

# Surface Tension of Water. The Fowler Model

B. Borštnik, D. Janežič, and A. Ažman

Boris Kidrič Institute of Chemistry, Ljubljana, Yugoslavia

Z. Naturforsch. **34a**, 1239–1242 (1979); received April 27, 1979

The surface tension and surface energy of water is calculated using the Fowler approximation. The direct Monte Carlo integration and the calculation using the atom-atom pair correlation functions are reported. The configuration interaction pair potential was used. The results show that feasible agreement with the experiment can be obtained.

## 1. Introduction

Computer simulation of liquid water has not yet been extended to heterogeneous systems such as liquid-crystal or liquid-vapour interfaces. All type of water-water pair potentials are expressed by rather complicated expressions so that the simulation of a heterogeneous system is very time consuming. For states close to the triple point, calculations on the homogeneous system can serve as the input for the evaluation of the surface tension. The Fowler model [1] connects the surface tension and excess internal surface energy with the distribution of the molecules in the homogeneous liquid phase. We have performed a direct evaluation of the Kirkwood-Buff-Fowler expression for the surface tension and surface energy by the Monte Carlo procedure. Besides this we have also investigated the possibility to evaluate both quantities with the atom-atom pair correlation functions of the homogeneous phase. The latter method leads to the possibility to express the surface tension and the surface energy with the experimentally available atom-atom pair correlation functions.

## 2. The Fowler Model of Surface Tension of Water

It was found by molecular dynamics and Monte Carlo calculations that close to the triple point the liquid-vapour interface of monoatomic [2] and diatomic [3] liquids extends across a few molecular diameters. This means that the Fowler model can be applied for the calculation of surface quantities. This model approximates the density profile at the liquid-vapour interface by a step function and neglects the density of the vapour phase. Unfortunately the value of the surface tension due to Fowler's model is very sensitive to details of the pair potential and radial distribution function [4].

The surface tension and the excess surface energy can be expressed in the following way [4, 5]:

$$\gamma = \frac{\pi}{8} \varrho^2 \int_0^\infty R_{00'}^4 \cdot \left\langle g(R_{00'} \boldsymbol{\omega} \boldsymbol{\omega}') \frac{\partial U(R_{00'} \boldsymbol{\omega} \boldsymbol{\omega}')}{\partial R_{00'}} \right\rangle_{\boldsymbol{\omega} \boldsymbol{\omega}'} dR_{00'} \quad (1)$$

$$u_s = \frac{\pi}{2} \varrho^2 \int_0^\infty R_{00'}^3 \cdot \langle g(R_{00'} \boldsymbol{\omega} \boldsymbol{\omega}') U(R_{00'} \boldsymbol{\omega} \boldsymbol{\omega}') \rangle_{\boldsymbol{\omega} \boldsymbol{\omega}'} dR_{00'} \quad (2)$$

where  $R_{00'}$  denotes the oxygen-oxygen distance,  $\varrho$  the density of water and  $g(R_{00'} \boldsymbol{\omega} \boldsymbol{\omega}')$  the pair distribution function of two water molecules. The three Euler angles defining the orientation of a molecule are represented by the vector  $\boldsymbol{\omega}$ .

On the other hand, if the positions and the orientations of the molecules are provided by a molecular dynamics or Monte Carlo simulation,  $\gamma$  and  $u_s$  can be evaluated by the expressions

$$\gamma = \frac{1}{16V} \left\langle \sum_{i>j} R_{00'}^2 \frac{\partial U(R_{00'} \boldsymbol{\omega} \boldsymbol{\omega}')}{\partial R_{00'}} \right\rangle, \quad (3)$$

$$u_s = \frac{1}{4V} \left\langle \sum_{i>j} R_{00'} U(R_{00'} \boldsymbol{\omega} \boldsymbol{\omega}') \right\rangle \quad (4)$$

The angular brackets mean canonical averages. The evaluation of  $\gamma$  and  $u_s$  on the basis of (3) and (4) leads to considerably better results [4] than the calculation based on (1) and (2).

