Relation between the Surface Tension and Roughness of the Intrinsic Liquid Surface

Pál Jedlovszky[a,b,c], Mária Darvas[d], and George Horvai[b,e]

[a] Laboratory of Interfaces and Nanosize Systems, Institute of Chemistry, Eötvös Loránd University, Pázmány Péter stny. 1/a, H-1117 Budapest, Hungary
[b] MTA-BME Research Group of Technical Analytical Chemistry, Szt. Gellért tér 4, H-1111 Budapest, Hungary
[c] EKF Department of Chemistry, Leányka u. 6, H-3300 Eger, Hungary
[d] SISSA, Department of Biological and Statistical Physics, 265 via Bonomea, Trieste, Italy
[e] Department of Inorganic and Analytical Chemistry, Budapest University of Technology and Economics, Szt. Gellért tér 4, H-1111 Budapest, Hungary

Reprint requests to P. J.; E-mail: pali@chem.elte.hu

Z. Naturforsch. **68a,** 123 – 129 (2013) / DOI: 10.5560/ZNA.2012-0096
Received September 28, 2012 / published online February 15, 2013

Dedicated to Prof. A. Klemm on the occasion of his 100th birthday

Previously published computer simulation data concerning the surface tension and surface roughness of various different liquid systems (i. e., binary water–methanol and water–dimethyl sulphoxide (DMSO) mixtures, water–poly-(ethylene-oxide) systems containing adsorbed sodium dodecyl sulphate, and room temperature ionic liquids) are re-analysed in order to find a relation between these quantities. It is found that the amplitude of the molecularly wavy liquid surface is inversely proportional to the logarithm of the surface tension while no clear correlation between the periodicity of the wavy surface and the surface tension is observed. It is also seen that the determination of the roughness parameters in a way analogous with the Langmuir formalism results in considerably more robust values than when an extra parameter is introduced in the procedure using a formula in analogy with the Langmuir–Freundlich isotherm.

Key words: Liquid–Vapour Interface; Surface Tension; Surface Roughness; Computer Simulation.

1. Introduction

Detailed investigations of the molecular level properties of the liquid/vapour interface have become the focus of intensive scientific efforts in the past two decades. The rapid increase of such studies has been initiated by the development of various surface sensitive experimental methods, such as nonlinear spectroscopy (e. g., sum frequency generation [1 – 5], second harmonic generation [6 – 9]) as well as X-ray and neutron reflectometry [10 – 12]. This development of experimental techniques able to selectively probe molecules located right at the surface of their phase was accompanied by the rapid increase of routinely available computing power, giving thus rise to computer simulation studies of such systems [13 – 37].

In a computer simulation study, i. e., when the system is seen at atomistic resolution, it is not a trivial task to detect the exact location of the liquid surface. The problem originates from the fact that the liquid surface is corrugated by capillary waves rather than being flat on the atomistic length scale. The problem of determining the exact location of the real, intrinsic surface of the liquid phase at every point (i. e., providing the function $X_{\mathrm{surf}} = f(Y,Z)$, where X_{surf} is the position of the surface along the macroscopic normal axis at the $\{Y,Z\}$ point of the macroscopic plane of the surface) is analogous with the problem of determining the full list of molecules that are located right at the liquid surface. It is obvious that any meaningful comparison of simulation results with surface sensitive experiments requires the accomplishment of this latter task to guarantee that the same set of molecules are considered in both cases. Although the majority of the existing simulation studies simply neglect the problem of determining the intrinsic surface and use a slab parallel with

the (macroscopic) Gibbs dividing surface instead, it is now clear that this treatment leads to large systematic errors in the calculated interfacial [26–29, 33] as well as thermodynamic properties [38] of the system.

In the past few years, several methods have been proposed to circumvent this problem [23, 26, 30, 32, 39, 40]. Among these methods, the identification of the truly interfacial molecules (ITIM) [26] turned out to be an excellent compromise between computational costs and accuracy [32]. In an ITIM analysis, the molecules that are accessible from the opposite phase (e. g., a vapour phase or an immiscible liquid) by a probe sphere of given radius are detected by moving the probe along test lines perpendicular to the macroscopic surface. The molecules that are first touched by the probe, moving from the bulk opposite phase along any of the test lines, are forming the list of the truly interfacial molecules.

