



On the ability of classic scaled particle theory to reproduce the cavity contact correlation function of water over a large hydrostatic pressure range

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ABSTRACT

The cavity contact correlation function $G(R_C)$ represents the density of liquid molecules in contact with the surface of a spherical cavity of R_C radius normalized to the bulk density. Recently, the $G(R_C)$ function of water has been determined in the TIP4P water model at 25 °C and over a large range of hydrostatic pressure, by means of Monte Carlo simulations [Floris, J. Mol. Liq. 218 (2016) 166]. It is shown that classic scaled particle theory relationships are able to reproduce in a satisfactory way the hydrostatic pressure dependence of $G(R_C)$ by using only two input data: the experimental density of water, and the effective hard sphere diameter of water molecules, 2.8 Å, assumed to be pressure-independent. No further information is needed, even though $G(R_C)$ should reflect structural features of water.

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1. Introduction

Water is a peculiar liquid and its special features manifest themselves also in the thermodynamic functions associated with the solvation (i.e., gas-to-liquid transfer) of nonpolar species [1,2]. In particular, the temperature and pressure dependence of such thermodynamic functions are strongly affected by the structural and fluctuating properties of the three-dimensional (3D) H-bonding network of water [3–6]. However, even subtle features of the hydration thermodynamics of nonpolar solutes (i.e., the positive Gibbs free energy change, the negative entropy change and the positive heat capacity change) can be reproduced by means of classic scaled particle theory, SPT, a simple hard sphere theory [7–10], that has a solid geometric ground [7,11]. Classic SPT allows the calculation of the reversible work to create a spherical cavity in the fluid (i.e., to insert a different hard sphere in the fluid), and this process proves to play a fundamental role in the thermodynamics of solvation. To apply classic SPT to a real liquid such as water, only two pieces of information are needed [8]: (a) its density (taking into account the temperature and pressure dependence); (b) an effective hard sphere diameter. The idea is that, once the density is fixed and determined by intermolecular attractions, the liquid can be treated as a hard sphere fluid [7]. In the case of water, the use of experimental densities corresponds to take into account the 3D H-bonding

network effect in a mean-field way. The effective hard sphere diameter assigned to water molecules is $\sigma_w = 2.8$ Å [10], close to the location of the first maximum in the oxygen oxygen radial distribution function of liquid water, determined by means of X-ray and neutron diffraction measurements [12,13], and close to the distance between two H-bonded water molecules in ordinary ice, 2.76 Å [14]. The reliability of the used σ_w is an important point to provide support for the ability of classic SPT to describe some properties of water.

Also, classic SPT allows the calculation of the so-called cavity contact correlation function, $G(R_C)$, a dimensionless quantity that represents the density of liquid molecules in contact with the cavity surface, normalized to the bulk density, as a function of cavity radius R_C [7,15]. Note that R_C is the radius of the spherical region from which the centres of liquid molecules are excluded, $R_C = r_c + r_1$, where r_c is the radius of the spherical region from which all parts of liquid molecules are excluded, and r_1 is the radius of liquid molecules. This cavity contact correlation function corresponds to the value of the cavity-liquid radial distribution function at contact distance. Of course, it can be determined directly by means of computer simulations, as shown by the pioneering work of Pratt and Pohorille [16], and its physical relevance is well established [7,15–17]. One of us pointed out that the $G(R_C)$ function determined in the TIP4P water model at 25 °C and 1 atm [18,19] can be reproduced more-than-qualitatively by means of classic SPT relationships [20]. This result confirmed that density and molecular size are sufficient to rationalize some features of water behaviour. Recently, the $G(R_C)$ function has been determined in the TIP4P water model at 25 °C,

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over a very large range of hydrostatic pressure, by means of Monte Carlo simulations by Floris [21]. It was also shown that the $G(R_C)$ hydrostatic pressure dependence cannot be reproduced by means of the “approximate SPT expression” [21]. It is important to underline that Floris did not use classic SPT, but a modified SPT approach which has no clear molecular ground.

