

## Reply to "Molecular Mechanics Models for the Image Charge"

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### ABSTRACT

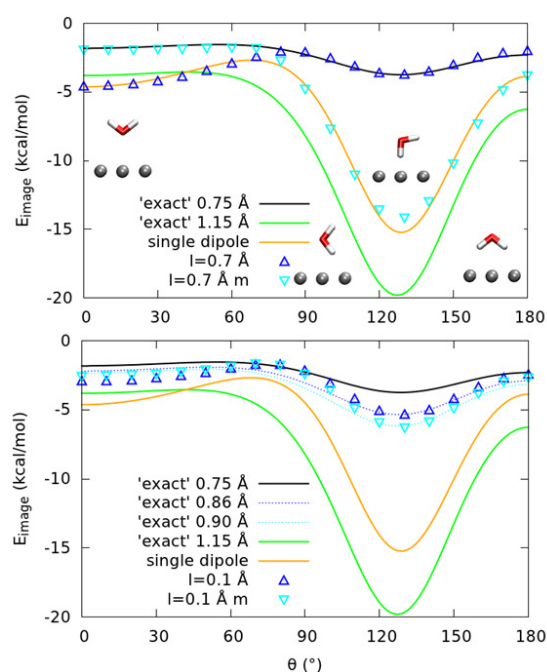
We have considered the systems investigated by Steinmann et al. by means of the image charge model originally proposed in J. Comput. Chem. 2008, 29,1656. Qualitatively correct results are obtained, that compare favorably with the relevant analytical benchmarks. We show that the effect of the asymmetry of the rod model can be controlled, when needed, as originally suggested, i.e., by using shorter rods. This strategy does not increase neither the complexity of the model nor its computational cost.

In their letter,<sup>1</sup> Steinmann et al. present an investigation of image charge interaction between a water molecule and a Pt (111) surface based on the rod model.<sup>2</sup> They claimed that such model gives qualitatively incorrect results for specific conditions and concluded that this is due to the asymmetry coded in the original rod model. Here we show instead that the image interaction is correctly reproduced, and that the effect of the asymmetry can be controlled, when required, by exploiting the strategy already described in ref. 2. This is in line with the successful use of the rod model in force fields developed by our group<sup>3-7</sup> and by others.<sup>8-11</sup> Finally we discuss whether it is meaningful to approximate the polarization interaction between a molecule and a metal surface with continuum electrostatic in the distance regime considered in ref. 1.

As discussed in ref. 2, the quantity that reproduces the image interaction with the rod model is the interaction *free* energy  $F_{\text{int}}$ . In fact, the latter determines the probability distribution in a MD simulation (as exemplified in Fig. S1), and should therefore be correct for the simulation to be reliable. When the linear response approximation holds,  $F_{\text{int}} = E_{\text{int}}/2$  where  $E_{\text{int}}$  is the interaction energy defined in eq.(A1) of the original work.<sup>2</sup> There is no reason to compare  $E_{\text{int}}$  directly to the analytical image interaction.<sup>1</sup> Here we shall calculate  $F_{\text{int}}$  by thermodynamic integration, without resorting to the linear response approximation, to avoid additional uncertainty. However, in the SI we show that  $E_{\text{int}}/2$  is a good approximation also for the setup considered here, equal to that in ref. 1 (see Fig. S2).

Following ref. 1, we have built a p(4x4) supercell for a 4 layer slab of metal atoms that are arranged as in Pt(111) (i.e., nearest neighbor distance of 2.77 Å). A water molecule is placed

on top of a metal atom, with the oxygen at a height of 2.4 Å from it.<sup>1</sup> The  $\theta$  angle, as defined in ref. 1, is then varied from 0° to 180° in step of 10°. Among the angles considered in ref. 1,  $\theta$  allows to span the most diverse water dipole orientations with respect to the surface (from perpendicular pointing up to perpendicular pointing down, see insets in Fig. 1). For each of the resulting configuration, a thermodynamic integration is run where the charges of the water molecules are created from 0 to their full values along the dynamics, with the slab thermostated at 300K. The same process is done for the water molecule alone without the slab to estimate (and then subtract out) the Coulomb interaction of water with its periodic replicas.  $F_{\text{int}}$  is then calculated as the difference between the water charge creation free energy with and without the slab. The resulting  $F_{\text{int}}$  for the rod model with rod length  $l=0.7$  Å are reported in Fig. 1, that should be compared with the upper panel of Fig. 1 in ref. 1.



