

Thermodynamics and Kinetics of Deeply Supercooled Water: a Computational Perspective

Pablo G. Debenedetti¹

¹Department of Chemical and Biological Engineering, Princeton University

e-mail: pdebene@princeton.edu

The physical properties of supercooled water have been a source of continued interest since the pioneering work of Speedy and Angell, who reported sharp increases in the response functions upon isobaric cooling [1]. One intriguing hypothesis that has been formulated to explain this behavior is the existence of a metastable liquid-liquid transition at deeply supercooled conditions [2]. The preponderance of experimental evidence is consistent with this hypothesis (e.g., [3], [4]), although no definitive proof exists to date. Computational studies have played an important role in this area [2], [5]-[13]. State-of-the-art free energy techniques provide clear evidence of a liquid-liquid transition in the ST2 model [14] of water [15], including the identification of three phases at the same, deeply supercooled thermodynamic conditions: two metastable liquids in equilibrium, and a stable crystal [15]. Recent calculations on tunable tetrahedral models support this key conclusion of the free energy results [16].

A coarse-grained implementation of the forward-flux sampling technique [17] allows the direct calculation of the rate of homogeneous ice nucleation in the TIP4P/Ice molecular model of water [18] and provides new insights into the mechanism of ice formation at deeply supercooled conditions. The early stages of nucleation are characterized by a competition between cubic and hexagonal ice polymorphs. Transition states are rich in cubic ice, rather than in the thermodynamically stable hexagonal ice.

Modern computational methods provide important insights into the thermodynamics and kinetics of deeply supercooled water, complementing ongoing experimental studies.

References

- [1] Speedy, R.J., Angell, C.A. *J. Chem. Phys.*, 65, 851 (1976).
- [2] Poole, P.H., Sciortino, F., Essmann, U., Stanley, H.E. *Nature*, 360, 324 (1992).
- [3] Mishima, O., Stanley, H.E. *Nature*, 392, 164 (1998).
- [4] Amann-Winkel, K., Gainaru, C., Handler, P.H., Seidl, M., Nelson, H., Böhmer, R., Loerting, T. *PNAS*, 110, 17720 (2013).
- [5] Liu, Y., Panagiotopoulos, A.Z., Debenedetti, P.G. *J. Chem. Phys.*, 131, 104508 (2009).
- [6] Moore, E.B., Molinero, V. *Nature*, 479, 506 (2011).
- [7] Limmer, D.T., Chandler, D. *J. Chem. Phys.*, 135, 134503 (2011).
- [8] Liu, Y., Palmer, J.C., Panagiotopoulos, A.Z., Debenedetti, P.G., *J. Chem. Phys.*, 137, 214505 (2012).
- [9] Poole, P.H., Bowles, R.K., Saika-Voivod, I., Sciortino, F. *J. Chem. Phys.*, 138, 034505 (2013).
- [10] Overduin, S.D., Patey, G.N. *J. Chem. Phys.*, 138, 184502 (2013).
- [11] Limmer, D.T., Chandler, D. *J. Chem. Phys.*, 138, 214504 (2013).
- [12] Kesselring, T.A., Lascaris, E., Franzese, G., Buldyrev, S.V., Stanley, H.E. *J. Chem. Phys.*, 138, 244506 (2013).
- [13] Li, Y.P., Li, J.C., Wang, F. *PNAS*, 110, 12209 (2013).
- [14] Stillinger, F.H., Rahman, A. *J. Chem. Phys.*, 60, 1545 (1974).
- [15] Palmer, J.C., Martelli, F., Liu, Y., Car, R., Panagiotopoulos, A.Z., Debenedetti, P.G. *Nature*, 510, 385 (2014).
- [16] Smallenburg, F., Fillon, L., Sciortino, F. *Nature Phys.*, 10, 653 (2014).
- [17] Allen, R.J., Warren, P.B. ten Wolde, P.R. *Phys. Rev. Lett.*, 94, 018104 (2005).
- [18] Abascal, J.L.F., Sanz, E., Fernández, R.G., Vega, C. *J. Chem. Phys.*, 122, 234511 (2005).