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# WATER’S SURFACE TENSION AND CAVITY THERMODYNAMICS

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The relationship between cavity thermodynamics in water and air-water surface tension is investigated in the present study. The effective hard sphere diameter of water molecules over a large temperature range is estimated from the experimental air-water surface tension, and cavity thermodynamics is calculated by means of classic scaled particle theory. The work of cavity creation proves to be a decreasing function of temperature and the cavity entropy change is a positive, practically constant, quantity, regardless of the cavity diameter, in marked contrast with well established theoretical and computer simulation results. This finding suggests that the relationship between cavity thermodynamics and surface tension is not a simple matter in the case of water.

***Keywords:*** *air-water surface tension, cavity thermodynamics, entropy convergence, isothermal compressibility, scaled particle theory*

## Introduction

The thermodynamic features of all the hydration processes, in particular of nonpolar molecules, are dominated by the thermodynamics of cavity creation [1–6]. The latter is an unavoidable step of solvation phenomena because liquids are a condensed state of the matter and a suitable cavity has to be created for the insertion of a solute molecule. Cavity creation cannot be studied by means of direct measurements, but only by means of theoretical statistical mechanical approaches and/or computer simulations [7–9]. Scaled particle theory, SPT, was developed by Reiss and colleagues to arrive at an expression for the work of cavity creation in hard sphere fluids and so to the equation of state [10, 11]. More than forty years ago, Pierotti was able to show that: (a) SPT can be applied to real liquids, also water; (b) SPT can reproduce the hydration thermodynamics of nonpolar molecules [12, 13]. A fundamental point for SPT application, apart the use of the experimental liquid density, is the knowledge of the effective hard sphere diameter of liquid molecules. Pierotti developed a reliable procedure to estimate the effective hard sphere diameter of liquid molecules on the basis of solubility data [12, 13].

It is also possible to obtain estimates of the effective hard sphere diameter of liquid molecules fitting the experimental isothermal compressibility, $\beta_T$, or the experimental liquid-vapour surface tension, $\gamma$, by means of the corresponding SPT relationships, as pioneered by Mayer and Reiss [11, 14]. This possibility has to be connected to the fact that the magnitude of the work of cavity creation in a liquid, $\Delta G_c$, is usually related, in an empirical/heuristic way, to the surface tension of the same liquid (i.e., $\Delta G_c$ is a large positive quantity in all liquids, but it is larger in water than in organic liquids simply because water has the largest surface tension) [15, 16]. Actually, this assumption is because the leading term in the SPT relationship for $\Delta G_c$ seems to represent the work to increase the surface area of the spherical cavity [see Eq. (1) below].

Recently, the relationship between $\Delta G_c$ and surface tension has been supported independently by Chandler [17], and Ashbaugh and Pratt [18]. In particular, Ashbaugh and Pratt have developed a revised/modified version of SPT incorporating the air-water surface tension to treat both small-size and large-size cavities (the dividing radius should be between 5 and 10 Å) [18]. In the present article I would like to show that, if the effective hard sphere diameter of water molecules is determined from the air-water surface tension over a large temperature range, $\sigma(H_2O, \gamma)$, the cavity thermodynamic functions calculated by means of classic/original SPT prove to be unreliable. The problem is not related to the magnitude of $\sigma(H_2O, \gamma)$ values, but to their too strong temperature dependence, suggesting that the relationship between cavity thermodynamics and surface tension is not trivial.

## Calculation procedure

Estimates of $\Delta G_c$ as a function of temperature are calculated by means of classic/original SPT [10, 11]. By assuming that the cavity size, $\sigma_c$, is the diameter of the spherical region from which any part of any liquid

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molecules is excluded, the SPT relationship for $\Delta G_c$ is the following [19]:

$$\Delta G_c=RT[K_0+K_1(\sigma_c/\sigma_1)+K_2(\sigma_c/\sigma_1)^2+K_3(\sigma_c/\sigma_1)^3] \quad (1)$$

