

Chem 860. Lecture 17

Derivation of Ewald summation

April 7, 2009

1 Periodic condition - Ewald summation

Lattice sum, or Ewald summation, is an elegant way to compute electrostatic interactions between charges in the primary cell and its (infinite number of) images. Using cubic PBC as an example, we can use $\mathbf{n} = (n_1, n_2, n_3)$ to label all cells. The goal is to compute electrostatic potential generated by all charges in the primary cell,

$$\phi(\mathbf{r}) = \sum_{\mathbf{n}} \sum_{i=1}^N \frac{q_i}{|\mathbf{r}_i + \mathbf{nL} - \mathbf{r}|} \quad (1)$$

This infinite series (in terms of \mathbf{n}) is conditionally convergent, so one has to be careful when doing the summation.

The basic idea of Ewald sum is to separate interactions into a short range part and a long range part; the former will be computed in the real space, while the latter will be computed in the reciprocal space.

To construct the short range part, we add a Gaussian to each point charge with the same magnitude but opposite sign ($-q_i(\beta/\sqrt{\pi})^3 \exp(-\beta^2 r^2)$). As a result, the interactions between different point charges are significantly screened and short ranged, which means the calculation can be truncated at a rather short distance. To remove contributions from those additional Gaussians, as the second step we add another set of Gaussians with the same sign and magnitude as the original point charges. Since these Gaussian charges are smooth spatially, the corresponding electrostatic problem is better solved in the reciprocal space with Fourier transform.

Referring to the screened charges as ρ_1 and the “correcting/compensating” Gaussians as ρ_2 , for any point \mathbf{r} NOT coincident with the point charges, the total electrostatic potential is simply the sum of ϕ_{ρ_1} and ϕ_{ρ_2} .

$$\phi_{\rho}(\mathbf{r}) = \phi_{\rho_1}(\mathbf{r}) + \phi_{\rho_2}(\mathbf{r}) \quad (2)$$

1.1 $\phi_{\rho_1}(\mathbf{r})$

One can show that the corresponding electrostatic potential is

$$\phi_{\rho_1}(\mathbf{r}) = \sum_{\mathbf{n}} \sum_{i=1}^N \frac{q_i \operatorname{erfc}(\beta |\mathbf{r}_i - \mathbf{r} + \mathbf{n}|)}{|\mathbf{r}_i - \mathbf{r} + \mathbf{n}|} \quad (3)$$

where β is a parameter that characterizes the width of the Gaussian.

Derivation: Consider a simple Gaussian charge at the origin, $\rho_{\text{Gaussian}}(\mathbf{r}) = q_i (\beta/\sqrt{\pi})^3 \exp(-\beta^2 r^2)$, for which we know the electrostatic potential in space:

$$\phi_{\text{Gaussian}}(\mathbf{r}) = \frac{q_i}{r} \operatorname{erf}(\beta r) \quad (4)$$

where $\operatorname{erf}(x) = 2/\sqrt{\pi} \int_0^x \exp(-u^2) du$ is the error function (note that when x is very large, $\operatorname{erf}(x) \rightarrow 1$; also note that the small value expansion of $\operatorname{erf}(x)$ can be easily derived with a Taylor expansion of the integrand, which leads to the result that $\operatorname{erf}(x \rightarrow 0) \approx 2x/\sqrt{\pi}$).

So for the screened charges, which are: $q_i - q_i (\beta/\sqrt{\pi})^3 \exp(-\beta^2 r^2)$, we should have,

$$\phi_{\rho_1, i}(\mathbf{r}) = \frac{q_i}{r} - \frac{q_i}{r} \operatorname{erf}(\beta r) = \frac{q_i}{r} \operatorname{erfc}(\beta r) \quad (5)$$

Note: The Poisson problem for a Gaussian charge can be solved by either the Green's function approach or by Fourier transform. Look up your favorite Math or EM book for that. It's useful to at least try to confirm the result by substitution, which we do here for fun. The Poisson Equation is,

$$-\nabla^2 \phi(\mathbf{r}) = 4\pi \rho(\mathbf{r}) \quad (6)$$

Since the problem is spherically symmetric, we use the spherical polar coordinate. Due to symmetry, we can ignore the angular derivatives. So we have

