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## Calculation of the long range interactions for interfacial properties

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# Calculation of the long range interactions for interfacial properties.

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## Abstract:

The molecular simulation of heterogeneous systems cannot be performed routinely. The results of such systems depend on the truncation procedures, size effects, long range corrections to the thermodynamic properties and on the way of calculating the Coulombic interactions. We propose here to illustrate the impact of the truncation procedures on the mechanical equilibrium of the liquid-vapor interface of alkanes. The importance of the long range corrections to the surface tension is established in alkanes, water, carbon dioxide and hydrogen sulfide liquid-vapor interfaces. The calculation of the electrostatic interactions in a slab geometry using a two-dimensional method and the standard three-dimensional Ewald summation technique is also reported.

*Keywords:* Heterogenous systems, molecular simulations, long range corrections, Coulombic interactions.

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# 1 INTRODUCTION

Most of the phenomena in surface science (adhesion, wetting, and lubrication) involve the combination of liquid-liquid, liquid-vapour, and liquid-solid interfaces. Many important fundamental problems in chemistry and biology lead to practical applications in ion separation and extraction, drug delivery, oil recovery, and detergents. Due to the difficulties of experimental probes to access the molecular level structure of the interface, direct molecular simulation methods have become powerful techniques to examine the nature of the interface region and to calculate interfacial properties.

However, the molecular simulation of heterogeneous systems cannot be considered as routine job because the nonuniformity of the local density along the direction normal to the surface gives rise to important issues. This heterogeneity makes problems concerning the truncation procedures involved in the calculation of the force and energy equations, the long range corrections to apply to the macroscopic properties and an accurate treatment of the Coulombic interactions. Additionally, when the system is modelled by a slab geometry that is periodic in two of the three directions, the calculation of the long range Coulombic interactions cannot be applied directly.

We propose to establish the mechanical equilibrium of the liquid-vapour interface of alkanes (Figure 1a) in Monte Carlo (MC) and Molecular Dynamics (MD) simulations. This example shows the importance of the truncation procedures in the force and energy equations for heterogeneous systems. We also show that the truncation procedures can affect significantly the results of surface tensions when they are calculated using different routes. We illustrate this point by calculating the surface tension of alkanes using both a truncated force and a force modified by a cubic spline function. We complete the study of the liquid-vapour interface by showing the order of magnitude of the long range corrections to the surface tension in alkanes, water, CO<sub>2</sub> and H<sub>2</sub>S systems.

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9 In a slab geometry system where periodic boundary conditions can be used in two of the  
10 three directions, the calculation of the long range electrostatic interactions cannot be per-  
11 formed directly using the standard Ewald summation method. It requires to adapt the  
12 dimensions of the simulation box. We propose here to compare a two-dimensional method  
13 (HKE) [1] and the standard three-dimensional Ewald summation (EW3D,EW3DC) tech-  
14 niques for the calculation of the Coulombic interactions. The two-dimensional method  
15 (HKE) [1] is better adapted to systems which are periodic in two directions only but it is  
16 20 times slower than standard three dimensional methods. The comparison between the  
17 different methods is carried out on systems constituted of monolayers of metal-chelating  
18 ligands grafted onto a graphite surface (see Figure 1b). These grafted monolayers are in-  
19 vestigated platforms in the development of applications such as electrochemical biosensors.  
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## 33 2 SIMULATIONS DETAILS

### 34 2.1 Liquid-vapour interface

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36 For the molecular simulations of the liquid-vapour interface, the total configurational en-  
37 ergy of the systems formed by  $N$  molecules consists of intramolecular and intermolecular  
38 interactions modelled by Lennard-Jones (LJ) 6-12 sites, electrostatic point charges and a  
39 long range correction (LRC) contribution.  
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$$49 U = U_{\text{INTRA}} + U_{\text{INTER}} + U_{\text{LRC}} \quad (1)$$

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51 The intermolecular interactions due to the repulsion-dispersion interactions are computed  
52 using the truncated LJ potential  $u_{\text{LJ}}(r_{iajb})$   
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$$\begin{aligned}
U_{LJ} &= \sum_{i=1}^{N-1} \sum_{j>i}^N \sum_{a=1}^{N_i} \sum_{b=1}^{N_j} u_{LJ}(r_{iajb}) \\
&= \sum_{i=1}^{N-1} \sum_{j>i}^N \sum_{a=1}^{N_i} \sum_{b=1}^{N_j} 4\epsilon_{ab} \left[ \left( \frac{\sigma_{ab}}{r_{iajb}} \right)^{12} - \left( \frac{\sigma_{ab}}{r_{iajb}} \right)^6 \right] \quad (2)
\end{aligned}$$

where  $r_{iajb}$  is the distance between atom  $a$  in molecule  $i$  and atom  $b$  in molecule  $j$ ,  $\epsilon_{ab}$  is the energy parameter of the interaction and  $\sigma_{ab}$  is the Lennard-Jones core diameter.  $N_i$  is the number of atoms in the molecule  $i$ . The LJ parameters for the interactions between unlike sites are calculated by using the Lorentz-Berthelot combining rules

$$\epsilon_{ab} = (\epsilon_{aa}\epsilon_{bb})^{1/2} \quad \sigma_{ab} = \frac{1}{2} (\sigma_{aa} + \sigma_{bb}) \quad (3)$$

In addition to the LJ interactions, the intermolecular interactions include the total electrostatic potential  $U_{ELEC}$  calculated using the Ewald sum method [2, 3, 4, 5] technique. For a box with orthogonal axis,  $U_{ELEC}$  is expressed as

$$\begin{aligned}
U_{ELEC} &= \frac{1}{2\epsilon_o V} \sum_{k \neq 0} Q(h) S(\mathbf{h}) S(-\mathbf{h}) \\
&+ \frac{1}{8\pi\epsilon_o} \sum_i \sum_a \sum_{j \neq i} q_{ia} \sum_b q_{jb} \operatorname{erfc}(\alpha r_{iajb}/r_{iajb}) \\
&- \frac{\alpha}{4\pi^{3/2}\epsilon_o} \sum_i \sum_a q_{ia}^2 \\
&- \frac{1}{8\pi\epsilon_o} \sum_i \sum_a \sum_{b \neq a} \frac{q_{ia} q_{ib}}{r_{iaib}} \operatorname{erf}(\alpha r_{iaib}) \quad (4)
\end{aligned}$$

where  $\operatorname{erfc}(x)$  is the complementary error function and  $\operatorname{erf}(x)$  is the error function.  $\alpha$  is chosen so that only pair interactions in the central cell need to be considered in evaluating the second term in Eq.(4). The functions  $S(\mathbf{h})$  and  $Q(h)$  are defined using Eqs.(5) and (6), respectively

$$S(\mathbf{h}) = \sum_i \sum_a q_{ia} \exp(i\mathbf{h} \cdot \mathbf{r}_{ia}) \quad (5)$$

$$Q(h) = \frac{1}{h^2} \exp\left(-\frac{h^2}{4\alpha^2}\right) \quad (6)$$

where the reciprocal lattice vector  $\mathbf{h}$  is defined as  $\mathbf{h} = 2\pi(l/L_x, m/L_y, n/L_z)$  where  $l, m, n$  take values of  $0, \pm 1, \pm 2, \dots \pm \infty$ . The reciprocal space sum is truncated at an ellipsoidal boundary at the vector  $|\mathbf{h}^{max}|$ .