where: $K_0=-\ln(1-\xi)$; $K_1=u=3\xi/(1-\xi)$; $K_2=u(u+2)/2$; $K_3=\xi Pv_1/RT$; $R$ is the gas constant; $\xi$ is the volume packing density of pure liquid, which is defined as the ratio of the physical volume of a mole of liquid molecules over the molar volume of the liquid, $v_1$ (i.e., $\xi=\pi\sigma_1^3N_{Av}/6v_1$); $\sigma_1$ is the hard sphere diameter of liquid molecules, and $P$ is the pressure. As claimed by other authors [19, 20], $P$ has to be the experimental hydrostatic pressure over the liquid, 1 atm; this value has been used in all the SPT calculations. In addition, I have used: (a) the experimental values of liquid water density at 1 atm over the 0–150°C temperature range compiled by Kell [21], and listed in the second column of Table 1 in terms of molar volume; (b) a temperature dependent hard sphere diameter for water molecules, $\sigma_1=\sigma(H_2O)$.

The temperature dependence of $\sigma(H_2O)$ has been obtained in two alternative ways (note that $\sigma_c$ is assumed to be temperature independent). Following the procedure of Mayer and Reiss [11, 14], $\sigma(H_2O, \gamma)$ values have been determined by fitting the experimental air-water surface tension over the 0–100°C temperature range [22] (the $\gamma$ values are listed in the third column of Table 1), by means of the following SPT relationship:

$$\gamma(\mathrm{SPT})=kT[(12\xi/1-\xi)+18(\xi/1-\xi)^2]/4\pi\sigma_1^2 \quad (2)$$

where $k$ is the Boltzmann constant. Some of these $\sigma(H_2O, \gamma)$ values and of those obtained by extrapolation up to 150°C are listed in the second column of Table 2, part A; it is evident that they decrease strongly with temperature, passing from 2.95 Å at 0°C to 2.59 Å at 150°C.

Alternatively, Soda determined $\sigma(H_2O)$ by reproducing the contact density function obtained from computer simulations at different temperatures [23]. Performing a polynomial fit of Soda's values over the 25–100°C range and an extrapolation to lower and higher temperatures, $\sigma(H_2O)$ values over the 0–150°C temperature range have been obtained [24], and are listed in the second column of Table 2, part B. The Soda's $\sigma(H_2O)$ values (a) decrease slightly with temperature, passing from 2.758 Å at 0°C to 2.662 Å at 150°C; (b) are in line with those determined from the analysis of gas solubility data over a smaller temperature range [13, 25].

The $\Delta S_c$ values have been calculated by direct application of the thermodynamic relation:

$$\Delta S_c=-(\partial\Delta G_c/\partial T)_P \quad (3)$$

**Table 1** Experimental values of molar volume, air-water surface tension, thermal expansion coefficient and isothermal compressibility of water over the temperature range 0–150°C, at 1 atm [21, 22]

| $T$/ °C | $v$/ cm$^3$ mol$^{-1}$ | $\gamma$/ dyne cm$^{-1}$ | $\alpha\cdot10^6$/ K$^{-1}$ | $\beta_T\cdot10^{12}$/ cm$^2$ dyne$^{-1}$ |
|---|---|---|---|---|
| 0 | 18.02 | 75.6 | –68 | 50.9 |
| 20 | 18.05 | 72.8 | 207 | 45.9 |
| 40 | 18.16 | 69.6 | 385 | 44.2 |
| 60 | 18.33 | 66.2 | 523 | 44.5 |
| 80 | 18.54 | 62.7 | 641 | 46.1 |
| 100 | 18.80 | 58.9 | 750 | 49.0 |
| 120 | 19.11 | – | 857 | 53.2 |
| 150 | 19.65 | – | 1028 | 62.3 |

## Results and discussion

Values of $\Delta G_c$ have been calculated, using the $\sigma(H_2O, \gamma)$ values determined from the air-water surface tension, for different cavity diameters, $\sigma_c$= 3, 5, 7, 10 and 15 Å, over the 0–150°C temperature range. The determined functions are shown in Fig. 1, and some values are reported in Table 2, part A. These $\Delta G_c$ functions, even though large positive at any temperature, have a monotonic decreasing trend on increasing temperature, regardless of the cavity diameter. The corresponding $\Delta S_c$ estimates are positive and roughly constant for each cavity size over the 0–150°C temperature range (i.e., $\Delta S_c$ (in J K$^{-1}$ mol$^{-1}$ units)≅37 for $\sigma_c$=3 Å, 152 for $\sigma_c$=5 Å, 176 for $\sigma_c$=7 Å, 347 for $\sigma_c$=10 Å, and 763 for $\sigma_c$=15 Å). These results should be considered to be unreliable for the following reasons.