We performed a Monte Carlo calculation [6] on a system of 64 water molecules. A modified version of Barsotti's Monte Carlo program was used [7]. The interaction of pairs of water molecules was described by the configuration interaction pair potential of Matsouka et al. [8]. It is expressed as a sum of terms depending upon  $R_{00'}$  and all other interatomic distances  $R_{ii'}$  (see Fig. 1). The deriva-

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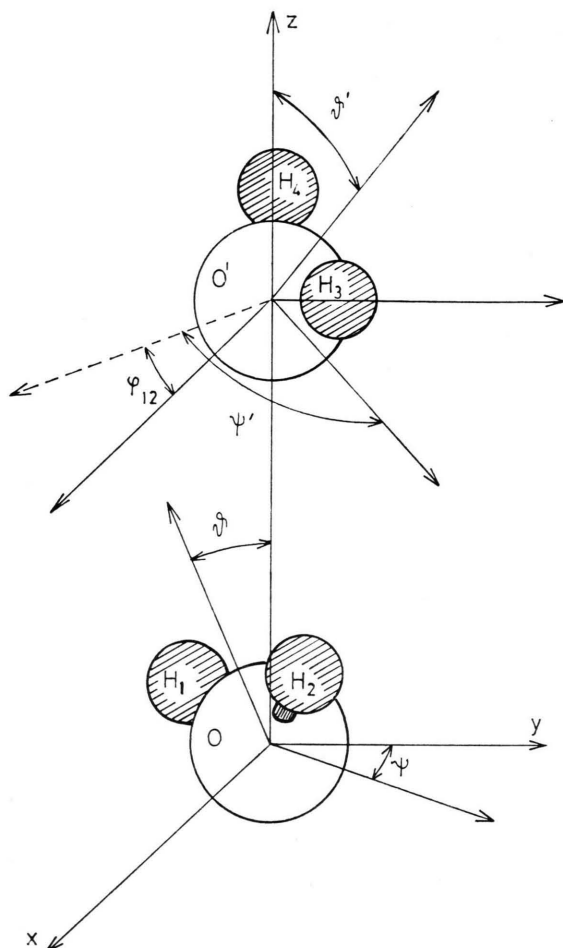


Fig. 1. The meaning of the variables concerning the angular averaging of the quantities depending upon two water molecules.

tives of the terms depending on  $R_{ii'}$  entering in (1) and (3), were expressed as follows:

$$\frac{\partial U(R_{ii'})}{\partial R_{00'}} = \frac{dU(R_{ii'})}{dR_{ii'}} \frac{\mathbf{R}_{ii'} \cdot \mathbf{R}_{00'}}{R_{ii'} R_{00'}} \quad (5)$$

Periodic boundary conditions were used and the potential was cut off at  $R = 6.44 \text{ \AA}$ . It was found [9, 10] that a peculiarity of the CI potential, if it is applied to the liquid, is an underestimation of the density in the vicinity of the triple point. Therefore we performed the calculation at  $\rho = 0.81 \text{ g/cm}^3$ .

The Monte Carlo run consisted of equilibration moves plus  $10^6$  moves for the evaluation of the surface tension and surface energy using (3) and (4). The resulting values were 18 dyne/cm for the surface tension and 160 dyne/cm for the surface

energy. The corrections for the neglected tail of the intermolecular potential has also to be taken into account. The corrections are due to dispersion forces and to electric multipole interactions. The dispersion forces are of the form  $C_6/R_{00'}^6$ . The value of the coefficient  $C_6$  depends upon the way it is determined (by the Kirkwood-Müller relation or by the London relation [11]). Taking the rounded value of  $C_6$  to be  $1000 \text{ kcal/mole/\AA}^6$  the contribution of the neglected tail of the potential to the surface tension and the surface energy is approximately equal to 29 dyne/cm and 20 dyne/cm, respectively. There is no simple way to evaluate the contribution of the long range electric multiple interactions to the surface tension and surface energy. The Onsager reaction field [12] can not be applied in the case of the Fowler Model because of the lack of spherical symmetry at the liquid surface. However, the Monte Carlo calculations [10] indicate the existence of orientational correlations at the liquid surface. These correlations affect the surface tension and surface energy but can not be taken into account in the context of the Fowler model.

