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Effect of the reference choice on the contribution of molecular dipoles to the local electric potential

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Abstract

The profile of the electric potential at interfaces is often employed in discussions of classical molecular dynamics models. However, in contrast to the total potential, the contribution of molecular dipoles to the potential depends on the choice of an arbitrary reference point within molecules. We show both analytically and in a simulation how this choice affects the dipole contribution in the bulk. The analytic derivation pinpoints the origin of the changes in the dipole contribution. The simulation verifies the analytic expression and shows the exact influence of the chosen molecular reference. This work highlights the inherent issues of the dipole contribution to the electric potential.

1. Introduction

Molecular dynamics (MD) is a well established tool in the study of solid-liquid [1, 2] and vapor-liquid [3, 4] interfaces as well as of bulk liquids [5, 6]. The electric potential is a fundamental quantity in the description of these interfaces. In MD models of interfaces, the electric potential can be computed along an axis z, normal to the interface. The values of this local electric potential are affected by ions and the orientation of neutral molecules within the liquid. Therefore, it may seem reasonable to analyze the orientation of molecular dipoles in order to illuminate the connection between molecular orientations and the electric potential at the interface. Indeed, many studies plot the dipole density as function of z, and further, calculate the contribution of this dipole density to the electric potential as a function of z [1–13]. However, the contribution of dipoles to the local potential is ill-defined because the dipole density depends on an arbitrary choice of a reference point within each molecule [14, 15].

The problems in the definition of the dipole contribution to the local electric potential $\Psi_P(z)$, even for neutral molecules, have been pointed out in [14]. We have demonstrated the severe magnitude of shifts in $\Psi_P(z)$ due to changes in the reference point for a model system (cf supplemental material of [15]). Here, we derive an analytic expression for an offset in the bulk potential, based on the the molecular reference choice. The derivation illustrates the underlying effect of the reference choice and proves that observed shifts are inherent to the definition of $\Psi_P(z)$. The derived expression is verified with a simple simulation cell of water, confined by two gold slabs. The simulation shows good agreement between observed and predicted differences of $\Psi_P(z)$ in the bulk region of water between reference choices.

2. Theory

We consider a system with slab geometry, with periodic boundary conditions in x and y-direction. The potential along the non-periodic z-direction

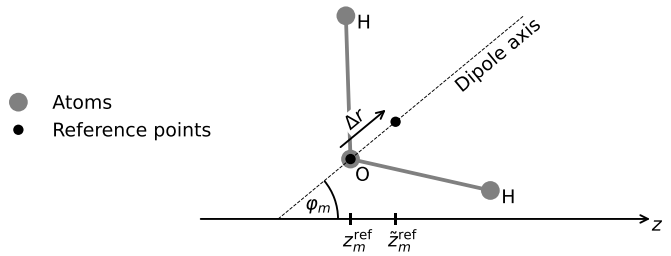

Figure 1. Schematic representation of a water molecule with an angle φ_m to the z-axis. Two choices for the reference point are shown: the oxygen position and the centroid position. The distance between the two points is Δr and the projections of their positions onto the z-axis are denoted as z_m^{ref} and $\tilde{z}_m^{\mathrm{ref}}$, respectively.

$$\Psi(z) = -\frac{1}{\epsilon_0}\int_{z_0}^{z} \mathrm{d}\zeta \int_{z_0}^{\zeta} \mathrm{d}\zeta' \rho(\zeta') \tag{1}$$

is obtained by averaging the charge density over the xy-plane and integrating twice over the z-coordinate. The potential is evaluated at the position z relative to an origin z_0. The charge density is written as a multipole expansion

$$\rho(z) = M(z) - \frac{\mathrm{d}}{\mathrm{dz}}P^{(z)}(z) + \frac{\mathrm{d}^2}{\mathrm{dz}^2}Q^{(zz)}(z) + \ldots, \tag{2}$$

with the molecular monopole density $M(z)$, dipole density $P^{(z)}(z)$ and quadrupole density $Q^{(zz)}(z)$ [14, 15]. The expansion allows for a separation of the potential into multipole contributions by inserting equation (2) into equation (1).

We construct a simple model for our derivation, comprising a liquid of only one type of neutral molecules with an interface to a vacuum region. Figure 1 shows a schematic view of a water molecule as an example for a neutral molecule.

