

Notes on the nonneutral system by Ewald summation method

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1. Ewald sum in 3D periodic boundary conditions

Electrostatic interaction is long range interaction forces, and it decays in an order of $1/r$. The tail correction formula for the dispersive interactions (e.g., 12-6 Lennard-Jones potential) is given by[1],

$$U^{tail} = \frac{N\rho}{2} \int_{r_c}^{\infty} u(r) 4\pi r^2 dr \quad (1.1)$$

where N is number of molecules; ρ is number density in the system; r_c is the cut-off radius of the intermolecular potential $u(r)$. If we use the same tail correction (Eq. (1.1)) for the electrostatic interactions, the tail energy will never converge because the convergence of Eq. (1.1) entails the intermolecular potential to decay faster than $1/r^3$. French physicist Ewald in 1927 developed a method to calculate such long-range interactions. The method introduces a compensating charge distribution in the real space to screen the original point charges, by doing so, we can then simply truncate the Coulomb interaction at distance r_c in the real space. However, in order to transform such modified charge distribution into the original point charges eventually, we need to introduce another charge distribution to cancel the artificial compensating charge distribution in the real space; such introduced charge distribution is treated in Fourier space because of the periodicity. The split of the electrostatic energy into the real space and the Fourier space utilizes the relation of

$$erfc(x) + erf(x) = 1 \quad (1.2)$$

Following Eq. (1.2), the introduced two charge distributions are naturally treated as Gaussian distribution. Of course, the choice of other distribution form is possible, only if the charge distributions cancels out each other in the real space and Fourier space. More details can be found in Ref. [1], [2].

If the system has net charges (non-neutral system), we can introduce a uniform background charge distribution to compensate the net charges and keep the system neutral. The total charge distribution in the system can be given by

$$\rho(\mathbf{r}) = \rho_{back} + \sum_i^N q_i \delta(\mathbf{r} - \mathbf{r}_i) \quad (1.3)$$

with

$$q_{tot} = \sum_i^N q_i \quad (1.4)$$

$$\rho_{back} = -\frac{q_{tot}}{V} \quad (1.5)$$

where V is the volume of the system or the total volume of the simulation box (including the vacuum space added to the box). We now apply the basic idea of the Ewald summation and split the density into two contributions,

$$\rho(\mathbf{r}) = \rho_{real} + \rho_{recip} \quad (1.6)$$

where ρ_{real} is the screened charge density in the real space,

$$\rho_{real} = \sum q_i \left(\delta(\mathbf{r} - \mathbf{r}_i) - \left(\frac{\alpha}{\sqrt{\pi}} \right)^{3/2} \exp(-\alpha^2 r^2) \right) \quad (1.7)$$

and ρ_{recip} is the Gaussian charge density in the reciprocal space (Fourier space),

$$\begin{aligned} \rho_{recip} &= \rho_{back} + \rho_{smooth} \\ &= \rho_{back} + \sum q_i \left(\frac{\alpha}{\sqrt{\pi}} \right)^{3/2} \exp(-\alpha^2 r^2) \end{aligned} \quad (1.8)$$

where the first term in Eq. (1.7) is the original point charges and the second term is the compensating Gaussian charge distribution which screens the original point charges. The corresponding electrostatic potentials are φ_{real} for the real space and φ_{recip} for the Fourier space by solving the Poisson equation in terms of ρ_{real} and ρ_{recip} . The total Coulombic energy can be written as

$$E_{elec} = E_{real} + E_{bc} + E_{recip} - E_{self} \quad (1.9)$$

where real-space energy E_{real} accounts for the ‘point-screened’ interactions and excludes the self-interactions ($i \neq j$),

$$E_{real} = \frac{1}{2} \sum_i \sum_{i \neq j} q_i \varphi_{real} \quad (1.10)$$

The real-space energy between the background charge density with the screened points is defined as

$$E_{bc} = \frac{1}{2} \int_V \rho_{back} \varphi_{real} d\mathbf{r} = \frac{\pi q_{tot}^2}{2V \alpha^2} \quad (1.11)$$

The reciprocal-space energy is defined as

$$E_{recip} = \frac{1}{2} \sum_k \tilde{\rho}_{recip} \tilde{\varphi}_{recip} \exp(i\mathbf{k}\mathbf{r}_i) \quad (1.12)$$

