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Molecular Dynamics Simulation of Surface Tension for Polar Molecules. Correction for Long-Range Interaction by Generalized van der Waals Theory†

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A new method, based on the Generalized van der Waals (GvdW) theory, for the correction of interaction truncation errors in the calculation of surface tensions from molecular dynamics simulations of polar liquids is presented and applied to SPC water. Several simulations using truncation radii ranging from 0.9 to 1.6 nm of a 4 nm thick SPC water slab are reported. The surface tension as obtained directly from the simulations grows with the cutoff from 56 to 80 mN m^{-1}, whereas the correction ranges from 24 to 8 mN m^{-1}, yielding resulting surface tensions between 74 and 88 mN m^{-1} with a minimum at a truncation radius of 1.2 nm. The minimum might reflect the shell structure in the liquid and the deviation from an ideal dipole (assumed in the GvdW calculation) for the SPC model.

The properties of fluids at equilibrium can be divided into two categories: (i) bulk properties and (ii) inhomogeneous fluid properties. Surface tension is, perhaps, the most important property of inhomogeneous fluids. Any kind of interface in the fluid is associated with a tension, i.e. a tendency to minimize the surface area. Most fundamentally the surface tension is a consequence of the fact that the fluid is stable in two forms corresponding to the bulk phases but unstable in the intermediate forms through which it must pass to connect physically the two stable bulk phases. The surface tension is of enormous practical importance, as is evident in all our everyday experiences with water whether it is as raindrops or dishwater. It is central to many industrial processes such as mineral flotation and oil recovery from depleted reservoirs. Surface tension is also a property of great fundamental interest, since it relates in a direct way to the strength and range of interactions in the fluid.

In comparison with bulk properties surface tension is more difficult to calculate, particularly for realistic molecular fluids.[1] However, molecular dynamics (MD) and Monte Carlo (MC) methods can be applied relatively straightforwardly. In molecular simulations one wants to model a macroscopic system by a very small system. One way to mimic a real system (which is 'infinitely' large on a simulation scale) is to use periodic boundary conditions. Usually the interactions are truncated at a certain distance ('cutoff radius') in order to make it possible to simulate such a system within reasonable computer time. This truncation will mainly affect the long-range electrostatic forces. An abrupt truncation could have devastating effects on the energy conservation in the simulation.[2] On the other hand, the smooth truncation schemes sometimes proposed will also affect the dynamics of the system in an unwanted way.[3] In order to include the long-range electrostatic interactions in a more or less approximate way there exist several methods. Among these is Ewald lattice summation,[4] which in principle consists of the summation over an infinite lattice of identical simulation boxes. Another method that is used[5] consists of dividing the system into several smaller subsystems. The interaction between non-adjacent subsystems is represented by a multipole expansion containing more terms the closer the subsystems are to each other. Both of these methods give a good representation of the distant electrostatic interactions but require large amounts of computer time. The Ewald sum, however, enhances the artificial periodicity applied to the system.

Whereas many isotropic properties are less affected by the use of a truncation, the surface tension is intrinsically affected.[6,7] Therefore, specific corrections have to be

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added. For non-polar systems the 'real' surface tension can be obtained from a simulation with a truncation of the force by applying a few correction terms[6,7] to the surface tension obtained directly from the pressures in different directions in the simulation. This relies on the assumption that the configurations obtained in the simulation with a truncation essentially are the same as in a simulation without truncation. In the case of Lennard-Jones potential an analytical expression for this correction under the assumption of a sharp interface has been obtained.[6]

In polar liquids the corrections are more difficult to calculate, since not only the spatial distributions of the molecules but also their orientations are of great importance. In order to estimate the surface tension for polar substances from simulations we have wanted to introduce simpler methods without losing much accuracy. A method that has proven useful to predict surface tension for non-polar molecules[8] is the so-called Generalized van der Waals (GvdW) theory.[9–11] It is, however, less accurate for polar interactions at short distances than for polar interactions at larger distances. In order to use the best of both methods we have combined the generalized van der Waals approach for long distances with explicit (atomic) simulation using forces truncated at a short distance.