The molecule has an arbitrary reference point and a molecular dipole μ. The dipole of the molecule with index m is oriented at an angle φ_m to the z-axis. Both quantities are projected onto the z-axis, yielding z_m^{ref} and $\mu_m^{(z)} = \mu \cos\varphi_m$, respectively. A shift Δr of the reference point along the direction of the dipole results in a changed position on the z-axis:

$$\tilde{z}_m^{\mathrm{ref}} = z_m^{\mathrm{ref}} + \Delta r \cos\varphi_m, \tag{3}$$

which is displayed in equation (1). The positions of atoms and their charges are unaffected by the shift Δr.

The issue of changes in $\Psi_P(z)$ due to Δr may be surprising because the molecular dipole $\mu_m^{(z)}$ itself is invariant w.r.t. the reference choice for neutral molecules and only the position of the reference point z_m^{ref} is changed. However, the z-component of the dipole density

$$P^{(z)}(z) = \frac{1}{A}\left\langle \sum_{m=1}^{N} \delta(z - z_m^{\mathrm{ref}})\mu_m^{(z)} \right\rangle, \tag{4}$$

with the area A in the xy-plane, is a function of the reference position z_m^{ref}. Equation (4) comprises a sum over the N molecules of the system and a sampling over the ensemble, indicated by the angle brackets. Consequently, the contribution of the dipole density to the potential

$$\Psi_P(z) = \frac{1}{\epsilon_0}\int_{z_0}^{z} \mathrm{d}\zeta P^{(z)}(\zeta) = \frac{1}{\epsilon_0 A}\int_{z_0}^{z} \mathrm{d}\zeta \left\langle \sum_{m=1}^{N} \delta(\zeta - z_m^{\mathrm{ref}})\mu_m^{(z)} \right\rangle, \tag{5}$$

where ϵ_0 is the vacuum permittivity, depends on z_m^{ref}, too.

We now derive the shift in $\Psi_P(z)$ for a simplified model system. First, we shift the molecular reference point by Δr along the molecular dipole direction [cf equation (4)]:

$$\begin{aligned}
\Delta\Psi(z;\Delta r) &= \frac{\mu}{\epsilon_0 A}\int_{z_0}^{z} \mathrm{d}\zeta \left\langle \sum_{m=1}^{N} \delta(\zeta - z_m^{\mathrm{ref}} - \Delta r\cos\varphi_m)\cos\varphi_m \right\rangle \\
&= \frac{\mu}{\epsilon_0 A}\left\langle \sum_{m=1}^{N} \cos\varphi_m \int_{z_0}^{z} \mathrm{d}\zeta\, \delta(\zeta - z_m^{\mathrm{ref}} - \Delta r\cos\varphi_m) \right\rangle \\
&= \frac{\mu}{\epsilon_0 A}\left\langle \sum_{m=1}^{N} \cos\varphi_m \Theta(z - z_m^{\mathrm{ref}} - \Delta r\cos\varphi_m) \right\rangle
\end{aligned} \tag{6}$$

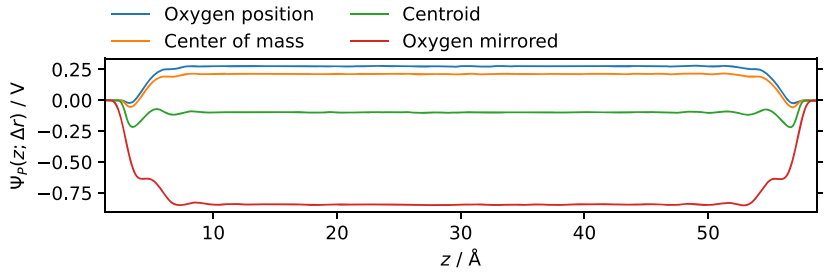

Figure 2. Contribution of water dipoles to the local electric potential for four different reference choices.

assuming $z_0 < z_m^{\mathrm{ref}} - \Delta r \ \forall \ m$, i.e., z_0 is in a vacuum region outside of the liquid. $\Theta(x)$ is the Heaviside step function.