Another possibility to calculate the surface tension and the surface energy due to the Fowler model is the use of (1) and (2). The angle dependent pair distribution function  $g(R_{00'} \omega \omega')$  plays the central role in this case. The angular dependence can be expressed with the atom-atom pair correlation functions  $g_{00'}(R)$ ,  $g_{0H}(R)$  and  $g_{HH}(R)$  using the superposition approximation. In the theory of simple monoatomic liquids, Kirkwood's superposition approximation [13] states that the triple distribution function can be expressed as the product of three pair distribution functions. This is a rather crude approximation. Exact expressions are known [14] correcting the triplet product of pair correlation functions by multiplying it with an exponential factor. Some authors tried to evaluate this factor [15] while others introduced phenomenological correction factors [16].

In our case, the pair distribution function of water molecules can be expressed in the superposition approximation as the product of atom-atom pair correlation functions for the pairs of atoms not belonging to the same molecule. The atom-atom pair correlation functions can be obtained by computer simulation of homogeneous systems or by experiments.

The relative motion of two water molecules has six degrees of freedom, which means that the product of six atom-atom pair correlation functions should suffice to express the pair distribution function of two water molecules. Since there are nine distinct pairs of atoms, it is not obvious which three pairs should not contribute to the pair distribution function. We retain the product of all nine factors and write

$$g(R_{00'}, \omega \omega') = A(R_{00'}) g_{00}(R_{00'}) w(R_{00'}, \omega \omega') \Pi_g, \quad (6a)$$

where

$$\begin{aligned} \Pi_g = & g_{0H}(r_{0H3}) g_{0H}(r_{0H4}) g_{0H}(r_{0'H1}) \\ & \cdot g_{0H}(r_{0'H2}) g_{HH}(r_{H1H3}) g_{HH}(r_{H1H4}) \\ & \cdot g_{HH}(r_{H2H3}) g_{HH}(r_{H2H4}) \end{aligned} \quad (6b)$$

and  $w(R_{00'}, \omega \omega')$  is the correction factor for the superposition approximation.

The factor  $A(R_{00'})$  was evaluated in the following way. Performing the angular averaging of (6a), while keeping the oxygen atoms fixed, the left hand side must be equal to  $g_{00}(R_{00'})$ . Thus from

$$A(R_{00'}) \langle w(R_{00'}, \omega \omega') \Pi_g \rangle_{\omega \omega'} = 1$$

the value of  $A(R_{00'})$  can be determined.

Angular averaging in Eqs. (1) and (2) involves the integration over the Euler angles of two water molecules. Because of symmetry arguments the integration over one of the six angles can be omitted and fivefold integration has to be carried out. The distance between the oxygens was kept fixed while all the other distances were varied by varying the orientations.

$$\begin{aligned} \langle f(\omega, \omega') \rangle_{\omega \omega'} = & \frac{1}{8\pi^3} \int_0^\pi \sin \vartheta d\vartheta \int_0^\pi \sin \vartheta' d\vartheta' \int_0^{2\pi} d\varphi_{12} \\ & \cdot \int_0^\pi d\psi \int_0^\pi d\psi' f(\omega, \omega'). \end{aligned} \quad (7)$$

The fivefold integrals were evaluated by the Monte Carlo procedure. Usually 20000 integration points gave sufficient accuracy. To test the numerical procedure we calculated also the second virial coefficient of the vapor and compared it with the results of Lie and Clementi [17]. The agreement was perfect.

