Molecular Dynamics using Non-variational Polarizable Force Fields: Theory, Periodic Boundary Conditions Implementation and Application to the Bond Capacity Model

Supplementary Information

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Alternative formulation of the Bond Capacity Equations

We here show that the BC charge equations can be derived from the minimization of an energy functional $\mathcal{E}_{BCM}$ given by the sum of the energy stored in a system of coupled

capacitors $\mathcal{E}_{cap}$ and the electrostatic energy arising from the set of induced BC charges $\mathbf{Q}_p$, $\mathcal{E}_p$.

$$\begin{aligned}\mathcal{E}_{BCM} &= \mathcal{E}_{cap} + \mathcal{E}_p = \frac{1}{2}\mathbf{V}^\dagger\mathbf{C}\mathbf{V} + \frac{1}{2}\mathbf{Q}_p^\dagger\widetilde{\mathbf{J}}\mathbf{Q}_p \\ \mathcal{E}_{BCM} &= \frac{1}{2}\Big[\chi + \widetilde{\mathbf{J}}(\mathbf{Q}_0 + \mathbf{Q}_p)\Big]^\dagger\mathbf{C}\Big[\chi + \widetilde{\mathbf{J}}(\mathbf{Q}_0 + \mathbf{Q}_p)\Big] + \frac{1}{2}\mathbf{Q}_p^\dagger\widetilde{\mathbf{J}}\mathbf{Q}_p\end{aligned} \tag{1}$$

The potential $\mathbf{V}$ from which $\mathcal{E}_{cap}$ is calculated is originated from the Coulomb potential arising from $\mathbf{Q} = \mathbf{Q}_p + \mathbf{Q}_0$ and from the electronegativity vector χ. Differentiation of eq 1 with respect $\mathbf{Q}_p$ gives eq 2.

$$\frac{\partial\mathcal{E}_{BCM}}{\partial\mathbf{Q}_p} = \chi^\dagger\mathbf{C}\widetilde{\mathbf{J}} + \mathbf{Q}_p^\dagger\widetilde{\mathbf{J}}\mathbf{C}\widetilde{\mathbf{J}} + \mathbf{Q}_0^\dagger\widetilde{\mathbf{J}}\mathbf{C}\widetilde{\mathbf{J}} + \mathbf{Q}_p^\dagger\widetilde{\mathbf{J}} = 0 \tag{2}$$

The terms containing $\mathbf{Q}_p$ can be collected to give eq 3.

$$\mathbf{Q}_p^\dagger(\widetilde{\mathbf{J}}\mathbf{C} + \mathbf{I})\widetilde{\mathbf{J}} = -\chi^\dagger\mathbf{C}\widetilde{\mathbf{J}} - \mathbf{Q}_0^\dagger\widetilde{\mathbf{J}}\mathbf{C}\widetilde{\mathbf{J}} \tag{3}$$

Assuming that the $\widetilde{\mathbf{J}}$ matrix is non-singular, both sides of eq 3 can be multiplied on the right by $\widetilde{\mathbf{J}}^{-1}$, transposed and $\mathbf{Q}_p$ isolated to obtain eq 4.

$$\mathbf{Q}_p = -(\mathbf{I} + \mathbf{C}\widetilde{\mathbf{J}})^{-1}\mathbf{C}\chi - (\mathbf{I} + \mathbf{C}\widetilde{\mathbf{J}})^{-1}\mathbf{C}\widetilde{\mathbf{J}}\mathbf{Q}_0 \tag{4}$$

Eq 4 represents the set of induced charges and we can add $\mathbf{Q}_0$ to both sides to obtain an expression for the total charge $\mathbf{Q}$, eq 5.

$$\mathbf{Q} = \mathbf{Q}_p + \mathbf{Q}_0 = -(\mathbf{I} + \mathbf{C}\widetilde{\mathbf{J}})^{-1}\mathbf{C}\chi - (\mathbf{I} + \mathbf{C}\widetilde{\mathbf{J}})^{-1}\mathbf{C}\widetilde{\mathbf{J}}\mathbf{Q}_0 + \mathbf{Q}_0 \tag{5}$$

Gathering the terms in $\mathbf{Q}_0$ and substituting the equality in 6 gives eq 7.

$$(\mathbf{I} + \mathbf{C}\widetilde{\mathbf{J}})^{-1} = \mathbf{I} - (\mathbf{I} + \mathbf{C}\widetilde{\mathbf{J}})^{-1}\mathbf{C}\widetilde{\mathbf{J}} \tag{6}$$

$$\mathbf{Q} = -(\mathbf{I} + \mathbf{C}\widetilde{\mathbf{J}})^{-1}\mathbf{C}\boldsymbol{\chi} + (\mathbf{I} + \mathbf{C}\widetilde{\mathbf{J}})^{-1}\mathbf{Q}_0 \tag{7}$$

The above derivation highlights that the set of BC charges are the result of the minimization of the electrostatic polarization energy $\mathcal{E}_p$ counterbalanced by an increase of the $\mathcal{E}_{cap}$ term which represents the energetic price to pay (positive work) for charge polarization in a system of fully coupled capacitors.

Finally, we note that the $\mathcal{E}_{BCM}$ energy reported in eq 1 is the same as the energy function employed in the charge response kernel methods.[1–5]

The Ewald summation method and the Smooth Particle Mesh Ewald reformulation

We define the $\mathbf{Q}$ array as the set of N charges $Q_1, \ldots, Q_i, \ldots, Q_N$ at positions $\mathbf{R}_1, \ldots, \mathbf{R}_i, \ldots, \mathbf{R}_N$ within an electrically neutral unit cell U defined by its edges $(\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3)$ and with volume $V = \mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)$. The reciprocal conjugate vectors $(\mathbf{a}_1^*, \mathbf{a}_2^*, \mathbf{a}_3^*)$ are related to their dual set by $\mathbf{a}_\alpha^* \cdot \mathbf{a}_\beta = \delta_{\alpha\beta}$, with $\alpha, \beta = \{1, 2, 3\}$ and $\delta_{\alpha\beta}$ being the Kronecker delta. For any integers n_1, n_2, n_3 and m_1, m_2, m_3 in $\mathbb{Z}^3$, the vectors $\mathbf{n}$ and $\mathbf{m}$ are defined in eq 8.

$$\mathbf{n} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3 \quad , \quad \mathbf{m} = m_1\mathbf{a}_1^* + m_2\mathbf{a}_2^* + m_3\mathbf{a}_3^* \tag{8}$$

The structure factor $S(\mathbf{m})$ for a given $\mathbf{m}$ is defined by eq 9.

$$S(\mathbf{m}) = \sum_{j=1}^{N} Q_j \exp 2\pi\mathbf{m} \cdot \mathbf{R}_j \tag{9}$$

The electrostatic potential $\phi(\mathbf{R}_i)$ at position $\mathbf{R}_i$ generated by $\mathbf{Q}$ and all its periodic images is given in eq 10.

$$\phi(\mathbf{R}_i) = \sum_{\mathbf{n}}^{*} \sum_{j=1}^{N} Q_j \frac{1}{\mid \mathbf{R}_j - \mathbf{R}_i + \mathbf{n} \mid} \tag{10}$$

The asterisk in the eq 10 summation indicates that the case $j = i$ is skipped for $\mathbf{n} = \mathbf{0}$. The potential in eq 10 represents a slowly and conditionally convergent series which is undesirable for efficiently treating long-range electrostatic interactions. The Ewald summation method[6,7] replaces the conditionally convergent series in eq 10 by the three absolute convergent terms $\phi(\mathbf{R}_i) = \phi_{dir}(\mathbf{R}_i) + \phi_{rec}(\mathbf{R}_i) + \phi_{self}(\mathbf{R}_i)$ shown in eq 11.

$$\begin{aligned}
\phi_{dir}(\mathbf{R}_i) &= \sum_{\mathbf{n}}^{*} \sum_{j=1}^{N} Q_j \frac{\operatorname{erfc}\left(\beta \mid \mathbf{R}_j - \mathbf{R}_i + \mathbf{n} \mid\right)}{\mid \mathbf{R}_j - \mathbf{R}_i + \mathbf{n} \mid} \\
\phi_{rec}(\mathbf{R}_i) &= \frac{1}{\pi V} \sum_{\mathbf{m} \neq \mathbf{0}} \frac{\exp\left(-\pi^2 \mathbf{m}^2 / \beta^2\right)}{\mathbf{m}^2} S(\mathbf{m}) \exp\left(-2i\pi \mathbf{m} \cdot \mathbf{R}_i\right) \\
\phi_{self}(\mathbf{R}_i) &= -\frac{2\beta}{\sqrt{\pi}} Q_i
\end{aligned} \tag{11}$$

In eq 11, β represents a positive parameter that balances the convergence ratio between the ϕ_{dir} and ϕ_{rec} terms. The original formulation of the Ewald summation in eq 11 addressed the electrostatic interactions in ionic crystals where none of the interactions were screened or damped. In force-field applications, however, the electrostatic interactions are often damped or scaled to exclude close neighbors. This is in practice done by setting up a list $M(i)$ containing the set of neighbors of atom i to be scaled, and translates into an additive term to ϕ_{dir} as shown in eq 12, which is the equation implemented in this work for the direct contribution of the potential.

$$\phi_{dir}(\mathbf{R}_i) = \sum_{\mathbf{n}}^{*} \sum_{j=1}^{N} Q_j \frac{\operatorname{erfc}\left(\beta \mid \mathbf{R}_j - \mathbf{R}_i + \mathbf{n} \mid\right)}{\mid \mathbf{R}_j - \mathbf{R}_i + \mathbf{n} \mid} - \sum_{j \in M(j)} Q_j \frac{1 - f_{ij}}{\mid \mathbf{R}_j - \mathbf{R}_i \mid}$$
$$f_{ij} = \begin{cases} f_{ij} = 0 & j \in M(i) \\ \\ f_{ij} = f(R_{ij}) & j \notin M(i) \end{cases} \tag{12}$$

Each of the complex exponentials in eqs 9 and 11 is in the SPME framework first rewritten in terms of the scaled fractional coordinates $u_{\alpha j}$, eq 13.

$$\begin{aligned} u_{\alpha j} &= K_\alpha \mathbf{a}_\alpha^* \cdot \mathbf{R}_j \qquad\qquad \alpha = \{1,2,3\} \ , \ K_\alpha \in \mathbb{N}^+ \\ \exp\left(2i\mathbf{m} \cdot \mathbf{R}_j\right) &= \exp\left(2i\pi m_1 \frac{u_{1j}}{K_1}\right) \exp\left(2i\pi m_2 \frac{u_{2j}}{K_2}\right) \exp\left(2i\pi m_3 \frac{u_{3j}}{K_3}\right) \end{aligned} \tag{13}$$

The exponentials in eq 13 are then interpolated by a p-degree B-spline function $\theta_p(u_{\alpha j} - n_\alpha)$ on a grid of size $K_1 \times K_2 \times K_3$ with the resulting approximated reciprocal potential shown in eq 14.

$$\phi_{rec}(\mathbf{R}_i) \approx \sum_{\mathbf{n}} \theta_p(u_{1i} - n_1)\theta_p(u_{2i} - n_2)\theta_p(u_{3i} - n_3)(G^R \star Q^R)(\mathbf{n}) \tag{14}$$

The $(G^R \star Q^R)$ in eq 14 is the convolution of the charge array Q^R and the pair potential G^R discussed by Sagui and coworkers, where the latter is defined in terms of its inverse discrete Fourier transform $G^F(\mathbf{m})$.[8] The use of B-splines makes the derivatives of ϕ_{rec}, and thus of the reciprocal contribution to the energy, analytical and the efficient FFT summation technique can be applied for evaluating eq 14. Once $\phi(\mathbf{R}_i)$ and all its components are computed, the electrostatic energy can be evaluated as shown in eq 15.

$$\mathcal{E}_{el} = \frac{1}{2} \sum_{i=1}^{N} \phi(\mathbf{R}_i) Q_i \tag{15}$$

From $\phi(\mathbf{R}_i)$, the electric field $\mathbf{F}(\mathbf{R}_i) = \mathbf{F}_{dir}(\mathbf{R}_i) + \mathbf{F}_{rec}(\mathbf{R}_i) + \mathbf{F}_{self}(\mathbf{R}_i)$ is derived by differentiating each of the $\phi_{dir}(\mathbf{R}_i)$, $\phi_{rec}(\mathbf{R}_i)$ and $\phi_{self}(\mathbf{R}_i)$ terms as shown in eq 16, where the direct and reciprocal contributions are taken from eqs 12 and 14, respectively.

$$
\begin{aligned}
\frac{\partial \boldsymbol{\phi}_{dir}}{\partial \mathbf{R}_i} &= -\mathbf{F}_{dir}(\mathbf{R}_i) = \frac{\partial}{\partial \mathbf{R}_i}\left[\sum_{\mathbf{n}}^{*}\sum_{j=1}^{N} Q_j \frac{\operatorname{erfc}\left(\beta \mid \mathbf{R}_j - \mathbf{R}_i + \mathbf{n} \mid\right)}{\mid \mathbf{R}_j - \mathbf{R}_i + \mathbf{n} \mid} - \sum_{j \in M(i)} Q_j \frac{f_{ij}}{\mid \mathbf{R}_j - \mathbf{R}_i \mid}\right] \\
\frac{\partial \phi_{rec}}{\partial \mathbf{R}_i} &= -\mathbf{F}_{rec}(\mathbf{R}_i) = \frac{\partial}{\partial \mathbf{R}_i}\left[\sum_{\mathbf{n}} \theta_p(u_{1i} - n_1)\theta_p(u_{2i} - n_2)\theta_p(u_{3i} - n_3)(G^R \star Q^R)(\mathbf{n})\right] \\
\frac{\partial \phi_{self}}{\partial \mathbf{R}_i} &= -\mathbf{F}_{self}(\mathbf{R}_i) = \mathbf{0}
\end{aligned}
\tag{16}
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