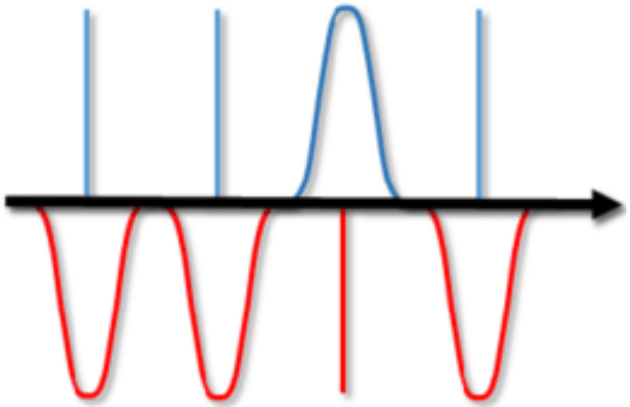
Course 13/2

Ewald summation (2/2)



- $E_c^{(1)}$: Long-range interaction (Fourier space)
- $E_c^{(2)}$: Self-interaction correction
- $E_c^{(3)}$: Short-range interaction (real space)
- Role of Ewald parameter

$E_c^{(1)}$: Long-range interaction (Fourier space)

$$E_c^{(1)} = \frac{1}{2} \sum_{\substack{I,\, \boldsymbol{n}J \\ \text{all}}} q_I \, \Phi^G_{\boldsymbol{n}J}(\vec{R}_I)$$

soft long-range interaction

We need to find the potential associated with the Gaussian charges!

$E_c^{(1)}$: Long-range interaction (Fourier space)

For a point charge in the origin, $\rho^{P}(r) = \delta(r)$, the associated Gaussian charge is

$$\rho^{G}(\vec{r}) = \left(\frac{1}{\sqrt{2\pi\sigma^2}}\right)^3 e^{-\frac{|\vec{r}|^2}{2\sigma^2}} = \left(\frac{\alpha}{\pi}\right)^{3/2} e^{-\alpha|\vec{r}|^2}$$

where $\alpha = \dfrac{1}{2\sigma^2}$ is the Ewald parameter.

The charge density associated with all the Gaussian ions then reads:

$$\rho_1(\vec{r}) = \sum_{J=1}^{N} \sum_{\boldsymbol{n}} q_J \left(\frac{\alpha}{\pi}\right)^{3/2} \exp\left[-\alpha\,|\vec{r} - (\vec{R}_J + \boldsymbol{n}L)|^2\right]$$

Transformation to Fourier space

$$\begin{cases} \rho_1(\vec{r}) = \sum_{\vec{k}} \tilde{\rho}_1(\vec{k})\, e^{\,i\vec{k}\cdot\vec{r}} \\ \tilde{\rho}_1(\vec{k}) = \frac{1}{V}\int_V d\vec{r}\,\rho_1(\vec{r})\, e^{-i\vec{k}\cdot\vec{r}} \end{cases}$$

V is the volume of the simulation cell

where the vectors $\vec{k}$ need to ensure that plane-waves $e^{\,i\vec{k}\cdot\vec{r}}$ used in the expansion satisfy the periodic boundary conditions of the unit cell.

$$\vec{k}\cdot\boldsymbol{n}L = 2\pi\cdot m \quad \Rightarrow \quad \vec{k} = \frac{2\pi}{L}\boldsymbol{n}$$

$\boldsymbol{n}$ = (0, 0, 0) ; (0, 0, 1) ; etc.

Full Gaussian charge density in Fourier space

In real space

$$\rho_1(\vec{r}) = \sum_{J=1}^{N} \sum_{\boldsymbol{n}} q_J \left(\frac{\alpha}{\pi}\right)^{3/2} \exp[-\alpha\,|\vec{r} - (\vec{R}_J + \boldsymbol{n}L)\,|^2]$$

