LONG-RANGE INTERACTION:

The interactions that decay slower than $r^{-n}$, where $n$ is the dimensionality of the system is known as long-range interaction. Those long-range interactions can be a problem as their range is often greater than half of the box length. During the simulations of charged species it is extremely important to properly model these long-range forces. The charge-charge interaction, which decays as $\frac{1}{r}$, is extremely difficult to handle properly during the simulations of charged species. Different methods, e.g. Ewald summations, the reaction field method, cell multiple method etc. have been developed to handle long-range interaction. We have used Ewald summation technique to handle long-range electrostatic interactions in chapter II and chapter III.

Ewald Summation Method:

This method was developed by Ewald to study the energetic of ionic crystals. In this method, a particle interacts with all other particles in the simulation box and with all possible images. The position of the image boxes can be related to the central box (assumed a cube of side $L$) by specifying a vector ($\pm n_x L$, $\pm n_y L$, $\pm n_z L$); $a, b, c = 0, 1, 2$ etc. The potential energy due to the charge-charge interaction in the central box containing ‘$N$’ charges can be written as:

$$V = \frac{1}{2} \sum_{i \neq j} \frac{q_i q_j}{4 \pi \varepsilon_0 r_{ij}},$$

where $r_{ij}$ is the minimum distance between the charges $i$ and $j$. In general, for a box at a cubic lattice point, $\vec{n} (= (n_x L, n_y L, n_z L)$ with $n_x, n_y, n_z$ being integers):

$$V = \frac{1}{2} \sum_{|\vec{n}|=0} \sum_{i \neq j} \frac{q_i q_j}{4 \pi \varepsilon_0 |\vec{r}_{ij} + \vec{n}|}$$

The ‘prime’ on the first summation indicates that the charge-charge interaction, $i=j$, for the primary simulation box is excluded. Now the series is conditionally convergent. The sum of a conditionally convergent series depends on the order in which its terms considered.

The sum is converted the summation into two series, each of which
converges much more rapidly. In this case we can write, \[ \frac{1}{r} = f(r) + \frac{1}{r} - f(r), \]
where \( f(r) \) is an appropriate function which deals with the rapid variation of \( \frac{1}{r} \) at small \( r \) and slow decay at long \( r \).

In Ewald sum method each charge is considered to be surrounded by a neutralizing charge distribution of equal magnitude but of opposite sign. The commonly used functional form is:

\[ \rho_i(\vec{r}) = q_i \frac{\alpha^3}{\pi^{3/2}} \exp(-\alpha^2 \vec{r}^2). \]

The sum over point charges is now converted to a sum of the interactions between the charges plus the neutralizing distributions.

The real space summation is given by:

\[ V_{\text{real}} = \frac{1}{2} \sum_{i \neq j} \sum_{\vec{r} \neq 0} q_i q_j \frac{4 \pi \varepsilon_0}{4 \pi \varepsilon_0} \text{erfc} \left( \frac{\alpha |\vec{r}_{ij} + \vec{n}|}{|\vec{r}_{ij} + \vec{n}|} \right) \]

where \( \text{erfc} \) is the complementary error function, which can be written as \( \text{erfc}(x) = \frac{2}{\sqrt{\pi}} \int_x^\infty \exp(-t^2) dt \). The new summation involving the error function converges very rapidly and beyond some cut-off distance its value can be considered negligible. The rate of convergence depends upon the width of the Gaussian charge distribution. The contribution comes from the neutralizing charge distribution is:

\[ V_{\text{reciprocal}} = \frac{1}{2} \sum_{i \neq j} \sum_{\vec{r} \neq 0} \frac{1}{\mathcal{L}^2} \sum_{\vec{r} \neq 0} q_i q_j \frac{4 \pi \varepsilon_0}{4 \pi \varepsilon_0} \exp \left( -\frac{k^2}{4 \alpha^2} \right) \cos(\vec{k} \cdot \vec{r}_{ij}) \]

where the vectors \( \vec{k} \) are reciprocal vectors and given by \( \vec{k} = \frac{2 \pi \vec{n}}{L} \). This summation is performed in reciprocal space. This reciprocal sum also converges much more rapidly than the original point-charge sum. For the reciprocal space summation the number of terms increases with the width of the Gaussian charge distribution. So, the value of ‘\( \alpha \)’ need to be chosen in such a way that it can balance real-space and reciprocal space summation. A value for \( \alpha \) of \( \frac{5}{L} \) and 100-200 reciprocal vectors \( \vec{k} \) provides an optimal solution. The sum of Gaussian functions in real space also includes the interaction of each Gaussian with itself. A third self-term therefore is
subtracted: \( V_{self} = -\frac{\alpha}{\sqrt{\pi} \sum_{k=1}^{N} \frac{q_k^2}{4 \pi \varepsilon_0}} \). A fourth term depending upon the surrounding medium is also included: \( V_{Corr} = \frac{2\pi}{3L} \left[ \sum_{k=1}^{N} \frac{q_k}{4 \pi \varepsilon_0} \right]^2 \).

The final expression of electrostatic interaction is thus:

\[
V_{total} = \frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{N} \sum_{k=1}^{N} q_i q_j \frac{\text{erfc} \left( \frac{\alpha \left| \mathbf{r}_{ij} + \mathbf{n} \right|}{\sqrt{\pi} \mathbf{r}_{ij}} \right)}{4 \pi \varepsilon_0} + \frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{N} \sum_{k=1}^{N} \frac{q_i q_j 4\pi^2}{4 \pi \varepsilon_0 \mathbf{k}^2} \exp \left( -\frac{k^2}{4\alpha^2} \right) + \cos(\mathbf{k} \cdot \mathbf{r}_{ij}) - \frac{\alpha}{\sqrt{\pi} \sum_{k=1}^{N} \frac{q_k^2}{4 \pi \varepsilon_0}} + \frac{2\pi}{3L} \left[ \sum_{k=1}^{N} \frac{q_k}{4 \pi \varepsilon_0} \right]^2.
\]

This is followed in chapter 4, chapter 5 and chapter 6 to study the different systems using molecular dynamics simulation.