Anomalous behaviour in a simple water/methanol model with two repulsive ranges

Enrique Lomba[a], Marcia Barbosa[b] and Alexandre Furlan[b]
[a] *IQFR-CSIC, Serrano 119, E-28006 Madrid, Spain*
[b] *Instituto de Física - UFRGS, CP15051 91501-970 - Porto Alegre - RS Brasil*

Water is well know for its thermodynamic, structural and dynamic anomalous behaviour[1], which can be interpreted as a result of the presence of two repulsive ranges of interaction stemming from a short range repulsion and a longer range contribution from the hydrogen network. In this connection the addition of small quantities of short chain alcohols alters the behaviour in a non monotonous fashion[4], due to the partial and progressive disruption of the hydrogen bond network. Since it is well known that the anomalies of water can be reproduced by simpler spherically shaped models with two ranges of repulsion[2], in this contribution, following the ideas of Su et al.[3], we construct a model for water/methanol mixtures in which water in modeled by means of an spherically shaped Lennard-Jones and two gaussian (LJ2G) potentials[5] and methanol using a dumbbell in which the methyl group is a simple Lennard-Jones and the hydroxil group is also represented by a LJ2G potential, thus accounting for the two repulsive ranges due to the hydogen bond network and the shorter range repulsion mostly induced by the oxygen atom. The cross interaction parameters of the model are adjusted so as to reproduce the experiemental excess properties of water-methanol mixtures. Calculations will be carried out using constant-pressure Molecular Dynamics simulations at various methanol concentrations in order to analyze the effect of the solute addition on the temperature of maximum density of water. The system will also be studied by means of the molecular Ornstein-Zernike approach[6] in particular in the low methanol concentration regime, for which water-water correlations can be modeled using a thermodynamic self-consistent approach that can reproduce the presence of thermodynamic anomalies.

---

* enrique.lomba@csic.es

[1] Poole, P. H.; Sciortino, F.; Essmann, U. and Stanley, H. E., Nature, **360**, 324 - 328 (1992).
[2] de Oliveira, A. B.; Netz, P. A.; Colla, T. and Barbosa, M. C., J. Chem. Phys., **125**, 084505 (2006).
[3] Su, Z.; Buldyrev, S. V.; Debenedetti, P. G.; Rossky, P. J. and Stanley, H. E., J. Chem. Phys., **136**, 044511 (2012)
[4] Wada, G. and Umeda, S., Bull. Chem. Soc. Jpn., **35**, 646 - 652 (1962)
[5] Bordin, J. R.; Diehl, A. and Barbosa, M. C., J. Phys. Chem. B, **117**, 7047 (2013)
[6] Anta, J.A.; Lomba, E.; Alvarez, M. ; Martin C., and Lombardero M., J. Chem. Phys., **106**, 2712 (1997)