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Aqueous solutions of ionic liquids: study of the solution/vapor interface using molecular dynamics simulations

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We performed a detailed molecular dynamics study of the interfacial structure of aqueous solutions of 1-butyl-3-methylimidazolium tetrafluoroborate in order to explain the anomalous dependence of the surface tension on concentration. At low concentrations the surface tension decreases with concentration. At higher concentrations the surface becomes saturated; a plateau is observed in simulations with a non-polarizable force field while a possible increase is detected in simulations with a polarizable force field. The structure is characterized by a surplus of cations at the surface (with hydrophobic butyl chains pointing toward vacuum) which at low concentrations is only partly compensated by the anions because of asymmetric solvation. A more hydrophobic 1-butyl-3-methylimidazolium hexafluoroarsenate is also simulated for comparison.

1. Introduction

Room-temperature ionic liquids or shortly ionic liquids (IL) are defined as salts that are molten at ambient conditions. They have attracted interest in recent years due to their favorable chemical and physical properties,1 being thermally stable solvents with negligible vapor tension at room temperature. ILs have been shown to have applicability in a wide range of areas including separation processes, catalysis and electrochemistry.2 ILs are usually composed of large asymmetric organic cations and inorganic or organic anions. The most extensively studied family of ILs contains 1-alkyl-3-methylimidazolium [CnMIM] cation combined with PF6-, BF4-, Cl-, etc.

A number of experiments have been carried out to gain fundamental understanding of bulk properties of ionic liquids.1 Although less frequent, several studies focused also on the characterization of surfaces of ionic liquids including direct recoil spectroscopy (DRS),3–5 neutron and X-ray reflection,6–8 surface tension,4,7,9 sum-frequency generation spectroscopy (SFG),9–14 and photoelectron spectroscopy.15–18 Various aspects of surface chemistry of ILs have been recently reviewed.19 Corresponding theoretical studies include quantum chemistry calculations,15,20,21 molecular dynamics (MD) simulations of IL/gas interface22–28 and IL/water interface.29–32 Wipff and coworkers performed series of IL/water mixing and demixing MD simulations and discussed the suitability of several models.29,31,32 Lynden-Bell and coworkers33 reported excess chemical potentials of water dissolved in dimethylimidazolium chloride.

For the purposes of MD simulations a number of force fields have been developed either on the basis of the Lennard-Jones potential27,28,34–42 or the Buckingham (exp-6) potential.34 Yan and coworkers developed a polarizable model of 1-ethyl-3-methylimidazolium [EMIM] nitrate and discussed the influence of polarizability on the IL/gas interfacial properties.34,28

In this study we focus on surfaces of aqueous solutions of ILs based on 1-butyl-3methylimidazolium [BMIM]. Interfacial properties of simple salts dissolved in water have been documented to be different than those in bulk with strongly specific surface ion propensities.33–45 The situation is expected to be even more intricate for ILs dissolved in water, since ILs involve more bulky complex ions. Here, different effects such as hydrophobicity, polarization, interactions with counterions, etc., can contribute to the surface behavior of these ions.

The properties of the IL-water interfaces may be strongly influenced by the nature of the cation and anion. Ionic liquids containing anions such as PF6-, AsF6- or Tf2N- are hydrophobic, while those with anions like BF4-, NO3- or ClO4- are water miscible.1 Water molecules preferentially interact with anions of these ILs,46 the interface then becomes strongly structured. In the case of pure imidazolium-based ionic liquids, the aromatic rings of the cations are preferentially aligned along the surface and the butyl chains point into vacuum.11,47 The effect of temperature and of the choice of the anion on the cationic orientation is small.23,48 Water affects the surface of hydrophobic ionic liquids more than the surface of the hydrophilic ones. The cationic ring of the hydrophobic ionic liquids is reoriented along the surface normal but remains parallel for the hydrophilic ones.47

Bowers et al.7 investigated the surface tension of aqueous solutions of imidazolium-based ionic liquids. The surface tension decreases until it reaches (at a certain concentration interpreted with the help of small-angle neutron scattering results as the critical aggregation or micellar concentration) a plateau or it slowly increases from this point. However, for [BMIM]BF4, which is of our main interest, this increase is
barely discernible; the critical molar fraction being about 0.015. Sung et al.\textsuperscript{9} observed the minimum at about the same molar fraction of [BMIM]BF\textsubscript{4} (0.016) and a small but significant increase as the concentration of IL increases. From SFG they inferred that at low concentrations only cations cover the surface (with butyls pointing out) while at higher concentrations the anions begin to appear at the surface, compensate the cations and the resulting large electrostatic interactions cause the surface tension to increase.

Here, we aim at understanding this phenomenon at a molecular level. To this end we performed a detailed MD study of the interfacial structure of aqueous solutions of 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM]BF\textsubscript{4}) and 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM]PF\textsubscript{6}). MD simulations have potential pitfalls, many of them caused by inaccuracies of the employed interaction potential. An important question in this context is whether the usual pairwise-additive force fields ignoring polarizability are suitable to model fluids dominated by electrostatic interactions like ionic liquids. Inclusion of polarizability was found to be important in the case of pure 1-ethyl-3-methylimidazolium nitrate,\textsuperscript{24,28} as well as for an accurate description of simple inorganic salts/water interfaces.\textsuperscript{44} In the present study we compare the results for aqueous ILs obtained using a non-polarizable vs. polarizable force fields and discuss the effect of polarizability on the interfacial properties.

2. Computational details

2.1 MD with a non-polarizable force field

Ionic liquids [BMIM]BF\textsubscript{4} and [BMIM]PF\textsubscript{6} were modeled by an all-atom pairwise force field.\textsuperscript{41} For water we used the new TIP4P/2005 model tailored to condensed phase calculations.\textsuperscript{49}

The standard slab geometry\textsuperscript{50} was used for the interface. The slab is perpendicular to the z-axis of the simulation cell which is periodic in the x and y directions. The sizes of the simulation box were fixed during simulation (NVT ensemble) to $L_x = L_y = 30 \text{ Å}$ and $L_z = 75 \text{ Å}$; this setup minimizes the influence of finite-size effects (capillary waves).\textsuperscript{51} The number of molecules was set so that the slab width be about 30 Å. Since the molar volume of RTIL is approximately ten times the molar volume of water, $n_{iw}$ ion pairs (from 0 to 64) were dissolved in $1000/C_0$ water molecules. The total mole fraction ($\gamma$) of the ionic liquid was set so that the slab width be about 30 Å. For these simulations a polarizable force field was employed. For [BMIM]$^+$ and BF$^-_4$ we used the general Amber force field (GAFF) parameter set\textsuperscript{56} while for water the POL3 model was employed.\textsuperscript{57} A force field based on GAFF was shown to provide a good description of bulk and surface properties of a pure IL recently.\textsuperscript{58} Partial charges for the ions were evaluated with the standard RESP procedure.\textsuperscript{59} Polarizable molecular dynamics simulations were performed using the Amber 8 program and the induced dipoles were converged in each step using a self-consistent procedure with the default convergence criterion.\textsuperscript{60} Note that the polarizable force field employed is not constructed as a non-polarizable one with just polarizabilities added because adding polarizabilities affects a balance of other terms (partial charges, London forces).

2.2 MD with a polarizable force field

Polarizable molecular dynamics simulations of aqueous solutions of the ionic liquid [BMIM]BF\textsubscript{4} were also performed in the slab geometry.\textsuperscript{60} We used a unit cell which contained 863 water molecules. The total mole fraction (i.e., the number of ion pairs divided by the total number of molecules) of the ionic liquid solute varied from 0.002 to 0.05. The size of the rectangular unit cell was approximately $30 \times 30 \times 100 \text{ Å}$, and the 3D periodic boundary conditions were applied.\textsuperscript{52}

Non-bonded interactions were cut off at 12 Å with long-range electrostatic interactions accounted for using the particle mesh Ewald procedure.\textsuperscript{55} A time step of 1 fs was employed and all bonds involving hydrogen atoms were constrained using the SHAKE algorithm.\textsuperscript{52} The systems were first subjected to energy minimization for removing possible bad contacts and then equilibrated for 500 ps. Production runs of at least 1.5 ns were performed in the NVT ensemble at 360 K.

For these simulations a polarizable force field was employed. For [BMIM]$^+$ and BF$^-_4$ we used the general Amber force field (GAFF) parameter set\textsuperscript{56} while for water the POL3 model was employed.\textsuperscript{57} A force field based on GAFF was shown to provide a good description of bulk and surface properties of a pure IL recently.\textsuperscript{58} Partial charges for the ions were evaluated with the standard RESP procedure.\textsuperscript{59} Polarizable molecular dynamics simulations were performed using the Amber 8 program and the induced dipoles were converged in each step using a self-consistent procedure with the default convergence criterion.\textsuperscript{60} Note that the polarizable force field employed is not constructed as a non-polarizable one with just polarizabilities added because adding polarizabilities affects a balance of other terms (partial charges, London forces).
3. Results and discussion

3.1 MD with a non-polarizable force field

The density profiles, as depicted in Fig. 1–3, are histogrammed distributions of selected atoms of the IL across the slab. In order to enable an easy comparison of atoms of different concentrations in one figure, we normalize the density profiles to the same integral; in other words, the areas under the curves are the same. In addition, we smooth the graphs by a convolution with a trapezoid of half-width of 0.75 Å.

These results give us the first insight into the structure of the interface. The density profiles are somewhat asymmetric; more at lower temperature and for dilute solutions. On the one hand, this asymmetry is a consequence of slow diffusion: Ions once adsorbed at the surface dissolve only slowly in the bulk and also slowly diffuse to the opposite side of the slab. On the other hand, sizable diffusion does occur on the present timescale because the initial distribution was symmetric.

In order to assess the convergence, the trajectories of individual ions were monitored. Fig. 4 shows the trajectories of 8 cations (atom N1) and 8 anions (B) in the system of Fig. 1; the thermal noise was filtered out by a trapezoidal filter of half-width 0.2 ns. It is seen that “hopping” of ions between both metastable surface positions is scarce.

In order to quantify the hopping kinetics, several approaches are possible. Direct calculation of the time autocorrelation function of the $z$-coordinate gives a set of $N$ functions for each cation and $N$ functions for each anion. The individual functions are scattered because a few hoppings are not sufficient to yield an accurate correlation function. Several correlation functions decrease very fast to zero (short correlation time). These functions correspond to ions which stay at the same layer and only randomly oscillate (with short typical time) around this metastable equilibrium value. The scattered bunch of functions give us an estimate of the correlation time; it is defined by an integral and can be obtained more simply by the time when the function value drops to $1/e$ because the functions are close to a decreasing exponential. The correlation times obtained in this way are in the range from 0.5 to 1 ns at 360 K which is less than the total simulation length of 4 ns. At 300 K the correlation time increases to about 2 ns and the...
results are more affected by poor equilibration. Anions are faster than cations.

Another approach is based on counting the hopping events. We define the hopping event as a trajectory which crosses the slab middle layer of width $D_z = 10 \text{Å}$; since the slab is about 30 Å thick, an ion must flip from the top third to the bottom third (or in the opposite direction) to be counted. Note that the dependence of the number of hoppings on $D_z$ exhibits a shoulder at roughly $D_z = 10 \text{Å}$ which suggests that this choice is optimal. The results are shown in Fig. 5. They are given as the number of flips per one ion pair; in turn, the low concentration results are subject to considerable uncertainty. At low concentrations of $[\text{BMIM}]\text{BF}_4$, there is about 1 flip ns$^{-1}$ for anions at 360 K and 0.3 flip ns$^{-1}$ at 300 K. The cations almost do not move at very low concentrations (they are stuck at the surface) and reach a maximum hopping rate slightly smaller than the anions. From a mole fraction about 0.02, the flipping rate decreases. This phenomenon includes both the changes in diffusivity and the propensity of ions to the surface. The kinetics of $[\text{BMIM}]\text{BF}_4$ is slower.

Therefore, for the used size of the simulation cell, $30 \times 30 \text{Å}$, the simulation time is just about sufficient. We have tested also larger cells, $45 \times 45 \text{Å}$, but it is hard to reach sufficiently long simulation times (in the Ewald summation, the time scales as $N^{3/2}$ and at the same time the diffusion time scales proportionally to the square of the slab width). The results with the larger systems are, therefore, unreliable and with the exception of pure water we do not present them.

It can be seen that the ions are preferentially concentrated at the surface. At low concentrations the propensity of cations is higher, as slightly more anions remain in the bulk. More details of the charge distribution are apparent from charge density profiles, both of individual molecules and the total charge density profile (see Fig. 6 and 7). They are given in units of $1 \text{me/Å}^3 = 1.6022 \times 10^9 \text{C m}^{-3}$. At higher concentrations the charges of the cations and of the anions effectively compensate each other. The total charge density profile (averaged charge profile across the slab) shows a small excess of positive charge at the surface (of surface charge density roughly 1 me Å$^{-2}$) followed by a negatively charged subsurface layer (the surface density of the dipole moment is about 0.03 D Å$^{-2}$); this is the same behavior as that observed for pure water. At lower concentrations there are slightly more cations than anions at the surface and this difference is partially compensated by orientation of water dipoles, in accordance with the work of Sung et al. He assumed that the BF$_4^-$ anions start to appear at mole fraction 0.016 until the anions and cations are equally populated at 0.05 or higher. The total charge density profile is nevertheless similar to that for higher concentrations. In other
Hydrogen bonding patterns at the interface and the energy/entropy interplay connected with the hydrogen-bond network can be analyzed by the concept of dangling hydrogens.62 A dangling hydrogen is defined as a hydrogen which is not engaged in any hydrogen bond; a hydrogen bond is defined for this purpose (from several available definitions) as an intermolecular O–H pair closer than 2.45 Å (this is a position of a deep minimum on the O–H correlation function). For pure water the number of dangling hydrogens at the surface layer is approximately twice the bulk value. We have found that the presence of ionic liquid slightly increases the concentration of dangling hydrogens in the bulk fluid but decreases it at the surface layer (another reason for the ionic liquid to move to the surface) so that the distribution is almost uniform across the slab.

The surface tension and structure of the [BMIM][BF₄]–water and [BMIM][PF₆]–water systems were studied at total mole fractions ranging from 0.004 to 0.15 and from 0.004 to 0.03, respectively.

Because of a propensity of the ions for the surface, the bulk concentration of the ionic liquid differs from the total concentration. The bulk mole fractions were determined from the density profiles at the center of the slab (see Table 1 and 2) and are a subject of statistical errors of roughly 10% (and that is why we will not use them in the figures of the surface tension). The total vs. bulk concentration plot in Fig. 9 shows that at bulk concentration of [BMIM][BF₄] about 0.01–0.02, the surface layer becomes saturated and at higher concentrations the surplus of ions is about the same (the line is parallel to the diagonal). The bulk concentration of [BMIM][PF₆] is lower. We have not simulated the high concentration range, but this behavior is consistent with low solubility of [BMIM][PF₆] in water, in agreement with experiment.

The surface tension in dependence on the total ionic liquid concentration is plotted in Fig. 10. We can see that the surface tension of [BMIM][BF₄] solution drops from that of the pure TIP4P/2005 water to lower values. In case of higher-temperature results, which are subject to smaller errors, it is clearly seen that a plateau is reached at a total molar fraction of about 0.04 (bulk 0.03); the lower-temperature results are not convincing. This behavior is closer to the experimental results in ref. 7 than in ref. 9. The results of [BMIM][PF₆] show

![Fig. 5](image1.png)  
**Fig. 5** Ion hopping between both surfaces as a function of total concentration. Full symbols and solid lines: cations, open symbols and dotted lines: anions; top curves: 360 K, bottom curves: 300 K.

![Fig. 6](image2.png)  
**Fig. 6** Charge density profiles of [BMIM][BF₄] at 360 K; total mole fraction 0.009 (left) and 0.045 (right). Simulation with non-polarizable force field.
a similar decrease in the considered range of concentrations; higher concentrations would probably show layers of immiscible IL at the water surface and a determination of surface tension would require a different simulation methodology.

The interpretation of the surface tension results is consistent with the saturation of the surface layer. Direct determination of the saturation mole fraction gives a value in agreement with both experiments, from surface tension we get a larger value (about 0.03), but the difference can still be explained by statistical errors. The non-polarizable model does not reproduce the minimum observed by the later experiment.

In addition to this traditional explanation valid also for higher alcohols in water, electric forces may modify the picture. At first glance, the density profiles and other structure

### Table 1

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data look qualitatively the same irrespective of concentration. A detailed view reveals a fine balance between the competing phenomena. The ionic liquid at low concentrations acts as a surfactant because hydrophobic (not charged) butyl groups do not prefer water environment, as follows from the atom density profiles and orientation order. No apparent micro-aggregation of butyls was observed in the bulk, only some degree of ion pairing, but we have not studied this phenomenon quantitatively.

As soon as the cations with butyl groups move towards the surface, the anions then must follow the cations in order to re-establish local electroneutrality. However, at low concentrations there is a small surplus of cations at the surface and polarization of water (orientation of water dipoles toward the bulk) is sufficient to maintain total neutrality, or at least to hide the anions enough below the surface so that they are not seen in the SFG signal.9 As the concentration increases, more anions must join the cations and the surface layer becomes saturated with both ions and further adding IL to the solution does not change the surface properties but (in case of soluble [BMIM]BF₄) influences the bulk.

Common (not surface-active) electrolytes exhibit a moderate increase of the surface tension with concentration, a phenomenon traditionally explained by strong ion-water association63,64 (more ions mean stronger ion–ion and ion–water interactions in the bulk as well as close to the surface). The question whether this increase eventually wins over the decrease caused by hydrophobicity of cations remains open; the non-polarizable results do not confirm this.

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**Table 2** Surface tension of [BMIM]PF₆ as a function of ionic liquid mole fraction obtained from molecular dynamics simulations with a non-polarizable force field.

![Fig. 9](image_url) **Fig. 9** Total simulation density vs. bulk density. Full circles: [BMIM]BF₄, open circles: [BMIM]PF₆; full line: 360 K, dotted line: 300 K.

![Fig. 10](image_url) **Fig. 10** Left: the simulated surface tension of [BMIM]BF₄ as a function of total concentration in the simulation box; full circles: a non-polarizable model (full squares: larger system), open circles: a polarizable model. Right: the simulated surface tension of [BMIM]PF₆ using a non-polarizable model.
The structure of molten salts and aqueous electrolytes is dominated by electrostatic interactions and repulsive forces, as exemplified by the so-called primitive model of electrolytes, i.e., charged hard spheres. Even the structure of water is dominated by short-range hydrogen bonds which are of electrostatic origin (or at least can be modeled by partial charges). This picture extends to ionic liquids with molecules of a complex shape, e.g., the energy of an optimized pair BMIM–BF₄ in vacuum is about 20 times lower than the energy minimum with all charges turned off and only dispersion forces are taken into account. A similar Coulomb/dispersion ratio appears in pure ILs. The presence of water as a solvent may modify this picture (and hinders the separation of different energy contributions). If water is treated as a dielectric continuum, the charge–charge attraction is scaled down 80 times (at 300 K) which is more than the above ratio. However, the above ratio is valid for an ionic pair at close contact and the London forces decrease very fast with the distance. In addition, bulky imidazolium rings are both positively charged and cannot appear close together to interact by dispersion forces. The standard explanation of the hydrophobic effect again accentuates the hydrogen bond network in water and not dispersion interactions. We therefore summarize that the leading microscopic forces in the explanation of IL solutions in water are electrostatic forces with repulsion along with the hydrogen bonding network in water.

3.2 MD with a polarizable force field

The structure and surface tension of the [BMIM]BF₄ aqueous solutions were studied at total mole fractions ranging from 0.002 to 0.05.

Fig. 11 depicts the density profiles for the two extreme concentrations investigated (0.002 and 0.05 mole fraction). At all concentrations both ions exhibit a much more pronounced surface propensity than in the case of the nonpolarizable model. At 0.002 mole fraction the ions practically do not visit the bulk region of the slab on the timescale of the simulation. At 0.05 mole fraction the ions populate the whole slab with peak surface enhancement of a factor of 3–4 compared to the bulk. It can also be seen from Fig. 11 that—similar to the nonpolarizable case—the peak of the terminal carbon of the aliphatic chain of the [BMIM]⁺ cations is shifted toward the vapor phase by 5 Å compared to the nitrogen peak. This indicates that these cations are strongly oriented in the surface layer with the hydrophobic chain pointing away from the bulk solution. On the contrary, the positively charged ring points toward the solution and its density peak overlaps with that of the counter-ions.

Accounting for the (partial) charges on the individual atoms the above density profiles can be translated to charge profiles displayed in Fig. 12. At a mole fraction of 0.002 the interfacial charge distribution is dominated by oriented water molecules, with positive dangling hydrogens pointing into the gas phase. Nevertheless, the signal from the ions is non-negligible with the cationic and anionic signals cancelling each other, but not perfectly at low concentrations, with more anions than cations in the bulk. At a mole fraction of 0.05 the charge distribution in the solution is already dominated by the [BMIM]⁺ and BF₄⁻ ions. Again, the cationic and anionic distributions cancel each other. In addition, as follows from the induced dipole density profiles (not shown), the induced dipoles tend to cancel the effect of the permanent charges, enhancing the effect of reorientation of water permanent dipoles.

The kinetics of the hopping between layers is slightly faster than in the nonpolarizable case which is in agreement both with higher diffusivity of the POL3 model itself and with faster (i.e., more realistic) diffusion of ILs modeled with a polarizable force field. Finally, we have used the simulations with a polarizable force field to evaluate the surface tension as a function of ionic liquid concentration in the 0.002–0.05 mole fraction range (Table 3 and Fig. 10). Despite the fact that the present water potential (POL3) underestimates the surface tension, the experimental trend upon adding the ionic liquid is well reproduced. Namely, the surface tension steeply decreases (faster than in the non-polarizable case) up to about 0.02 total mole fraction, after which it starts to slowly rise again. The statistical inaccuracies are approximately the same as for the non-polarizable model and, therefore, the differences between the...
two force fields are at the limit of confidence. It is, however, known that polarizability enhances the stability of bulky ions at the surface;\textsuperscript{43,44} therefore, this sharper decrease and a possible minimum around 0.02 are likely to occur. To summarize, we need polarizability to explain the anomalous minimum of the surface tension in dependence on concentration.

4. Conclusions

We performed molecular dynamics simulations with both non-polarizable and polarizable force fields for aqueous solutions of [BMIM]BF\textsubscript{4} and [BMIM]PF\textsubscript{6} ionic liquids. We reproduced the experimentally observed decrease in surface tension in dilute solutions of ionic liquids and related it to the surface propensity of hydrophobic 1-butyl-3-methylimidazolium cations (acting as a surface active species), accompanied only partly by anions; the surplus of positive charge is compensated by polarizing water. The butyl chains tend to point towards vacuum and the imidazolium rings are preferentially parallel to the surface.

The experimentally observed increase in the surface tension at higher concentrations of [BMIM]BF\textsubscript{4} was reproduced by a polarizable force field only. This increase, which is however barely above the statistical error, can be explained by adding the “normal” increase in solutions of electrolytes after the surface becomes saturated. To be taken into account, a quantitative combination of both competing phenomena requires polarizability forces which further stabilize the ions at the water surface.

Appendix

4.1 Surface tension

The surface tension is defined as

\[ \gamma = \frac{\partial F}{\partial A} \]

where \( A \) is the surface area and \( F \) is the Helmholtz free energy,

\[ F = -kT \ln \left[ \frac{1}{N!} \sum \exp \left(-\beta U d\mathbf{r}^N\right) \right]. \]

\( U = U(\mathbf{r}^N) \) is the potential energy as a function of coordinates of all \( N \) atoms, \( \lambda \) is the de Broglie thermal wavelength, \( k \) is the Boltzmann constant and \( T \) the absolute temperature. The partial derivative in eqn (1) must be calculated at constant volume which is best accomplished by using rescaled coordinates (marked by underlined symbols) keeping the volume \( V \) as well as the volume element constant,

\[ \mathbf{\underline{r}}_i = \left( \frac{A}{2} \right)^{1/2} \mathbf{x}_i, \left( \frac{A}{2} \right)^{1/2} \mathbf{y}_i, \left( \frac{A}{2} \right)^{1/2} \mathbf{z}_i. \]

Note that there are two surfaces in the slab and therefore \( A/2 = L_xL_y \) where \( L_x, L_y, L_z \) are the dimensions of the periodic simulation box. The resulting surface tension is

\[ \gamma = \frac{\partial F}{\partial A} \left[ \sum_i \left( x_i^2 + y_i^2 + z_i^2 \right) \right] \]

where \( U \) is the interaction potential (a function of atom coordinates). In the case of pair forces, \( u_i(r_{ij}) \), \( U \) is given by \( U = \sum_{i<j} u_i(r_{ij}) \) and the above equation adopts the well-known form\textsuperscript{51}

\[ \gamma = \frac{1}{2A} \left( \sum_{i<j} u'_{ij}(r_{ij}) (x_{ij} y_{ij} - 2z_{ij}) \frac{\partial U}{\partial \mathbf{r}_{ij}} \right) \]

\[ = \frac{1}{4L_xL_y} \left( \sum_{i<j} u'_{ij}(r_{ij}) \frac{x_{ij}^2 + y_{ij}^2 - 2z_{ij}^2}{r_{ij}} \right) \]
or, in terms of the pressure tensor
\[ \gamma = \frac{L_z}{2} \left( p_{zz} - \frac{p_{xx} + p_{yy}}{2} \right). \] (6)

In the Ewald summation method, the formulae are more complicated. However, if the vapor pressure is negligible, one can neglect the z-component of the pressure tensor and replace \(-2z_i\) in (5) by \(+z_i\) a small vapor pressure \(p^\prime\) can be easily corrected for, if necessary. Finally, we get
\[ \gamma = -\frac{3L_z}{4}(p - p^\prime), \] (7)
where \(p\) is the “pressure” formally calculated by the same formula as in the homogeneous system, particularly with the virial of electrostatic forces replaced by the electrostatic energy, as follows from the virial theorem.

4.2 Cutoff corrections in the slab geometry

We write the total interatomic potential as
\[ u_{ij} = u_{ij, \text{short}} + \Delta u_{ij} \tag{8} \]

In particular, MACSIMUS\textsuperscript{61} implements
\[ \Delta u(r) = \begin{cases} 0, & \text{for } r \in [0, c_1], \\ u(r) - C(r^2 - c_2^2)^2, & \text{for } r \in [c_1, c_2], \\ u(r), & \text{for } r \in [c_2, \infty], \end{cases} \tag{9} \]
where constants \(C\) and \(c_1\) are determined from the cutoff \(c_2\) and the potential so that both \(\Delta u(r)\) and its derivative \(\Delta u'(r)\) are continuous for all positive \(r\).

Let \(\zeta(z)\) denote the z-density profile of atom \(i\). The correction in the averaged potential energy \(E\) (residual internal energy) can be approximated by integration over all (assuming uncorrelated) positions of pairs \(ij\) and then by summing over all pairs

\[ \Delta E = \sum_{i<j} \int \zeta_i(z_i)d\zeta_i \int \zeta_j(z_j)d\zeta_j \Delta u_{ij}(r_{ij}). \tag{10} \]

This can be partly integrated and rearranged to a 3D integral,
\[ \Delta E = \sum_{i<j} \int \zeta_i(z_i)d\zeta_i \int \zeta_j(z_j)d\zeta_j \int \Delta u_{ij}(z_i - z_j) dz_i dz_j. \tag{11} \]

where
\[ I_j(z) = \int_0^\infty 2\pi r dr \Delta u_j(\sqrt{r^2 + z^2}) = 2\pi \int_0^{1/\max(z_i, z_j)} \frac{d\gamma}{\gamma} \Delta u_j(1/\gamma). \tag{12} \]

In practical evaluation we first calculate, for all atom type pairs \(ij\), tables \(I_j(z)\) by a fourth-order Gaussian integration over \(dz\). We use the grid of 1 Å for both \(I_j(z)\) and \(\zeta(z)\). Then the integrals over \(dz_i\) and \(dz_j\) are numerically evaluated by the trapezoidal rule with the same grid as \(\zeta(z)\). For determining the surface tension correction, term \(\Delta u\) in the above formulae should be replaced by
\[ \Delta u \rightarrow \frac{L_z}{4V} \frac{\gamma^2 + \gamma^2 - 2\gamma}{r} \Delta u'(r) \tag{13} \]

and then
\[ I_j(z) = \frac{L_z}{8\pi} \int_0^{1/\max(z_i, z_j)} \frac{d\gamma}{\gamma^2} |1/\gamma^2 - 3\gamma^2| \Delta u_j'(1/\gamma). \tag{14} \]
in eqn (11) gives \(\Delta E\) instead of \(\Delta E\).

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