As the geometry of the system shows an heterogeneity along the axis normal to the interface ( $z$ -axis), we calculate the long range correction (LRC) to the repulsion-dispersion energy as a function of  $z_k$  by splitting the cell into slabs of width  $\delta z$ . The total long range correction energy  $U_{LRC}$  is then calculated by summing up all of the local contributions of each slab. The long range corrections to the total energy within each  $k$ th slab are defined by two parts [6]

$$U_{LRC} = \sum_{i=1}^{N_s} u_{lrc}(z_k) = \sum_{i=1}^{N_s} \left( u_{lrc}^{(1)}(z_k) + u_{lrc}^{(2)}(z_k) \right) \text{ with}$$

$$u_{lrc}^{(1)}(z_k) = \frac{8\pi}{3} \rho(z_k)^2 V_s \sum_{a=1}^{N_i} \sum_{b=1}^{N_j} \epsilon_{ab} \left[ \frac{1}{3} \left( \frac{\sigma_{ab}^{12}}{r_c^9} \right) - \left( \frac{\sigma_{ab}^6}{r_c^3} \right) \right] \quad (7)$$

$$u_{lrc}^{(2)}(z_k) = \pi \rho(z_k) V_s \int_{r_c}^{\infty} dr \int_{-r}^r d\Delta z \sum_{i=1}^{N_s} [\rho(z_{k+i}) - \rho(z_{k+i-1})] r U_{LJ,m}(r) \quad (8)$$

where  $\rho(z_k)$  and  $V_s$  are respectively the density and the volume of the slab  $k$ .  $\Delta z$  is defined as the difference  $z - z_k$ .  $N_s$  is the number of slabs between  $z$  and  $z_k$ .  $r_c$  is the cutoff radius,  $U_{LJ,m}(r)$  is the intermolecular energy and  $r$  the distance between the two centers of mass.

$$U_{LJ,m}(r) = \sum_a^{N_i} \sum_b^{N_j} 4\epsilon_{ab} \left[ \left( \frac{\sigma_{ab}}{r} \right)^{12} - \left( \frac{\sigma_{ab}}{r} \right)^6 \right] \quad (9)$$

The first part of the long range contribution has an analytical form identical to the one associated with a homogeneous system but uses the local density  $\rho(z_k)$  of the slab. The second part consists of a double integral which contains a series of density differences which render this part cumbersome to calculate.

## 2.2 Grafted metal-chelating monolayers onto a graphite surface

For the modelling of the grafted monolayers, we use the all-atom (AA) version of the Cornell force field AMBER [7]. The general potential function is of the form

$$\begin{aligned}
 U = & \sum_{\text{bonds}} k_b (r - r_o)^2 \\
 & + \sum_{\text{angles}} k_\theta (\theta - \theta_o)^2 \\
 & + \sum_{\text{dihedrals}} k_\phi [1 + \cos(l\phi + \delta)] \\
 & + \sum_{i=1}^{N-1} \sum_{j=i+1}^N \left\{ 4\epsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] + \sum_l' \frac{q_i q_j}{|\mathbf{r}_{ij} + \mathbf{n}L|} \right\} \quad (10)
 \end{aligned}$$

where  $k_b$ ,  $k_\theta$  and  $k_\phi$  are the force constants for deformation of bonds, angles and dihedrals, respectively. The equilibrium values of bond distances and valence angles correspond to  $r_o$  and  $\theta_o$ , respectively. In the dihedral angle term,  $l$  is the periodicity and  $\delta$  is the phase factor. The intermolecular and intramolecular interactions consist of a van der Waals repulsion-dispersion term calculated using the Lennard-Jones (6-12) potential, represented by the penultimate term in Eq.(10). In the AMBER force field, the nonbonded interactions between atoms separated by exactly three bonds (1-4 van der Waals interactions) are reduced by a factor of 0.5 [7]. The Lennard Jones potential parameters for the interactions between unlike atoms were calculated by using the Lorentz-Berthelot mixing rules (quadratic and arithmetic rules for  $\epsilon_{ij}$  and  $\sigma_{ij}$  parameters, respectively). The water molecules were represented with the TIP4P/2005 model [8].

When the last term in Eq.(10) is calculated with Eq.(4), the method is called EW3D and refers to the standard Ewald summation technique. When Eq.(4) is changed by the addition of  $\frac{1}{2\epsilon_o V} M_z^2$ , the method is called EW3DC.  $M_z$  is the net dipole moment of the simulation cell given by  $\sum_{i=1}^N q_i \mathbf{r}_i$ . This contribution is the correction term from Yeh and Berkowitz [9] which results by the plane-wise summation method proposed by Smith [3].



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7 Adding this term to the total energy amount to using a  $z$ -component force for each atom  
8 given by  
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$$F_{i,z} = -\frac{q_i}{\epsilon_o V} M_z \quad (11)$$

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12 The EW3DC method differs from the standard EW3D method only by the presence of  
13 this dipole correction. However, these two three-dimensional method require to change the  
14 primary simulation box by adding two empty spaces between the periodic image in order  
15 to dampen out the interslab interactions [9, 10, 11].  
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23 The total Coulombic interactions for a two-dimensional periodic system which is finite in  
24 the  $z$ -dimension can be calculated using the Hautman and Klein method [1]. This method  
25 is in fact an adaptation of the Ewald technique for systems which are periodic in two di-  
26 mensions only. The operational expressions of the total electrostatic interactions can be  
27 found elsewhere [1] for completeness.  
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35 The computational procedures of the molecular simulation of the liquid-vapour interface  
36 can be found in previous papers [12, 13, 14, 15, 16, 17]. The force-field used in the molecular  
37 modelling of the grafted system and the description of the computational procedures can  
38 be also found elsewhere [11]. Figures 1a and 1b show typical configurations of the liquid-  
39 vapour interface of the  $n$ -pentane and of the NTA grafted system, respectively. In these  
40 snapshots,  $z$  refers to the direction of the heterogeneity.  
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### 49 **3 RESULTS AND DISCUSSIONS**

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51 We propose here to illustrate the importance of the truncation procedures for the mechan-  
52 ical equilibrium of the liquid-vapour interface of alkanes. The impact of the discontinuities  
53 in the force and energy equations is also studied for the different definitions of the sur-  
54 face tension. The long range corrections to the surface tension are reported for systems  
55 involving both electrostatic and dispersion-repulsion energy contributions. We finish by  
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the calculation of the electrostatic interactions in a slab geometry system.

