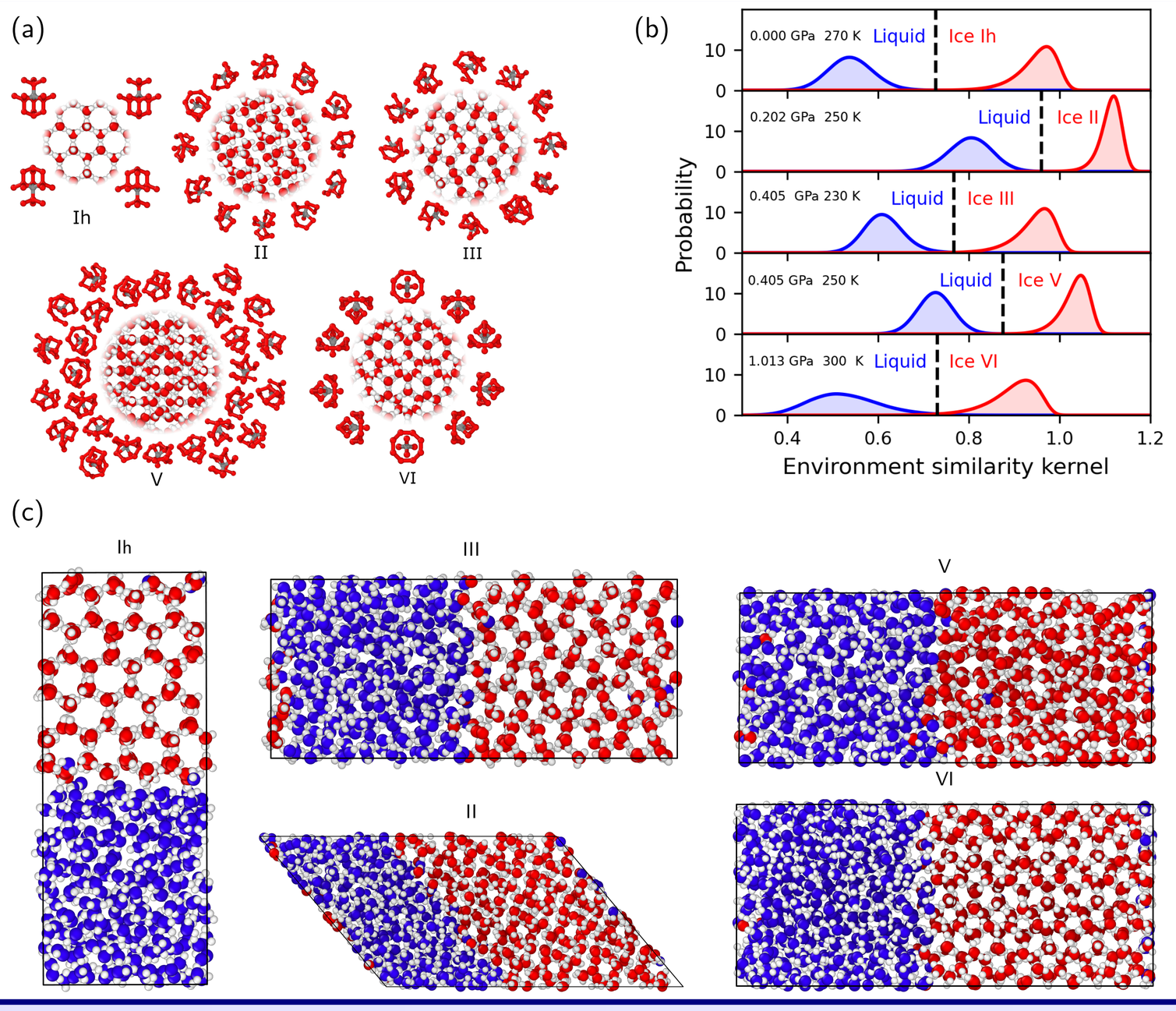
$$\Delta G(n_{ice}) = -k_B T \log P(n_{ice}).$$

Third, the chemical potential difference from liquid to ice is estimated by:

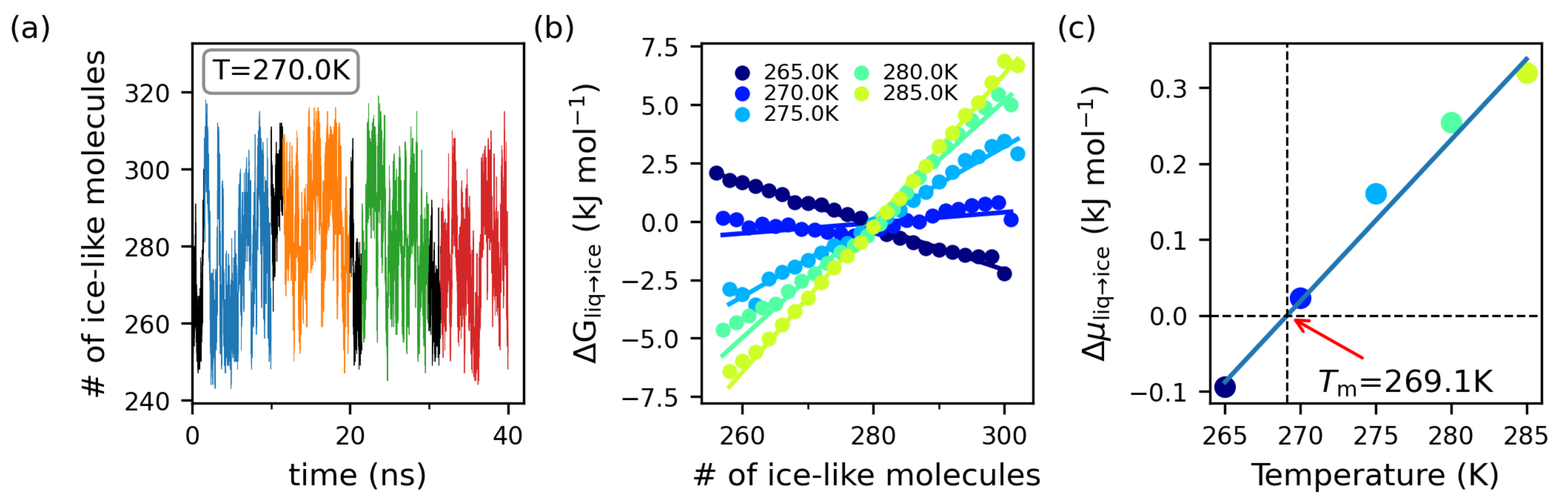
$$\frac{\Delta G(n_{ice} + \Delta n_{layer}) - \Delta G(n_{ice})}{\Delta n_{layer}} = \mu_{ice} - \mu_{liq},$$

the slope of the free energy profiles (Panel IIc). Finally, the melting point is estimated at zero chemical potential difference.

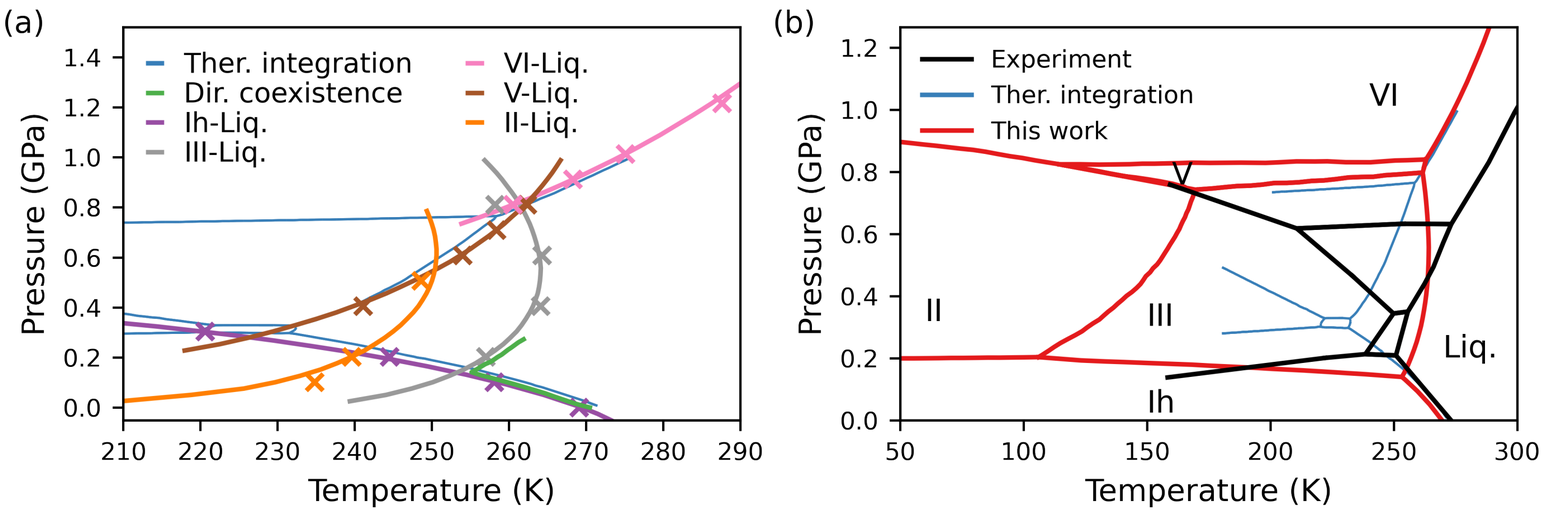
I) Collective variable for enhanced sampling simulations



II) The melting point for ice I_h



III) The phase diagram of TIP4P/Ice



Acknowledgements

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References

[1] S. L. Bore, P. M. Piaggi, R. Car, and F. Paesani, "Phase diagram of the TIP4P/Ice water model by enhanced sampling simulations", J. Chem. Phys. **in press** (2022).

[2] M. Invernizzi, P. M. Piaggi, and M. Parrinello, "Unified approach to enhanced sampling", Phys. Rev. X **10**, 041034 (2020).