We now assume a system with random angle distribution with probability density $\sin(\varphi_m)/2$ on the interval $\varphi_m \in [0, \pi]$. For $\Delta r = 0$ this uniform distribution within the interval $[z_0, z]$, yields $\Psi_P(z) = 0$ in the bulk region. Therefore, $\Delta\Psi(z;\Delta r)$ is the offset in the potential from this particular choice. $z_m^{'} = z - z_m^{\mathrm{ref}}$ is used for brevity in the following. We perform the integration over φ_m by substituting with $s = \Delta r \cos\varphi_m$:

$$\begin{aligned}\Delta\Psi(z;\Delta r) &= \frac{\mu}{2\epsilon_0 A}\left\langle \sum_{m=1}^{N}\int_0^{\pi} \mathrm{d}\varphi_m\, \Theta(z_m^{'} - \Delta r\cos\varphi_m)\cos\varphi_m \sin\varphi_m \right\rangle \\ &= \frac{\mu}{2\epsilon_0 A \Delta r^2}\left\langle \sum_{m=1}^{N}\int_{-\Delta r}^{\Delta r} \mathrm{d}s\, \Theta(z_m^{'} - s)s \right\rangle \\ &= -\frac{\mu}{4\epsilon_0 A}\left\langle \sum_{m=1}^{N}\left[1 - \left(\frac{z_m^{'}}{\Delta r}\right)^2\right][\Theta(z_m^{'} + \Delta r) - \Theta(z_m^{'} - \Delta r)] \right\rangle. \end{aligned} \tag{7}$$

Finally, we sample over the molecule positions by integrating $z_m^{'}$ over $\mathbb{R}$. We assume a uniform distribution with the number density $\rho = \langle N\rangle/(A\ 2\Delta r)$, where $\langle N\rangle$ is the expected number of molecules within the interval $[z-\Delta r, z+\Delta r]$, given by the Heaviside functions. The integration yields the dipole contribution to the electric potential

$$\Delta\Psi(z;\Delta r) = -\frac{\mu\rho}{4\epsilon_0}\int_{-\Delta r}^{\Delta r} \mathrm{d}z_{\mathrm{m}}^{'}\ 1 - \left(\frac{z_m^{'}}{\Delta r}\right)^2 = -\frac{\mu\rho\Delta r}{3\epsilon_0}. \tag{8}$$

The result shows that the contribution of molecular dipoles in a bulk region, relative to a vacuum region, is shifted by a value proportional to a shift Δr along the molecular dipole. For the derivation we have assumed a simplified model with a vacuum region, immediately followed by a bulk region. However, the expression in equation (8) is valid for systems with an arbitrary interface between vacuum and bulk regions, because $\Delta\Psi_P(z;\Delta r)$ is a linear function of Δr and the offset due to the interface vanishes when two reference choices are compared.

3. Results

In order to verify the derived expression in equation (8), a system is simulated using the classical MD implementation in LAMMPS [16]. The system comprises 5460 TIP3P water molecules [17] confined by two gold slabs [18] with three layers each and an area of $A = 52 \times 60$ Å^2. The simulation uses periodic boundary conditions in the x and y-direction and non-periodic boundary conditions in the z-direction, perpendicular to the gold slabs. The distance between slabs was equilibrated at atmospheric pressure and subsequently a trajectory in the NVT ensemble was obtained.

The sampled values of $\Psi_P(z)$ are displayed for four different reference choices in figure 2. The reference points are: the oxygen position, the center of mass, the centroid of the triangle formed by the atoms in the water molecule, and the oxygen position mirrored across the axis between the hydrogen atoms. Even between the results for the reference point at the oxygen position and at the center of mass, which are separated by only $\Delta r = 0.07$ Å, the difference is clearly visible. For the centroid and mirrored position, $\Psi_P(z)$ in the bulk region changes to a negative value. Further, the choice of reference may affect a qualitative analysis. For instance, the peaks at the interface appear more pronounced with the centroid position as reference as opposed to the relatively smooth profile with the oxygen position as reference.

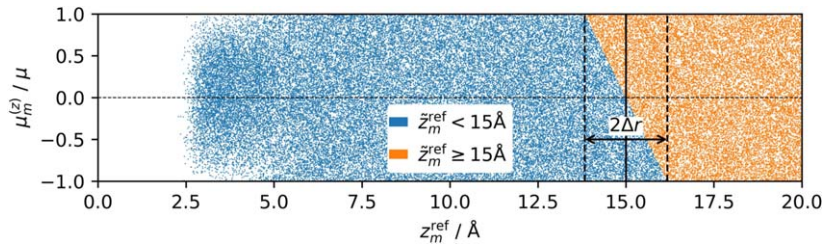

Figure 3. Scatter plot of molecules with positions z_m^{ref} and dipoles $\mu_m^{(z)}$ for the oxygen position as reference point. Colors indicate whether position $\tilde{z}_m^{\mathrm{ref}}$ would be left or right of $z = 15$ Å if the reference point was the mirrored oxygen position with $\Delta r = 1.17$ Å.

