Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Classical polarizable model for simulations of water and ice: Supplementary material (theory)

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Pressure tensor for Drude oscillators

Let $\vec{r}_i'$ be positions of the Drude charges and shortly $r = \{r_i\}_{i=1}^N$, $r' = \{r_i'\}_{i=1}^N$. Let us denote $U' = U'(r, r')$ the potential energy as a function of all point charges (normal and Drude). We are interested in the self-consistent potential energy,

$$U(r) = \min_{r'} \left[U'(r, r') + \sum_i \frac{K_i}{2} (\vec{r}_i' - \vec{r}_i)^2 \right] \tag{1}$$

The minimum condition is equivalent to

$$\frac{\partial U'}{\partial r_i'} + K_i(r_i' - r_i) = 0 \tag{2}$$

Let us calculate $U(r + \mathrm{d}r)$:

$$U(r + \mathrm{d}r) = \min_{r''} \left[U'(r + \mathrm{d}r, r'') + \sum_i \frac{K_i}{2} (\vec{r}_i'' - \vec{r}_i - \mathrm{d}\vec{r}_i)^2 \right] \tag{3}$$

Here $r'' = r' + \mathrm{d}r'$, where $\mathrm{d}r'$ is of the same order as $\mathrm{d}r$. However, the minimum is quadratic in r' and therefore replacing $r'' \approx r'$ in (3) will lead to a second order error which can be neglected. From the Taylor expansion of $U(r + \mathrm{d}r)$ (or simply taking $\partial/\partial\vec{r}_i$ of [...] in (1)) we get

$$\frac{\partial U}{\partial \vec{r}_i} = \frac{\partial U'}{\partial \vec{r}_i} - K_i(\vec{r}_i' - \vec{r}_i) = \frac{\partial U'}{\partial \vec{r}_i} + \frac{\partial U'}{\partial \vec{r}_i'} \tag{4}$$

The computer code (r- and k- space Ewald sums for both real and Drude charges) calculates the following components of the pressure tensor

$$\frac{1}{V} \sum_i \left(\vec{r}_i \vec{f}_i + \vec{r}_i' \vec{f}_i' \right) = -\frac{1}{V} \sum_i \left(\vec{r}_i \frac{\partial U'}{\partial \vec{r}_i} + \vec{r}_i' \frac{\partial U'}{\partial \vec{r}_i'} \right)$$

However, from (4) it follows that it should be

$$-\frac{1}{V}\sum_i \vec{r}_i \frac{\partial U}{\partial \vec{r}_i} = -\frac{1}{V}\sum_i \left(\vec{r}_i \frac{\partial U'}{\partial \vec{r}_i} + \vec{r}_i \frac{\partial U'}{\partial \vec{r}'_i} \right)$$

Therefore, the following correction should be added

$$\frac{1}{V}\sum_i (\vec{r}'_i - \vec{r}_i) \frac{\partial U'}{\partial \vec{r}_i} = -\frac{1}{V}\sum_i (\vec{r}'_i - \vec{r}_i) \vec{f}'_i$$

where $\vec{f}'_i$ is the force acting on the Drude charge. Since in our model the force on the Drude charge is entirely electrostatic, the trace of the above term (contribution to the virial pressure), the above term is $-(2/V)E_{\mathrm{self}}$.

Lone dependant mechanics

Let us denote the positions of the three parents (as atoms O, H and H in water) as $\vec{r}_a$, $a = 1, 2, 3$. The calculations need a local orthonormal coordinate system $(\hat{x}, \hat{y}, \hat{z})$, where vectors $\hat{x}, \hat{y}$ are in the plane of the parents and $\hat{z}$ is perpendicular:

$$\begin{aligned} \hat{x} &= \sum_a x_a \vec{r}_a \qquad (\sum_a x_a = 0), \\ \hat{y} &= \sum_a y_a \vec{r}_a \qquad (\sum_a y_a = 0), \\ \hat{z} &= \hat{x} \times \hat{y}. \end{aligned}$$

Constants x_a, y_a are pre-calculated.

The dependant position is

$$\vec{r} = \sum_a w_a \vec{r}_a + w_z \hat{z} \qquad (\sum_a w_a = 1) \tag{5}$$

where again w_a and w_z are pre-calculated.

To distribute force f on the dependant back to the parents, we first calculate its components in the local coordinate system,

$$f_x = \hat{x} \cdot \vec{f}, \quad f_y = \hat{y} \cdot \vec{f}, \quad f_z = \hat{z} \cdot \vec{f}.$$

The force on parent a, $a = 1, 2, 3$, is

$$\vec{f}_a = w_a \vec{f} + (t_{x,a} f_x + t_{y,a} f_y)\hat{z}.$$

The 'torque constants' $t_{x,a}$, $t_{y,a}$ are again pre-calculated.

Pressure tensor calculation

The force-calculating module also calculates the virial of force and optionally also components of the pressure tensor. For the "Lone" dependants, a correction must be made because of force redistribution,

$$V\Delta\overleftrightarrow{P} = \sum_a \vec{f}_a(\vec{r}_a - \vec{r}) = \sum_a (t_{x,a}f_x + t_{y,a}f_y)\hat{z}(\vec{r}_a - \vec{r}) - w_z\vec{f}\hat{z}$$

where we used (5) to simplify the expression. The virial of force correction is the trace,

$$V\mathrm{Tr}\Delta\overleftrightarrow{P} = \sum_a (t_{x,a}f_x + t_{y,a}f_y)\hat{z}\cdot(\vec{r}_a - \vec{r}) - w_z f_z$$

Note that the above corrections are zero for the "Middle" dependants (like site M in the TIP4P model).