THE LIQUID-LIQUID TRANSITION OF ST2 WATER, REVISITED

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The question of whether supercooled water exhibits a liquid-liquid transition will ultimately be resolved by experiment. From a theoretical and computational perspective, on the other hand, it is of interest to know which models exhibit this behavior and which don't. This is a challenging question, given the low temperatures and high degree of metastability involved. In 2009 we published a study[1] of the low-temperature fluid phase behavior of the ST2 model of water[2], suitably modified to account for long-ranged electrostatic forces. That work, which employed histogram reweighting methods[3], concluded that the ST2 model shows a metastable first-order transition between two liquid phases. This conclusion was also reached by Sciortino *et al*.[4] using similar computational methods but a different treatment of electrostatics. Limmer and Chandler[5], on the other hand, computed the free energy surface as a function of density and bond-orientational order[6], and concluded that the liquid-liquid transition is really a liquid-crystal transition in the ST2 model, as well as in Molinero's mW modified Stillinger-Weber model of water[7]. By comparing the time scales for equilibration and nucleation, Molinero and Moore[8] showed that the mW model does not exhibit a liquid-liquid phase transition. We report new calculations of the free energy surface of the ST2 model as a function of density and bond-orientational order, which clearly show a liquid-liquid transition. We explain the origin of the discrepancy between our findings and those of Limmer and Chandler.

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