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Short Communication

Probability of cavity creation in water and *corresponding* Lennard-Jones liquid

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ABSTRACT

It has recently been reported that "the probability of forming a sufficiently large cavity is higher in water than in the *corresponding* Lennard-Jones fluid" [Abe and Koga, J. Mol. Liq. 200 (2014) 7]. This finding seems to contrast with the widely recognized fact that the magnitude of the reversible work of cavity creation is larger in water than in common organic liquids. In the present analysis, it is shown that the *corresponding* Lennard-Jones liquid of Abe and Koga can be described as consisting of particles larger in size than water molecules and, possessing the same number density of water, is characterized by a larger volume packing density that, in turn, leads to a marked decrease in the probability of cavity creation.

1. Introduction

It is widely accepted that the poor solubility of nonpolar species in water is due to the magnitude of the reversible work of cavity creation, Wcav [1–3]. The latter quantity is positive in all liquids, and proves to be markedly larger in water than in common organic liquids, as a consequence of the small size of water molecules [1,3–5]. By assuming that a molecule can be represented as a simple sphere, the effective diameter of a water molecule is 2.8 Å [6], that of an ethanol molecule is 4.4 Å [7], that of a benzene molecule is 5.3 Å [8], that of a carbon tetrachloride molecule is 5.4 Å [8], and that of a cyclohexane molecule is 5.6 Å [8]. It has been shown that the effect of molecular size overwhelms the effect of volume packing density, ξ (i.e., $\xi = \pi \cdot \sigma^3 \cdot N_{Av}/6 \cdot v_m$, is the ratio of the volume really occupied by a mole of liquid molecules to the molar volume v_m of the liquid itself; it represents the fraction of filled space in the liquid), whose value is smaller in the case of water (i.e., at 25 °C and 1 atm, $\xi = 0.383$ for water, and is around 0.5 for the above liquids) [1,4]. This happens because, fixed the liquid density, the effective diameter determines the number density of the liquid and so water has the largest number density among the above liquids: at 25 °C and 1 atm, $\rho \cdot 10^3$(molecules Å^{-3}) = 33.33 for water, 10.26 for ethanol, 6.74 for benzene, 6.20 for carbon tetrachloride, and 5.54 for cyclohexane [9]. Of course, the partitioning of void volume depends upon the liquid number density and particle size, so that the latter plays the role of a fundamental length-scale of the liquid [6,10,11].

This view originated from the successful application of classic scaled particle theory [12], SPT (a hard sphere theory based on statistical geometry [13]), to describe the solubility of nonpolar gases in real liquids, also water [14]. As originally pointed out by Reiss [12], the ground for the use of classic SPT to describe real liquids is the following: the attractive interactions among liquid molecules (either van der Waals attractions or H-bonds) determine the density of the liquid; then the latter can be described as consisting of hard spheres (confined in the volume fixed by the density), whose behaviour is governed by the solvent-excluded volume effect. The latter is a purely entropic effect accounting for the decrease in translational entropy of hard spheres associated with the decrease in configurational space caused by the insertion of another hard sphere (i.e., the creation of a cavity) in the liquid [15]. Of course, the classic SPT approach does not allow the calculation of the liquid density that is an input parameter, carrying implicit information about the strength of attractive interactions among liquid molecules. This means that water-water H-bonds, playing the fundamental role in determining the density of water and its temperature dependence, are implicitly taken into account in performing classic SPT calculations [14,15].

A further, more subtle question is related to the possibility that the H-bonding network of water is the factor controlling the magnitude of the solvent-excluded volume effect in such a liquid (i.e., the Wcav magnitude) [10,11,16]. To address this point, the H-bonding potential has been switched off in detailed water models, under the condition of constant volume, producing a liquid characterized by the same Lennard-Jones, LJ, parameters of the original water model (i.e., the *corresponding*

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LJ liquid) [17–19]. Madan and Lee, on the basis of Monte Carlo simulation results, pointed out that, by simply switching off the H-bonding potential in the TIP4P water model [20], the particles of the LJ liquid prove to be larger in size than the water molecules (this is readily verified by determining the location of the first maximum in the radial distribution function of the LJ liquid). In fact, in all the water models constructed so far, the LJ diameter is fixed around 3.2 Å, but the first peak in the obtained oxygen-oxygen radial distribution function is located at 2.8 Å [17,20], in line with X-ray and neutron diffraction measurements [21]. This implies that H-bonds are so strong to bunch up water molecules well beyond their LJ size. Therefore, if the LJ particle size is not adjusted to 2.8 Å, the *corresponding* LJ liquid would consist of particles with a diameter around 3.2 Å, and would have a volume packing density markedly larger than that of water (i.e., at 25 °C, $\xi = 0.383$ in water with $\sigma =$ 2.8 Å, and 0.572 in the LJ liquid with $\sigma = 3.2$ Å, by using the experimental density of liquid water for both liquids; see below). This would render such a *corresponding* LJ liquid not strictly correct to test the role played by the water molecule size versus the H-bonding network, in determining the Wcav magnitude. I have already underscored this problem in order to rationalize the results obtained by Sanchez and coworkers for the cavity size distribution in water versus a *corresponding* LJ liquid [6,22].

Madan and Lee showed that, by adjusting the diameter of LJ particles to 2.8 Å, and by calculating the reversible work of cavity creation under the constant volume condition, the Wcav magnitude proved to be similar in the TIP4P water model and the *corresponding* LJ liquid [17]. Note that switching off the H-bonding potential under the constant volume condition is a critical point because: (a) the *corresponding* LJ liquid has to possess the same density of water; (b) the *corresponding* LJ liquid can exist only under very high pressure, and the reversible work of cavity creation will contain a large contribution from the pressure-volume term, if the cavity creation process were performed under the constant pressure condition [17,23]. Therefore, the constant volume condition, by keeping fixed the density and by eliminating the pressure-volume contribution, allows one to carry out a meaningful comparison between water and the *corresponding* LJ liquid. The results by Madan and Lee and by others clarified that the probability of cavity creation is similar in water and in the *corresponding* LJ liquid with the particle diameter suitably adjusted to be identical to that of water molecules [17–19]. This means that, fixed the density, the molecular diameter, not the H-bonding network, is the factor controlling the magnitude of the solvent-excluded volume effect in water.