In the present work we show that a straightforward application of classic SPT produces $G(R_C)$ curves whose hydrostatic pressure dependence is in good agreement with that emerged from Monte Carlo simulations in the TIP4P water model. The significance of this finding is carefully discussed.

2. Theory section

Simple geometric arguments lead to the following exact relationship for the reversible work of cavity creation when $R_C \leq r_1$ (i.e., at most one molecular centre can be found in the cavity for $0 \leq R_C \leq r_1$):

$$\Delta G_C = -RT \cdot \ln \left[1 - (4/3)\pi \cdot \rho_1 \cdot R_C^3 \right] \quad (1)$$

where ΔG_C is the Gibbs free energy change associated with cavity creation, R is the gas constant, $\rho_1 = N_{AV} / v_1$ is the number density of the liquid and v_1 its molar volume. For $R_C \geq r_1$, Reiss and colleagues provided the following approximate formula for ΔG_C [7], that can be derived also by means of geometric arguments [11]:

$$\Delta G_C = RT \cdot \left[-\ln(1-\xi) + u(\sigma_C/\sigma_1) + (u/2) \cdot (u+2) \cdot (\sigma_C/\sigma_1)^2 \right] + P \cdot v_C \quad (2)$$

in this relation ξ is the volume packing density of the liquid, which is defined as the ratio of the physical volume of a mole of liquid molecules over the molar volume of the liquid (i.e., $\xi = \pi \cdot \sigma_1^3 \cdot N_{AV} / 6 \cdot v_1$), and $u = 3\xi / (1 - \xi)$; $\sigma_C = 2 \cdot r_C$ and $\sigma_1 = 2 \cdot r_1$ are the hard sphere diameter of the cavity and of liquid molecules, respectively; v_C is the van der Waals volume of the spherical cavity (i.e., $v_C = \pi \cdot \sigma_C^3 \cdot N_{AV} / 6$), the spherical region from which all parts of liquid molecules are excluded, not to be confused with the partial molar volume of the cavity [5,6]; and P is the hydrostatic pressure over the liquid. The last term in Eq. (2) represents the pressure-volume contribution to the reversible work of cavity creation, whose magnitude is negligibly small at 1 atm, but may become significant on increasing P [6].

The cavity contact correlation function $G(R_C)$, which is the conditional solvent density just outside a spherical cavity of radius R_C , is given by the derivative of ΔG_C with respect to R_C , normalized to the cavity surface area and bulk liquid density [7,20]:

$$G(R_C) = (1/4\pi \cdot \rho_1 \cdot R_C^2) \cdot [\partial(\Delta G_C/RT)/\partial R_C] \quad (3)$$

Performing the derivatives one obtains the following relationships:

$$G(0 \leq R_C \leq r_1) = 1 / \left[1 - (4/3)\pi \cdot \rho_1 \cdot R_C^3 \right] \quad (4)$$

$$G(R_C \geq r_1) = \left(1/2\pi \cdot \rho_1 \cdot R_C^2 \right) \cdot \left\{ (u/\sigma_1) + [u \cdot (u+2)/\sigma_1^2] \cdot \sigma_C + [3 \cdot P \cdot v_C/RT \cdot \sigma_C] \right\} \quad (5)$$

To perform classic SPT calculations, it has been used: (a) the experimental density of water at the different hydrostatic pressures and 25 °C [22]; (b) the effective hard sphere diameter of water molecules, $\sigma_W = 2.8 \text{ \AA}$, which has been considered to be pressure-independent because the location of the first peak in the oxygen oxygen radial distribution function is little affected on increasing hydrostatic pressure [13,23].