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \frac{q_i}{r} \operatorname{erf}(\beta r) \right) \quad (7)$$

$$= \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{q_i}{r} \frac{2\beta}{\sqrt{\pi}} e^{-\beta^2 r^2} - q_i \operatorname{erf}(\beta r) \right) \quad (8)$$

where we used the identity, $\frac{d}{dx} \int_0^x f(u) du = f(x)$ to get the derivative w.r.t the error function. Carry on the second partial derivative, we have,

$$= \frac{q_i}{r^2} \left(\frac{2\beta}{\sqrt{\pi}} e^{-\beta^2 r^2} + r \frac{2\beta}{\sqrt{\pi}} e^{-\beta^2 r^2} (-2\beta^2 r) - \frac{2\beta}{\sqrt{\pi}} e^{-\beta^2 r^2} \right) \quad (9)$$

$$= \frac{-4q_i \beta^3}{\sqrt{\pi}} e^{-\beta^2 r^2} = -4\pi \rho_{\text{Gaussian}} \quad (10)$$

1.2 $\phi_{\rho_2}(\mathbf{r})$

The electrostatic problem (Poisson) associated with a set of Gaussians in periodic boundary condition is straightforward to solve in the reciprocal space - i.e., first perform discrete Fourier transform of the Poisson Equation,

(Recall: $f(\mathbf{r}) = \frac{1}{V} \sum_{\mathbf{k}} \hat{f}(\mathbf{k}) e^{i\mathbf{k}\cdot\mathbf{r}}$ and $\hat{f}(\mathbf{k}) = \int_V d\mathbf{r} f(\mathbf{r}) e^{-i\mathbf{k}\cdot\mathbf{r}}$)

$$k^2 \hat{\phi}_{\rho_2}(\mathbf{k}) = 4\pi \hat{\rho}_2(\mathbf{k}) \quad (11)$$

(If you don't remember the derivative rule of Fourier transform, you can get the result by inspection:

$$-\nabla^2 \phi(\mathbf{r}) = -\nabla^2 \phi \left(\frac{1}{V} \sum_{\mathbf{k}} \hat{\phi}(\mathbf{k}) e^{i\mathbf{k}\cdot\mathbf{r}} \right) = \frac{1}{V} \sum_{\mathbf{k}} k^2 \hat{\phi}(\mathbf{k}) e^{i\mathbf{k}\cdot\mathbf{r}} \quad (12)$$

and

$$\rho(\mathbf{r}) = \frac{1}{V} \sum_{\mathbf{k}} \hat{\rho}(\mathbf{k}) e^{i\mathbf{k}\cdot\mathbf{r}} \quad (13)$$

)

meaning, $\hat{\phi}_{\rho_2}(\mathbf{k}) = \frac{4\pi}{k^2} \hat{\rho}_2(\mathbf{k})$.

What is the Fourier transform of $\rho_2(\mathbf{r})$?

$$\hat{\rho}_2(\mathbf{k}) = \int_V d\mathbf{r} \rho_2(\mathbf{r}) e^{-i\mathbf{k}\cdot\mathbf{r}} \quad (14)$$

which is

$$= \int_V d\mathbf{r} e^{-i\mathbf{k}\cdot\mathbf{r}} \sum_j \sum_{\mathbf{n}} q_j \left(\frac{\beta}{\sqrt{\pi}} \right)^3 e^{-\beta^2 |\mathbf{r} - (\mathbf{r}_j + \mathbf{nL})|^2} \quad (15)$$

Take periodicity into account, we can move the summation over \mathbf{n} out, which makes the integration change from within the cell (with volume V) to the entire space,

$$= \int_{all\ space} d\mathbf{r} e^{-i\mathbf{k}\cdot\mathbf{r}} \sum_j q_j \left(\frac{\beta}{\sqrt{\pi}} \right)^3 e^{-\beta^2 |\mathbf{r} - \mathbf{r}_j|^2} \quad (16)$$