**Figure 1.** Upper panel. Image interaction energy calculated as a function of the angle  $\theta$  between the

water dipole moment and the normal to the surface. 'Exact' values refer to analytical results obtained for a semi-infinite semiconductor slab whose surface is positioned at various distances from the outermost metal atomic plane (0.75 Å and 1.15 Å). 'Single dipole' refers to the Coulombic interaction of the water molecule with a single polarizable atom (see Method for details). For ' $l=0.7$  Å',  $E_{\text{image}}$  is the interaction free energy  $F_{\text{int}}$  of water obtained with rods of length 0.7 Å (the negative rod end is at the center of the atom, the positive rod end is free to rotate); in ' $l=0.7$  Å m' the negative and positive ends have been swapped. Lower panel. Same as upper panel, but shorter rods ( $l=0.1$  Å) have been used, keeping the overall dipole the same by using proportionally larger charges.

We have performed the calculations both with the negative end fixed and the positive one moving (" $l=0.7$  Å" in Fig. 1), as in GoIP, and the opposite choice (" $l=0.7$  Å m"). In the figure we also report the image interaction with a semi-infinite perfect conductor (called 'exact' to use the same nomenclature as in ref. 1), for the values of the outermost metal atom-plane-image plane displacements suggested there (0.75 Å and 1.15 Å). Since the distance between the water molecule and the closest rod atom ( $\leq 2.4$  Å) is smaller than 2.77 Å, the distance between two contiguous rod-atoms (i.e., the granularity of the model of the surface), we also included in the figure the interaction energy with the single polarizable atom closest to water for comparison. The expressions used for the image interaction and the interaction with such polarizable atom are reported in the Method section.

It is apparent that the resulting  $E_{\text{image}}$  (i.e., the model estimates of the image charge energy  $F_{\text{int}}$ ) are fully coherent with the analytical ('exact') benchmark, being in-between the

analytical image energy obtained for the plane placed at 0.75 Å and that for the interaction with a single dipole (as well as for the image energy for a plane displacement of 1.15 Å).

Therefore, we could not reproduce the qualitatively wrong results claimed by ref. 1. In fact, our results are quite different from those in ref. 1. Compare for example the curve " $l=0.7$  Å" (blue triangles) in Fig.1 with that " $\text{Pt}^- \text{R}^+$ " (also blue triangles) in Fig.1, upper panel of ref.1, that should be identical. The former is ranging from about -5 kcal/mol to -2 kcal/mol, with minima around  $\theta=0^\circ$  and  $\theta=130^\circ$ ; the latter is increasing monotonically between -12 kcal/mol to +11 kcal/mol (approximately). The same large qualitative and quantitative discrepancy exists for " $l=0.7$  Å m" vs " $\text{Pt}^+ \text{R}^-$ " (cyan triangles in both figures), that should also be equal. In particular, we do not find positive interaction energies.<sup>1</sup> A positive (i.e., unfavorable) interaction energy is a particularly puzzling result for a system of charge in front of a polarizable object, however inaccurate the model of the polarization may be. Since the polarizable object has degrees of freedom that can adapt to the external field, it should end up in a conformation where the interaction with such field is favorable, i.e., negative interaction energy, or at least not unfavorable (i.e., zero interaction energy).

As a further check, we verified that our results are independent of the software used (here GROMACS).<sup>12</sup> To this end, we have repeated the " $l=0.7$  Å" calculation with NAMD<sup>13</sup> (unfortunately AMBER, used in ref. 1, is not available to us at the time of writing). The resulting  $F_{\text{int}}(\theta)$  is the same found with GROMACS, with differences well below  $kT$  (see Fig. S4). In running NAMD tests, we noticed that its default behavior is to ignore some energy

terms associated to fixed atoms to save computer time, unless `fixedAtomsForces` is set to `on`. The  $F_{\text{int}}$  values obtained with the default setting were large in modulus and positive for some orientations.