In Fourier space

$$\tilde{\rho}_1(\vec{k}) = \frac{1}{V}\int_V d\vec{r}\;\rho_1(\vec{r})\;e^{-i\vec{k}\cdot\vec{r}}$$

$$= \frac{1}{V}\int_V d\vec{r}\;e^{-i\vec{k}\cdot\vec{r}} \sum_{J=1}^{N} \sum_{\boldsymbol{n}} q_J \left(\frac{\alpha}{\pi}\right)^{3/2} \exp[-\alpha\,|\vec{r} - (\vec{R}_J + \boldsymbol{n}L)\,|^2]$$

change of variable and $\vec{k}\cdot\boldsymbol{n}L = 2\pi\cdot m$

$$= \frac{1}{V}\int_{\substack{\text{all}\\ \text{space}}} d\vec{r}\;e^{-i\vec{k}\cdot\vec{r}} \sum_{J=1}^{N} q_J \left(\frac{\alpha}{\pi}\right)^{3/2} \exp[-\alpha\,|\vec{r} - \vec{R}_J\,|^2]$$

change of variable and Fourier transform of a Gaussian

$$= \frac{1}{V}\sum_{J=1}^{N} q_J\,e^{-i\vec{k}\cdot\vec{R}_J} \exp[-k^2/(4\alpha)]$$

Potential of full Gaussian charge density

Poisson equation in real space: $$-\nabla^2 \phi_1(\vec{r}) = 4\pi \rho_1(\vec{r})$$

The potential expanded in plane waves: $$\phi_1(\vec{r}) = \sum_{\vec{k}} \tilde{\phi}_1(\vec{k})\, e^{i\vec{k}\cdot\vec{r}}$$

Poisson equation in Fourier space: $$k^2 \tilde{\phi}_1(\vec{k}) = 4\pi \tilde{\rho}_1(\vec{k})$$

For $\vec{k} \neq 0$:

$$\tilde{\phi}_1(\vec{k}) = \frac{4\pi}{k^2} \tilde{\rho}_1(\vec{k}) = \frac{4\pi}{k^2} \frac{1}{V} \sum_{J=1}^{N} q_J\, e^{-i\vec{k}\cdot\vec{R}_J} \exp[-k^2/(4\alpha)]$$

$$\phi_1(\vec{r}) = \frac{1}{V} \sum_{\substack{\vec{k} \\ \vec{k}\neq 0}} \sum_{J=1}^{N} \frac{4\pi q_J}{k^2}\, e^{i\vec{k}\cdot(\vec{r}-\vec{R}_J)} \exp[-k^2/(4\alpha)]$$

- For $\vec{k} = 0$, the potential cannot be determined, but the average potential does not affect the energy for a neutral system.
- This potential is periodic and thus consistent with a vanishing electric field.

Calculation of long-range interaction $E_c^{(1)}$

$$E_c^{(1)} = \frac{1}{2} \sum_{I=1}^{N} q_I \sum_{\boldsymbol{n}J} \Phi^{G}{}_{\boldsymbol{n}J}(\vec{R}_I) = \frac{1}{2} \sum_{I=1}^{N} q_I \, \phi_1(\vec{R}_I)$$

$$= \frac{1}{2} \frac{1}{V} \sum_{\substack{\vec{k} \\ \vec{k} \neq 0}} \sum_{I,J=1}^{N} \frac{4\pi}{k^2} q_I q_J \, e^{i \vec{k} \cdot (\vec{R}_I - \vec{R}_J)} \exp[-k^2/(4\alpha)]$$

$$= \frac{V}{2} \sum_{\substack{\vec{k} \\ \vec{k} \neq 0}} \frac{4\pi}{k^2} |\tilde{\rho}(\vec{k})|^2 \exp[-k^2/(4\alpha)]$$

where $\tilde{\rho}(\vec{k}) = \frac{1}{V} \sum_{I=1}^{N} q_I \, e^{-i \vec{k} \cdot \vec{R}_I}$

Fourier components of the density of point charges

- The term $\exp[-k^2/(4\alpha)]$ guarantees a fast convergence with k.
- Delocalized charge from electron wave functions can be added up to $\tilde{\rho}(\vec{k})$.

