Simulations of water: challenges after fifty years

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In 1969, the first paper dealing with computer simulations of water was published by Barker and Watts [1] followed by the pioneering papers of Rahman and Stillinger [2]. Typically, water is described since the classical paper of Bernal and Fowler [3] by using simple models that use partial charges and Lennard Jones centers. In the early days, computer simulations focused mostly in obtaining the properties of water in the liquid phase. The parameters of the potential were obtained to reproduce the radial distribution function, densities and vaporization enthalpies. Studies about phase equilibria started in the late 80's. Firstly the vapor-liquid equilibria was determined using new developed methodologies. Freezing properties and phase diagrams were calculated in the last fifteen years. That allowed to develop a model TIP4P/2005 that probably represents the limit of what can be done with a simple non-polarizable potential. The failure of the model teaches a lot about the physics of water: the importance of nuclear quantum effects, the special role of the dielectric constant in the modeling of water, and also the importance of polarizability. Important progress has been done in the recent years with polarizable models and more recently on neural networks to describe water interactions. The increase in computer power allowed to study problems such as nucleation of ice, quasi-liquid layer , or even speculating on the behavior of supercooled water and its possible liquid-liquid transition. Finally I shall discuss the kind of problems we face in computer simulation of mixtures by presenting some results for two simple systems: salt solutions and hydrates. Both of them illustrate that there is nothing wrong in leaving standard combination rules or even with more provocative ideas to describe ions in water.

[1] J. A. Barker and R. O. Watts,Chem.Phys.Lett.,3,144,(1969)
[2] A. Rahman and F.H. Stillinger,J.Chem.Phys.,55,3336,(1971)
[3] J. D. Bernal and R. H. Fowler,J.Chem.Phys.,1,515,(1933)