Undoubtedly, the choice of the sign of the charges on the rod makes a difference for this short molecule-metal distance (compare curves " $l=0.7$  Å" with " $l=0.7$  Å" m in Fig. 1 upper panel). This is not surprising if we consider that for  $\theta \sim 128^\circ$ , one of the two Hydrogens is only 1.4 Å from a metal atom. Admittedly, the model was not created for this unphysical conditions. Yet, the results for both choice of charge distribution are within the expected range of analytical benchmarks, which is what the model is expected to do. The choice of using  $l=0.7$  Å in GoIP and GoIP-CHARMM<sup>3,5,6</sup> as well as of letting the positive end to be mobile (instead of the negative one) is related to a specific feature for classical force field for water and biomolecular simulations. Such force fields typically represent H-bond by letting the polar hydrogen atoms without a vdW radius, or with a small one. This fictitiously increases the interaction of polar H with the metal surface, and we found that exploiting the asymmetry of the Drude rod model was a computationally inexpensive way to quench such overestimation. In passing we note that also the harmonic Drude model is intrinsically asymmetric, since the virtual site charge will move by a finite length to or from an external charge depending on its sign. Further comparison with ab initio MD simulations<sup>14</sup> showed that a small H-metal Lennard-Jones repulsion were also needed, as discussed in recent works.<sup>5</sup>

The effect of the rod asymmetry was extensively commented in the original work under the section *Effects Related to the Finite*

*Size of the Rods.*<sup>2</sup> In particular, Fig.7 of the original work<sup>2</sup> presents the image results obtained for shorter rods (0.3 Å instead of 0.7 Å) and higher charges ( $q=\pm 0.7$  instead of  $q=\pm 0.3$ , to keep the same dipole), and it demonstrates that the effect of the finite rod size is substantially reduced. As discussed there, rod shortening offers a simple strategy to deal with asymmetry whenever it is an undesired feature of the model. To show that the effect of the finite rod size can be controlled also for the system presented here, we repeated the calculations leading to the upper panel of Fig.1, this time with rods 0.1 Å long. The results are shown in the lower panel of Fig. 1. Now the effect of asymmetry is minor: in the worst case, when H is 1.4 Å from the metal atom ( $\theta\sim 128^\circ$ ), the difference is still less than 1 kcal/mol. Such uncertainty is the same related to a uncertainty in the position of the image plane of 0.04 Å (from 0.86 Å to 0.90 Å), whatever it means a continuum model description for a system where an H atom is penetrating deeply in one of the surface atoms.

In fact, the approximation of representing the polarization interaction between external charges and a metal slab with the analytical image potential is known to break down at short distances. Finnis et al. found a minimum acceptable distance around 2.5 Å for Al surfaces and a unitary test charges;<sup>15</sup> Fernández-Torre et al. considered neutral molecules on Ni(111) and did not explore distances smaller than 5 Å, at which distance the trends were qualitatively correct but relative deviations were already non-negligible.<sup>16</sup> The tests presented in this work have therefore an internal consistency, rather than a physical, relevance, i.e., they show that, contrary to what stated in ref. 1, the model keeps the expected behavior also in these "extreme" conditions.

In conclusion, we have shown that the Drude rod model introduced previously<sup>2</sup> do provide correct results also when it is tested for very short molecule-metal distances, and that the effect of the finite size of the rod can be controlled, when needed, by exploiting the original suggestion of using shorter rods.<sup>2</sup> Thus, there is no need to increase the computational burden of the approach by introducing additional sites (5 instead of 2 per each atom) and fixed bonds (9 instead of 1 per each atom, based on Fig. SI-2)<sup>1</sup> as in the symmetric (but still finite size) model of ref. 1.

## Methods

*Slab geometry.* The p(4x4) supercell was build by placing the atoms as a fcc lattice, with a nearest-neighbor distance of 2.77 Å, based on the experimental bulk structure that was not further relaxed. 4 atomic layers were used.<sup>1</sup> The rod atoms were initially manually placed along x, y, z directions and randomization occurs in the first few ps of the simulations. The resulting cell is quite small in the surface plane (x and y directions) leading to a small but non-negligible interaction of the water molecule with its replicas. This is why  $F_{\text{int}}$  is to be obtained by subtracting out such term. For the  $l=0.7$  Å rod simulations, the mass of the mobile site was chosen to be 2 amu, as in ref. 1. For the  $l=0.1$  Å rods simulations, the mass was increased to 5.3 amu to keep the same moment of inertia, and thus the same characteristic dynamical time.<sup>2</sup>

