Lecture 8: Molecular Dynamics Simulation: Coulomb Interaction and Ewald Summation

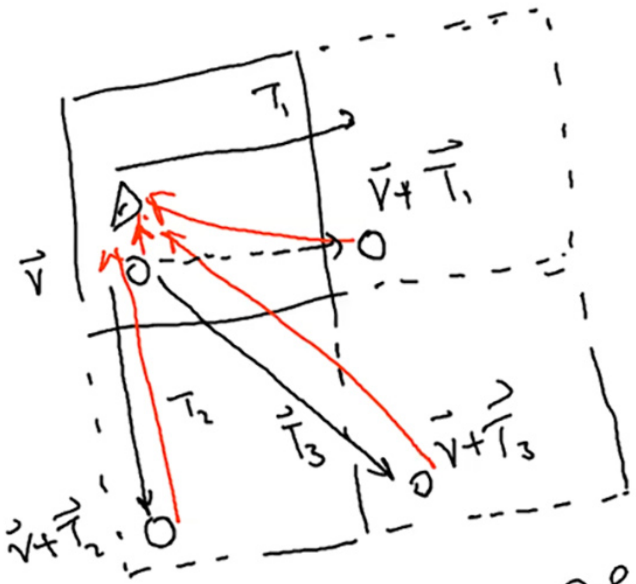
Theories in Statistical Mechanics and Molecular Dynamics Simulations

PBC and non-PBC

$$f(r) = \frac{\mathrm{erf}(\alpha r)}{r} \qquad r = |\vec{r}|$$

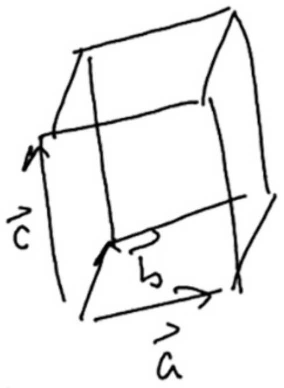
PBC

Non PBC $\longrightarrow$ All pairwise interactions



$$\sum_{\vec{T}} \frac{\mathrm{erf}(\alpha|\vec{r}+\vec{T}|)}{|\vec{r}+\vec{T}|} \equiv f(\vec{r})$$

$$\vec{T} = n_1\vec{a} + n_2\vec{b} + n_3\vec{c}$$



periodic $f(\vec{r}+\vec{T}) = f(\vec{r})$

$\Rightarrow$ Fourier Series

Fourier Transform

$$f(\vec{r}) = \sum_{\vec{T}} \frac{\mathrm{erf}(\alpha|\vec{r}+\vec{T}|)}{|\vec{r}+\vec{T}|} = \frac{1}{V} \sum_{\vec{g}} C_{\vec{g}}\, e^{i\vec{g}\cdot\vec{r}}$$

$$C_{\vec{g}} = \int_V d\vec{r}\, f(\vec{r})\, e^{-i\vec{g}\cdot\vec{r}} = \int_V d\vec{r} \sum_{\vec{T}} \frac{\mathrm{erf}(\alpha|\vec{r}+\vec{T}|)}{|\vec{r}+\vec{T}|} e^{-i\vec{g}\cdot\vec{r}}$$

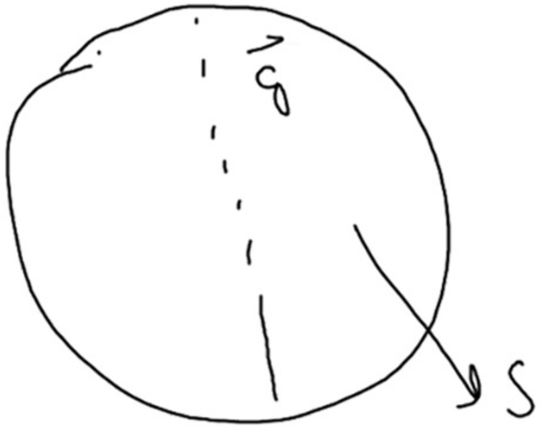
$$= \sum_{\vec{T}} \int_V d\vec{r}\, \frac{\mathrm{erf}(\alpha|\vec{r}+\vec{T}|)}{|\vec{r}+\vec{T}|} e^{-i\vec{g}\cdot\vec{r}}$$

$$= \int_{\mathbb{R}^3} \frac{\mathrm{erf}(\alpha r)}{r} e^{-i\vec{g}\cdot\vec{r}}\, d\vec{r}$$

$$= \frac{4\pi}{|\vec{g}|^2} e^{-|\vec{g}|^2/4\alpha^2}$$

Lagrangian force

$$U_{long}(\vec{r}_1 \cdots \vec{r}_N) = \frac{1}{V}\sum_{i,j} q_i q_j \sum_{\vec{g}} \frac{4\pi}{|\vec{g}|^2} e^{-|\vec{g}|^2/4\alpha^2} e^{i\vec{g}\cdot(\vec{r}_i-\vec{r}_j)}$$



