Summary

Water is the most important liquid on Earth, but despite an enormous effort put into research, it is not yet fully understood. A number of thermodynamic anomalies have been identified in water (e.g. the maximum of density at 4°C) and their occurrence intuitively linked to a strong intermolecular associative force, i.e., hydrogen bonding. Nevertheless, so far no rigorous molecular theory has been formulated.

The present work attempts to propose and apply a rigorous statistical-mechanical approach to water. The approach is based on recent findings that the structure of associating fluids is determined mainly by the short-range forces (both repulsive and attractive). This fact enables us to apply the perturbation theory taking a short-range model as a reference. The properties of the short-range reference model are then estimated by means of a simple, so-called primitive, model. Primitive models are analytically constructed to reproduce the structure of the short-range reference model keeping the interactions simple enough for theory. The contribution of the primitive model evaluated by Wertheim's TPT2 is used as a reference term in the perturbation expansion. The equation of state is then completed by adding dispersion and dipole-dipole correction terms.

Main results of the work are as follows: (i) The behavior of the simple equation of state based on the primitive-model reference term is investigated. It shows that, in principle, such an equation is capable of describing several anomalies, namely the maximum of density, the minimum of the constant-pressure heat capacity, and the minimum of the isothermal compressibility. The equation is then fitted to VLE of data TIP4P water with good prediction of the temperature of the maximum of density. (ii) The improved version of the reference model is proposed, exhibiting the above anomalies without the need of corrections. Complex temperature-pressure dependence of density is also reproduced. (iii) The MC simulations are performed and the theory is suggested for the modified dipolar hard-sphere system in order to evaluate the dipole-dipole correction term. The theory fails to describe the simulation because of the onset of the of the ferroelectric transition.

Keywords: Water; Anomalies; Equation of state; Perturbation theory; Primitive model; Dipolar hard sphere.