A review of classical Ewald method

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Problem Statement

Consider N ions in vacuum, at locations $\boldsymbol{r}_1, \boldsymbol{r}_2, \boldsymbol{r}_3, \ldots, \boldsymbol{r}_N$, and possessing point charges $q_1, q_2, q_3, \ldots, q_N$, respectively. The total Coulomb interaction energy is

$$E = \frac{1}{4\pi\varepsilon_0} \sum_{(i,j)} \frac{q_i q_j}{|\boldsymbol{r}_{ij}|}$$

where $\boldsymbol{r}_{ij} = \boldsymbol{r}_j - \boldsymbol{r}_i$ and the sum is over all $N(N-1)/2$ ionic pairs (i, j).

Under periodic boundary condition (PBC) and three transition lattice vectors $\boldsymbol{c}_1, \boldsymbol{c}_2, \boldsymbol{c}_3$, there will be equivalent ions at

$$r_i + n_1\boldsymbol{c}_1 + n_2\boldsymbol{c}_2 + n_3\boldsymbol{c}_3$$

To simple notations, let $n_1\boldsymbol{c}_1 + n_2\boldsymbol{c}_2 + n_3\boldsymbol{c}_3$ be $\boldsymbol{n}L$, where L represents the characteristic length of the supercell.

The total Coulomb interaction energy under PBC is

$$E = \frac{1}{4\pi\varepsilon_0}\sum_{\boldsymbol{n}}\sum_{(i,j)}\frac{q_i q_j}{\left|\boldsymbol{r}_{ij} + \boldsymbol{n}L\right|}$$

Rewriting the sum over pairs into sums over all ions, and with a factor of ½ to cancel the double counting:

$$E = \frac{1}{4\pi\varepsilon_0}\frac{1}{2}\sum_{\boldsymbol{n}}\sum_{i=1}^{N}\sum_{j=1}^{N'}\frac{q_i q_j}{\left|\boldsymbol{r}_{ij} + \boldsymbol{n}L\right|}$$

where the ’ symbol means to exclude the term $i = j$ if and only if $\boldsymbol{n} = 0$.

PROBLEM!

This expression not only converges very slowly but also is conditionally convergent, meaning that the result depends on the order of the summation.

The Ewald method evaluates E by transforming it into summations that converges not only rapidly but also absolutely.

The potential field generated by all N ions together with their periodic images under PBC is

$$\phi(\boldsymbol{r}) = \frac{1}{4\pi\varepsilon_0} \sum_{\boldsymbol{n}} \sum_{j=1}^{N} \frac{q_j}{\left|\boldsymbol{r} - \boldsymbol{r}_j + \boldsymbol{n}L\right|}$$

Defining $\phi_{[i]}(\boldsymbol{r})$ as the potential field generated by all the ions plus their images, excluding ion i:

$$\phi_{[i]}(\boldsymbol{r}) = \phi(\boldsymbol{r}) - \phi_i(\boldsymbol{r}) = \frac{1}{4\pi\varepsilon_0} \sum_{\boldsymbol{n}} \sum_{j=1}^{N'} \frac{q_j}{\left|\boldsymbol{r} - \boldsymbol{r}_j + \boldsymbol{n}L\right|}$$

again the ’ symbol means to exclude the term $i = j$ if and only if $\boldsymbol{n} = 0$.

Combing the equations, we find that

$$E = \frac{1}{2} \sum_{i=1}^{N} q_i \phi_{[i]}(\boldsymbol{r}_i)$$

Charge Distribution Function

The charge density distribution for the system of point charges are described by a collection of delta functions.

