Boundaries

In macroscopic systems, the effect of boundaries on the dynamics of biomolecules is minimal. In MD simulations, however, the system size is much smaller and one has to worry about the boundary effects.

- Using nothing (vacuum) is not realistic for bulk simulations.
- Minimum requirement: water beyond the simulation box must be treated using a continuum representation (reaction field). An intermediate zone is treated using stochastic boundary conditions.
- Most common solution: periodic boundary conditions. The simulation box is replicated in all directions just like in a crystal. The cube and rectangular prism are the obvious choices for a box shape, though there are other shapes that can fill the space (e.g. hexagonal prism and rhombic dodecahedron).
Periodic boundary conditions in two dimensions: 8 nearest neighbours

Particles in the box freely move to the next box, which means they appear from the opposite side of the same box.

In 3-D, there are 26 nearest neighbours.
Treatment of long-range interactions

Problem: the number of non-bonded interactions grows as $N^2$ where $N$ is the number of particles. This is the main computational bottle neck that limits the system size. A simple way to deal with this problem is to introduce a cutoff radius for pairwise interactions (together with a switching function), and calculate the potential only for those within the cutoff sphere. This is further facilitated by creating non-bonded pair lists, which are updated every 10-20 steps.

- For Lennard-Jones (6-12) interaction, which is weak and falls rapidly, this works fine and is adapted in all MD codes.
- Coulomb interaction, however, is very strong and falls very slowly. [Recall the Coulomb potential between two unit charges, $U=560 \text{ kT/r (Å)}$] Hence use of any cutoff is problematic and should be avoided.
Ewald summation method

The coulomb energy of N charged particles in a box of volume \( V = L_x L_y L_z \)

\[
U_{\text{Coul}} = \frac{1}{2} \sum_{i=1}^{N} q_i \phi(r_i), \quad \phi(r_i) = \sum_{j=1}^{N} \sum_{n} \frac{q_j}{|r_{ij} + r_n|}
\]

Here \( r_n = (n_x L_x, n_y L_y, n_z L_z) \) with integer values for \( n \).

The prime on the sum signifies that \( i = j \) is not included for \( n = 0 \).

Ewald’s observation (1921): in calculating the Coulomb energy of ionic crystals, replacing the point charges with Gaussian distributions leads to a much faster convergence of the sum in the reciprocal (Fourier) space.

The remaining part (point particle – Gaussian) falls exponentially in real space, hence can be computed easily.
The Poisson equation and it’s solution:

\[ \nabla^2 \varphi = -4\pi \rho \quad \rightarrow \quad \varphi = \int \frac{\rho(r')}{|r - r'|} \, d^3 r' \]

For a point charge \( q \) at the origin:

\[ \rho_{\text{point}} = q \delta(r) \quad \rightarrow \quad \varphi = \frac{q}{r} \]

When the charge \( q \) has a Gaussian distribution:

\[ \rho_{\text{Gauss}}(r) = q \frac{\alpha^3}{\pi^{3/2}} e^{-\alpha^2 r^2}, \quad \int \rho_{\text{Gauss}}(r) \, d^3 r = q \]

\[ \varphi(r) = q \frac{\alpha^3}{\pi^{3/2}} \int \frac{e^{-\alpha^2 r'^2}}{|r - r'|} \, d^3 r' = \frac{q}{r} \text{erf}(\alpha r) \]

where \( \text{erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-u^2} \, du \) is the error function
This result is obtained most easily by integrating the Poisson equation

\[
\frac{1}{r} \frac{d^2}{dr^2} r \varphi = -4\pi q \frac{\alpha^3}{\pi^{3/2}} e^{-\alpha^2 r^2}
\]

\[
\int_\infty^r \frac{d^2}{dr'^2} r' \varphi \, dr' = -4\pi q \frac{\alpha^3}{\pi^{3/2}} \int_\infty^r e^{-\alpha^2 r'^2} \, r' \, dr'
\]

\[
\frac{d}{dr} r \varphi = -4\pi q \frac{\alpha^3}{\pi^{3/2}} \frac{-1}{2\alpha^2} e^{-\alpha^2 r^2}
\]