The generalized van der Waals theory is probably the simplest free energy density functional theory accounting for all the major mechanisms in equilibrium fluid phenomena. At the heart of the theory is an estimate of entropy by a functional which incorporates excluded volume effects and resolves the range of these effects. Binding energy is obtained by a mean-field approximation. It is possible to incorporate temperature and density dependence of the effective hard-sphere diameter used in the theory and to quantize the theory in order to account for quantum effects in applications involving light fluids at low temperatures (see Ref. 10 and references cited therein).

We chose as a model system a slab of water with an approximate thickness of 4 nm. The main reasons for this choice was that water surfaces have been the subject of several studies with different water models with both Monte Carlo and molecular dynamics simulations.[12–18] Several simulations of water interfaces have been performed for different water models yielding different surface tensions, all differing from the experimental value of 72 mN m^{-1} at 298 K.[19] The quantum-chemically determined MCY[20] and CC[21] potentials both yield surface tensions that are far too low, 24 (MCY)[14] and 30 (CC)[15] mN m^{-1}, respectively. Effective potentials fitted to experimental properties of water normally yield much higher surface tensions. Thus a Monte Carlo simulation of ST2[22] water yielded a surface tension of 97 mN m^{-1},[13] whereas a surface tension of 132 mN m^{-1} at 325 K[16] was obtained for TIP4P[23] water and 124 mN m^{-1} for flexible SPC-water.[17] Of the water models studied, the rigid SPC model[24] and the SPC-E model[25] appear to give the best agreement with the experimental surface tension, 59 and 72 mN m^{-1}, respectively, with a rather short twin range cutoff (0.8/1.2 nm) according to our previous studies.[18] Since the uncertainties for all surface tensions from simulations are large, one should be careful before drawing any definite conclusions from these results. However, we believe that the main reason for the differences between the models is that surface tension is strongly dependent on the dipole moment; the leading term in the GvdW expression (see below) for the surface tension is proportional to the dipole moment to the power 4. The dipole moments differ by only 3% between SPC and SPC-E water, but anyway they give a difference in surface tension of about 20% according to simulation. Since we expected that including long-range forces would increase the surface tension we chose to use the standard SPC model which, with a short cutoff, yields a somewhat low surface tension, to study the effect of long-range forces on the surface tension.

Methods

Molecular dynamics simulations. Three molecular dynamics simulations using different truncation radii of a water slab containing 2111 SPC water molecules were performed. The SPC (Simple Point Charge) model[24] is a three-centre model in which the centre that represents the oxygen carries a charge of $-0.82e$, whereas the two centres representing hydrogen atoms carry a charge of $+0.41e$ each. These hydrogen centres are located 0.100 nm from the oxygen and form a tetrahedral angle of 109.47°. Only the oxygen carries a Lennard-Jones (6–12) potential with a well depth $\varepsilon = 0.638$ kJ mol^{-1} (corresponding to 76 K) and radius $\sigma = 0.317$ nm. The molecular dynamics simulations were made using a slightly modified version of the molecular dynamics package Gromos.[26]

During the simulations the pressure components in the x-, y- and z-directions were calculated separately using a molecular virial method. From the difference between the pressure parallel and perpendicular to the surface the surface tension was obtained, cf. Ref. 27. All simulation parameters are given in Table 1. The temperature was kept constant by coupling to an external bath.[28] With this form of temperature coupling the system centre-of-mass motion may be accelerated when the resulting temperature is less than the desired. In order to prevent this any system centre-of-mass motion was removed every time step.

The generalized van der Waals theory. The generalized van der Waals (GvdW) theory[29–36] is based on the original ideas of van der Waals[37] concerning energy and entropy of a fluid. A simple but accurate free-energy density functional has been developed and found capable of predicting both surface tension and interface width of a two-phase Lennard-Jones fluid anywhere from the small region close to the critical point, where the critical density

Table 1. Simulation parameters and thermodynamic averages.[a]

Simulation:	Long	Medium	Short	Double
r_{cut} nm	1.6	1.2	0.9	0.9/1.2
Number of H_2O	2111	2111	2111	2111
Simulation length ps	180	265	250	150
Analyzed period ps	50	200	200	100
Temperature coupling time ps	0.5	0.5	0.1	0.1
Solvent temperature K	299(3)	301(3)	300(3)	303(3)
Simulation surface tension mN m^{-1}	80(4)	60(2)	56(3)	60(5)

