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A model for molecular emulsions: Water and “weak water” mixtures

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ABSTRACT

The SPC/E water model is mixed with three ⟨⟨weaker⟩⟩ versions of it, obtained by reducing the initial partial charges by multiplicative factors of 1/3, 2/3 and 4/5, respectively, while keeping the same diameter as water, and adjusting only the energy parameters such as to keep each neat substance in a dense liquid phase under ambient conditions. These models cover the observed behaviour of many realistic aqueous mixtures, ranging from demixing (the 1/3 model) to fully mixed hydrophobic-like (2/3) or hydrophilic-like (4/5) situations, the latter both showing strong and weak micro-heterogeneity, respectively. The simulations show that micro-segregation arises even when all constituents have the same length scale, under the sole influence of hydrogen bonding interactions. However, this micro-heterogeneity itself introduces a second length scale by producing domain oscillations in the distribution functions in the nanometer range, that can be captured by making a formal analogy with micro-emulsions. This approach explains the origin of the anomalously large Kirkwood–Buff integrals, often obtained in simulations of realistic aqueous mixtures, as a transient behaviour in the domain range. The analogy can be used to calculate the correct integrals by accounting for domain statistics, without the need to perform expensive large scale simulations.

1. Introduction

Liquids are fundamentally disordered systems, excluding the large class of liquid crystalline materials. Considered from this sole point of view, water and aqueous mixtures would be on a par with argon or other such simple liquids, as well as their mixtures. However, water is characterised by a strong tetrahedral order, and since this order is not global—such as in crystalline ice, for example—water is considered as a “complex” disordered liquid [1]. Yet, the nature of the order in water, and in particular tetrahedral order, remains a controversial subject. Two approaches seem to be prevalent in this matter. One is based on ideas inspired from the earlier work of Franks [2], that water is patched with domains of locally ordered hydrogen-bonded water molecules, and could even be a binary mixture of an ordered and disordered forms of the same liquid, and that a corresponding liquid–liquid critical point might be hidden in the low-temperature/high-density part of the phase diagram [3]. The other type of approaches infers that most properties of water and mixtures can be explained by the smallness of the water molecule, when compared to most types of molecules, in the sense that size effects are of leading importance [4–7]. In these latter approaches, the hydrogen bonding property has clearly a secondary importance.

The role played by the geometry and the magnitude of the tetrahedral interactions in many natural substances such as water and silica, for example, has been studied by Angell and co-workers [8]. The importance of tetrahedrality in the charge distribution of water has been recently examined by Lynden-Bell and co-workers [9–11], where they varied the geometry of the charge distribution while keeping the charges the same. In the present work, we take a similar approach, and examine the relative importance of the magnitude of the charges that produces the hydrogen-bond (H-bond) interaction

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from the classical point of view, while keeping the geometry the same. In other words, the two basic length-scales of the water–water interactions, which are the diameter and the hydrogen bonding distance, are kept the same. In order to sort out the importance of the size of the water molecule, we consider several models of "weak water", which differ from the neat SPC/E water model [12] only by scaling down the charges on the oxygen and hydrogen sites by a factor λ, otherwise keeping the same geometry and diameter of the SPC/E model. We consider three values of λ. The first is $\lambda = 1/3$, for which we find that the corresponding "weak water" does not mix with water, except at mole solute fractions smaller than $x = 0.1$ or larger than 0.9. The second is $\lambda = 2/3$, for which we find full mixing at all concentrations, but with high micro-heterogeneity (MH), displayed by the tendency of water and "weak water" to micro-segregate. The last is $\lambda = 4/5$, for which full mixing is equally obtained, with noticeably moderate micro-heterogeneity. In the latter two cases, we find that it is water that prefers to stay with its own kind, hence segregating the various forms of "weak water". This study shows that it is not necessary to have hydrophobic groups to induce the nano-scale micro-segregation observed in many alcohol–water mixtures [13–15], for example. From this point of view, these "weak water" models mimic the behaviour of real solutes in water, even though they have the same size as the water molecule. For $\lambda = 0$ "weak water" reduces to a standard Lennard-Jones (LJ) particles. Mixtures of LJ particles with SPC/E water have been previously studied at very low concentrations where hydrophobic aggregative behaviour has been reported [16].

The paper is organised as follows. In the first part we describe model details and computer simulation protocols. The second part contains our principal results. The last part gathers some discussion and our conclusions.