Recently, my attention has been captured by an interesting article in which Abe and Koga [24] showed that the probability of cavity creation in water is higher than that in the *corresponding* LJ liquid, obtained by switching off the H-bonding potential under the constant volume condition. Abe and Koga performed MD simulations to determine the solubility of nonpolar molecules across the liquid-vapour interfaces of the TIP4P/2005 water model [25], and the *corresponding* LJ liquid, by means of the test particle insertion method [26]. They determined also the solubility of hard spheres across such interfaces and so they practically determined the probability of cavity creation. In particular, Abe and Koga investigated the solubility of a hard sphere (i.e., a cavity) whose size corresponds to the LJ diameter of the oxygen atom in the TIP4P/2005 water model, $\sigma = 3.1589$ Å [24]. They found that the solubility of this hard sphere in water is higher than that in the *corresponding* LJ liquid when plotted as a function of the density across the whole interface region (see Fig. 4 in their article). The Abe and Koga study offers a further opportunity to test the rightness of the rationalization presented above.

2. Results and discussion

I would like to take advantage of the Abe and Koga findings to show that an approach grounded on the solvent-excluded volume effect can be useful to provide a reliable interpretation. Specifically, the aim is to reproduce the Abe and Koga results across the liquid-vapour interfaces by means of classic SPT calculations, in the assumption that the LJ liquid consists of particles larger in size than water molecules, so that its volume packing density is markedly larger than that of water. Classic SPT provides analytical formulas to calculate Wcav that have proven to be quantitatively reliable [1,4,6,15–17], and from which the pressure-volume contribution can easily be removed [14,27]. I have performed a comparison between water, consisting of spheres with $\sigma = 2.8$ Å, and the *corresponding* LJ liquid, consisting of spheres with $\sigma = 3.2$ Å (i.e., the one with no adjustment of particle diameter). Classic SPT calculations have been done under the constant volume condition, in order to neglect the pressure-volume contribution that would be large in the LJ liquid, by using the actual density of water at 25 °C and 1 atm [28], as starting condition. Then the density has been systematically lowered, up to values close to a vapour phase, trying to capture a fundamental feature of the liquid-vapour interfaces investigated by Abe and Koga [24], but ignoring the sigmoidal dependence of the density upon the distance from the interface (see Fig. 1 in the Abe and Koga article [24]). All the considered cases, that should model different slices in going from the bulk liquid to the vapour phase, are listed in Table 1 for water, and Table 2 for the *corresponding* LJ liquid. The two liquids have the same density in the bulk phase by construction, because the H-bonding potential of water is switched off by keeping fixed the volume. Different density values have been assigned to them in going toward the vapour phase, exactly to show how the devised procedure works. This implies that the present approach (using toy liquid models) cannot reproduce in a quantitative way the Abe and Koga results, obtained by means of MD computer simulations on realistic liquid models.

At 25 °C, the volume packing density $\xi = 0.572$ for the *corresponding* LJ liquid and 0.383 for water, so that the reversible work to create a spherical cavity with a diameter $\sigma_{cav} = 3.2$ Å proves to be Wcav = 41.9 kJ mol^{-1} in the former liquid and 18.1 kJ mol^{-1} in the latter. The Wcav magnitude in the *corresponding* LJ liquid is markedly larger than that in water. In other words, the probability of cavity creation, by molecular-scale density fluctuations at equilibrium, in the *corresponding* LJ liquid is markedly smaller than that in water. The ξ value plays the dominant role in determining the magnitude of the solvent-excluded volume effect, because the diameters of the liquid particles are not so different (i.e., 2.8 Å versus 3.2 Å), and the number density of the two liquids is identical (something similar occurs on adding NaCl to water at 25 °C and 1 atm [29]). This conclusion proves to be robust to changes in cavity (hard sphere) diameter.

Moreover, it is possible to calculate the local solubility quantity, defined by $\ln\Sigma = \exp[-\text{Wcav}/RT]$, that should provide a picture of the hard sphere solubility in the different slices across the liquid-vapour interface [24]. The calculated numbers, listed in the last column of Tables 1

Table 1
Values of the density, molar volume and volume packing density of water slices across the liquid-vapour interface; the first line corresponds to bulk water at 25 °C and 1 atm, while the last line is close to a vapour phase. Estimates of the reversible work to create a cavity of 3.2 Å diameter, under the condition of constant volume, Wcav, and of the local solubility, lnΣ, calculated by means of classic SPT, are listed in the last two columns. All these numbers refer to 25 °C.

d g cm^{-3}	v cm^3 mol^{-1}	ξ	Wcav kJ mol^{-1}	lnΣ
0.997	18.07	0.383	18.1	−7.3
0.937	19.23	0.360	16.0	−6.4
0.885	20.36	0.340	14.3	−5.8
0.833	21.63	0.320	12.7	−5.1
0.781	23.07	0.300	11.4	−4.6
0.729	24.72	0.280	10.1	−4.1
0.677	26.62	0.260	8.9	−3.6
0.547	32.96	0.210	6.5	−2.6
0.417	43.26	0.160	4.4	−1.8
0.260	69.22	0.100	2.5	−1.0
0.130	138.43	0.050	1.1	−0.5
0.052	346.09	0.020	0.5	−0.2