[a] The medium simulation was started from an equilibrated box of 216 water molecules that was multiplied and cut in order to form a cube with side 4 nm. This cube was placed in periodic simulation box with sides 10×4×4 nm resulting in modelling a 4 nm thick water slab with periodic repeat in the *y*- and *z*-directions. Also in the *x*-direction there was a periodic repeat representing the vapour phase. At start random velocities (taken from a Maxwell–Boltzmann distribution) were assigned at 250 K and the temperature slowly scaled to 300 K. The "Long" and "Double" simulations were started from a configuration of the "Medium" simulation taken out after 15 ps of equilibration, whereas the "Short" simulation was taken out from the "Double" simulation after 110 ps of simulation. In all simulations the time step was 2 fs. In the "Double" simulations forces between atoms more than 0.9 but less than 1.2 nm apart from each other were updated every 10 time steps. The numbers in parenthesis are RMS fluctuations. For simulated surface tensions in all simulations except "Long", RMS fluctuations of 50 ps subaverages are given within parenthesis. For the "Long" simulation RMS fluctuations of the 10 ps subaverages are given instead.

fluctuations dominate the behavior, to the triple point. An important advancement on the original van der Waals idea is the incorporation of non-local entropic phenomena through an analysis of the range of the excluded volume effect. The non-local entropy is found to reduce the surface tension.[32] The main idea in GvdW theory is to write the configurational partition function as a functional integral in which the integration variable is an appropriately coarse-grained particle density.[29] It is assumed that all important contributions to the integral come from a narrow region around a well defined particle density (corresponding to a cell structure). The theory reduces the role of the radial distribution function by setting up a free-energy density based on estimated entropic and energetic contributions.

We have recently reconsidered the optimal form of the GvdW functional for simple fluids and presented a new form called GvdW(HS-B_2) (hard-sphere second virial coefficient).[8] It is very simple, i.e. it yields a simple cubic equation of state and retains a density-independent form of the range of non-locality in the entropy, but provides an accurate equation of state and accurate interface properties for simple fluids. We have in mind to apply this functional to molecular fluids of greater complexity through the use of effective pair potentials developed on the basis of statistical-mechanical principles to represent asymmetric interactions in a simple spherically symmetric form.

We will study the gas–liquid interface in a fluid described by an effective Lennard-Jones potential. At first one may think that a spherically symmetric potential must fail in this application because of the orientational ordering that is expected to occur at the interface.[38–41] However, this turns out to be a very minor effect with respect to the magnitude of the surface tension as verified in several recent investigations by density functional methods where the orientations are explicitly incorporated.[42] In the present work we approach the problem of the 'cutoff' in MD simulation by using a long-range correction term calculated by the generalized van der Waals theory with an effective potential.

The effective potential. The use of effective pair potentials, which despite a simple spherically symmetric form represent asymmetric interactions, is old and widespread but rarely recognized and justified by detailed analysis. The best example in our present context is the Keesom potential representing orientationally averaged dipole–dipole interactions at sufficiently large separations.[43,44] More recently, Woodward and Nordholm[45] extended the work on the effective dipole–dipole potential showing that it yields reasonable bulk thermodynamic properties for hard spheres with embedded dipoles and for Stockmayer fluids, i.e. Lennard-Jones interacting particles with additional dipole–dipole interactions. It was shown possible to quantize the orientational correlations and incorporate the consequences of an ordering external field in the form of the effective potential.

In the effective potential we represent the orientational correlation in a polar fluid by a pair potential depending only on the separation r between the two molecules and the temperature. The effective potential method has been established in earlier papers,[31,46–49] so we will omit the details. The general strategy we have used is described below.