Once the intrinsic liquid surface is determined, not only the aforementioned systematic error is eliminated, but detailed analyses of the properties of the intrinsic surface itself become also possible. One of these properties concerns the molecular-scale roughness of this surface. In characterizing this roughness, one has to realize that this information cannot be condensed to one single value; the characterization of the roughness of a wavy surface requires the use of at least two parameters, i. e., a frequency-like and an amplitude-like one [26].

In describing the properties of a liquid surface, the probably most important thermodynamic quantity is the surface tension, being the free energy cost of increasing the surface area by unity. On the molecular level, the surface tension originates from the virtual lack of attractive interactions on the surface molecules from the vapour side. Since this lack is primarily experienced by the molecules that are located right at the (intrinsic) surface, it is sensible to assume that surface tension is almost exclusively determined by the interfacial layer of the molecules. Furthermore, it is also clear that in the limiting case of zero entropy surface tension leads to a perfectly smooth liquid surface even on the molecular scale; the existence of the aforementioned capillary waves is of purely entropic nature. Therefore, one can expect that any decrease of the surface tension is accompanied by larger fluctuations, in other words, an enhanced roughness of the intrinsic liquid surface.

The development of various intrinsic surface analysing methods, such as ITIM, in computer simulations now opens the possibility of investigating in detail the relation between the surface tension and the molecular-scale roughness of the liquid surface. In this paper, we address this point by using, and partly re-analysing, surface roughness data from previously published simulations of a number of different liquid–vapour interfacial systems. For the purpose of the present study, the exact composition and thermodynamic state of the systems considered are irrelevant since we focus here solely on the relation between surface tension and surface roughness, both in terms of frequency and amplitude.

2. Methods

2.1. Characterizing the Surface Roughness

In order to quantify the roughness of the intrinsic liquid surface in computer simulations in terms of a parameter pair related to the frequency and amplitude of the surface, respectively, we proposed the following procedure [31]. The average normal distance $\overline{d}$ of two surface points (i. e., their distance along the macroscopic surface normal axis X) exhibits saturation behaviour as a function of their lateral distance l (i. e., their distance when their positions are projected orthogonally into the macroscopic plane of the surface, YZ). Fitting the function

$$\overline{d} = \frac{a\xi l}{a + \xi l} \tag{1}$$

to the calculated $\overline{d}(l)$ data then provides the frequency-like parameter ξ (i. e., the steepness of the $\overline{d}(l)$ curve at small lateral distances) and the amplitude-like parameter a (i. e., the value of $\overline{d}$ at large lateral distances) [31]. It should be noted that (1) is formally analogous with the Langmuir equation used for the description of adsorption isotherms [41].

Recently Lísal et al. [36] realized that the fit of the simulated data points can be substantially improved by using the following formula instead of (1) in the fitting procedure:

$$\overline{d} = \frac{a_{\mathrm{L}}\xi_{\mathrm{L}} l^{b_{\mathrm{L}}}}{a_{\mathrm{L}} + \xi_{\mathrm{L}}, l^{b_{\mathrm{L}}}}\,. \tag{2}$$

This description, being formally analogous with the Langmuir–Freundlich adsorption isotherm [42], uses three parameters among which a_{L} is an amplitude-like quantity whilst ξ_{L} and b_{L} are related to the frequency of the rough surface.

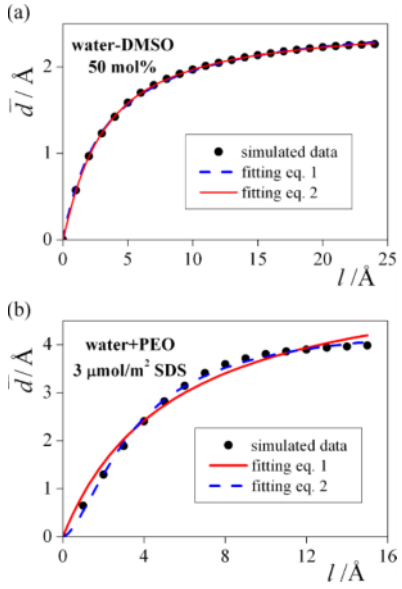

Fig. 1 (colour online). Average normal distance of two surface points as a function of their normal distance in the equimolar mixture of water and DMSO [33] (top panel) and in the water–PEO system containing SDS at the surface density of 3 μmol/m^2 [35] (bottom panel). The curves fitted to the simulated data with (1) and (2) are shown as red solid and blue dashed lines, respectively.