2. Models and simulation details

The extended Berendsen SPC/E model [12] is used as the reference solvent for water. This model has been widely used for simulating aqueous mixtures, therefore it provides a good testing ground. There are several other water models that are equally popular, such as those belonging to the TIPnP family [17–19]. However, In view of our earlier studies comparing these two categories of models, we do not expect that other types of water models would drastically change any of the conclusions we reach for the type of study conducted herein.

Realistic solutes are often multi-site molecules, having both hydrophobic and hydrophilic sites. It is very difficult to produce a sufficiently realistic force field for a given solute, and even more difficult to adapt this force field to model the corresponding realistic aqueous mixture. For these reasons, we consider here the simplest solute that would be compatible with water, having the same geometry as the SPC/E water model, except that the partial charges are scaled down with a factor λ. We recall that the SPC/E water model is defined by a centre with parameters $(\epsilon_W/k_B, \sigma_W) = (78.22\text{ K}, 3.165\text{ Å})$ (where k_B is the Boltzmann constant and ϵ_W the energy parameter with ϵ_W/k_B expressed here in Kelvins and the diameter σ_W in Ångströms), and the partial charges $q_H = 0.4238|e|$ on each of the 2 hydrogen sites (H) (where e is the charge of the electron) and $q_O = -2q_H$ on the oxygen site (O) that is placed at the Lennard-Jones (LJ) center, each H-site distant from the centre by 1 Å with the angle $H\hat{O}H = 109.47°$. In what follows, we will denote by a subscript "W" all quantities related to ordinary water, and with "w" those related to "weak water". These "weak water" models have the same geometry, with two sites Y corresponding to the H sites, with partial charge $q_Y = \lambda q_H$, and one site X corresponding to the O site, with partial charge $q_X = \lambda q_O = -2q_Y$. In this work, we choose to study three different values of λ, $\lambda = 1/3$, 2/3 and 4/5. Since we want each of these neat "weak waters" to be in the liquid state under ambient conditions, we need to increase the LJ energy parameter in order to compensate for the decrease of the partial charges. Indeed, water being liquid is the result of the H-bond interaction. If we remove the charges by setting $\lambda = 0$ then water would be a gas under ambient conditions just like nitrogen. Hence, when reducing λ from 1, it is necessary to increase the LJ parameter in order to keep the "weak water" liquid. In order to achieve this, we have aimed at keeping the molar volumes between 28 cm^3/mol which corresponds to the volume of many simple liquids close to their triple point and 18 cm^3/mol, which is the value for neat water. With a molecular diameter identical to that of water $\sigma_w = \sigma_W = 3.165$ Å, this leads to the following energy parameters: for $\lambda = 1/3$ we get $\epsilon_w/k_B = 273$ K which is 3.5 times that of the SPC/E model, for $\lambda = 2/3$ we settled for $\epsilon_w/k_B = 155.44$ K, double that of the SPC/E water, and for $\lambda = 4/5$ we settled for $\epsilon_w/k_B = 117$ K which is 1.5 times that of SPC/E. In this latter case, the molar volume for "weak water" is close to that of real water with 23 cm^3/mol, whereas for the previous two it is closer to 28 cm^3/mol. In fact, for these "weak water" models, it was quite difficult to obtain a dense liquid phase under ambient conditions of $T = 300$ K and 1 atm, while keeping the molar volumes about that of real water. Indeed, for smaller volumes than those we use here, we observed that these systems tend to be in the glassy or supercooled regime, especially for small values of λ. Avoiding this problem was one of the main motivations for choosing the actual values of the molar volumes. There does not seem to be an easy recipe of scaling both the LJ energy parameter and the λ parameter, such as for example to keep their ratio constant. One of the reasons for this could come from the fact the strong *anisotropic* (tetrahedral) interaction leads to a specific local organisation, which cannot be compensated by the *isotropic* LJ interaction, and does not allow for a variant of the law of corresponding states found for simple LJ fluids.

All the simulations are conducted in the NPT ensemble under ambient conditions and with $N = 2048$ molecules. The DLPOLY-2 simulation package [20] was used. The integration time step was set to 2 fs and Ewald summation techniques were used to handle the electrostatic part of the interactions. The "weak water" mole fraction increment was set to $\delta x = 0.1$ and mole fractions x ranging from 0.1 to 1 (neat solute) were studied. In a few cases, intermediate points were studied. For each concentration, the mixtures were first allowed to reach equilibrium for 0.5 ns, followed then by production runs ranging from 1 to 3 ns. Mole fractions $x = 0.2$, 0.5 and 0.8 received particular attention since they represent typical situations of