We start from a Stockmayer potential modified by turning the soft core into a hard sphere. The pair potential for our system of dipolar hard spheres with Lennard-Jones attraction is given by

$$U(r_{12}, \Omega_1, \Omega_2) = U_0(r_{12}) + U_d(r_{12}, \Omega_1, \Omega_2) \quad (1)$$

with

$$U_0 = \begin{cases} U_{LJ}(r_{12}), & r \geq \sigma \\ \infty, & r < \sigma \end{cases} \quad (2)$$

and

$$U_d(r_{12}, \Omega_1, \Omega_2) = -m^2 r_{12}^{-3} [2 \cos\theta_1 \cos\theta_2 - \sin\theta_1 \sin\theta_2 \cos(\phi_1 - \phi_2)] \quad (3)$$

Here U_{LJ} is the Lennard-Jones (12–6) potential, the subscript $i = 1,2$ labels the coordinates locating the centre of the hard sphere r_i and the angles specifying the direction of the dipole $\Omega_i = (\theta_i, \phi_i)$ with respect to the inter-hard-sphere axis $r_{12} = r_1 - r_2$. The hard-sphere diameter d is taken to be σ. $m = \mu/4\pi\varepsilon_0$ is the strength of the ideal point dipole which is embedded in the hard core of diameter σ. The hard-sphere separation is given by $r_{12} = |r_{12}|$. We introduce an effective potential in terms of the angle-averaged Boltzmann factor $\exp[-\beta U(r_{12}, \Omega_1, \Omega_2)]$

$$\exp[-\beta U_{eff}] = \int \frac{d\Omega_1}{\Omega} \int \frac{d\Omega_2}{\Omega} \exp[-\beta U(r_{12}, \Omega_1, \Omega_2)] \quad (4)$$

where β is the inverse reduced temperature $[\beta = (k_B T)^{-1}]$, k_B is Boltzmann's constant and T is the absolute temperature. We rewrite eqn. (4) and proceed by expanding the angular term in a power series of r^{-6}. From this we generate a series representation of the dipole–dipole interaction:

$$\beta U_{eff} = \beta U_0 + \sum_{n=1}^{\infty} (\beta m^2 r^{-3})^{2n} \frac{V_{2n}}{2n} \quad (5)$$

Values of the coefficients V_{2n} are given in Appendix A in Ref. 45, where the behaviour of the series for higher values of $\beta m^2 r^{-3}$ is also discussed. This series, when it converges ($0 < \beta m^2 r^{-3} \lesssim 2.4$), provides a numerically useful expression for $U_{eff}(r)$.

Now U_{eff} can be treated as an orientation-independent effective pair potential between two interacting hard spheres. For values of $\beta m^2 r^{-3} << 1$ we can truncate the series in eqn. (5) after the second term. The idea behind this is to have an asymptotic form of U_{eff} which only depends on $1/r^6$ and $1/r^{12}$:

$$U_{eff} = U_{LJ} - 1/3 \frac{\beta m^4}{r^6} + 0.01555 \frac{\beta^3 m^8}{r^{12}} \quad (6)$$

Since the additional terms due to dipole–dipole interaction will be of the same form as those already present in the symmetric potential, in our case an LJ (12–6) potential, we can add them together and make an effective LJ (12–6) potential with effective parameters σ_{eff} and ε_{eff}:

$$\sigma_{eff} = \left(\frac{\frac{c_2}{(k_B T)^3 4\varepsilon\sigma^6} + \sigma^6}{1 - \frac{c_1}{k_B T 4\varepsilon\sigma^6}} \right)^{1/6} \quad (7)$$

$$\varepsilon_{eff} = \frac{(4\varepsilon\sigma^6 - c_1/k_B T)^2}{4[4\varepsilon\sigma^{12} + c_2/(k_B T)^3]} \quad (8)$$

where $c_1 = -\frac{1}{3}m^4$ and $c_2 = 0.01555\, m^8$.

We have now obtained a representation of polar molecule interaction which is expected to be useful for dipole moments that are not too large or for large dipole moment and large separation (which is the case when we are dealing with calculations of water and a long-range correction).