The integral over the radius in (1) was divided into three regions

$$0 \leq R_{00'} \leq 2.4 \text{ \AA}, \quad 2.4 \text{ \AA} \leq R_{00'} < 5.1 \text{ \AA}$$

and  $R_{00'} \geq 5.1 \text{ \AA}$ .

In the first region the integrand is equal to zero. In the second region the trapez rule was applied. In the third region the atom-atom pair distribution functions were supposed to have the limiting value unity and the integral over the radius was evaluated analytically.

Three different prescriptions for  $w(R_{00'}, \omega \omega')$  were used

$$w_I(R_{00'}, \omega \omega') = 1 \quad (8)$$

$$w_{II}(R_{00'}, \omega \omega') = \exp(-U(R_{00'}, \omega \omega')/kT), \quad (9)$$

$$w_{III}(R_{00'}, \omega \omega') = \begin{cases} \exp(-U(R_{00'}, \omega \omega')/kT) & \text{for } U(R_{00'}, \omega \omega') > 0 \\ 1 & \text{for } U(R_{00'}, \omega \omega') \leq 0. \end{cases} \quad (10)$$

To test the adequacy of the upper expressions we calculated also the mean potential energy of homogeneous liquid

$$\langle u \rangle = 2\pi \rho \int_0^\infty R_{00'}^2 \langle g(R_{00'}, \omega \omega') \rangle_{\omega \omega'} dR_{00'}. \quad (11)$$

The results obtained by (1), (2) and (11) are presented in Table 1. It can be seen that the values resulting from  $w_I$  and  $w_{II}$  in the first two columns of Table 1 are not encouraging. Since in the first column both, the surface tension and surface energy result with wrong sign we can speculate that the contribution of the configurations with the repulsive interactions exceeds the contributions of the configurations with the attractive part of the pair potential. This can be expected because the crude superposition approximation neglects all the correlations between the distances of pairs of atoms entering in (6b). The results in the second column of Table 1 indicate that the Boltzmann factor gives

Table 1. Values of the surface tension ( $\gamma$ ), surface energy ( $u_s$ ) and mean potential energy  $\langle u \rangle$  per particle.

		$w_I$	$w_{II}$	$w_{III}$	Direct Monte Carlo	Experiment
$\gamma$	dyne/cm	< 0	235	90 <sup>a)</sup> 51 <sup>b)</sup>	47 <sup>c)</sup>	72
$u_s$	dyne/cm	< 0		170	180	116
$\langle u \rangle$	kcal/mole	> 0	-21	-9.8	-9.1	

<sup>a)</sup> atom-atom pair correlation functions based on isothermal isobaric MC calculation [9],

<sup>b)</sup>  $g(R)$  based on isothermal isobaric MC calculation [18],

<sup>c)</sup> the contribution of dipole-dipole interaction beyond  $R_{00} = 6.44 \text{ \AA}$  not taken into account.

an excess weight to the configurations of any pair of water molecules with negative potential energy. The values in the third column of Table 1 agree quite well with the values obtained by direct Monte Carlo integration (fourth column).

### 3. Conclusion

We can conclude that the calculation of the surface tension and surface energy of water by the Fowler model is feasible. Close to the triple point the liquid-vapour interface is thin and Fowler's supposition of zero thickness does not represent serious obstruction. Also the extension of the bulk pair distribution function to the interface region can be acceptable. The direct Monte Carlo integration of the expressions for the surface tension

and surface energy leads to sufficient agreement with experiment.

The evaluation of the surface properties with the help of atom-atom pair correlation functions is tedious since it is difficult to express the angle dependent pair correlation functions with the atom-atom pair correlation functions. We used the superposition approximation and we found that an adequate correction factor can be found to obtain feasible results.

### Acknowledgement

The authors thank Prof. E. Clementi for sending us the computer program. The financial support of Research Community of Slovenia is gratefully acknowledged.

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