### 3.1 Calculation of the normal and tangential pressure components

In the case of a planar liquid-vapour surface lying in the  $x,y$  plane where the heterogeneity takes place along the  $z$  direction normal to the surface, the calculation of the normal and tangential pressure components along this axis is meaningful for the validation of the mechanical equilibrium. The components of the pressure tensor calculated from the Irving and Kirkwood definition [18, 19, 20] are expressed by

$$p_{\alpha\beta}(z_k) = \langle \rho(z_k) \rangle k_B T \mathbf{I} + \frac{1}{A} \left\langle \sum_{i=1}^{N-1} \sum_{j>i}^N (\mathbf{r}_{ij})_{\alpha} (\mathbf{F}_{ij})_{\beta} \frac{1}{|z_{ij}|} \theta \left( \frac{z_k - z_i}{z_{ij}} \right) \theta \left( \frac{z_j - z_k}{z_{ij}} \right) \right\rangle \quad (12)$$

where  $\mathbf{I}$  is the unit tensor and  $T$  is the input temperature.  $\alpha$  and  $\beta$  represent  $x$ ,  $y$  or  $z$  directions.  $\theta(x)$  is the unit step function defined by  $\theta(x) = 0$  when  $x < 0$  and  $\theta(x) = 1$  when  $x \geq 0$ .  $A$  is the surface area normal to the  $z$  axis. The distance  $z_{ij}$  between two molecular centers-of-mass is divided into  $N_s$  slabs of thickness  $\delta z$ . Following Irving and Kirkwood, the molecules  $i$  and  $j$  give a local contribution to the pressure tensor in a given slab if the line joining the centers-of-mass of molecules  $i$  and  $j$  crosses, starts or finishes in the slab. Each slab has  $1/N_s$  of the total contribution from the  $i - j$  interaction. The normal component  $p_N(z_k)$  is equal to  $p_{zz}(z_k)$  whereas the tangential component is given by  $\frac{1}{2}(p_{xx}(z_k) + p_{yy}(z_k))$ .  $\mathbf{F}_{ij}$  in Eq.(12) is the intermolecular force between molecules  $i$  and  $j$  and is expressed as the sum of all the site-site forces acting between these two molecules.

$$\begin{aligned} \mathbf{F}_{ij} &= \sum_{a=1}^{N_i} \sum_{b=1}^{N_j} (\mathbf{f}_{iajb}) \\ &= - \sum_{a=1}^{N_i} \sum_{b=1}^{N_j} \frac{\mathbf{r}_{iajb}}{r_{iajb}} \frac{dU(r_{iajb})}{dr_{iajb}} \end{aligned} \quad (13)$$

For the simulation of the liquid-vapour interface of alkanes, the total intermolecular energy  $U$  is calculated by using the LJ potential  $U_{LJ}$  because no electrostatic interactions are

involved in the model. In our MC simulations, the LJ potential is truncated at the cutoff radius ( $r_c = 12 \text{ \AA}$ ) according to  $U_T$

$$U_T(r_{iajb}) = \begin{cases} U_{LJ}(r_{ij}) & r_{iajb} < r_c \\ 0 & r_{iajb} \geq r_c \end{cases} \quad (14)$$

The calculation of the pressure components requires the use of the derivative of the potential. This derivative can be calculated using either the truncated force expressed as

$$f_T(r_{iajb}) = \begin{cases} -\frac{\partial U_{LJ}}{\partial r_{iajb}} & r_{iajb} < r_c \\ 0 & r_{iajb} \geq r_c \end{cases} \quad (15)$$

or the truncated force modified by the addition of an impulse contribution [21] defined by

$$f_{TC}(r_{iajb}) = \begin{cases} -\frac{\partial U_{LJ}}{\partial r_{iajb}} & r_{iajb} < r_c \\ +\frac{U_{LJ}(r_c)}{\Delta r} & r_c < r_{iajb} < r_c + \Delta r \\ 0 & r_{iajb} \geq r_c + \Delta r \end{cases} \quad (16)$$

where  $\Delta r$  is equal to  $0.05 \text{ \AA}$  for a cutoff of  $12 \text{ \AA}$ . In the most cases, the MD simulations used a truncated force and the MC simulations a truncated potential. Figure 2 shows the profiles of the normal  $p_N$  and tangential  $p_T$  components of the pressure tensor calculated from MC and MD configurations. For a planar surface, the mechanical equilibrium requires to have  $p_N(z)$  and  $p_T(z)$  constant and equal to  $p$  in the bulk phases. In the interfacial region,  $p_T$  exhibits two negative peaks indicating that the liquid phase is under tension. The normal and tangential components of the pressure calculated from MD are shown in Figure 2a. These profiles establish the mechanical equilibrium of these MD configurations as expected for a method that uses the forces to generate the evolution of the system. On the other hand, in MC configurations when the forces are calculated from Eq.(15), the profiles of  $p_N$  and  $p_T$  highlight that the configurations are not in mechanical equilibrium. This can be explained by the fact that MC uses the configurational energy to generate the configurations and that the pressure is calculated from the derivative of the configurational

energy. When the configurational energy is calculated with a truncated potential which is not differentiable at the cutoff radius, the truncated force used in the calculation of the pressure does not correspond to the truncated potential. To match the force and energy equations, the force must be corrected by an addition term. When the force is corrected as in Eq.(16), the profiles of the normal and tangential components of Figure 2b show that the mechanical equilibrium is satisfied within the MC configurations.