Integrate 0 to \( r \) :  \[
\varphi(r) = q \frac{2\alpha}{\sqrt{\pi}} \int_0^r e^{-\alpha^2 r'^2} \, dr' = q \frac{2}{\sqrt{\pi}} \int_0^{\alpha r} e^{-u^2} \, du = q \text{erf}(\alpha r)
\]

\[
\varphi(r) = \frac{q}{r} \text{erf}(\alpha r)
\]
Writing the charge density as

$$\rho_{\text{point}} = \rho_{\text{Gauss}} + (\rho_{\text{point}} - \rho_{\text{Gauss}})$$

For the second part, the potential due to a charge $q_i$ at $r_i$ is given by:

$$\varphi(r_j) = \frac{q_i}{r_{ij}} \left[ 1 - \text{erf}(\alpha r_{ij}) \right] = \frac{q_i}{r_{ij}} \text{erfc}(\alpha r_{ij})$$

Where $\text{erfc}(x)$ is the complementary error function which falls as $e^{-\alpha^2 r^2}$

Thus choosing $1/\alpha$ about an Angstrom, this potential converges quickly.

Typically, it is evaluated using a cutoff radius of $\sim 10$ Å, so the original box with $N$ particles is sufficient for this purpose (with the nearest image convention). The direct (short-range) part of the energy of the system is:

$$U_{\text{direct}} = \frac{1}{2} \sum_{i=1}^{N} q_i \varphi(r_i), \quad \varphi(r_i) = \sum_{j=1}^{N} \frac{q_j}{r_{ij}} \text{erfc}(\alpha r_{ij}),$$
The Gaussian part converges faster in the reciprocal (Fourier) space hence best evaluated as a Fourier series

\[ f(\mathbf{r}) = \frac{1}{V} \sum_{n} \tilde{f}(\mathbf{k}) e^{i \mathbf{k} \cdot \mathbf{r}}, \quad \mathbf{k} = 2\pi \left( \frac{n_x}{L_x}, \frac{n_y}{L_y}, \frac{n_z}{L_z} \right) \]

\[ \tilde{f}(\mathbf{k}) = \int_{V} f(\mathbf{r}) e^{-i \mathbf{k} \cdot \mathbf{r}} d^3r \]

The Poisson equation in the Fourier space

\[ \nabla^2 \left( \frac{1}{V} \sum_{n} \tilde{\phi}(\mathbf{k}) e^{i \mathbf{k} \cdot \mathbf{r}} \right) = -4\pi \frac{1}{V} \sum_{n} \tilde{\rho}(\mathbf{k}) e^{i \mathbf{k} \cdot \mathbf{r}} \]

\[ k^2 \tilde{\phi}(\mathbf{k}) = 4\pi \tilde{\rho}(\mathbf{k}) \]

For a point charge \( q \) at the origin:

\[ \tilde{\rho}(\mathbf{k}) = \int q \delta(\mathbf{r}) e^{-i \mathbf{k} \cdot \mathbf{r}} d^3r = q \quad \rightarrow \quad \tilde{\phi}(\mathbf{k}) = \frac{4\pi q}{k^2} \]
When the charge $q$ has a Gaussian distribution:

$$
\tilde{\rho}(k) = q \frac{\alpha^3}{\pi^{3/2}} \int e^{-\alpha^2 r^2} e^{-i \mathbf{k} \cdot \mathbf{r}} \, d^3 r
$$

$$
= q \frac{\alpha^3}{\pi^{3/2}} \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy \int_{-\infty}^{\infty} dz \, e^{-\alpha^2 (x^2 + y^2 + z^2)} e^{-i(k_x x + k_y y + k_z z)}
$$

Multiply each integral by $e^{\pm k^2 / 4 \alpha^2}$ to complete the square

Each Gaussian integral then gives $\sqrt{\pi} / \alpha$

$$
\tilde{\rho}(k) = q e^{-(k_x^2 + k_y^2 + k_z^2) / 4 \alpha^2} = q e^{-k^2 / 4 \alpha^2}
$$