Evaluating the integral (3D Gaussian integral, $\int_{all\ space} e^{-a\mathbf{r}^2 + i\mathbf{k}\cdot\mathbf{r}} d\mathbf{r} = \left(\frac{\pi}{a}\right)^{3/2} e^{-k^2/4a}$, which is simply the product of three 1D Gaussian integral), we get

$$= \sum_j q_j e^{-i\mathbf{k}\cdot\mathbf{r}_j} e^{-k^2/4\beta^2} \quad (17)$$

which means

$$\hat{\phi}(\mathbf{k}) = \frac{4\pi}{k^2} e^{-k^2/4\beta^2} \sum_j q_j e^{-i\mathbf{k}\cdot\mathbf{r}_j} \quad (18)$$

where we make the choice that $\hat{\phi}(\mathbf{k}) = 0$ when $\mathbf{k} = \mathbf{0}$.

Then carry out the reverse Fourier transform, the result is

$$\phi(\mathbf{r}) = \frac{1}{V} \sum_{\mathbf{k} \neq \mathbf{0}} \frac{4\pi}{k^2} e^{-k^2/4\beta^2} \sum_j q_j e^{i\mathbf{k} \cdot (\mathbf{r} - \mathbf{r}_j)} \quad (19)$$

Note that the wave vector \mathbf{k} can be expressed in terms of an integer vector, \mathbf{m} , as, $\mathbf{k} = \mathbf{m}2\pi/L$, and some prefers an alternative expression in terms of \mathbf{m} (as used in the ppt, in which I unfortunately used \mathbf{k} as the integer label),

$$\phi_{\rho_2}(\mathbf{r}) = \frac{1}{\pi L} \sum_{\mathbf{m} \neq \mathbf{0}} \frac{e^{-\pi^2 m^2 / (\beta^2 L^2)}}{m^2} S(\mathbf{m}) e^{2\pi i \mathbf{m} \cdot \mathbf{r} / L}$$

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

$$S(\mathbf{m}) = \sum_i q_i e^{-2i\pi \mathbf{m} \cdot \mathbf{r}_i / L}$$

1.3 Electrostatic Energy

For computing electrostatic energies, we need the electrostatic potential at the sites of the point charges. In this case, we should NOT include the contribution from the charge at the site. For the real-space part, we simply do not include contribution from the current site, i.e.,

$$\phi'_{\rho_1}(\mathbf{r}_i) = \sum'_{\mathbf{n}} \sum_{j=1}^N \frac{q_j \text{erfc}(\beta |\mathbf{r}_j - \mathbf{r} + \mathbf{n}|)}{|\mathbf{r}_j - \mathbf{r} + \mathbf{n}|}$$

where the ' in the summation sign indicates that the summation does not include $j = i$ when $\mathbf{n} = \mathbf{0}$.

For ϕ_{ρ_2} , it turns out that it's convenient to include all the Gaussians because it's easier to solve for a truly periodic problem. This means, however, we have to correct the result to be consistent with the modification we have done for the short range part. This gives rise to the so-called self-interaction term,

$$\phi^{self} = -\frac{q_i}{\sqrt{\pi}} 2\beta$$

To sum up, the total electrostatic potential at the site of a point charge in the primary cell is,

$$\phi_{Ewald}(\mathbf{r}_i) = \sum'_{\mathbf{n}} \sum_{j=1}^N \frac{q_j \text{erfc}(\beta |\mathbf{r}_j - \mathbf{r} + \mathbf{n}|)}{|\mathbf{r}_j - \mathbf{r} + \mathbf{n}|} + \frac{1}{\pi L} \sum_{\mathbf{k} \neq \mathbf{0}} \frac{e^{-\pi^2 k^2 / (\beta^2 L^2)}}{k^2} S(\mathbf{k}) e^{2\pi i \mathbf{k} \cdot \mathbf{r} / L} - \frac{q_i}{\sqrt{\pi}} 2\beta$$

The total electrostatic interaction energy is nothing but

$$U^{Ewald} = \frac{1}{2} \sum_{i=1}^N q_i \phi_{Ewald}(\mathbf{r}_i)$$

Without going into details, we simply note that if the primary cell is NOT charge neutral, an additional correction should be added, which is equal to

$$-\frac{\pi Q}{2L^3\beta^3}$$

where Q is the total charge of the primary cell.