The charge density for point charge q_i is

$$\boldsymbol{\rho}_i(\boldsymbol{r}) = q_i \delta(\boldsymbol{r} - \boldsymbol{r}_i)$$

where the associated potential field is described by the Poisson's equation

$$\nabla^2 \phi_i(\boldsymbol{r}) = -\frac{\rho_i(\boldsymbol{r})}{\varepsilon_0}$$

The general solution of Poisson's equation is

$$\phi_i(\boldsymbol{r}) = \frac{1}{4\pi\varepsilon_0}\int \frac{\rho_i(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}\,d^3\boldsymbol{r}'$$

The total Coulomb interaction energy can be written as,

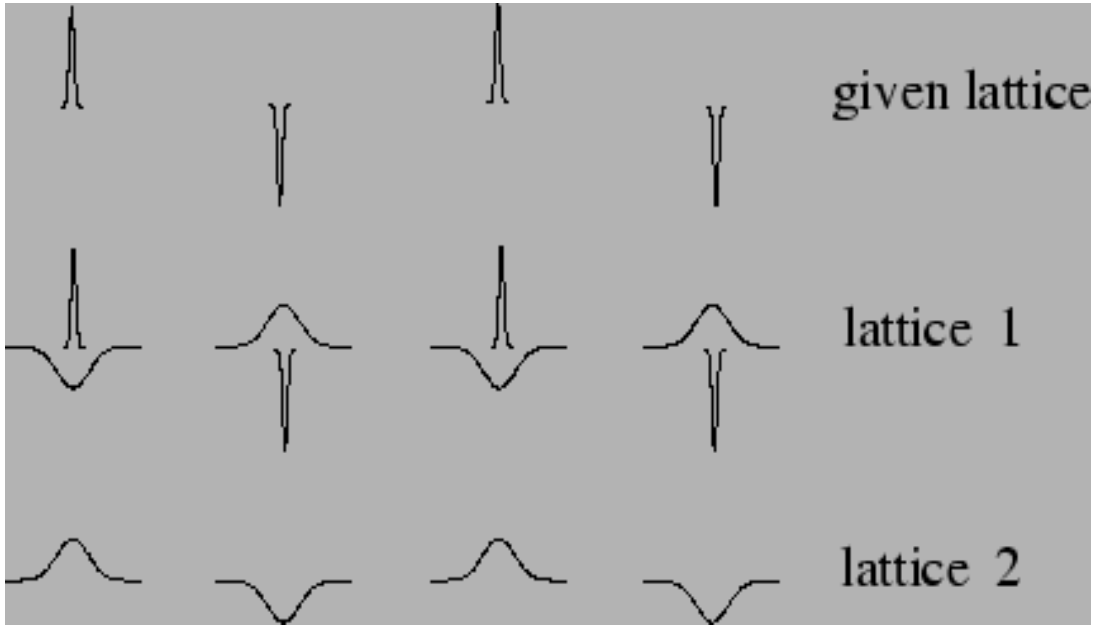
$$E = \frac{1}{4\pi\varepsilon_0}\frac{1}{2}\sum_{\boldsymbol{n}}\sum_{i=1}^{N}\sum_{j=1}^{N'}\iint \frac{\rho_i(\boldsymbol{r})\rho_j(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'+\boldsymbol{n}L|}\,d^3\boldsymbol{r}\,d^3\boldsymbol{r}'$$

and the potential field generated by all ions excluding ion i is

$$\phi_{[i]}(\boldsymbol{r}) = \frac{1}{4\pi\varepsilon_0}\sum_{N}\sum_{j=1}^{N'}\int \frac{\rho_j(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'+\boldsymbol{n}L|}\,d^3\boldsymbol{r}'$$

Splitting the Charge Distribution

The solution is to split up the potential in two well-behaved parts, one being represented in r-space and the other in k-space by rapidly converging series.



$$\rho_i(\boldsymbol{r}) = \rho_i^S(\boldsymbol{r}) + \rho_i^L(\boldsymbol{r})$$

$$\rho_i^S(\boldsymbol{r}) = q_i\delta(\boldsymbol{r} - \boldsymbol{r}_i) - q_i G_\sigma(\boldsymbol{r} - \boldsymbol{r}_i))$$

$$\rho_i^L(\boldsymbol{r}) = q_i G_\sigma(\boldsymbol{r} - \boldsymbol{r}_i)$$

The original charge densities are split into two terms by adding and subtracting a Gaussian distribution, where

$$G_\sigma(\boldsymbol{r}) = \frac{1}{(2\pi\sigma^2)^{3/2}} \exp\left[-\frac{|\boldsymbol{r}|^2}{2\sigma^2}\right]$$