$E_c^{(2)}$: Self-interaction correction

For a Gaussian charge in the origin:

$$\rho^{G}{}_{I}(\vec{r}) \;=\; q_I \left(\frac{\alpha}{\pi}\right)^{3/2} e^{-\alpha|\vec{r}|^2}$$

To find the associated potential, we need to solve the Poisson equation:

$$-\nabla^2 \phi^{G}{}_{I}(r) \;=\; 4\pi\, \rho^{G}{}_{I}(r)$$

To address this a problem of spherical symmetry, we express the Laplacian in spherical coordinates:

$$\nabla^2 \phi^{G}{}_{I}(r) \;=\; \frac{1}{r}\,\frac{\partial^2(r\,\phi^{G}{}_{I})}{\partial r^2}$$

The problem becomes:

$$-\,\frac{1}{r}\,\frac{\partial^2(r\,\phi^{G}{}_{I})}{\partial r^2} \;=\; 4\pi\, \rho^{G}{}_{I}(r)$$

Solution of Poisson equation by radial integration

Poisson equation: $$-\frac{\partial^2(r\,\phi^G{}_l)}{\partial r^2} = 4\pi\, r\, \rho^G{}_l(r)$$

We integrate both sides from ∞ to r:

$$\left[-\frac{\partial(r\,\phi^G{}_l)}{\partial r} \right]_\infty^r = 4\pi q_l \left(\frac{\alpha}{\pi}\right)^{3/2} \int_\infty^r dr\; r\, e^{-\alpha r^2}$$

For $r \to \infty$, $\phi^G \to 1/r \quad \Rightarrow \quad (r\,\phi^G) \to 1 \quad \Rightarrow \quad \frac{\partial(r\,\phi^G)}{\partial r} \to 0$

$$-\frac{\partial(r\,\phi^G{}_l)}{\partial r} = 2q_l \left(\frac{\alpha}{\pi}\right)^{1/2} \left[-e^{-\alpha r^2} \right]_\infty^r$$

We integrate both sides from 0 to r:

$$-\left[r\,\phi^G{}_l \right]_0^r = 2q_l \left(\frac{\alpha}{\pi}\right)^{1/2} \int_0^r dr\; e^{-\alpha r^2}$$

Potential from a Gaussian charge distribution

change of variable

$$r\,\phi^{G}{}_{I} \;=\; 2q_I\left(\frac{\alpha}{\pi}\right)^{1/2}\frac{1}{\sqrt{\alpha}}\int_0^{\sqrt{\alpha}\,r} dr\;\mathrm{e}^{-r^2} \;=\; q_I\;\mathrm{erf}\,(\sqrt{\alpha}\,r)$$

$$\boxed{\phi^{G}{}_{I} \;=\; \frac{q_I\;\mathrm{erf}\,(\sqrt{\alpha}\,r)}{r}}$$

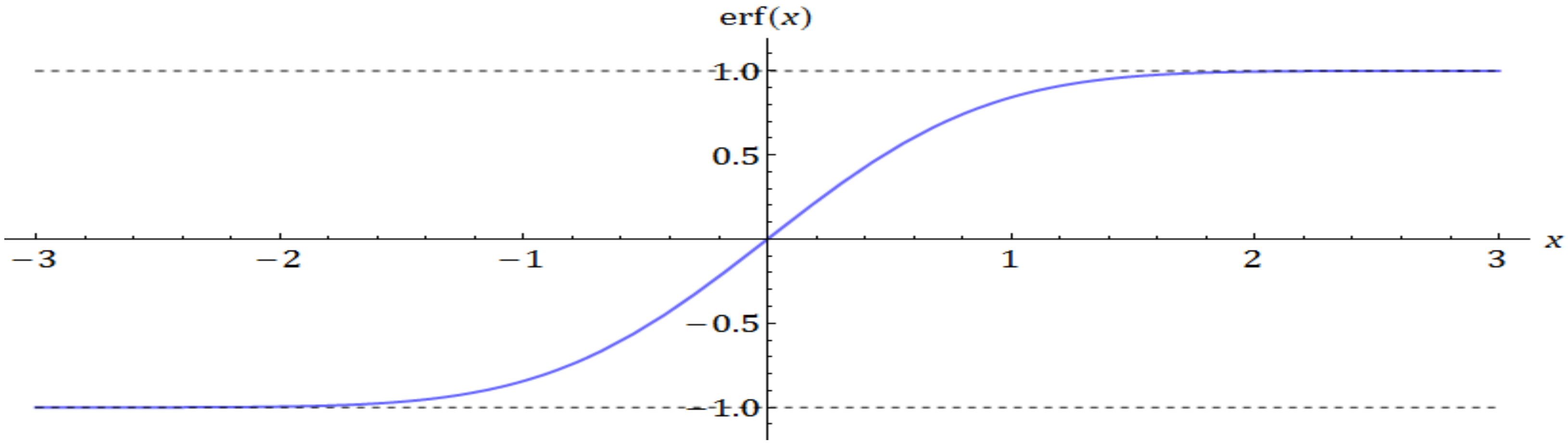
potential from a Gaussian
charge distribution