First of all, a parabolic shape has been obtained for $\Delta G_c$ in water over a large temperature, for cavities

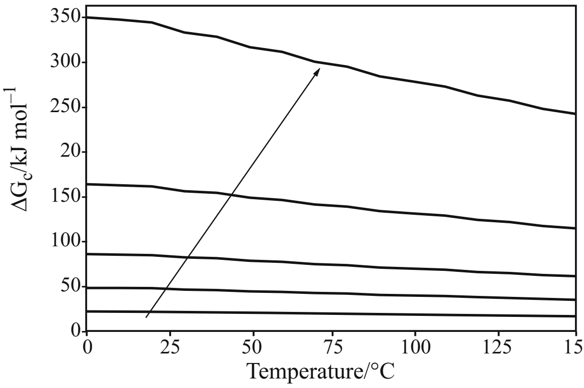

**Fig. 1** Temperature dependence of $\Delta G_c$ functions, calculated by means of SPT Eq. (1), using the $\sigma(H_2O, \gamma)$ values listed in the second column of Table 2, part A, for different cavity diameters. The arrow indicates $\Delta G_c$ functions for cavities with $\sigma_c$=3, 5, 7, 10 and 15 Å. The magnitude of $\Delta G_c$ functions increases with cavity diameter

**Table 2** For spherical cavities whose diameter is reported at the top, SPT estimates of $\Delta G_c$ (in kJ mol$^{-1}$ units), over the 0–150°C temperature range, are listed: part A, numbers calculated by using the $\sigma(H_2O, \gamma)$ values determined fitting the experimental air-water surface tension by means of SPT Eq. (2); part B, numbers calculated by using the Soda’s $\sigma(H_2O)$ values. See text for further details

| | $T$/°C | $\sigma(H_2O)$/Å | ξ | 3 Å | 5 Å | 7 Å | 10 Å | 15 Å |
|---|---|---|---|---|---|---|---|---|
| A | 0 | 2.95 | 0.449 | 19.8 | 46.3 | 84.1 | 162.2 | 349.1 |
| | 20 | 2.91 | 0.430 | 19.6 | 45.7 | 82.9 | 159.6 | 343.3 |
| | 40 | 2.86 | 0.406 | 18.9 | 43.8 | 79.3 | 152.4 | 327.2 |
| | 60 | 2.81 | 0.382 | 18.1 | 41.7 | 75.4 | 144.7 | 310.3 |
| | 80 | 2.76 | 0.358 | 17.3 | 39.7 | 71.6 | 137.2 | 293.8 |
| | 100 | 2.71 | 0.334 | 16.4 | 37.7 | 67.8 | 129.7 | 277.4 |
| | 120 | 2.66 | 0.311 | 15.6 | 35.7 | 64.1 | 122.4 | 261.6 |
| | 150 | 2.59 | 0.279 | 14.5 | 33.1 | 59.3 | 113.0 | 241.1 |
| B | 0 | 2.758 | 0.367 | 14.1 | 32.5 | 58.7 | 112.5 | 241.2 |
| | 20 | 2.750 | 0.363 | 14.9 | 34.3 | 61.9 | 118.7 | 254.3 |
| | 40 | 2.741 | 0.358 | 15.5 | 35.6 | 64.3 | 123.2 | 263.9 |
| | 60 | 2.730 | 0.350 | 15.9 | 36.5 | 65.9 | 126.1 | 270.1 |
| | 80 | 2.718 | 0.341 | 16.2 | 37.1 | 66.9 | 128.0 | 273.9 |
| | 100 | 2.704 | 0.332 | 16.3 | 37.3 | 67.2 | 128.5 | 274.8 |
| | 120 | 2.688 | 0.315 | 16.3 | 37.2 | 66.9 | 127.8 | 273.0 |
| | 150 | 2.662 | 0.303 | 16.0 | 36.6 | 65.6 | 125.3 | 267.4 |

having a radius smaller than 10 Å, by several authors by means of computer simulations and/or theoretical approaches: (a) Guillot and Guissani using the test particle insertion method coupled with molecular dynamics simulations [26]; (b) Pratt and colleagues using both the test particle insertion method and an information theory model [27, 28]; (c) Huang and Chandler using computer simulations and the Lum–Chandler–Weeks theoretical approach [29, 30]; (d) Garde and Ashbaugh using Monte Carlo simulations in an isotropic single site model of water [31]; (e) Ashbaugh, Truskett and Debenedetti [32], and Graziano [33] using statistical mechanical models based on a van der Waals treatment of the excluded volume effect.