1.4 Practical issues of Ewald calculations

Basically we have to choose β (width of the Gaussian), range of real-space calculation and range of reciprocal space calculation; all these are related. One may choose β such that real space sum is negligible beyond $L/2$. In this case, the real space sum is N^2 while the reciprocal sum is N . Alternatively, one can choose larger β so that one can truncate the real space part at a fixed cutoff (e.g., 10\AA); in this case, the reciprocal sum scales as N^2 (because more \mathbf{k} sums are needed). The best balance can make Ewald summation scale as $N^{3/2}$. Rule of thumb is that $\beta \sim \frac{4-5}{r_{cut}}$; however, one should always vary β , r_{cut} and the number of \mathbf{k} sums such that errors in force is small ($< 10^{-3}$ kcal/mol $\cdot\text{\AA}$).

A slightly more careful derivation: The errors due to truncation in the real space (r_{cut}) and reciprocal space ($|\mathbf{k}| < k_{cut}$) have been analyzed and both depend on the function of the form e^{-x^2}/x^2 . By setting the error ϵ to be the same order of magnitude of e^{-s^2}/s^2 , we can derive that the r_{cut} and k_{cut} are related:

$$r_{cut} = s/\beta$$

and

$$k_{cut} = \frac{sL\beta}{\pi} = \frac{s^2L}{\pi r_{cut}}$$

The cost of calculations can be estimated by counting how many calculations are needed:

$$\tau = \tau_R N_R + \tau_F N_F$$

where $N_R = \frac{4\pi r_{cut}^3}{3L^3} N^2$ and $N_F = \frac{4\pi k_{cut}^3}{3} N$.

Since both r_{cut}/k_{cut} depend on β , for a given s , one can choose β such that the computational cost (τ) is minimized. The result shows that the resulting scaling is indeed $N^{3/2}$.

More recent developments have further sped up Ewald summations. For example, a popular approach is the so-called Particle-mesh-Ewald, which computes the reciprocal sum using Fast Fourier Transform (FFT). This makes the calculation essentially scales as $N \log N$.

Finally, we emphasize once again that whenever possible, one should systematically check the convergence of results with respect to the size of the primary cell. For discussions, see, for example, Smith and Pettitt, *J. Chem. Phys.*, **1996**, 105, 4289; McCammon et al. *J. Phys. Chem. B* **2000**, 104, 3668

1.5 Note: Gaussian integral

For your future reference, I included the derivation of the (complex) Gaussian integral.

$$I = \int_{-\infty}^{\infty} e^{iax-bx^2} dx \quad (20)$$

First, complete square, we have

$$I = e^{-a^2/4b} \int_{-\infty-i(a/2b)}^{\infty-i(a/2b)} e^{-bz^2} dz \quad (21)$$

where apparently, $z = x - ia/2b$. Using a rectangular contour and noticing that there is no pole within the contour as well as the fact that the integration along the lines perpendicular to the real axis (at $\pm\infty$) doesn't contribute, we have,

$$I = e^{-a^2/4b} \int_{-\infty}^{\infty} e^{-bz^2} dz \quad (22)$$

where we integrate simply along the real axis. Since the integral on the r.h.s. is just the standard Gaussian integral, which can be evaluated using a polar coordinate trick (*hint*: $\int e^{-z^2} dz = (\int e^{-x^2} dx)^{1/2} (\int e^{-y^2} dy)^{1/2}$) to be $\sqrt{\pi/b}$, we have

$$\int_{-\infty}^{\infty} e^{iax-bx^2} dx = \sqrt{\pi/b} e^{-a^2/4b} \quad (23)$$