The surface tension. The calculations of the surface tension are based on the fact that the particle density $n(x)$ depends only upon the variable x, which is the coordinate describing the location of planes in the direction orthogonal to the interface. In our case $n(x)$ is provided from the simulations. The surface tension is the cost in terms of free energy per unit area of establishing an interface,[8,32] i.e.

$$\gamma = \lim_{h \to \infty} \Delta\mathcal{F}(\alpha, h) = \lim_{h \to \infty} \mathcal{F}(\alpha, h) - \mathcal{F}^{(0)}(h) \quad (9)$$

where $[-h, h]$ is the finite interval on which the calculations are carried out. The finite range will introduce an error which can be made small by making h large and assuming that we have bulk densities outside the interval $[-h, h]$. The first term on the right-hand side is the free energy containing the interface and non-local interaction. This can be calculated as

$$\mathcal{F}(\alpha, h) = \int_{-h}^{h} dx f_c(x) n(x) \quad (10)$$

where $f_c(x)$ is the free energy per particle at x,

$$f_c(x) = -k_B T \left[\ln(n(x)^{-1} - \sigma^3) - \left(\frac{2\pi}{3} - 1\right) \sigma^3 \bar{n}(x) \right] + \frac{1}{2} \int_{-\infty}^{\infty} dx' n(x') \phi_{s1}(|x - x'|) \quad (11)$$

The relationship between the fine-grained n and coarse-grained particle densities $\bar{n}$, is

$$\bar{n}(x) = (3/4\sigma^3) \int_{x-\sigma}^{x+\sigma} ds n(s)[\sigma^2 - (s - x)^2] \quad (12)$$

The second term $\mathcal{F}^{(0)}(h)$ in eqn. (9) is the free energy of the corresponding interval of the fluid but with the range of entropic and energetic interactions set to zero. This will give us zero surface tension and a step function for the interface.

Combination of molecular dynamics simulation and Generalized van der Waals theory. The aim of this work is to approach the problem of force truncation in the MD simulations by using a long-range correction term calculated by GvdW theory. In the sections above we have noted the ability of GvdW theory and the effective po-

tential approximation to resolve the surface tension at long range. We will use this approach to calculate a long-range correction of MD simulation results for surface tension. The approach is to calculate the surface tension by the GvdW theory, without any cutoff in the effective potential and with the cutoff radius used in the simulation, and then take the difference between these as the correction. The interface profile used in the calculation is taken from simulation. The reduced potential in one dimension acting between planes parallel to the interface (obtained by integration of the Lennard-Jones 6–12 potential) is defined by:

(i) without truncation

$$\phi_{s1}(x) = \begin{cases} -6\pi\varepsilon_{eff}\sigma_{eff}^2/5, & |x| \le \sigma \\ 4\pi\varepsilon_{eff}[\frac{1}{5}(\sigma_{eff}/x)^{10} - \frac{1}{2}(\sigma_{eff}/x)^4] & |x| > \sigma \end{cases} \quad (13)$$

(ii) with truncation

$$\phi_{s1}(x) = \begin{cases} 4\pi\varepsilon_{eff}\sigma_{eff}^2\{[\frac{1}{5}(\sigma_{eff}/r_{cut})^{10} - \frac{1}{2}(\sigma_{eff}/r_{cut})^4] - \frac{3}{10}\}, & |x| \le \sigma \\ 4\pi\varepsilon_{eff}\sigma_{eff}^2\{[\frac{1}{5}(\sigma_{eff}/r_{cut})^{10} - \frac{1}{2}(\sigma_{eff}/r_{cut})^4] \\ \quad - [\frac{1}{5}(\sigma_{eff}/x)^{10} - \frac{1}{2}(\sigma_{eff}/x)^4]\}, & \sigma < |x| \le r_{cut} \\ 0, & |x| > r_{cut} \end{cases} \quad (14)$$

By subtraction of the surface tension obtained by use of eqn. (14) from that obtained by eqn. (13) we will account for the long-range ($x > r_{cut}$) contribution to the surface tension.

Results and discussion

We start here by presenting the pure MD results, then proceed to the Generalized van der Waals correction and finally discuss the outcome of the combination of both. The results for the surface tension at different cutoff radii are given in Table 1. As expected, the uncorrected surface tension increases with increasing cutoff radius. The surface tension is somewhat underestimated at short cutoff radii, whereas it is slightly overestimated at the long cutoff radius as compared to experimental results, but altogether our results confirm that the SPC model gives a decent agreement with experimental surface tension, better than any other water model known to us. When comparing the simulated values to the experimental surface tension one should remember that the water model was fitted to experimental properties using a cutoff of 0.85 nm.[24] A more unexpected result is that the increase between the short and medium simulations is much smaller than between the medium and large simulations. This will be discussed further below.