Table 1. Shifts in reference positions, Δr, and potential offsets $\Delta\Psi_P(z; \Delta r)$ in the bulk from the simulation and the analytic expression. All values are relative to results with the oxygen position as reference.

Reference choice	Δr/Å	$\Delta\Psi_P^{\mathrm{sim}}(\Delta r)$/V	$\Delta\Psi_P^{\mathrm{analytic}}(\Delta r)$/V
Center of mass	0.07	−0.063	−0.063
Centroid	0.39	−0.373	−0.374
Oxygen mirrored	1.17	−1.120	−1.121

For a comparison with the analytic expression in equation (8), the bulk region is defined as interval from 15 Å to 45 Å. The simulated values $\Delta\Psi_P^{\mathrm{sim}}(\Delta r)$ are obtained by averaging over the bulk region and calculating the value relative to the oxygen position. The analytic values $\Delta\Psi_P^{\mathrm{analytic}}(\Delta r)$ are calculated using the molecular dipole $\mu = 0.489$ eÅ of the TIP3P water model and the number density $\rho = 0.0325$ Å^{-3}, measured in the bulk region of the simulation. The resulting values are collected in table 1 and show good agreement between simulation and theory. Differences between $\Delta\Psi_P^{\mathrm{sim}}(\Delta r)$ and $\Delta\Psi_P^{\mathrm{analytic}}(\Delta r)$ are only ~ 1 mV and are attributed to the sampling over a finite number of time steps.

The computational system enables an illustration of the mechanism behind the potential shift. Figure 3 illustrates the derivation in equations (6) to (8), which ended with an integration over the interval $[z - \Delta r, z + \Delta r]$ in equation(8). For this, molecules with positions z_m^{ref} and dipoles $\mu_m^{(z)}$ from the NVT trajectory are shown in a scatter plot. The reference for the position in the scatter plot is the oxygen position. To calculate $\Psi_P(z)$ according to equation (5), one would add up all dipole values left of a specific value, e.g. $z = 15$ Å. For a different reference choice, the plot would be skewed and this is indicated by the color of points. Due to the changed value of $\tilde{z}_m^{\mathrm{ref}}$, points near the integration limit can move into or out of the integral. For the reference choice of a mirrored oxygen position, molecules that would be inside the integral are blue and those that would not are orange. Because the reference point inside the molecule is moved in the direction of the dipole, the z-component of the reference position increases for molecules with $\mu_m^{(z)} > 0$ and vice versa. Hence, one can clearly see molecules with a positive dipole moving out of the integral, i.e., they have an orange color even though $z_m^{\mathrm{ref}} < 15$ Å for the original reference choice of the oxygen position. This movement across the integration bound causes the potential offset which is quantified by equation (8).

4. Conclusion

In conclusion, we have analyzed the change in the contribution of molecular dipoles to the local electric potential $\Psi_P(z)$ due to a change in the reference point. For the contribution to the potential in the bulk, we have derived an analytic expression [cf equation (8)]. This expression has been verified using a computational system. Further, the analysis of the simulation shows the drastic effect of the reference choice. The results clearly show that $\Psi_P(z)$ is ill-defined due to the arbitrary reference choice and therefore it should not be employed in the analysis of computational models. It should be stressed that there is no specific reference choice which would remedy this issue. In particular, the choice which sets $\Psi_P(z) = 0$ in the bulk was useful in the derivation, but should not be misinterpreted as an advantageous choice for the analysis of computational models.

Potential profiles, $\Psi(z)$, directly calculated from partial charges in classical MD do not depend on a reference choice within molecules. Therefore, they do not suffer from the same issue as the dipole contribution. For the contribution of quadrupole moments to the potential $\Psi_Q(z)$, we have previously demonstrated a similar issue as for the dipole contribution $\Psi_P(z)$ [15]. Though, we have not investigated this in more detail here, the molecular quadrupole itself depends on the choice of reference and thus its contribution to the potential depends on the

reference, too. The multipole expansion approximates the charge density [cf equation (2)]. Therefore the sum of their contributions—obtained by insertion into equation (1)—should yield a good approximation to the potential [14]. In the supplementary material of [15], we have shown that the sum of multipole contributions is barely affected by the reference choice for a computational model. Nevertheless, the decomposition into the dipole and quadrupole contributions depends on the reference choice and can give no insight into the underlying physics.

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The authors have no conflicts to disclose.

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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