where the error function erf is defined as

$$\mathrm{erf}\,x \;=\; \frac{2}{\sqrt{\pi}}\int_0^{x}\mathrm{e}^{-u^2}\,du$$

Error function

$$\text{erf}\, x = \frac{2}{\sqrt{\pi}} \int_0^x e^{-u^2}\, du$$



Properties:

1. $$\sqrt{\pi} = \int_{-\infty}^{+\infty} e^{-u^2}\, du = 2\int_0^{\infty} e^{-u^2}\, du \Rightarrow \lim_{x \to \infty} \text{erf}\,(\,x\,) = 1$$

2. $$\lim_{x \to 0} \frac{\text{erf}\,(\,x\,)}{x} = \lim_{x \to 0} \frac{2}{x\sqrt{\pi}} \int_0^x e^{-u^2} du = \lim_{x \to 0} \frac{2}{x\sqrt{\pi}} \int_0^x (\,1 - u^2 \ldots\,)\, du = \frac{2}{\sqrt{\pi}}$$

Calculation of self-interaction correction $E_c^{(2)}$

Potential from a Gaussian charge distribution

$$\boxed{\phi^{G}_{I} = \frac{q_I \,\mathrm{erf}\,(\sqrt{\alpha}\, r)}{r}}$$

NB For $r \gg 1/\sqrt{\alpha}$, $\phi^{G}_{I} \rightarrow q_I / r$
point-charge behavior!

Self-interaction of a point charge with its corresponding Gaussian charge:

$$E_G^{\mathrm{SELF}} = \frac{1}{2}\, q_I \cdot \phi^{G}_{I}(r = 0) = \frac{1}{2}\, q_I^{\,2} \cdot \sqrt{\alpha} \cdot \frac{2}{\sqrt{\pi}}$$

$E_c^{(2)}$ corrects for the self-interaction (minus sign) of all Gaussian charges:

$$E_c^{(2)} = -\sqrt{\frac{\alpha}{\pi}} \sum_{I=1}^{N} q_I^{\,2}$$

NB independent on atomic positions;
can be calculated once in MD.

$E_c^{(3)}$: Short-range interaction (real space)

Potential due to both point charge and Gaussian charge at ***nJ*** :

$$\Phi_{\boldsymbol{n}J}^{\text{short-range}}(\vec{r}) = \Phi^{P}_{\boldsymbol{n}J}(\vec{r}) - \Phi^{G}_{\boldsymbol{n}J}(\vec{r})$$

$$= \frac{q_J}{|\vec{r} - \vec{R}_J + \boldsymbol{n}L|} - \frac{q_J \,\mathrm{erf}\,(\sqrt{\alpha}\,|\vec{r} - \vec{R}_J + \boldsymbol{n}L|)}{|\vec{r} - \vec{R}_J + \boldsymbol{n}L|}$$

$$= \frac{q_J \,\mathrm{cerf}\,(\sqrt{\alpha}\,|\vec{r} - \vec{R}_J + \boldsymbol{n}L|)}{|\vec{r} - \vec{R}_J + \boldsymbol{n}L|}$$