Another way of removing the discontinuities in the energy and force equations is to use the Lennard-Jones potential modified by a cubic spline. The potential and force equations become

$$U_{SP}(r_{iajb}) = \begin{cases} U_{LJ}(r_{iajb}) - U_{LJ}(r_s) + a & r_{iajb} < r_s \\ -\frac{b}{3}(r_{iajb} - r_c)^3 - \frac{c}{4}(r_{iajb} - r_c)^4 & r_s \leq r_{iajb} < r_c \\ 0 & r_{iajb} \geq r_c \end{cases} \quad (17)$$

$$f_{SP}(r_{ij}) = \begin{cases} -\frac{\partial U_{LJ}}{\partial r_{iajb}} & r_{iajb} < r_s \\ +b(r_{iajb} - r_c)^2 + c(r_{iajb} - r_c)^3 & r_s \leq r_{iajb} < r_c \\ 0 & r_{iajb} \geq r_c \end{cases} \quad (18)$$

Using such expressions, the potential and its derivative are continuous at the cutoff. The parameters  $a, b$  and  $c$  are calculated by requiring that the first and second derivatives of the  $u_{SP}$  potential be continuous at  $r_s$  and  $r_c$ .

$$\begin{aligned} c &= +\frac{\frac{\partial^2 U_{LJ}}{\partial r_{ij}^2}(r_s)}{(r_s - r_c)^2} - 2\frac{\frac{\partial U_{LJ}}{\partial r_{ij}}(r_c)}{(r_s - r_c)^3} \\ b &= -\frac{\frac{\partial^2 U_{LJ}}{\partial r_{ij}^2}(r_s)}{(r_s - r_c)} + 3\frac{\frac{\partial U_{LJ}}{\partial r_{ij}}(r_s)}{(r_s - r_c)^2} \\ a &= -\frac{b}{3}(r_s - r_c)^3 - \frac{c}{4}(r_s - r_c)^4 \end{aligned} \quad (19)$$

Figures 3a and 3b display the profiles of the normal and tangential pressure components calculated over MC and MD configurations using the potential and force of Eqs. (17) and (18), respectively. The profiles match very well within the MC and MD methods and indicates the primary importance of the discontinuity of the potential at the cutoff. Additionally, the total local chemical potential calculated from Eq.(20) exhibits a flat profile as expected for a planar liquid-vapour interface at equilibrium:

$$\mu(z_k) = kT \ln \left( \left\langle \frac{\Lambda^3 \rho(z_k)}{\exp(-\Delta U/k_B T)} \right\rangle_{z_k, NVT} \right) \quad (20)$$

where  $\Lambda$  is the de Broglie thermal wavelength and  $U$  is the potential changed by a cubic spline function.  $\Delta U$  represents the energy of the ghost ( $N + 1$ ) particle with the  $N$  particles. The local expression of the chemical potential was established by Widom [22].

The discontinuity in the force and energy equations was not considered as crucial in the simulations of a homogeneous fluid where there was a compensation between the forces affecting a particle from outside is cutoff sphere. In the case of heterogeneous system, this assumption is not longer valid and the equivalence between MC and MD is recovered only when the discontinuities are removed. In this case, the MC and MD simulations are performed with the same potential.

### 3.2 Calculation of the surface tension

In the case of the calculation of the surface tension, the discontinuities in the energy and forces expressions can lead to significant differences between the different routes. Some definitions use the potential energy in their working expressions. For instance, the test-area (TA) method [23] recently developed uses the perturbation formalism to express the surface tension. Other expressions (KB [24]) and (IK [25, 19, 20]) are based upon the mechanical definition of the surface tension and use the derivative of the potential in their operational expressions. Table 1 shows that the intrinsic part of the surface tension calculated from the potential energy (TA) is different with that calculated from the derivative of the potential energy (IK,KB). However, when the discontinuities are removed in the expressions of the force and energy with a cubic spline function, the intrinsic part is identical within IK, KB and TA approaches. The equivalence between the different operational expressions can be also recovered by making the potential and force equations consistent [14].

An other important contribution to the surface tension is the long range contribution due to the fact that interactions are neglected from the cutoff region. The appropriate LRC of the normal and tangential components of the pressure tensor within the IK definition have been derived by Guo and Lu [6] and are composed of two parts as expressed in Eqs. (21) and (22).

$$\begin{aligned}
 p_{N,LRC}(z_k) &= p_{N,LRC}^{(1)}(z_k) + p_{N,LRC}^{(2)}(z_k) \\
 &= -\frac{2\pi}{3}\rho^2(z_k) \int_{r_c}^{\infty} dr r^3 \frac{dU_{LJ,m}(r)}{dr} \\
 &\quad - \pi\rho(z_k) \int_{r_c}^{\infty} dr \int_{-r}^r d\Delta z [\rho(z) - \rho(z_k)] \frac{dU_{LJ,m}(r)}{dr} (\Delta z)^2
 \end{aligned} \tag{21}$$

As concerns the tangential pressure, the first term is identical to the first term of the normal component whereas the second term is expressed by

$$p_{T,LRC}^{(2)}(z_k) = -\frac{\pi}{2}\rho(z_k) \int_{r_c}^{\infty} dr \int_{-r}^r d\Delta z [\rho(z) - \rho(z_k)] \frac{dU_{LJ,m}(r)}{dr} [r^2 - (\Delta z)^2] \tag{22}$$

The first term of  $p_{N,LRC}(z_k)$  and  $p_{T,LRC}(z_k)$  is identical to that used in homogeneous molecular simulations by using a local density  $\rho(z_k)$  instead of a scalar density  $\rho$  whereas the second term takes into account the density differences between the slabs. From these LRC expressions, it is then possible to calculate the LRC parts relative to the surface tension. From a mechanical viewpoint, the surface tension can be also calculated from the integration of the difference of the normal and tangential components of the pressure tensor [18, 19, 20] across both interfaces according to

$$\begin{aligned}
 \gamma &= \gamma_I + \gamma_{LRC} \\
 &= \frac{1}{2} \int_{-L_z/2}^{+L_z/2} dz (p_N(z_k) - p_T(z_k)) + \frac{1}{2} \int_{-L_z/2}^{+L_z/2} dz (p_{N,LRC}(z_k) - p_{T,LRC}(z_k))
 \end{aligned} \tag{23}$$

where the first term is related to the intrinsic part of the surface tension and the second one corresponds to the LRC part.