2.2. Description of the Systems Considered

In this study, we focus on the relation between the roughness of the liquid surface and surface tension, and hence the actual systems to be considered are of minor importance. To avoid the arbitrariness of the system chosen, however, we consider here four different sets of simulated systems, for which both surface tension and surface roughness data are available in the literature. The first two sets of systems consist of the liquid surface of water–methanol [28] and water–DMSO [33] mixtures of seven and nine different compositions, respectively, ranging from neat water to neat methanol or DMSO. The third set consists of systems of poly(ethylene-oxide) (PEO) dissolved in water and/or adsorbed at its surface, and sodium dodecyl sulphate (SDS) adsorbed at the liquid surface in seven different surface densities up to saturation [35].

For these three sets of systems, studied by our group, we reported previously both the surface tension values and the a and ξ roughness parameters. However, for the water–methanol mixtures no fitting to (1) was performed at that time, therefore we have recalculated here these roughness parameter values according to (1). Furthermore, we have now also determined the parameters a_L, ξ_L, and b_L by performing the fitting procedure proposed by Lísal et al. [36, (2)] for these three sets of systems.

Finally, the fourth set of systems is the liquid surface of three room temperature ionic liquids (RTILs) built up from 1-alkyl-3-methylimidazolium ([$C_n$mim]) cations and bis(trifluoromethylsulphonyl) imide ([T_f2N]) anions, simulated by Lísal et al. [36]. For these systems, besides the surface tension, only the a_L, ξ_L, and b_L roughness parameter values were reported; values for the roughness parameters a and ξ are not available. The four sets of systems considered show a great variety in chemical composition as well as in the size and polarity of the particles, which can give some confidence in the general validity of the conclusion that might be drawn from their analyses.

3. Results and Discussion

Two examples for fitting of the $\bar{d}(l)$ data are given in Figure 1, according to both (1) and (2). As it is seen, in the case of the equimolar mixture of water and DMSO, (1) yields an almost perfect fit to the simulated $\bar{d}(l)$ data, whereas in the case of the water–PEO system, containing SDS at 3 μmol/m^2 surface density, a noticeably better fit is obtained with the formula proposed by Lísal et al.

The dependence of a and ξ of (1) on the surface tension γ is shown in Figure 2, whereas that of a_L, ξ_L, and b_L of (2) is presented in Figure 3. As it is seen, the a and a_L amplitude parameters both exhibit a clear and continuous decrease with increasing surface tension. This decrease is rapid at small γ values, and the sensitivity of the amplitude parameters on the surface tension decreases rapidly as the latter value increases. The trend is very clear in the case of the $a(\gamma)$ data, as the simulated points all lie along a smoothly decreasing curve. The noise overlaying this trend is much larger in the case of a_L (see Fig. 3), in particular, in the intermediate surface tension range of 30 mN/m $< \gamma <$ 60 mN/m. The data obtained for the two sets of binary mixtures follow the same trend as those for the other two systems (and the same as the one seen for $a(\gamma)$), however, there seems to be a shift of about 10 – 20 mN/m between these two groups of $a_L(\gamma)$ data, which overlap in the 30 – 60 mN/m surface tension range.