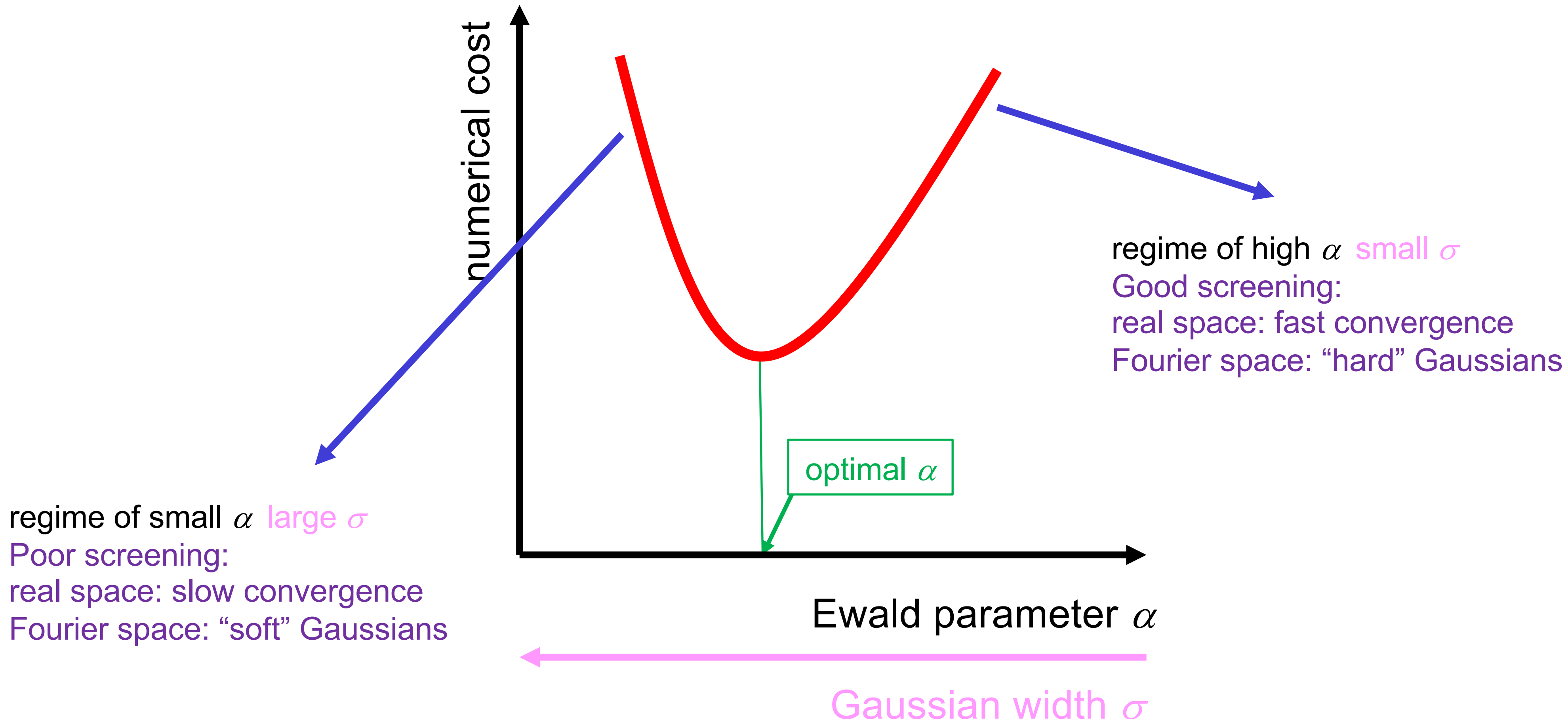
where $\mathrm{cerf}\,(x) = 1 - \mathrm{erf}\,(x)$, hence $\lim_{x \to \infty} \mathrm{cerf}\,(x) = 0$.

$E_c^{(3)}$ can then be written as

$$E_c^{(3)} = \frac{1}{2} \sum_{\substack{I,\, \boldsymbol{n}J \\ I \neq \boldsymbol{0}J}} \frac{q_I \, q_J}{|\vec{r} - \vec{R}_J + \boldsymbol{n}L|} \; \mathrm{cerf}\,(\sqrt{\alpha}\,|\vec{r} - \vec{R}_J + \boldsymbol{n}L|)$$

Fast convergence since contributions vanish quickly for $r \gg 1/\sqrt{\alpha}$

Role of Ewald parameter



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