3. Results and discussion

The $G(R_C)$ curves calculated at 25 °C and over the 1–8000 atm pressure range by means of classic SPT relationships, Eqs. (4) and (5), are shown in panel A of Fig. 1. They are in good agreement with those determined by means of Monte Carlo simulations in the TIP4P water model [21], as emphasized by the comparison with blue and black filled circles referring to 1 atm and 8000 atm, respectively (see panel B of Fig. 1). It is worth noting that the $G(R_C)$ function determined at 25 °C and 1 atm in the SPC/E water model over a smaller cavity size range [24,25] does not correspond to that obtained in the TIP4P water model (compare the blue and green filled circles in panel B of Fig. 1). In particular, the $G(R_C)$ function in SPC/E water is always smaller than that in TIP4P water, and its maximum occurs at $R_C \approx 2.4 \text{ \AA}$, whereas in TIP4P water it occurs at $R_C \approx 2.8 \text{ \AA}$. We do not have an explanation for this discrepancy.

Classic SPT relationships are able to reproduce both the presence of the maximum (even though at a cavity radius smaller than that determined in the two water models, $R_C \approx 2.1 \text{ \AA}$), and the continuous decrease of the $G(R_C)$ function on increasing the cavity radius at 25 °C and 1 atm [20]. These two features have been considered unequivocal indications of cavity dewetting, a fundamental point of the lengthscale dependence of hydrophobicity claimed by Lum-Chandler-Weeks [26,27]. The location of the $G(R_C)$ maximum has been used to distinguish between two mechanisms of cavity creation [28]: (a) the entropic one guided by the solvent-excluded volume effect, holding for small cavities; (b) the energetic one guided by the surface thermodynamics, holding for large cavities. Since the $G(R_C)$ maximum occurs at $R_C < 3 \text{ \AA}$, one should conclude that a cavity suitable to host a methane molecule

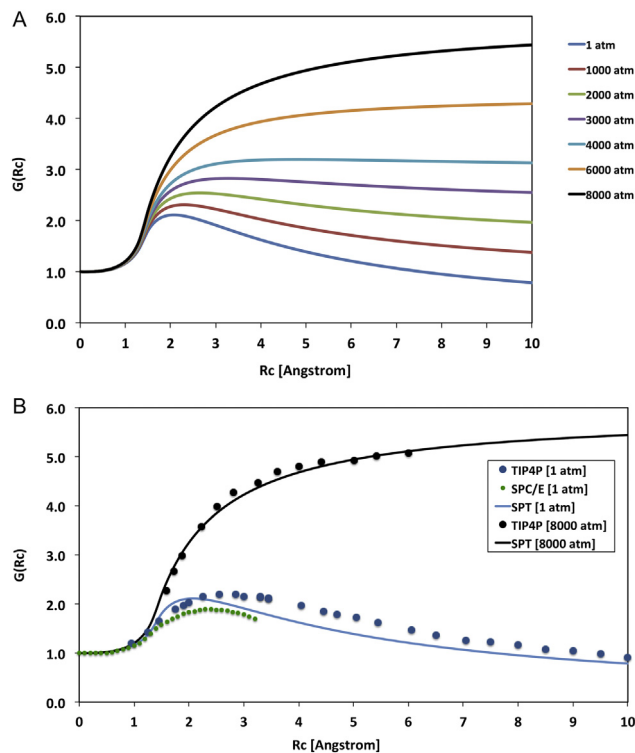


Fig. 1. Panel A. Trend of the cavity contact correlation function $G(R_C)$ of water calculated by means of classic SPT at 25 °C, over a large range of hydrostatic pressure, using the experimental density values. Panel B. The blue and black lines represent the $G(R_C)$ function calculated at 1 atm and 8000 atm, respectively, by means of classic SPT, using the experimental density values. The blue and black filled circles represent the $G(R_C)$ function obtained at 25 °C in TIP4P water at 1 atm and 8000 atm, respectively, by means of Monte Carlo simulations [18,21]. The green filled circles represent the $G(R_C)$ function obtained in SPC/E water at room temperature and 1 atm, by means of MD simulations [24]. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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