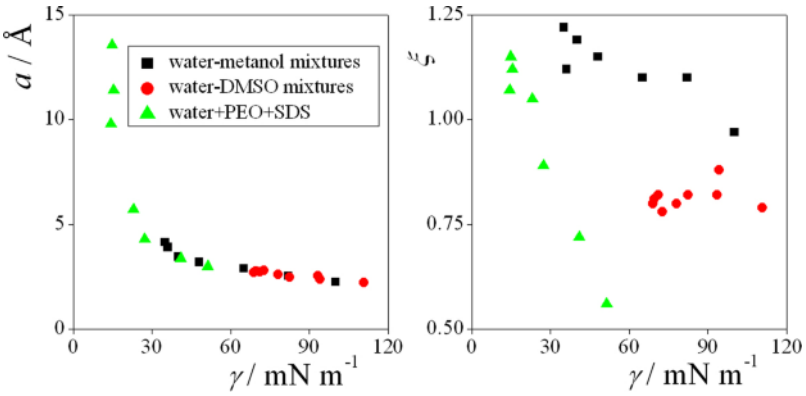

Fig. 2 (colour online). Dependence of the amplitude parameter a (left panel) and frequency parameter ξ (right panel) of (1) on the surface tension in water–methanol [28] (black squares) and water–DMSO mixtures [33] (red circles), as well as in water–PEO-SDS systems [35] (green up triangles).

The parameters ξ and ξ_L also show a clearly decreasing trend with surface tension within each set of systems. However, this trend seems to be system-specific, as no trend can be observed when the full set of data, corresponding to all 26 systems considered, are taken into account. This finding suggests that the frequency of the roughness of the liquid surface, besides the surface tension itself, strongly depends also on the composition of the system. This finding is understandable considering that ξ and ξ_L describe the slope of the $\overline{d}(l)$ curve at small lateral distances, i. e., at distances comparable with the size of the molecules in the system.

Finally, the parameter b_L does not show a clear trend with surface tension. To see whether the two frequency-related parameters of the Lísal formalism (2) are really independent of each other, we plotted the dependence of ξ_L on the values of b_L in the inset of Figure 3. Although the $\xi_L(b_L)$ data show a rather broad scattering around a trend line, their correlation is evident, indicating that the parameters of (2) are not completely independent from each other.

Since the obtained $a(\gamma)$ data (Fig. 2) as well as the two separate groups of $a_L(\gamma)$ data (Fig. 3) strongly resemble a hyperbola, we plotted also the reciprocal values of these amplitude parameters as a function of γ in Figures 4 and 5, respectively. The corresponding reciprocal amplitude vs. surface tension points indeed follow a straight line above the surface tension value of about 30 mN/m (in the case of $a_L^{-1}(\gamma)$ there are

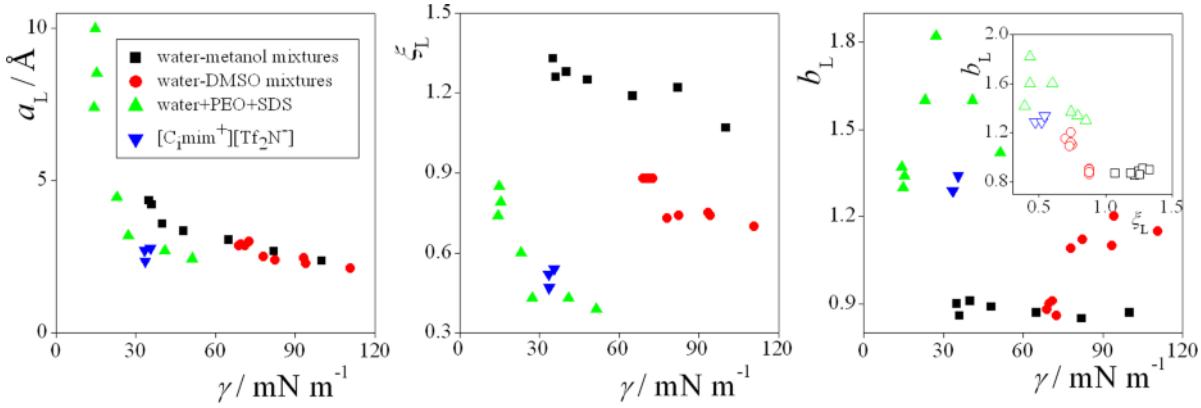

Fig. 3 (colour online). Dependence of the amplitude parameter a_L (left panel) and frequency parameters ξ_L (middle panel) and b_L (right panel) of (2) on the surface tension in water–methanol [28] (black squares) and water–DMSO mixtures [33] (red circles), water–PEO-SDS systems [35] (green up triangles), and RTILs [36] (blue down triangles). The inset shows the dependence of b_L on the other frequency-related parameter, ξ_L, in these systems (shown by open symbols).