In the double simulation of SPC water a twin range cutoff, similar to many other MD simulations, was used. This means that interactions between atoms within a smaller distance from each other than the inner radius are updated at every time step, whereas interactions at intermediate distances are updated only once in a few (in our case 10) time steps. In this simulation the two radii were 0.9 and 1.2 nm, and the surface tension obtained was 60 ± 5 mN m^{-1}, i.e. very close to the medium simulation (with a 1.2 nm cutoff). These results are in good agreement with our earlier simulation of SPC water with a double cutoff (0.8 and 1.2 nm),[18] where a surface tension of 59 ± 7 mN m^{-1} was obtained. The results also indicate that thermodynamic (but not necessarily dynamic) properties in a twin-range simulation are somewhat closer to the properties of a system with the longer cutoff than to a system with the shorter cutoff. Since the differences in surface tension between these systems are small, this result is, however, not beyond doubt. Energy conservation is much worse in a system with a double cutoff than in a system with a simple short cutoff, as can be seen from the higher temperature with the same coupling time to the external bath. This effect has been noticed in earlier simulation studies with multiple cutoffs[50] and could in our opinion be due to the step-wise change in forces at the time steps when the long-range forces are updated (reflected in a stepwise decaying force correlation function).[51] In the light of these results we abstain from using the double cutoff simulation in the further discussion.

In the GvdW calculations the dipole strength corresponding to SPC water is $15.27\sigma^3\varepsilon$. The calculations are carried out at the temperature 300 K. In Table 2 we show the results for three different cutoff distances: short, medium and long. The first column shows the cutoff, the second the calculated surface tension with cutoff, the third the surface tension without any cutoff, the fourth the difference between these and the fifth the surface tension from the simulation corrected for the long-range interaction. We can see that as we decrease the cutoff the correction decreases.

The trends in both the simulation results and the GvdW correction are intuitive: the larger the cutoff ra-

Table 2. Long-range correction of MD simulations.[a]

Simulation	r_{cut} /nm	$\gamma_{GvdW}(r_{cut})$ /mN m^{-1}	γ_{GvdW} /mN m^{-1}	$\Delta\gamma_{GvdW}$ /mN m^{-1}	$\gamma_{Sim}+\Delta\gamma_{GvdW}$ /mN m^{-1}
Short	0.9	29.4	55.4	26.0	82
Medium	1.2	39.6	53.8	14.2	74
Long	1.6	43.0	51.0	8.0	88

[a] The first column shows the cutoff, the second and the third the surface tension calculated with GvdW with and without the cutoff, the fourth the long-range correction and the fifth the surface tension with long-range correction.

dius, the larger the surface tension from the simulation and the smaller the GvdW correction. However, whereas the results from the short and the long simulations are in decent agreement with each other, the resulting surface tension from the medium simulation is much smaller. This result may partially be due to deficiencies in the simulation, such as insufficient equilibration, or to inappropriate approximations in the GvdW calculation. Since the surface tensions and other thermodynamic entities appear stable in all simulations we do not believe that a lack of equilibration is the culprit, even though some slow processes might be involved in the change of interface profile. This argument applies also to statistical fluctuations (with exception for 'very long-lived' ones). The GvdW correction is based on a mean field approximation ignoring the radial correlations in the fluid. This may be a less well founded approximation in the case of water than most other fluids. The treatment of orientational correlations by pairwise perturbation theory is also an approximation open to question. Another possible explanation is that the water molecules are no ideal dipoles but an assembly of three-point charges within a Lennard-Jones sphere, whereas the GvdW assumes the water molecules to be ideal dipoles. In order to resolve the origin of the surface tension variation we intend to perform further studies of both water and simple Stockmayer-type molecules in the future.

Conclusions

We have reported an attempt to calculate the surface tension of water including an account of interactions at all separations by the use of a correction of MD results for long-range interactions by use of a density functional method. Given the notorious difficulty of such surface tension calculations for the highly structured water fluid the results are encouraging. We get a more consistent and plausible surface tension with our long-range GvdW correction. There is still a considerable variation in the corrected results which needs investigation, but we are encouraged to believe to that it may be possible to speed up simulations of realistic fluids by use of a relatively short cutoff combined with long-range correction. The method can be applied to other fluids and properties providing substantial improvements in efficiency.

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