*MD simulation details.* All the simulations have been performed by using GROMACS 4.5.5 (the version available on the local workstation at the time of writing). Time-step for the simulation was 2 fs, the metal and the water atoms were kept fixed with the freeze option. The Bussi, Donadio, Parrinello thermostat was used,<sup>17</sup> with a relaxation time of 0.4ps. PME was used for long-range electrostatics; the Ewald tolerance

(ewald\_rtol) was set at  $1e-6$ , the Fourier grid spacing at 0.1nm, PME interpolation order (PME\_order) at 4, the direct space cut-off at 0.52nm (due to the small size of the used cell). Constraints on rod lengths were imposed with the LINCS algorithm.<sup>18</sup> For water, we have used the TIP3P charges and geometry.

**Free energy simulation.** The thermodynamic integration algorithm of GROMACS (free\_energy=yes) was used. The water charges are switched on linearly from the initial to the final point of the simulations, that lasted 10ns. Due to this very long simulation time, we did not perform any preliminary equilibration and start all the simulations by the same slab geometry. We did not observe any instabilities, although in the first 100fs of the simulations with  $l=0.1 \text{ \AA}$  a few rods rotated more than  $30^\circ$  (but less than  $45^\circ$ ). We repeated the free-energy simulations for a test case ( $l=0.7 \text{ \AA}$ ), starting from the last snapshot of the long simulation and switching on the water charges in 100ps instead of 10ns. The resulting free energies were within 1 kcal/mol of the long simulations (Fig. S3).

**Calculations of  $E_{int}$ .** For the case  $l=0.7 \text{ \AA}$ , we have tested the linear response approximation, i.e. the calculation of  $F_{int}$  as  $E_{int}/2$  (Fig. S2). To do so, we have performed a straight MD simulation of 10ns from each of the water molecule orientation. Following the definition of  $E_{int}$  given in ref. 2, we have calculated  $E_{int}=\langle H_{int} \rangle_1 = \langle H_{tot} - H_{slab} - H_{water} \rangle_1 = \langle V_{tot} - V_{slab} - V_{water} \rangle_1$  where  $H_{tot}$  ( $V_{tot}$ ) is the total Hamiltonian (potential energy) of the system, and  $H_{slab}$  ( $V_{slab}$ ) and  $H_{water}$  ( $V_{water}$ ) are those of the metal slab and water alone, respectively. Potential energy here is just the Coulomb term (short range + long range PME terms). The subscript 1 recalls that the average is done with the Hamiltonian of the fully interacting system (i.e.,  $H_{tot}$ ). In practice,  $\langle V_{slab} \rangle_1$  is obtained by switching off the charges on water and recalculating the Coulomb energy along the 10ns trajectory, and  $\langle V_{water} \rangle_1$  by switching off the charges on the slab (since

water is frozen, this provides the same Coulomb energy for all the snapshots).

**Image interaction** The interaction energy of the water molecule with its image has been calculated as

$$E_{image} = 1/2 \sum_{ij} q_i q_j G_{image}(\mathbf{r}_i, \mathbf{r}_j) \quad (1)$$

$$G_{image}(\mathbf{r}_i, \mathbf{r}_j) = -1/\sqrt{((x_i - x_j)^2 + (y_i - y_j)^2 + (z_i + z_j - 2z_0)^2)} \quad (2)$$

where  $q_i$  are the charges of the water molecules,  $\mathbf{r}_i$  are their positions and  $z_0$  is the  $z$  coordinate of the image plane.

The interaction of the water molecule with a single polarizable atom has been calculated as

$$E_{single} = -1/2 \alpha E_{water}^2$$

where  $E_{water}$  is the modulus of the electric field produced by the water molecule on the atom, and  $\alpha$  is the orientational polarizability given by  $\mu^2/3kT$ .<sup>2</sup>

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**Keywords:** image interaction, Drude rod model, classical MD simulation

Additional Supporting Information may be found in the online version of this article.

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**GRAPHICAL ABSTRACT**

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Reply to "Molecular Mechanics Models for the Image Charge"

The Drude rod model introduced to include image interaction in molecular dynamics simulations [J. Comput. Chem. 2008, 29,1656] is tested for the water-metal distances explored by Steinmann et al. It is shown that such model provides qualitatively correct results, in contrast with Steinmann et al.'s findings. The effects associated to the finite rod length can be controlled by using shorter rods, as suggested in the original work.