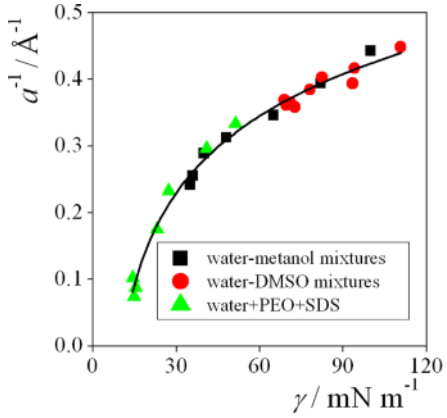

Fig. 4 (colour online). Dependence of the reciprocal of the amplitude parameter a of (1) on the surface tension in water–methanol [28] (black squares) and water–DMSO mixtures [33] (red circles), as well as in water–PEO-SDS systems [35] (green up triangles). The logarithmic function (see (3)) fitted to these data is shown as a solid line.

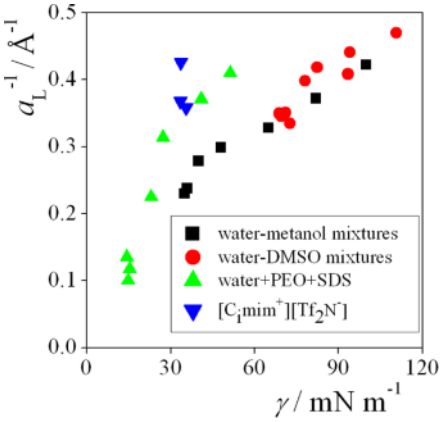

Fig. 5 (colour online). Dependence of the reciprocal of the amplitude parameter a_L of (2) on the surface tension in water–methanol [28] (black squares) and water–DMSO mixtures [33] (red circles), water–PEO-SDS systems [35] (green up triangles), and RTILs [36] (blue down triangles).

two, more or less parallel, trend lines), however, below 30 mN/m the reciprocal amplitude values drop rapidly below this line. The $a^{-1}(\gamma)$ data still follow a smooth curve, and can excellently be fitted by a logarithmic function in the form of

$$a^{-1} = A + B\ln(\gamma + C). \tag{3}$$

In understanding why the simpler and less accurate Langmuir-like formula of (1) results in amplitude values that are much more clearly related to the surface tension than what can be obtained by the Freundlich-like formula of Lísal et al., in spite of the fact that the latter formalism certainly results in a better fit of the simulated $\overline{d}(l)$ data, the observed correlation between ξ_L and b_L (Fig. 3) has to be taken into account. This clear correlation reveals that the improvement in the fitting of the simulated $\overline{d}(l)$ data when using (2) instead of (1) can largely be attributed to the extra fitting parameter in (2), which is not independent from the other two. In other words, the price paid for the better fit of the $\overline{d}(l)$ data is that the physical meaning of the parameters of (2) is somewhat lost. Since the three fitting parameters are not independent from each other, this loss of physical meaning affects also the amplitude parameter, although to a considerably smaller extent than the frequency-related ones.

It should also be noted that one of the two separate groups of $a_L(\gamma)$ data corresponds to systems consisting of small molecules of rather uniform sizes (i. e., water–methanol and water–DMSO mixtures), for which (1) already gives a practically as good a fit as (2), whilst the other group corresponds to systems consisting also of molecules of particular shapes, being considerably larger than the probe sphere used in the ITIM analysis (i. e., water–PEO-SDS systems and RTILs). In the case of these latter systems, the $\overline{d}(l)$ data are much more sensitive to the details of the ITIM analysis, and hence are more strongly affected by any possible inappropriateness of the particular choice of its parameters than in the case of the binary mixtures. However, these small inaccuracies caused by non-optimally chosen parameters are then also well fitted by (2) because of the presence of an extra fitting parameter, which, as mentioned, further destroys the physical meaning of these parameters.