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7 Figure 4a shows the profiles of the difference between the normal and tangential compo-  
8 nents as a function of the  $z$  direction. We observe that the two profiles are well symmetric  
9 with a well established liquid bulk phase. The integral of the profile is represented on  
10 the right axis. The integral allows to check that the contributions to the surface tension  
11 are the same for the two interfaces with a flat profile between them. Figure 4b plots the  
12 profile of the long range corrections to  $p_N - p_T$  difference with the integral of this property  
13 represented on the right axis. The profile of the long range corrections to the pressure  
14 components indicates that the contribution of each interface is identical and there is no  
15 contribution in the bulk phases. The total value of the long range correction to the surface  
16 tension is far from being negligible: in this case, it represents up to 30 % of the total surface  
17 tension. The calculation of the surface tension requires the use of appropriate long range  
18 corrections; each operational expression of the surface tension must be corrected by specific  
19 long range corrections. This was described in detail elsewhere [14]. Interestingly, Table 2  
20 shows the intrinsic surface tension with its long range corrections for some alkanes, water,  
21 carbon dioxide and hydrogen sulfide. In water, the long range corrections to the surface  
22 tension are small whereas the electrostatic contribution to the surface tension is negative.  
23 In  $\text{CO}_2$  and  $\text{H}_2\text{S}$ , the dispersion-repulsion contributions are greater than the electrostatic  
24 interactions; the long range corrections to the surface tension represents then about 30 %  
25 of the total value.  
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### 48 3.3 Calculation of the electrostatic interactions in a slab geometry

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50 The calculation of the electrostatic interactions in a system represented by a slab ge-  
51 ometry must be carefully undertaken. The use of two-dimensional method such as the  
52 Hautmann-Klein method (HKE) [1] is recommended for systems which are periodic in  
53 two dimensions only. However, the two-dimensional methods are cumbersome and time-  
54 consuming. The HKE method is about 20 times slower than the standard Ewald methods  
55 (EW3D, EW3DC). It is then fundamental from a methodological viewpoint to check that  
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7 the 2D and 3D methods lead to the same energetical, structural and electrical proper-  
8 ties in slab geometry systems. We propose to check these points on a system formed by  
9 negatively charged monolayers of chelating copper (NTA) compounds immobilized onto a  
10 HOPG graphite surface in aqueous solution. The use of a three-dimensional method in a  
11 slab geometry system requires to elongate the simulation box in the  $z$  direction in order to  
12 dampen out the interslab interactions. Figure 5a depicts the number of hydrogen bonds  
13 between water molecules in the region close to the surface. The criteria used for the calcu-  
14 lation of the number of hydrogen bonds can be found in a previous paper [11]. This figure  
15 demonstrates that the number of hydrogen bonds between water molecules close to the  
16 grafted surface does not depend on the method used for the calculation of the electrostatic  
17 interactions indicating that KHE, EW3D and EW3DC methods give the same structure  
18 of water. The charge density profiles of water molecules is reported in part b of Figure 5  
19 for each method. This figure tends to establish that the distribution of charges of water  
20 molecules is slightly perturbed close to the surface. This is due to the presence of grafted  
21 molecules that are able to interact preferentially with water molecules to give hydrogen  
22 bonds. However, from 20 Å, the charge density profile recovers an expected zero value.  
23 We observe that the three methods give the same charge density profiles. The analysis of  
24 the electric field profile  $E(z)$  (Figure 5c) calculated from the integral of the charge density  
25 profile confirms that the electric field reaches a constant zero from 20 Å. From this value of  
26  $z$ , the distribution of water molecules is isotropic as expected for a bulk-like region. This  
27 indicates that the surface and the grafted molecules do not influence significantly the water  
28 molecules within this region. Additionally, the calculation of these electric properties al-  
29 lows to validate the use of three-dimensional methods for the calculation of the Coulombic  
30 interactions in a slab geometry.  
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## 4 Conclusions

We have shown that the use of truncated potential and truncated force may lead to significant differences in the mechanical equilibrium and surface tensions of liquid-vapour systems governed by dispersion-repulsion interactions. Removing the discontinuities in the potential and force equations amounts to recovering the equivalence between MC and MD and to making consistent the different routes of the calculation of the surface tension. Whereas the effects of these discontinuities are compensated in the simulation of bulk phases, they must be taken into account in the simulation of two-phase systems.

The simulation of slab geometry system requires to do a compromise between an accurate treatment of the Coulombic interactions, the use of fully developed system and the number of steps to obtain a good convergence of the thermodynamic and electrical properties. A solution consists in using a slight modified three-dimensional Ewald summation method with the addition of empty space between the primary simulation cell. We have compared the results between three-dimensional methods and a two-dimensional method. We have concluded that the standard Ewald summation technique can be used with confidence in such slab geometries.

## References

- [1] J. Hautmann and M. L. Klein, *An ewald summation method for planar surfaces and interfaces*, Mol. Phys., 75 (1992), 379.
- [2] M. P. Allen and D. J. Tildesley, *Computer Simulation of Liquids*, Clarendon Press, Oxford, (1989).
- [3] E. R. Smith, *Electrostatic energy in ionic crystals*, Proc. R. Soc. Lond. A., 375 (1981), 475.
- [4] D. M. Heyes, *Pressure tensor of partial-charge and point-dipole lattices with bulk and surface geometries*, Phys. Rev. B, 49 (1994), 755.
- [5] J. Alejandre, D. J. Tildesley, and G. A. Chapela, *Molecular dynamics simulation of the orthobaric densities and surface tension of water*, J. Chem. Phys., 102 (1995), 4574.
- [6] M. Guo and B. C. Y. Lu, *Long range corrections to thermodynamic properties of inhomogeneous systems with planar interfaces*, J. Chem. Phys., 106 (1997), 3688.
- [7] W. D. Cornell, P. Cieplak, C. I. Bayly, I. R. Gould, K. M. Merz, D. M. Ferguson Jr, D. M. Fox, T. Spellemer, J. W. Caldwell, and P. Kolleman, *A second generation force field for the simulation of proteins, nucleic acids, and organic molecules*, J. Am. Chem. Soc., 117 (1995), 5179.
- [8] J. L. F. Abascal and C. Vega, *A general purpose model for the condensed phases of water: Tip4p/2005*, J. Chem. Phys., 123 (2005), 234505.
- [9] I. C. Yeh and M. L. Berkowitz, *Ewald summation for systems with slab geometry*, J. Chem. Phys., 111 (1999), 3155.