Secondly, the parabolic shape of $\Delta G_c$ *vs.* $T$ produced cavity entropy functions $\Delta S_c$ that converge above 100°C – there is a temperature at which the $\Delta S_c$ functions for different cavity diameters attain the same value [24, 27, 32, 33]. In this respect, it is important to note that entropy convergence is a specific feature of the experimental hydration thermodynamics of hydrocarbons, noble gases and *n*-alcohols [24, 34–37].

The fundamental point is that the same SPT expression of $\Delta G_c$, Eq. (1), produces a parabolic temperature dependence using alternative sets of $\sigma(H_2O)$ values: (a) those determined on the basis of Soda’s results [24]; (b) those determined on the basis of the experimental $\beta_T$ values of water over the 0–150°C temperature range [37]. In particular, the $\Delta G_c$ functions calculated using the Soda’s $\sigma(H_2O)$ values, are shown in Fig. 2 for different cavity diameters, $\sigma_c$=3, 5, 7, 10 and 15 Å, over the 0–150°C temperature range, and some values are reported in Table 2, part B. These $\Delta G_c$ functions possess a flat maximum around 100°C; performing a second-degree polynomial fit, it results that: $T_{max}$≅109°C for $\sigma_c$=3 Å, 104°C for $\sigma_c$=5 Å, 102°C for $\sigma_c$=7 Å, 100°C for $\sigma_c$=10 Å, and 99°C for $\sigma_c$=15 Å. The $\Delta S_c$ functions, calculated by numerical

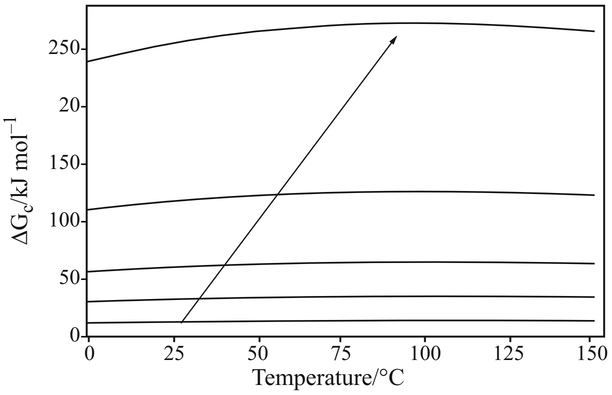

**Fig. 2** Temperature dependence of $\Delta G_c$ functions, calculated by means of SPT Eq. (1), using the Soda’s $\sigma(H_2O)$ values listed in the second column of Table 2, part B, for different cavity diameters. The arrow indicates $\Delta G_c$ functions for cavities with $\sigma_c$=3, 5, 7, 10 and 15 Å. The magnitude of $\Delta G_c$ functions increases with cavity diameter

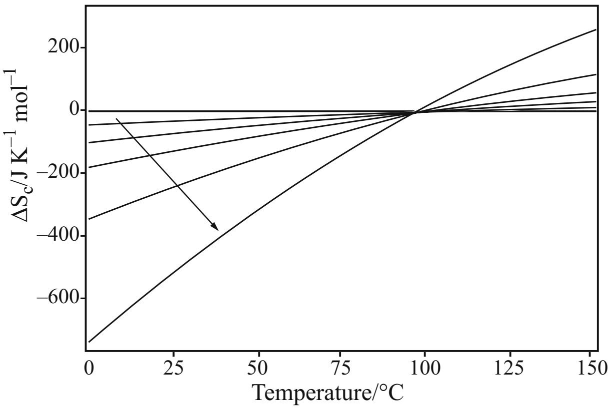

**Fig. 3** $\Delta S_c$ functions calculated by temperature derivative of the $\Delta G_c$ curves of Fig. 2. The arrow indicates entropy curves for cavities with $\sigma_c$=3, 5, 7, 10 and 15 Å. The convergence temperature is close to 100°C