Furthermore, an important source of small systematic errors in such analyses is the finite size effect, i. e., that because of the finite cross section of the basic simulation box, large amplitude capillary waves do not appear in the simulated system (and hence cannot be taken into account). This loss of the large amplitude capillary waves results in a smaller saturation value of the $\overline{d}(l)$ data than what would correspond to an infinite system. Again, due to the presence of an extra fitting parameter this error can be perfectly fitted by the formula of Lísal et al., while it can, at least partly, be compensated using the Langmuir-

like formula of (1), consisting of physically more meaningful parameters, in the fitting procedure (see Fig. 1).

All these considerations lead us to the conclusion that the amplitude parameter obtained by (1) is much more robust, being considerably less sensitive to the details and to a possibly slightly inappropriate choices of the ITIM analysis as well as to the error due to finite size effect, and hence it is much more closely related to the real physical meaning of surface roughness than that obtained by (2).

Furthermore, the parallel shape of the two groups of $a_L^{-1}(\gamma)$ data (and their parallel shape with the $a^{-1}(\gamma)$ data set) suggests that the small differences and inappropriate choices of some parameters in the ITIM analysis are primarily reflected in a shift of the $a^{-1}(\gamma)$ and $a_L^{-1}(\gamma)$ data, and hence among the three parameters of (3) the two shifting parameters, A and C, are far less important than the third value, B. The value of B resulted in about 0.2 Å^{-1} both for the two groups of $a_L^{-1}(\gamma)$ data, and also for the $a^{-1}(\gamma)$ data.

It should also be noted that the parameters a and a_L are not the amplitude of the wavy surface, just quantities that are related to it, as they represent the *average* normal distance of two sufficiently distant surface points, whilst the amplitude of the rough surface itself is the *largest* possible distance of two such points. This consideration further emphasizes the importance of the shape rather than the exact position of the $a^{-1}(\gamma)$ curve, i. e., the importance of parameter B with respect to A and C of (3).

Taking all these facts into account, we conclude from the analysis of the 26 data points of the four sets of simulations that the reciprocal amplitude of the molecularly-rough liquid surface is proportional to the logarithm of the surface tension for any kind of liquid systems.

Acknowledgement

This work is supported by the Hungarian OTKA Foundation under project Nos. 75328 and 104234.