Noting that the reciprocal energy calculated here includes the ‘self-point-point’ and ‘self-background-background’ interactions. And that’s why the self-interaction from the reciprocal space, E_{self} , should be subtracted from the total energy. Because ρ_{back} is a constant, its Fourier transform is an impulse function at zero frequency, and that the amplitude of the impulse is the constant value (for nonzero frequency, its value is just zero). So $\tilde{\rho}_{back} \tilde{\varphi}_{recip}$ is just zero for $k \neq 0$. In another words, φ_{recip} contains the information of the background charge density only at Fourier space vector $k = 0$. And because the total charge in ρ_{recip} is zero, $\tilde{\varphi}_{recip}(k = 0)$ in the Fourier space is just zero. Leaving out the ‘self-back-back’ interaction finally comes down to dropping the $k=0$ term¹. Therefore, E_{self} only contains the ‘self-point-point’ interactions in the reciprocal space. Following Eq. (1.2), we can see that the combination of the energies in the real space and Fourier space eventually goes to the direct Coulombic interactions of the point-point and point-background.

Generally, for either a neutral system or a non-neutral system, the equation of Ewald summation is the same, but with $E_{bc} = 0$ for the neutral system. In conclusion, it is only meaningful to apply the Ewald method to a physically neutral system. While for a physically non-neutral system, Ewald method will still converge but its value will depend on the choice of a non-physical parameter α . So it is meaningful only when a neutralizing background charge density is implicitly added (i.e., including Eq. (1.11) in the total energy and thus avoid the dependence of the total energy on α). In another words, Ewald method is meaningless when applied to a non-neutral system without neutralizing background charges. People actually use this feature of Ewald method in some special cases where the inclusion of explicit neutralizing counterions is very hard (either in a technical or physical way). Because this implicit neutralizing background energy introduced in Ewald method is uniformly distributed, special attentions should be payed when applying it to a inhomogeneous system with different dielectric composition throughout the system[3]. It is possible to apply this uniform neutralizing background charge in a specific region of the system, but this could change the force field of the original system. Further investigation should be made to verify such treatment will not alter the correct chemical physical properties of the original (correct) force field.

¹ Derivations of the reciprocal space energy in http://users.ugent.be/~tovrstra/labnotes/html/ewald_sum.html is not correct in some steps. Be cautious when referring to it.

2. Ewald Summation in 2D periodic boundary conditions

When applying the conventional 3D Ewald summation method to a slab geometry (i.e., periodic boundary conditions are only applied in two directions), the tin-foil boundary condition used in 3D Ewald summation should be changed, and a surface term should be added[4]. For a 2D non-neutral system, it is technically possible to calculate its electrostatic energy. The final equation is

$$E_{elec,2D} = E_{elec} + E_{surf} - E_{bcc} \quad (1.13)$$

where E_{elec} is defined by Eq. (1.9) and noting that E_{bc} term (Eq. (1.11)) must be included to avoid α -dependence of the Coulombic energy; E_{surf} is the surface term correction for a slab geometry[4]; E_{bcc} is the contribution due to the implicit background-background and background-point charge interaction. Eq. (1.13) states that for a 2D non-neutral system, an implicit neutralizing charge distribution should be added first like in the 3D method, then the contributions due to this background charge are subtracted to reveal the final energy of the non-neutral system.

3. Comparison between 3D method and 2D method

3D Ewald cannot physically account for a non-neutral system without applying a background neutralizing charge density, while 2D Ewald is able to account for a non-neutral system.

Reference

- [1] D. Frenkel and B. Smit, *Understanding molecular simulation: from algorithms to applications*, 2nd ed. San Diego: Academic Press, 2002.
- [2] M. P. Allen and D. J. Tildesley, *Computer Simulation of Liquids*. Clarendon Press, 1989.
- [3] J. S. Hub, B. L. de Groot, H. Grubmüller, and G. Groenhof, “Quantifying Artifacts in Ewald Simulations of Inhomogeneous Systems with a Net Charge,” *J. Chem. Theory Comput.*, vol. 10, no. 1, pp. 381–390, Jan. 2014.
- [4] I.-C. Yeh and M. L. Berkowitz, “Ewald summation for systems with slab geometry,” *J. Chem. Phys.*, vol. 111, no. 7, p. 3155, 1999.