differentiation of the $\Delta G_c$ curves with respect to temperature according to Eq. (3), are plotted over the 0–150°C temperature range in Fig. 3. They are large negative and increase in magnitude with the cavity size at room temperature. In addition, the $\Delta S_c$ functions increase markedly with temperature, and show convergence slightly below 100°C, where $\Delta S_c \cong -4\ \mathrm{J\ K^{-1}\ mol^{-1}}$, regardless of the cavity diameter. It is worth noting that, at the convergence temperature, $\Delta S_c$ is negative, in qualitative agreement with experimental findings for the hydration of hydrocarbons, noble gases and *n*-alcohols [24, 37], even though its magnitude is significantly smaller. Part of the discrepancy is because the entropy contribution associated with turning on solute-water interactions, that should be a negative quantity, has been neglected.

Application of SPT Eq. (1), using the experimental density of liquid water and temperature dependent $\sigma(H_2O)$ values leads to: (a) $\Delta G_c$ functions that decrease in a monotonic way with temperature (Fig. 1), and so to positive and roughly constant $\Delta S_c$ values, if the $\sigma(H_2O)$ values are determined by fitting the air-water surface tension with respect to SPT Eq. (2); (b) $\Delta G_c$ functions that show a non-monotonic temperature dependence with a flat maximum around 100°C (Fig. 2), and so to $\Delta S_c$ functions that converge to a common negative value slightly below 100°C (Fig. 3), if the $\sigma(H_2O)$ values are determined on the basis of Soda's computer simulation results. Clearly, these data confirm the sensitivity of SPT calculations to the choice of the effective hard sphere diameter for liquid molecules [4, 19, 24], and so I have not attempted an analysis of error propagation.

Since the second set of results is the qualitatively correct one, it appears that the unreliable first set of results originates from the exaggerated temperature dependence of the $\sigma(H_2O, \gamma)$ values. This argument was advanced also by Pierotti [38] in a reply to Ben-Naim and Friedman [39], who were the first to point out that $\Delta S_c$ assumes positive values in water at room temperature if $\sigma(H_2O)$ and its temperature dependence are determined from the experimental air-water surface tension. Pierotti claimed that the isothermal compressibility $\beta_T$ should be a less questionable property to evaluate $\sigma(H_2O)$ over a large temperature range than the air-water surface tension [38]. In fact, according to its statistical mechanical definition [40], $\beta_T$ of a system is a measure of the ensemble fluctuations in local number density, and, fixed the liquid average density by intermolecular attractions, any further isothermal compression can be treated as the repacking of hard spheres [11]. I agree with Pierotti's claim, and I have already shown that the $\sigma(H_2O)$ values determined from $\beta_T$, when inserted in SPT Eq. (1), produce parabolic $\Delta G_c$ curves as a function of temperature and entropy convergence [37].

Classic/original SPT is a hard sphere theory and it is very strange to expect that it should be able to correctly reproduce the air-water surface tension [18], whose magnitude and temperature dependence are surely related to the properties of water–water H-bonds [41]. Nevertheless, SPT Eq. (2) can reproduce $\gamma$ for water over a large temperature range, but at the expense of an unreasonably large temperature dependence of $\sigma(H_2O)$ [11, 14], and, in fact, the cavity thermodynamics calculated by means of SPT with $\sigma(H_2O, \gamma)$ prove to be not correct. Pierotti exactly wrote [38]: 'There is no question that $\sigma_1$ should have some temperature dependence especially for non-spherical molecules, but the very nature of a collision diameter implies that there exists a large energy gradient with respect to distance and hence a small change in kinetic energy should not appreciably change the collision diameter.' On this matter, I would like to point out that the significant decrease of $\gamma$ with temperature is not paralleled by the behaviour of other thermodynamic properties of water, such as the isothermal compressibility $\beta_T$, that changes very little with temperature, and the thermal expansion coefficient, $\alpha$, that increases markedly with temperature [21] (see the values listed in Table 1). In all probability, this is because each physical quantity accounts for different features of the H-bonded network of water.

I have already pointed out that there is no clear relationship between the $\Delta G_c$ values calculated by means of classic/original SPT and the liquid-vapour surface tension for several liquids at room temperature [42]. The present results further confirm that the relationship between cavity thermodynamics and surface tension is not straightforward in the case of water.

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