[1] Y. R. Shen, Nature **337**, 519 (1989).
[2] G. L. Richmond, Chem. Rev. **102**, 2693 (2002).
[3] E. A. Raymond, T. L. Tarbuck, M. G. Brown, and G. L. Richmond, J. Phys. Chem. B **107**, 546 (2003).
[4] W. Gan, D. Wu, Z. Zhang, R. Feng, and H. Wang, J. Chem. Phys. **124**, 114705 (2006).
[5] M. J. Shultz, P. Bisson, H. Groenzin, and I. Li, J. Chem. Phys. **133**, 054702 (2010).
[6] V. Vogel, C. S. Mullin, Y. R. Shen, and M. W. Kim, J. Chem. Phys. **95**, 4620 (1991).
[7] D. Zimdars, J. I. Dadap, K. B. Eisenthal, and T. F. Heinz, J. Phys. Chem. B **103**, 3425 (1999).
[8] A. J. Fordyce, W. J. Bullock, A. J. Timson, S. Haslam, R. D. Spencer-Smith, A. Alexander, and J. G. Frey, Mol. Phys. **99**, 677 (2001).
[9] Y. Rao, Y. Tao, and H. Wang, J. Chem. Phys. **19**, 5226 (2003).
[10] J. Daillant and A. Gibaud, X-Ray and Neutron Reflectivity: Principles and Applications, Springer, Berlin 1999.
[11] D. Mitrinovic, Z. Zhang, S. M. Williams, Z. Huang, and M. L. Schlossman, J. Phys. Chem. B **103**, 1779 (1999).
[12] G. Luo, S. Malkova, S. V. Pingali, D. G. Schultz, B. Lin, M. Meron, I. Benjamin, P. Vanysek, and M. L. Schlossman, J. Phys. Chem. B **110**, 4527 (2006).
[13] I. Benjamin, Phys. Rev. Lett. **73**, 2083 (1994).
[14] T. M. Chang, K. A. Peterson, and L. X. Dang, J. Chem. Phys. **103**, 7502 (1995).
[15] R. S. Taylor, L. X. Dang, and B. C. Garrett, J. Phys. Chem. **100**, 11720 (1996).
[16] M. Tarek, D. J. Tobias, and M. L. Klein, J. Chem. Soc. Faraday Trans. **92**, 559 (1996).
[17] M. A. Wilson and A. Pohorille, J. Phys. Chem. B **101**, 3130 (1997).
[18] T. M. Chang, L. X. Dang, and K. A. Peterson, J. Phys. Chem. B **101**, 3413 (1997).
[19] I. Benjamin, Int J. Chem. Phys. **110**, 8070 (1999).
[20] F. Goujon, P. Malfreyt, A. Boutin, and A. H. Fuchs, J. Chem. Phys. **116**, 8106 (2002).
[21] L. X. Dang and T. M. Chang, J. Chem. Phys. **119**, 9851 (2003).
[22] R. S. Taylor and R. L. Shields, J. Chem. Phys. **119**, 12569 (2003).
[23] E. Chacón and P. Tarazona, Phys. Rev. Lett. **91**, 166103 (2003).
[24] P. Tarazona and E. Chacón, Phys. Rev. B **70**, 235407 (2004).
[25] E. Chacón, P. Tarazona, and J. Alejandre, J. Chem. Phys. **125**, 14709 (2006).
[26] L. B. Pártay, Gy. Hantal, P. Jedlovszky, Á. Vincze, and G. Horvai, J. Comp. Chem. **29**, 945 (2008).
[27] G. Hantal, M. Darvas, L. B. Pártay, G. Horvai, and P. Jedlovszky, J. Phys. Condens. Matter **22**, 284112 (2010).
[28] L. B. Pártay, P. Jedlovszky, Á. Vincze, and G. Horvai, J. Phys. Chem. B **112**, 5428 (2008).

[29] L. B. Pártay, P. Jedlovszky, and G. Horvai, J. Phys. Chem. C **113**, 18173 (2009).
[30] A. P. Wilard and D. Chandler, J. Phys. Chem. B **114**, 1954 (2010).
[31] M. Darvas, L. B. Pártay, P. Jedlovszky, and G. Horvai, J. Mol. Liq. **153**, 88 (2010).
[32] M. Jorge, P. Jedlovszky, and M. N. D. S. Cordeiro, J. Phys. Chem. C. **114**, 11169 (2010).
[33] K. Pojják, M. Darvas, G. Horvai, and P. Jedlovszky, J. Phys. Chem. C **114**, 12207 (2010).
[34] Gy. Hantal, M. N. D. S. Cordeiro, and M. Jorge, Phys. Chem. Chem. Phys. **13**, 21230 (2011).
[35] M. Darvas, T. Gilányi, and P. Jedlovszky, J. Phys. Chem. B **115**, 933 (2011).
[36] M. Lísal, Z. Posel, and P. Izák, Phys. Chem. Chem. Phys. **14**, 5164 (2012).
[37] Gy. Hantal, I. Voroshylova, M. N. D. S. Cordeiro, and M. Jorge, Phys. Chem. Chem. Phys. **14**, 5200 (2012).
[38] L. B. Pártay, P. Jedlovszky, and G. Horvai, J. Phys. Chem. C **114**, 21681 (2010).
[39] J. Chowdhary and B. M. Ladanyi, J. Phys. Chem. B **110**, 15442 (2006).
[40] M. Jorge and M. N. D. S. Cordeiro, J. Phys. Chem. C **111**, 17612 (2007).
[41] J. Langmuir, J. Am. Chem. Soc. **38**, 2221 (1916).
[42] H. Freundlich, Colloid and Capillary Chemistry, E. P. Dutton and Company, New York 1922.