The corresponding potential in the Fourier space

$$
\tilde{\varphi}(k) = \frac{4\pi q}{k^2} e^{-k^2 / 4 \alpha^2}
$$
The Gaussian charge density for the periodic box

\[ \rho_{\text{Gauss}}(\mathbf{r}) = \sum_{j=1}^{N} \sum_{n} q_j \frac{\alpha^3}{\pi^{3/2}} e^{-\frac{\alpha^2}{2}\sum_{n} \left| \mathbf{r} - (\mathbf{r}_j + \mathbf{r}_n) \right|^2} \]

\[ \tilde{\rho}_{\text{Gauss}}(\mathbf{k}) = \int_{V} d^3 r \ e^{-i\mathbf{k} \cdot \mathbf{r}} \sum_{j=1}^{N} \sum_{n} q_j \frac{\alpha^3}{\pi^{3/2}} e^{-\frac{\alpha^2}{2}\left| \mathbf{r} - (\mathbf{r}_j + \mathbf{r}_n) \right|^2} \]

\[ = \int_{\text{all space}} d^3 r \ e^{-i\mathbf{k} \cdot \mathbf{r}} \sum_{j=1}^{N} q_j \frac{\alpha^3}{\pi^{3/2}} e^{-\frac{\alpha^2}{2}\left| \mathbf{r} - \mathbf{r}_j \right|^2} \]

\[ = \sum_{j=1}^{N} q_j \ e^{-i\mathbf{k} \cdot \mathbf{r}_j} e^{-\frac{k^2}{4\alpha^2}} \]

Which yields for the potential

\[ \tilde{\phi}_{\text{Gauss}}(\mathbf{k}) = \frac{4\pi}{k^2} \sum_{j=1}^{N} q_j \ e^{-i\mathbf{k} \cdot \mathbf{r}_j} e^{-\frac{k^2}{4\alpha^2}} \]
Transforming back to the real space

\[ \varphi_{\text{Gauss}}(\mathbf{r}) = \frac{1}{V} \sum_{n \neq 0} \tilde{\varphi}_{\text{Gauss}}(\mathbf{k}) e^{i\mathbf{k} \cdot \mathbf{r}} \]

\[ = \frac{1}{V} \sum_{n \neq 0} \sum_{j=1}^{N} 4\pi q_j e^{-k^2/4\alpha^2} e^{i\mathbf{k} \cdot (\mathbf{r} - \mathbf{r}_j)} \]

The reciprocal space (long-range) part of the system’s energy:

\[ U_{\text{recip}} = \frac{1}{2} \sum_{i=1}^{N} q_i \varphi_{\text{Gauss}}(\mathbf{r}_i) \]

\[ = \frac{1}{2V} \sum_{n \neq 0} \sum_{i, j=1}^{N} 4\pi q_i q_j e^{-k^2/4\alpha^2} e^{i\mathbf{k} \cdot (\mathbf{r}_i - \mathbf{r}_j)} \]

\[ = \frac{1}{2V} \sum_{n \neq 0} \frac{4\pi}{k^2} |\tilde{\varphi}(\mathbf{k})|^2 e^{-k^2/4\alpha^2} \]
This energy includes the self-energy of the Gaussian density which needs to be removed

\[ \varphi_{\text{Gauss}}(r) = \frac{q}{r} \text{erf}(\alpha r) \]

\[ \varphi_{\text{self}}(r=0) = \frac{2q\alpha}{\sqrt{\pi}} \]

\[ U_{\text{self}} = \frac{1}{2} \sum_{i=1}^{N} q_i \varphi_{\text{self}}(r_i) \]

\[ = \frac{\alpha}{\sqrt{\pi}} \sum_{i=1}^{N} q_i^2 \]

So the total energy is: \[ U_{\text{total}} = U_{\text{direct}} + U_{\text{recip}} - U_{\text{self}} \]