# EPAPS supplementary information for the JCP article "Molecular Dynamics Scheme for Precise Estimation of Electrostatic Interaction via Zero-Dipole Summation Principle"

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# Further analysis of the heuristic derivation

The heuristic derivation, based on the idea of introducing mirror image charges (MICs), of the force and energy in the current zero dipole method is described in detail. In particular, general issues regarding the number and positions of MICs are considered.

Supposing the interaction $\frac{1}{2}\sum_{i\in\mathcal{N}}\sum_{j\in\mathcal{N}_i} q_i q_j V(r_{ij})$, we fix an arbitrary $i \in \mathcal{N}$ and consider $j \in \mathcal{N}_i$ such that $r_{ij} < r_{\mathrm{c}}$. We introduce $M$ MICs for each $j$ with values $a_1^j, \ldots, a_M^j$ and with coordinates $R_1^j, \ldots, R_M^j$, respectively (Although we should denote them as $a_1^{i,j}, \ldots, R_1^{i,j}, \ldots$, we omit the suffix $i$ for simplicity). First, we pose a zero dipole condition along with associated conditions, i.e., for every $j$,

$$\sum_{k=1}^{M} a_k^j (x_i - R_k^j) + q_j x_{ij} = 0 \in \mathbb{R}^d, \tag{A1a}$$

$$\sum_{k=1}^{M} a_k^j = 0 \in \mathbb{R}, \tag{A1b}$$

$$\left\| x_i - R_k^j \right\| = r_{\mathrm{s}}, \quad k = 1, \ldots, M. \tag{A1c}$$

Namely, $\{a_k^j\}_{k=1,\ldots,M}$ are introduced to cancel the dipole $q_j x_{ij}$ [Eq. (A1a)], and they are placed on a sphere with a radius $r_{\mathrm{s}}$ [Eq. (A1c)]; Eq. (A1b) is a supplementary condition such that the added MICs do not affect the total charge. Then, the force acting on particle $i$ from particle $j$ and from the MICs is

$$\begin{aligned} f_{ij} &= q_i q_j F(r_{ij}) \frac{x_{ij}}{r_{ij}} + \sum_{k=1}^{M} q_i a_k^j F(r_{\mathrm{s}}) \frac{x_i - R_k^j}{r_{\mathrm{s}}} \\ &= q_i q_j F(r_{ij}) \frac{x_{ij}}{r_{ij}} + q_i F(r_{\mathrm{s}}) \frac{-q_j x_{ij}}{r_{\mathrm{s}}} \\ &= q_i q_j f(r_{ij}) \frac{x_{ij}}{r_{ij}}, \end{aligned}$$

where $F = -DV$ and

$$f(r) \equiv F(r) - \frac{F(r_{\mathrm{s}})}{r_{\mathrm{s}}} r. \tag{A2}$$

Namely, the effect of the MICs is turned into a redefinition of the force interaction. Taking into account all of the contributions from every $j \in \mathcal{N}_i$ inside the cutoff sphere and from the associated MICs, the force acting on particle $i$ is

$$\sum_{\substack{j\in\mathcal{N}_i \\ r_{ij}<r_{\mathrm{c}}}} f_{ij} = \sum_{\substack{j\in\mathcal{N}_i \\ r_{ij}<r_{\mathrm{c}}}} q_i q_j f(r_{ij}) \frac{x_{ij}}{r_{ij}}.$$

A natural interaction in which $f(r_\mathrm{c}) = 0$ can only be obtained if

$$r_\mathrm{s} = r_\mathrm{c} \tag{A3}$$

for e.g., the target $F$. We thus employ Eq. (A3), yielding $f(r)$ equal to Eq. (2) in the text. In other words, we place the MICs on the cutoff surface, which is compatible with the physical consideration that the counter-dipole objects should be near the excess-dipole generated around the cutoff surface. Now, the energy that leads to this force is thus, aside from constants, given as

$$\frac{1}{2}\sum_{i\in\mathcal{N}}\sum_{\substack{j\in\mathcal{N}_i \\ r_{ij}<r_\mathrm{c}}} q_i q_j u(r_{ij}), \tag{A4}$$

with $u$ defined in Eq. (3) in the text.

In the above procedure, we hold a nonzero net charge in general, because we have not used a ZC condition; actually, there is no room for using such a condition in order to consider a force function. Hence, second, we employ a protocol that explicitly uses a ZC condition. This corresponds to the original Wolf approach, but here we suppose we should keep the ZD condition attained in the above procedure. Namely, for any fixed $i$ and every $j$ (involving $i$) such that $r_{ij} < r_\mathrm{c}$, we pose the following conditions on additional MICs with charges $\{b_k^j\}_{k=1,\ldots,L}$ and coordinates $\{S_k^j\}_{k=1,\ldots,L}$ :

$$\sum_{k=1}^{L} b_k^j + q_j = 0 \in \mathbb{R}, \tag{A5a}$$

$$\sum_{k=1}^{L} b_k^j (x_i - S_k^j) = 0 \in \mathbb{R}^d, \tag{A5b}$$

$$\left\| x_i - S_k^j \right\| = r_\mathrm{c}, \quad k = 1, \ldots, L. \tag{A5c}$$

Through these two procedures, both the total charge and dipole, yielded by $q_j$ and the accompanying MICs, result in zero:

$$\sum_{k=1}^{M} a_k^j + \sum_{k=1}^{L} b_k^j + q_j = 0 \ (j \in \mathcal{N}_i), \tag{A6a}$$

$$\sum_{k=1}^{L} b_k^i + q_i = 0; \tag{A6b}$$

$$\sum_{k=1}^{M} a_k^j (x_i - R_k^j) + \sum_{k=1}^{L} b_k^j (x_i - S_k^j) + q_j x_{ij} = 0 \ (j \in \mathcal{N}_i), \tag{A6c}$$

$$\sum_{k=1}^{L} b_k^i (x_i - S_k^i) = 0. \tag{A6d}$$

By the application of the MICs $\{b_k^j\}$ to the pair potential $u$, the total energy, Eq. (A4), is transformed into

$$\begin{aligned} &\frac{1}{2} \sum_{i \in \mathcal{N}} \sum_{\substack{j \in \mathcal{N}_i \\ r_{ij} < r_{\mathrm{c}}}} \left[ q_i q_j u(r_{ij}) + \sum_{k=1}^{L} q_i b_k^j u(r_{\mathrm{c}}) \right] + \frac{1}{2} \sum_{i \in \mathcal{N}} \sum_{k=1}^{L} q_i b_k^i u(r_{\mathrm{c}}) \\ &= \frac{1}{2} \sum_{i \in \mathcal{N}} \sum_{\substack{j \in \mathcal{N}_i \\ r_{ij} < r_{\mathrm{c}}}} q_i \left[ q_j u(r_{ij}) - q_j u(r_{\mathrm{c}}) \right] - \frac{1}{2} \sum_{i \in \mathcal{N}} q_i^2 u(r_{\mathrm{c}}). \end{aligned} \tag{A7}$$

Hence we again have Eq. (4) in the text.

One of the simplest solutions $\{a_k^j, R_k^j\}_{k=1,\ldots,M}$, $\{b_k^j, S_k^j\}_{k=1,\ldots,L}$, satisfying Eqs. (A1), (A3), and (A5) for every $j$, is, as described in Sec. IIB in the text,

$$a_1^j = -a_2^j = q_j r_{ij}/2r_{\mathrm{c}}, \ R_1^j = x_i + r_{\mathrm{c}} d^j, \ R_2^j = x_i - r_{\mathrm{c}} d^j \ (j \in \mathcal{N}_i),$$
$$b_1^j = b_2^j = -q_j/2, \ S_1^j = x_i + r_{\mathrm{c}} e^j, \ S_2^j = x_i - r_{\mathrm{c}} e^j \ (j \in \mathcal{N}),$$

where $d^j \equiv x_{ij}/r_{ij}$ and $e^j$ is an arbitrary unit vector (even if e.g., $d^j = d^{j'}$ for $j \neq j'$, which yields $R_1^j = R_1^{j'}$, there is no problem; MICs never interact with each other). The number of MICs should be greater than 1 in order to meet the conditions (except for the trivial case, $q_j = 0$), so we have used $M = L = 2$. However, the results are irrelevant to the details of the solutions (the number of the MICs, and their values and positions on the surface).

Note that the supplementary conditions, Eqs. (A1b) and (A5b), have not been explicitly used to derive Eq. (A7), but they are required to meet Eq. (A6). We may have to remove these conditions, according to a theoretical choice. The choice concerns the combination and the ordering of the treatment about (i) the basic condition (ZC or ZD) with the corresponding supplementary condition and (ii) the quantity (force or potential). As stated in Sec. IIB in the text, the results also depend on these issues in the above general consideration, and the difference between individual results is not simply a coordinate-irrelevant constant in general.

Other heuristic derivations would be possible, e.g., not introducing MICs against each particle $j$ in the cutoff sphere, but simply introducing a single dipole quantity to cancel out the total dipole inside the cutoff sphere.