## A. Traditional Ewald Sum

Because Coulombic interactions decay very slowly, these interactions are frequently handled using the Ewald (lattice) sum method.[1,2] In an Ewald sum, the total Coulombic potential $U_C$ is divided into a real space portion $U_C^{real}$ and reciprocal $k$-space portion $U_C^{recip}$ as

$$U_C = U_C^{real} + U_C^{recip} - U_C^{self}, \tag{1}$$

where $U_C^{self}$ is a self-correction term which must also be included (see below).

The real-space portion of the energy is calculated for $r \leq r_{cut}$ as

$$U_C^{real} = \frac{1}{4\pi\,\varepsilon_0} \sum_{i,j<i} \frac{q_i\,q_j \text{erfc}\,(\alpha\,r_{ij})}{r_{ij}}, \tag{2}$$

where $\alpha$ is the constant that controls how the potential is divided between real and reciprocal space.

The $k$-space portion of the energy is efficiently handled using a Fourier series as

$$U_C^{recip} = \frac{1}{2\,V\,\varepsilon_0} \sum_{\mathbf{k}\neq 0} \Gamma(k)\,\chi(\mathbf{k}), \tag{3}$$

where $\mathbf{k}$ are the reciprocal lattice vectors, $k = |\mathbf{k}|$, and $\Gamma(k)$ are Fourier coefficients given as

$$\Gamma(k) = k^{-2}\,e^{-k^2/4\alpha^2}. \tag{4}$$

The quantity $\chi(\mathbf{k})$ can be defined as a double sum over particle positions as

$$\chi(\mathbf{k}) = \sum_{i=1}^{N} \sum_{j=1}^{N} q_i\,q_j\,e^{\mathbf{i}\,\mathbf{k}\cdot\mathbf{r}_{ij}} \tag{5}$$

where $N$ is the total number of atoms, $\mathbf{i}$ is the imaginary number, and $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$. However, the double sum in Eq. 5 is very expensive, so normally one reduces the double sum in Eq. 5 to a single sum as

$$\chi(\mathbf{k}) = \sum_{i=1}^{N} \sum_{j=1}^{N} q_i \, q_j \, e^{\mathbf{i}\,\mathbf{k}\cdot\mathbf{r}_{ij}}$$

$$= \sum_{i=1}^{N} q_i \, e^{\mathbf{i}\,\mathbf{k}\cdot\mathbf{r}_i} \sum_{j=1}^{N} q_j \, e^{-\mathbf{i}\,\mathbf{k}\cdot\mathbf{r}_j}$$

$$= S(\mathbf{k}) \, S(-\mathbf{k}) \,, \tag{6}$$

where $S(\mathbf{k})$ is the structure factor:

$$S(\mathbf{k}) = \sum_{i=1}^{N} q_i \, e^{\mathbf{i}\,\mathbf{k}\cdot\mathbf{r}_i} \,. \tag{7}$$

In the traditional lattice sum, a particle interacts with itself, all periodic images of itself, all of its neighbors, and all periodic images of its neighbors. Because a particle interacts with itself, a energy self-correction term must be subtracted from the total energy:

$$U_{\mathrm{C}}^{\mathrm{self}} = \frac{\alpha}{4\pi^{3/2}\,\varepsilon_0} \sum_{i} q_i^2 \,. \tag{8}$$

## B.  Group-Group Ewald Sum

Eq. 5 includes a double sum over particles. In order to get interactions of group A atoms on group B atoms, one can restrict the double sum in Eq. 5 to include only groups A and B as:

$$\chi(\mathbf{k}) = \sum_{i=1}^{N_\mathrm{A}} \sum_{j=1}^{N_\mathrm{B}} q_i \, q_j \, e^{\mathbf{i}\,\mathbf{k}\cdot\mathbf{r}_{ij}}$$

$$= \sum_{i=1}^{N_\mathrm{A}} q_i \, e^{\mathbf{i}\,\mathbf{k}\cdot\mathbf{r}_i} \sum_{j=1}^{N_\mathrm{B}} q_j \, e^{-\mathbf{i}\,\mathbf{k}\cdot\mathbf{r}_j}$$

$$= S_\mathrm{A}(\mathbf{k}) \, S_\mathrm{B}(-\mathbf{k}) \,, \tag{9}$$

where $N_\mathrm{A}$ is the number of atoms in group A, $N_\mathrm{B}$ is the number of atoms in group B, $S_\mathrm{A}(\mathbf{k})$ is the group A structure factor:

$$S_\mathrm{A}(\mathbf{k}) = \sum_{i=\mathrm{type\,A}} q_i \, e^{\mathbf{i}\,\mathbf{k}\cdot\mathbf{r}_i} \,. \tag{10}$$

and $S_\text{B}(\mathbf{k})$ is the group B structure factor:

$$S_\text{B}(\mathbf{k}) = \sum_{j=\text{type B}} q_j \, e^{\mathbf{i}\,\mathbf{k}\cdot\mathbf{r}_j} \,. \tag{11}$$

One can think of this as all group A atoms and periodic images interacting with all group B atoms and periodic images. If an atom is in both groups A and B, one must also include the energy self-correction for that atom (see Eq. 8). One can obtain group-group forces in a similar manner by using the same group structure factors.

## C.   Per-atom Ewald Sum

In a similar manner, one can think of per-atom energy as one atom interacting with a group of all other atoms. Per-atom values can therefore be obtained by replacing $\chi(\mathbf{k})$ in Eqs. 9 with a per-atom version[3–5]

$$\begin{aligned}
\chi_i(\mathbf{k}) &= \sum_i q_i \, q_j e^{\mathbf{i}\,\mathbf{k}\cdot\mathbf{r}_{ij}} \\
&= S(-\mathbf{k})S_i(\mathbf{k}) \,,
\end{aligned} \tag{12}$$

where $S_i(\mathbf{k})$ is a per-atom structure factor defined as

$$S_i(\mathbf{k}) = q_i \, e^{\mathbf{i}\,\mathbf{k}\cdot\mathbf{r}_i} \,. \tag{13}$$

One must also include a per-atom version of the self-correction term (Eq. 8).

## D.   PPPM

In the PPPM method, group-group energy and force can be obtained in a similar manner. One interpolates charges for groups A and B to a mesh and then uses two forward FFTs (one for each group) to obtain group A and B structure factors. Total energy and force are then obtained using these group structure factors in a manner very similar to the Ewald sum.

3

## REFERENCES

[1] M. Allen and D. Tildesley, *Computer simulation of liquids* (Oxford Science, 1989).

[2] N. Karasawa and W. A. Goddard, "Acceleration of convergence for lattice sums," J. Chem. Phys. **93**, 7320–7327 (1989).

[3] D. M. Heyes, "Pressure tensor of partial-charge and point-dipole lattices with bulk and surface geometries," Phys. Rev. B **49**, 755–764 (1994).

[4] N. Galamba, C. A. N. de Castro, and J. F. Ely, "Thermal conductivity of molten alkali halides from equilibrium molecular dynamics simulations," J. Chem. Phys. **120**, 8676–8682 (2004).

[5] J. Sonne, F. Y. Hansen, and G. H. Peters, "Methodological problems in pressure profile calculations for lipid bilayers," J. Chem. Phys. **122** (2005).