Similarly, the potential can also be split:

$$\phi_i(\boldsymbol{r}) = \phi_i^S(\boldsymbol{r}) + \phi_i^L(\boldsymbol{r})$$

$$\phi_i^S(\boldsymbol{r}) = \frac{q_i}{4\pi\varepsilon_0} \int \frac{\delta(\boldsymbol{r}' - \boldsymbol{r}_i) - G_\sigma(\boldsymbol{r}' - \boldsymbol{r}_i)}{|\boldsymbol{r} - \boldsymbol{r}'|} d^3\boldsymbol{r}'$$

$$\phi_i^L(\boldsymbol{r}) = \frac{q_i}{4\pi\varepsilon_0} \int \frac{G_\sigma(\boldsymbol{r}' - \boldsymbol{r}_i)}{|\boldsymbol{r} - \boldsymbol{r}'|} d^3\boldsymbol{r}'$$

And also

$$\phi_{[i]}(\boldsymbol{r}) = \phi^{S}_{[i]}(\boldsymbol{r}) + \phi^{L}_{[i]}(\boldsymbol{r})$$

This leads to the splitting of the Coulomb interaction energy

$$E = \frac{1}{2}\sum_{i=1}^{N} q_i \phi^{S}_{[i]}(\boldsymbol{r}_i) + \frac{1}{2}\sum_{i=1}^{N} q_i \phi^{L}(\boldsymbol{r}_i) - \frac{1}{2}\sum_{i=1}^{N} q_i \phi^{L}_{i}(\boldsymbol{r}_i)$$

$$E = E^{S} + E^{L} - E^{self}$$

The self-interaction terms is extracted from the long range part.

Note that in E_L the potential generated by ion *i* itself is no longer excluded.

Potential Field of a Gaussian Charge Distribution

By the solving the Poisson's equation for a charge distribution of the Gaussian form, we get

$$\phi_\sigma = \frac{1}{4\pi\varepsilon_0 r}\,\mathrm{erf}\left(\frac{r}{\sqrt{2}\sigma}\right)$$

where $\mathrm{erf}(z) = \frac{2}{\sqrt{\pi}}\int_0^z e^{-t^2}\,dt$.

Then we can get

$$\phi_i^S(\boldsymbol{r}) = \frac{1}{4\pi\varepsilon_0}\frac{q_i}{|\boldsymbol{r}-\boldsymbol{r}_i|}\operatorname{erfc}\left(\frac{|\boldsymbol{r}-\boldsymbol{r}_i|}{\sqrt{2}\sigma}\right)$$

$$\phi_i^L(\boldsymbol{r}) = \frac{1}{4\pi\varepsilon_0}\frac{q_i}{|\boldsymbol{r}-\boldsymbol{r}_i|}\operatorname{erf}\left(\frac{|\boldsymbol{r}-\boldsymbol{r}_i|}{\sqrt{2}\sigma}\right)$$

where $\operatorname{erfc}(z) \equiv 1 - \operatorname{erf}(z)$.

Since $\lim_{n\to\infty} \operatorname{erf}(z) = 1$, we find that

- $\phi_i^S(\boldsymbol{r})$ is a short-range singular potential.
- $\phi_i^L(\boldsymbol{r})$ is a is a long-range non-singular potential.

Given this result,

$$\phi^S_{[i]}(\boldsymbol{r}) = \frac{1}{4\pi\varepsilon_0}\sum_{\boldsymbol{n}}\sum_{j=1}^{N'}\frac{q_j}{\left|\boldsymbol{r}-\boldsymbol{r}_j+\boldsymbol{n}L\right|}\operatorname{erfc}\left(\frac{\left|\boldsymbol{r}-\boldsymbol{r}_j+\boldsymbol{n}L\right|}{\sqrt{2}\sigma}\right)$$

And given that $E^S = \frac{1}{2}\sum_{i=1}^{N} q_i\phi^S_{[i]}(\boldsymbol{r}_i)$,

$$E^S = \frac{1}{4\pi\varepsilon_0}\frac{1}{2}\sum_{\boldsymbol{n}}\sum_{i=1}^{N}\sum_{j=1}^{N'}\frac{q_iq_j}{\left|\boldsymbol{r}_i-\boldsymbol{r}_j+\boldsymbol{n}L\right|}\operatorname{erfc}\left(\frac{\left|\boldsymbol{r}_i-\boldsymbol{r}_j+\boldsymbol{n}L\right|}{\sqrt{2}\sigma}\right)$$

The erfc term that truncates the potential function at large distances.