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4  
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7 [10] S. Crozier, R. L. Rowley, E. Spohr, and D. Henderson, *Comparison of charged sheets*  
8 *and corrected 3d ewald calculations of long-range forces in slab geometry electrolyte*  
9 *systems with solvent molecules.* J. Chem. Phys., 112 (2000), 9253.  
10  
11  
12  
13 [11] F. Goujon, C. Bonal, B. Limoges, and P. Malfreyt, *Molecular simulations of grafted*  
14 *metal-chelating monolayers: methodology, structure and energy,* Mol. Phys., 106  
15 (2008), 1397.  
16  
17  
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19  
20 [12] F. Goujon, P. Malfreyt, A. Boutin, and A.H. Fuchs, *Direct monte carlo simulations of*  
21 *the equilibrium properties of the n-pentane liquid-vapor interface,* J. Chem. Phys.,  
22 116 (2002), 8106.  
23  
24  
25  
26  
27 [13] F. Goujon, P. Malfreyt, J.M. Simon, A. Boutin, B. Rousseau, and A. H. Fuchs, *Monte*  
28 *carlo versus molecular dynamics simulations in heterogeneous systems: An application*  
29 *to the n-pentane liquid-vapor interface,* J. Chem. Phys., 121 (2004), 12559.  
30  
31  
32  
33  
34 [14] C. Ibergay, A. Ghoufi, F. Goujon, P. Ungerer, A. Boutin, B. Rousseau, and P. Mal-  
35 *freyt, Molecular simulations of the n-alkane liquid-vapour interface: interfacial prop-*  
36 *erties and their long range corrections,* Phys. Rev. E, 75 (2007), 051602.  
37  
38  
39  
40  
41 [15] A. Ghoufi, F. Goujon, V. Lachet, and P. Malfreyt, *Expressions for local contributions*  
42 *to the surface tension from the virial route,* Phys. Rev. E, 77 (2008), 031601.  
43  
44  
45  
46 [16] A. Ghoufi, F. Goujon, V. Lachet, and P. Malfreyt, *Calculation of the surface tension*  
47 *of acid gases and water from monte carlo simulations,* J. Chem. Phys., 128 (2008),  
48 154716.  
49  
50  
51  
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53 [17] A. Ghoufi, F. Goujon, V. Lachet, and P. Malfreyt, *Multiple histogram reweighting*  
54 *method for the surface tension calculation,* J. Chem. Phys., 128 (2008), 154718.  
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58 [18] J. S. Rowlinson and B. Widom, *Molecular Theory of Capillarity.* Clarendon Press,  
59 Oxford, (1982).  
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7 [19] J. P. R. B. Walton, D. J. Tildesley, J. S. Rowlinson, and J. R. Henderson, *The pressure*  
8 *tensor at the planar surface of a liquid*, Mol. Phys., 48 (1983), 1357.  
9  
10  
11 [20] J. P. R. B. Walton and K. E. Gubbins, *The pressure tensor in an inhomogeneous fluid*  
12 *of non-spherical molecules*, Mol. Phys., 58 (1986), 1013.  
13  
14  
15  
16 [21] A. Trokhymchuk and J. Alejandre, *Computer simulations of liquid/vapor interface in*  
17 *lennard-jones fluids: Some questions and answers*, J. Chem. Phys., 111 (1999), 8510.  
18  
19  
20  
21 [22] B. Widom, *Structure of interfaces from uniformity of the chemical potential*, J. Stat.  
22 *Phys.*, 19 (1978), 563.  
23  
24  
25  
26 [23] G. J. Gloor, G. Jackson, F. J. Blas, and E. de Miguel, *Test-area simulation method*  
27 *for the direct determination of the interfacial tension of systems with continuous or*  
28 *discontinuous potentials*, J. Chem. Phys., 123 (2005), 134703.  
29  
30  
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32  
33 [24] J. G. Kirkwood and F. P. Buff, *The statistical mechanical theory of surface tension*,  
34 *J. Chem. Phys.*, 17 (1949), 338.  
35  
36  
37  
38 [25] J. H. Irving and J. G. Kirkwood, *The statistical mechanical theory of transport pro-*  
39 *cesses. iv. the equations of hydrodynamics* J. Chem. Phys., 18 (1950), 817.  
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Table 1: Surface tensions of methane ( $\text{mN m}^{-1}$ ) calculated from MC simulations using a truncated LJ potential and a modified LJ potential using the KB, IK and TA approaches. The cutoff radius is fixed to 12 Å.

$\gamma_{\text{KB}}$	$\gamma_{\text{IK}}$	$\gamma_{\text{TA}}$
Truncated potential		
9.5	9.5	10.6
Spline potential		
8.5	8.5	8.5

Table 2: Lennard-Jones, electrostatic and long range corrections contributions to the surface tension ( $\text{mN m}^{-1}$ ) calculated from MC simulations in different liquid-vapour systems.

	$\gamma_{LJ}$	$\gamma_{ELE}$	$\gamma_{LRC}$	$\gamma_{TOT}$	$\gamma_{EXP.}$
CH <sub>4</sub>	9.5		3.8	13.3	11.3
<i>n</i> C <sub>5</sub>	12.0		5.6	17.6	15.3
<i>n</i> C <sub>10</sub>	6.0		4.3	10.3	10.4
H <sub>2</sub> O	-87.6	117.7	3.5	33.6	36.5
CO <sub>2</sub>	6.1	2.9	2.5	11.5	12.0
H <sub>2</sub> S	21.0	9.3	8.0	38.3	37.5