$$= \frac{2}{V}\sum_{i>j} q_i q_j \sum_{\vec{g}\in S} \frac{4\pi}{|\vec{g}|^2} e^{-|\vec{g}|^2/4\alpha^2} e^{i\vec{g}\cdot(\vec{r}_i-\vec{r}_j)}$$

$$= \frac{1}{V}\sum_{i,j} q_i q_j \sum_{\vec{g}\in S} \frac{4\pi}{|\vec{g}|^2} e^{-|\vec{g}|^2/4\alpha^2} e^{i\vec{g}\cdot(\vec{r}_i-\vec{r}_j)}$$

$$- \underbrace{\frac{1}{V}\sum_{i} q_i^2 \sum_{\vec{g}\in S} \frac{4\pi}{|\vec{g}|^2} e^{-|\vec{g}|^2/4\alpha^2}}_{\to\ i=j}$$

Ewald Summation

$$\frac{1}{V}\sum_{ij} q_i q_j \sum_{\vec{g}\in S} \frac{4\pi}{|\vec{g}|^2} e^{-|\vec{g}|^2/4\alpha^2} e^{i\vec{g}\cdot(\vec{r}_i-\vec{r}_j)}$$

$$= \frac{1}{V}\sum_{\cancel{\vec{g}\in S}} \frac{4\pi}{|\vec{g}|^2} e^{-|\vec{g}|^2/4\alpha^2} \left|\underbrace{\sum_i q_i e^{i\vec{g}\cdot\vec{r}_i}}\right|^2$$

$\vec{g}\in S,\ \vec{g}\neq 0$

$\vec{g}=0$?

$S(\vec{g})$: Structure factor

$$\frac{1}{2V}\sum_i q_i^2 \sum_{\vec{g}} \frac{4\pi}{|\vec{g}|^2} e^{-|\vec{g}|^2/4\alpha^2}$$

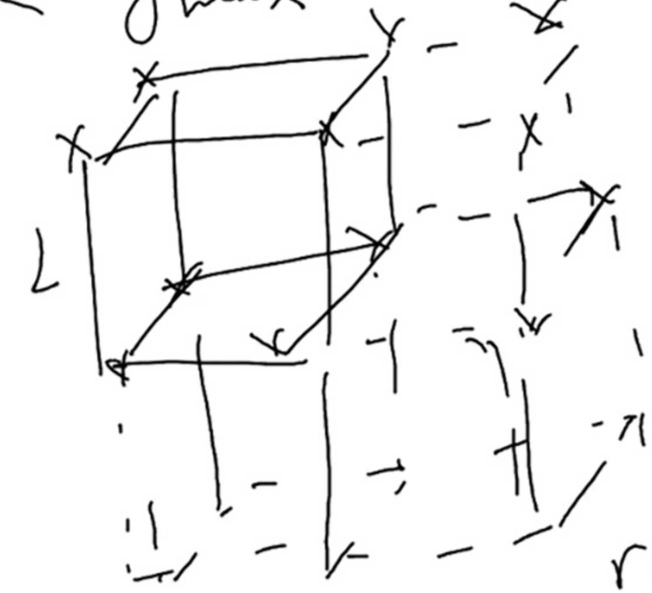
$$\frac{1}{V}\sum_{g} \frac{4\pi}{|\vec{g}|^2} e^{-|\vec{g}|^2/4\alpha^2} = \lim_{r\to 0}\frac{\mathrm{erf}(\alpha r)}{r} = \frac{2\alpha}{\sqrt{\pi}}$$

Ewald Summation

Structure factor

$$S(\vec{g}) = \sum_i q_i e^{i\vec{g}\cdot\vec{r}_i}$$

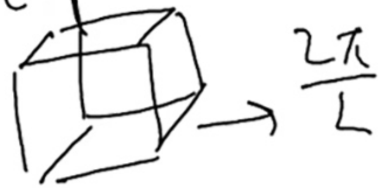
Truncation. $|\vec{g}| \leq g_{max}$



→ Real space Lattice

reciprocal space

→

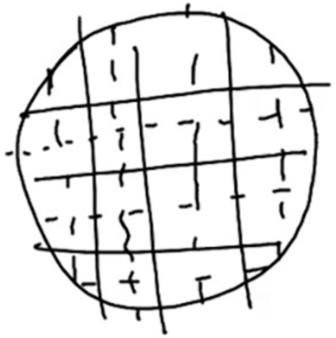


General space lattice

$$\vec{a}, \vec{b}, \vec{c} \longrightarrow \vec{k}_a = \frac{2\pi\, \vec{b}\times\vec{c}}{V}$$

$$\vec{k}_b = \frac{2\pi\, \vec{c}\times\vec{a}}{V}$$

$$\vec{k}_c = \frac{2\pi\, \vec{a}\times\vec{b}}{V}$$



$$|k| \longrightarrow \frac{|k|}{2}$$

grids($\vec{g}$) × 8

atom × 8

$$\vec{g} = \tilde{n}_1 \vec{k}_a + \tilde{n}_2 \vec{k}_b + \tilde{n}_3 \vec{k}_c$$

$V, N \longrightarrow 8V, 8N$

$L \rightarrow 2L$