Due to the erfc truncation, E^S can be directly computed from a ***sum in real space***.

Self energy term

A spurious contribution to the potential energy from the interactions of Gaussian charge clouds with themselves.

Since analytic expression for the long-range potential is obtained, we can easily get the self energy term $E^{self} = \frac{1}{2}\sum_{i=1}^{N} q_i \phi_i^L(\boldsymbol{r}_i)$.

$$\lim_{z\to\infty} \mathrm{erf}(z) = \frac{2}{\sqrt{\pi}} z$$

$$\phi_i^L(\boldsymbol{r}_i) = \frac{q_i}{4\pi\varepsilon_0}\sqrt{\frac{2}{\pi}}\frac{1}{\sigma}$$

$$E^{self} = \frac{1}{4\pi\varepsilon_0}\frac{1}{\sqrt{2\pi}\sigma}\sum_{i=1}^{N} q_i^2$$

Long Range Potential in Reciprocal Space

The long-range interaction E^L cannot be directly computed by a sum in real space.

Given that this potential is no longer singular, it can be transformed into a sum in the reciprocal space.

Since the total charge densities

$$\rho^L(\boldsymbol{r}) = \sum_{\boldsymbol{n}} \sum_{i=1}^{N} \rho_i^L(\boldsymbol{r} + \boldsymbol{n}L)$$

is a periodic function, so is $\phi^L(\boldsymbol{r})$, which warrants the use of Fourier transform technique.

Let $\hat{\phi}^L(\boldsymbol{k})$ and $\hat{\rho}^L(\boldsymbol{k})$ be the Fourier transform of $\phi^L(\boldsymbol{r})$ and $\rho^L(\boldsymbol{r})$ respectively.

$$\hat{\phi}^L(\boldsymbol{k}) = \int_V \phi^L(\boldsymbol{r}) e^{-i\boldsymbol{k}\cdot\boldsymbol{r}} d^3\boldsymbol{r}$$

$$\hat{\rho}^L(\boldsymbol{k}) = \int_V \rho^L(\boldsymbol{r}) e^{-i\boldsymbol{k}\cdot\boldsymbol{r}} d^3\boldsymbol{r}$$

The integral is over the volume V of the supercell. The inverse Fourier transform is

$$\phi^L(\boldsymbol{r}) = \frac{1}{V}\sum_{\boldsymbol{k}} \hat{\phi}^L(\boldsymbol{k}) \boldsymbol{e}^{i\boldsymbol{k}\cdot\boldsymbol{r}}$$

$$\rho^L(\boldsymbol{r}) = \frac{1}{V}\sum_{\boldsymbol{k}} \hat{\rho}^L(\boldsymbol{k}) \boldsymbol{e}^{i\boldsymbol{k}\cdot\boldsymbol{r}}$$

Transforming the Poisson's equation

$$\nabla^2 \phi^L(\boldsymbol{r}) = -\frac{\rho^L(\boldsymbol{r})}{\varepsilon_0}$$

into reciprocal space will result in

$$k^2 \hat{\phi}^L(\boldsymbol{k}) = \frac{\hat{\rho}^L(\boldsymbol{k})}{\varepsilon_0}$$

Steps:

1. Firstly obtain the Fourier transform of the charge density
2. Dividing the result by k^2 we obtain the Fourier transform of the long range potential
3. The long-range potential in real space is then obtained by inverse Fourier transform

$$\rho^L(\boldsymbol{r}) = \sum_{\boldsymbol{n}} \sum_{j=1}^{N} q_j G_\sigma(\boldsymbol{r} - \boldsymbol{r}_j + \boldsymbol{n}L)$$

$$\hat{\rho}^L(\boldsymbol{k}) = \int_V \sum_{j=1}^{N} q_j G_\sigma(\boldsymbol{r} - \boldsymbol{r}_j + \boldsymbol{n}L) e^{-i\boldsymbol{k}\cdot\boldsymbol{r}}\, d^3\boldsymbol{r}$$

$$= \sum_{j=1}^{N} q_j \int_{\boldsymbol{R}^3} G_\sigma(\boldsymbol{r} - \boldsymbol{r}_j) e^{-i\boldsymbol{k}\cdot\boldsymbol{r}}\, d^3\boldsymbol{r}$$

$$= \sum_{j=1}^{N} q_j e^{-i\boldsymbol{k}\cdot\boldsymbol{r}_j} e^{-\sigma^2 k^2/2}$$

where $k = |\boldsymbol{k}|$ and $\int_{\boldsymbol{R}^3}$ means integration over the entire 3-dimensional space

Then the potential field in reciprocal space is

$$\hat{\phi}^L(\boldsymbol{k}) = \frac{1}{\varepsilon_0}\sum_{j=1}^{N} q_j e^{-i\boldsymbol{k}\cdot\boldsymbol{r}_j}\frac{e^{-\sigma^2 k^2/2}}{k^2}$$

Applying inverse Fourier transform,

$$\phi^L(\boldsymbol{r}) = \frac{1}{V}\sum_{\boldsymbol{k}\neq\boldsymbol{0}} \hat{\phi}^L(\boldsymbol{k})\boldsymbol{e}^{i\boldsymbol{k}\cdot\boldsymbol{r}}$$

$$= \frac{1}{V\varepsilon_0}\sum_{k\neq 0}\sum_{j=1}^{N}\frac{q_j}{k^2}e^{i\boldsymbol{k}\cdot(\boldsymbol{r}-\boldsymbol{r}_j)}e^{-\sigma^2 k^2/2}$$

The contribution to the $\boldsymbol{k} = 0$ term is zero if the supercell is charge neutral.

The long-range interaction energy is

$$E^L = \frac{1}{2}\sum_{i=1}^{N} q_i \phi^L(\boldsymbol{r}_i)$$

$$= \frac{1}{2V\varepsilon_0}\sum_{k\neq 0}\sum_{i=1}^{N}\sum_{j=1}^{N}\frac{q_i q_j}{k^2} e^{i\boldsymbol{k}\cdot(\boldsymbol{r_i}-\boldsymbol{r}_j)} e^{-\sigma^2 k^2/2}$$

For convenience, the structure factor $S(\boldsymbol{k})$ of the charge distribution is defined

$$S(\boldsymbol{k}) = \sum_{i=1}^{N} q_i e^{i\boldsymbol{k}\cdot\boldsymbol{r}_i}$$

Then the long-range interaction energy can be simply expressed as

$$E^L = \frac{1}{2V\varepsilon_0} \sum_{k \neq 0} \frac{e^{-\sigma^2 k^2/2}}{k^2} |S(\boldsymbol{k})|^2$$

The Ewald energy expression

Combing all terms, the total Coulomb interaction energy can be finally written as

$$E = E^S + E^L - E^{self}$$

$$= \frac{1}{4\pi\varepsilon_0}\frac{1}{2}\sum_{\boldsymbol{n}}\sum_{i=1}^{N}\sum_{j=1}^{N\prime}\frac{q_i q_j}{\left|\boldsymbol{r}_i - \boldsymbol{r}_j + \boldsymbol{n}L\right|}\operatorname{erfc}\left(\frac{\left|\boldsymbol{r}_i - \boldsymbol{r}_j + \boldsymbol{n}L\right|}{\sqrt{2}\sigma}\right)$$

$$+\frac{1}{2V\varepsilon_0}\sum_{k\neq 0}\frac{e^{-\sigma^2 k^2/2}}{k^2}|S(\boldsymbol{k})|^2 - \frac{1}{4\pi\varepsilon_0}\frac{1}{\sqrt{2\pi}\sigma}\sum_{i=1}^{N} q_i^2$$

The E^S sum is short-ranged in real space (truncated by the erfc function)

The E^L sum is short-ranged in reciprocal space (truncated by $e^{-\sigma^2 k^2/2}$).