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7 **Fig. 1** a) Configurations of the *n*-pentane liquid-vapour interface at  $T = 350$  K. b)  
8 Snapshot of a MD configuration of 10 grafted NTA-Cu(II) complexed onto the  
9 HOPG surface with the water molecules.  
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13 **Fig. 2** a) Normal and tangential pressure components calculated in the liquid-vapour  
14 interface of the *n*-pentane at  $T = 325$  K a) from MC using a truncated potential  
15 and MD using a truncated force; b) from MC using both a truncated force  $f_T$   
16 and a truncated force modified by an additional impulse  $f_{TC}$ .  
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22 **Fig. 3** Normal and tangential pressure components calculated in the liquid-vapour  
23 interface of the *n*-pentane at  $T = 325$  K from a) MC and b) MD using a  
24 Lennard-Jones potential and a force changed by a cubic spline function. c)  
25 Total chemical potential of the liquid-vapour interface of methane at  $T = 120$   
26 K calculated from MC simulations using a LJ potential changed by a cubic  
27 spline function.  
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35 **Fig. 4** a) Difference between the normal and tangential pressure profiles for the liquid-  
36 vapour interface of the *n*-pentane at  $T = 300$  K; b) Difference between the  
37 normal and tangential components of the long range corrections to the pressure  
38 tensor. On the right axis, the integral of each difference is plotted as a function  
39 of  $z$ .  
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47 **Fig. 5** a) Profiles of the number of hydrogen bonds between water molecules along  
48 the direction normal to the surfaces. b) charge density and c) electric field  
49 profiles along the direction normal to the surface.  
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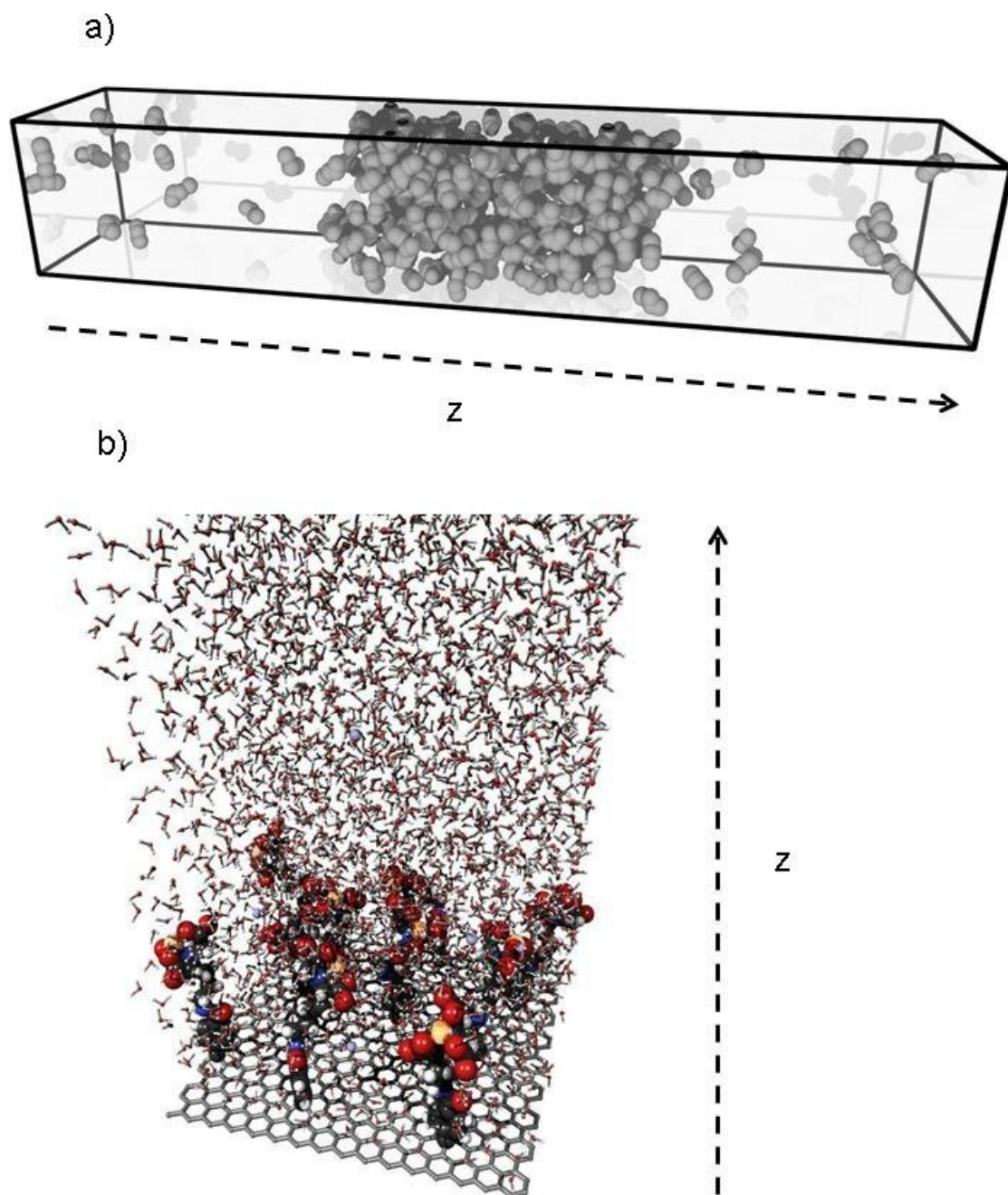


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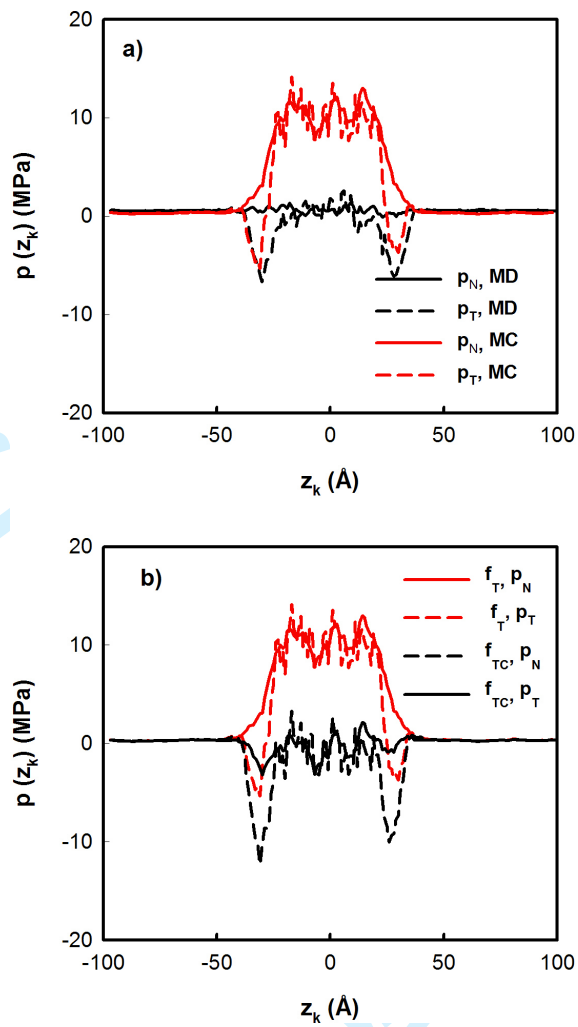


Figure 2:

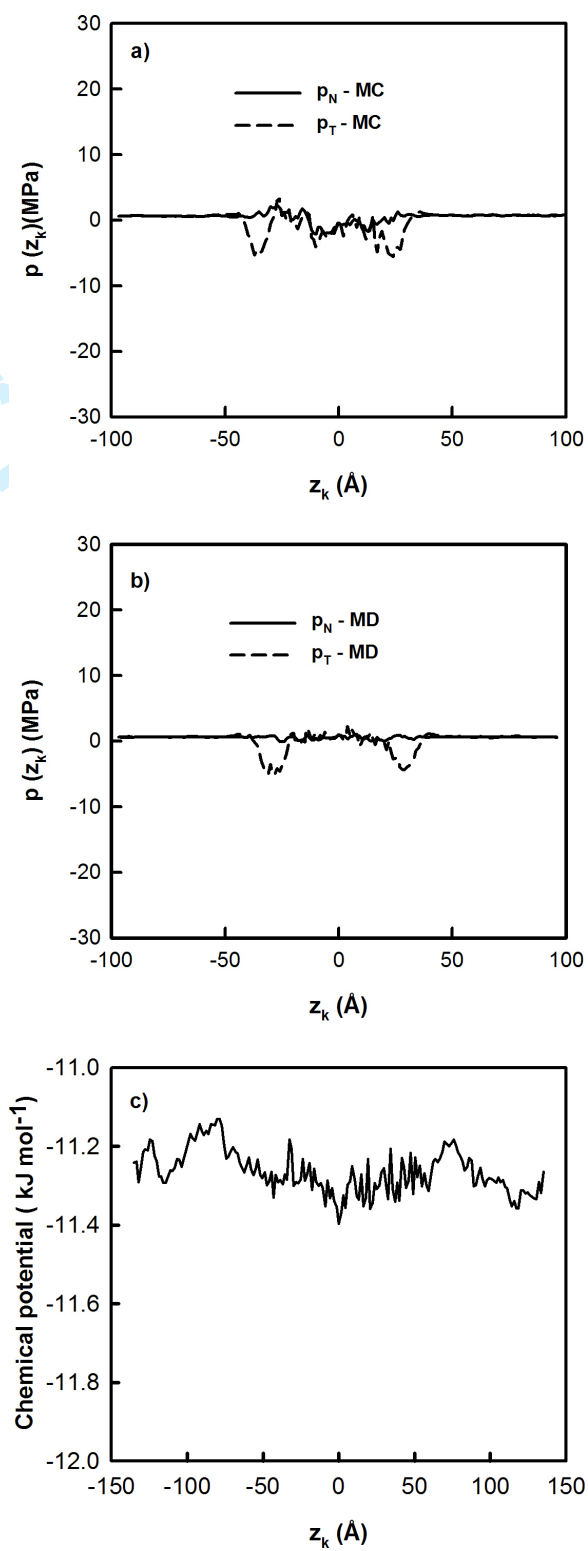


Figure 3:

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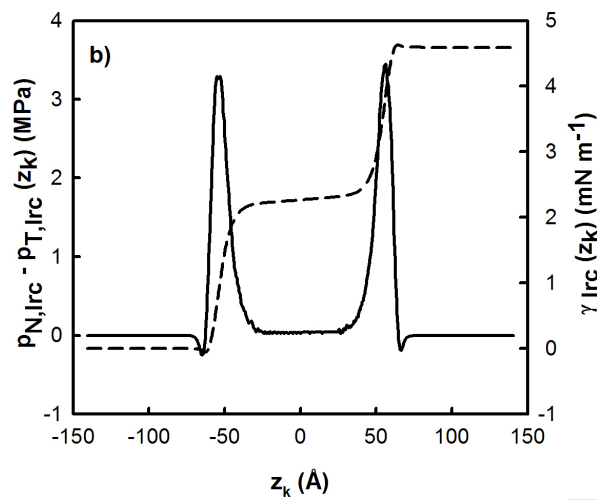
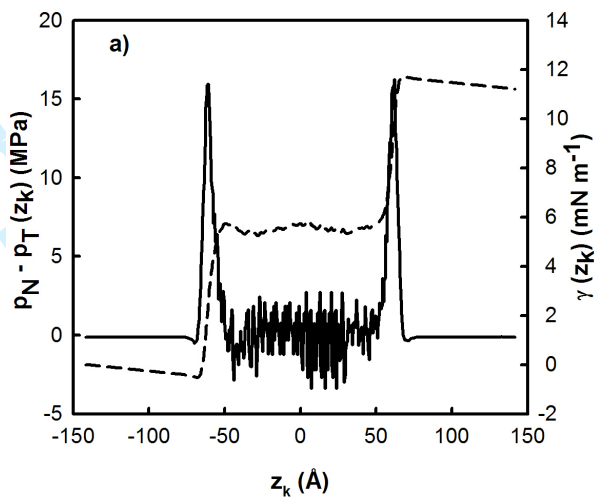


Figure 4:

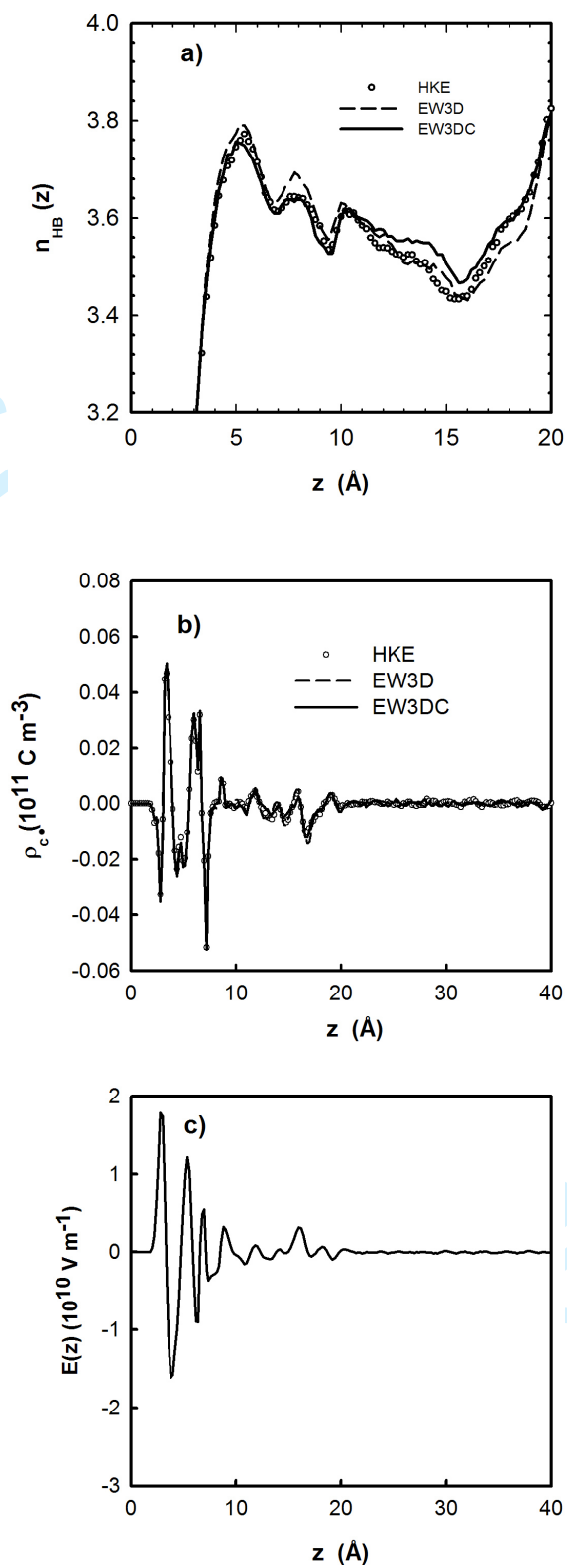


Figure 5: