Course 13/1

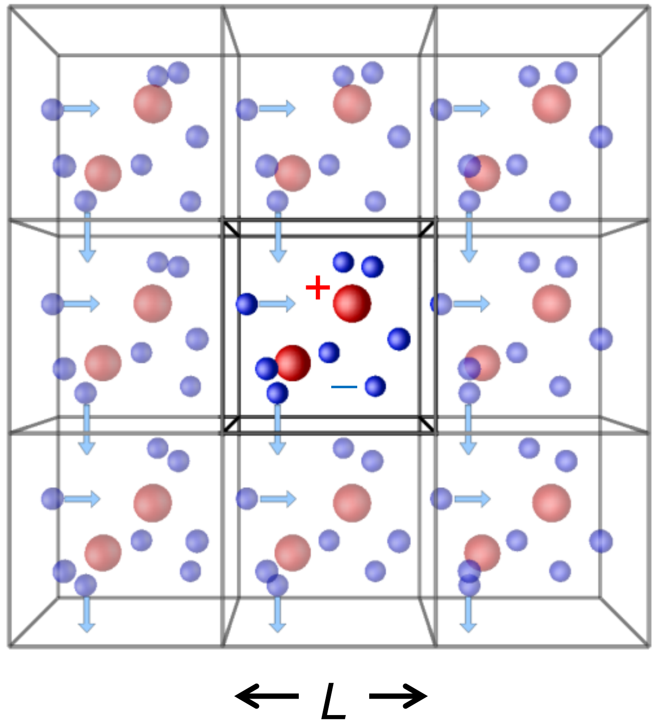
Ewald summation (1/2)

- Electrostatic Coulomb energy
- Problem
- General idea
- Decomposition of the energy

Paul Peter Ewald
(1888-1985)

Electrostatic Coulomb energy

$$U_c = \frac{1}{2} \sum_{\substack{I,\,J \\ I \neq J}} \frac{q_I\, q_J}{|\vec{R}_I - \vec{R}_J|}$$



However, when using periodic boundary conditions, this energy diverges for a charged unit cell.

Hence: $$\sum_{I=1}^{N} q_I = 0$$

For a cubic unit cell:

$$U_c = \frac{1}{2} \sum_{\substack{I,\,\boldsymbol{n}J \\ I \neq \boldsymbol{0}J}} q_I\, \Phi^{P}{}_{\boldsymbol{n}J}(\vec{R}_I)$$

where

$$\Phi^{P}{}_{\boldsymbol{n}J}(\vec{r}) = \frac{q_J}{|\vec{r} - \vec{R}_J + \boldsymbol{n}L|}$$

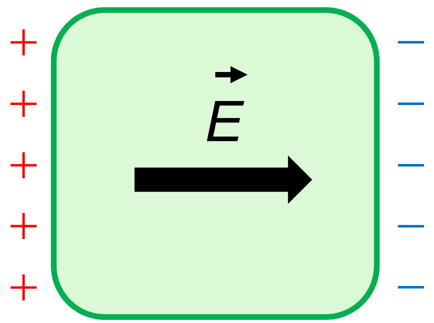
Potential of a point charge q_J located at $\vec{R}_J - \boldsymbol{n}L$

Further condition for periodic systems

$$U_c = \frac{1}{2} \sum_{\substack{l,\, \boldsymbol{n}J \\ l \neq \boldsymbol{0}J}} q_l \, \Phi^{P}{}_{\boldsymbol{n}J}(\vec{R}_l)$$

This expression is *conditionally convergent*, which means that the result depends on the order of summation.

This reflects that the periodic approximation neglects surface charges, which affect U_c.



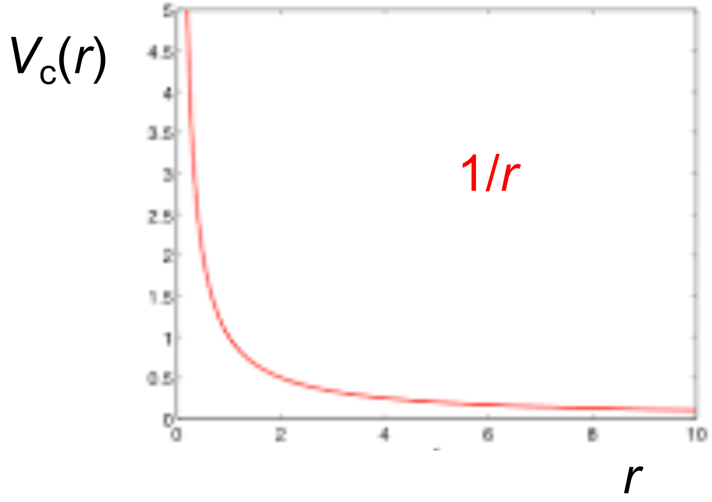
The residual indetermination is due to the possible presence of a finite electric field.

Calculations in periodic systems are usually carried out under the condition of vanishing electric field.

Problem

Real space

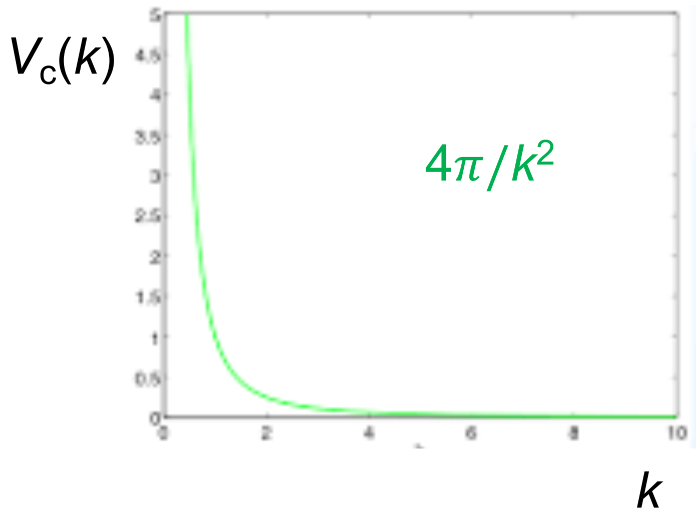
The Coulomb potential $1/r$ is long-ranged !



Fourier space

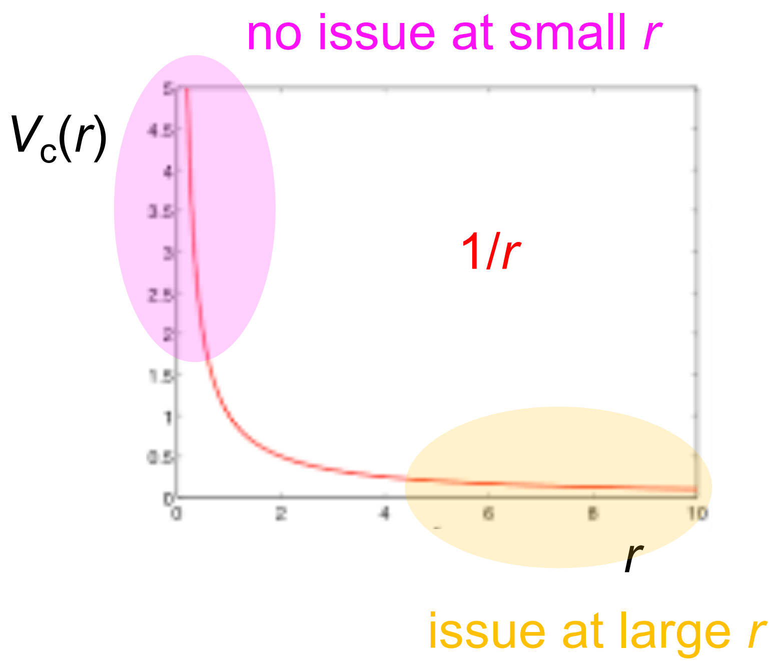
The interaction becomes: $1/r \;\rightarrow\; 4\pi/k^2$

This is somewhat better but still does not solve the convergence problem: too many k's are needed. The convergence with increasing k is slow.

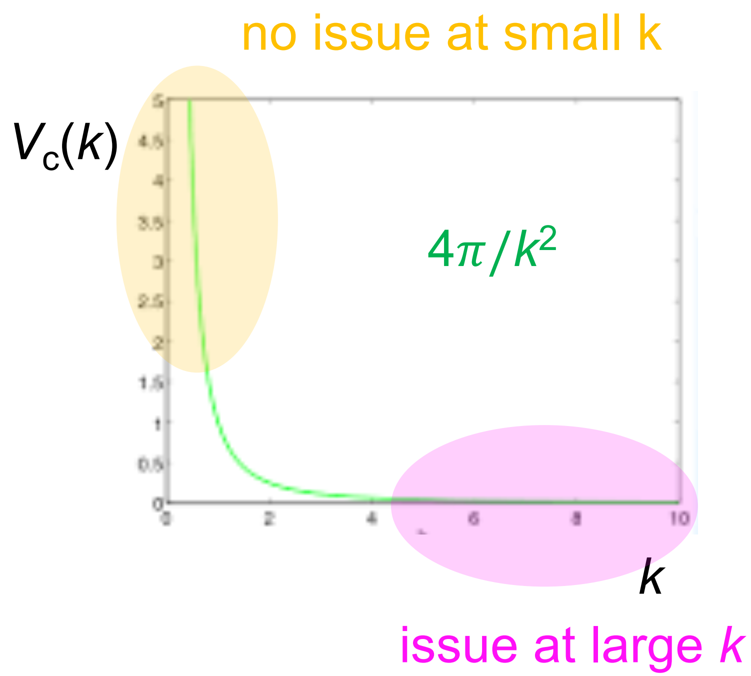


Remark: these are two different issues!

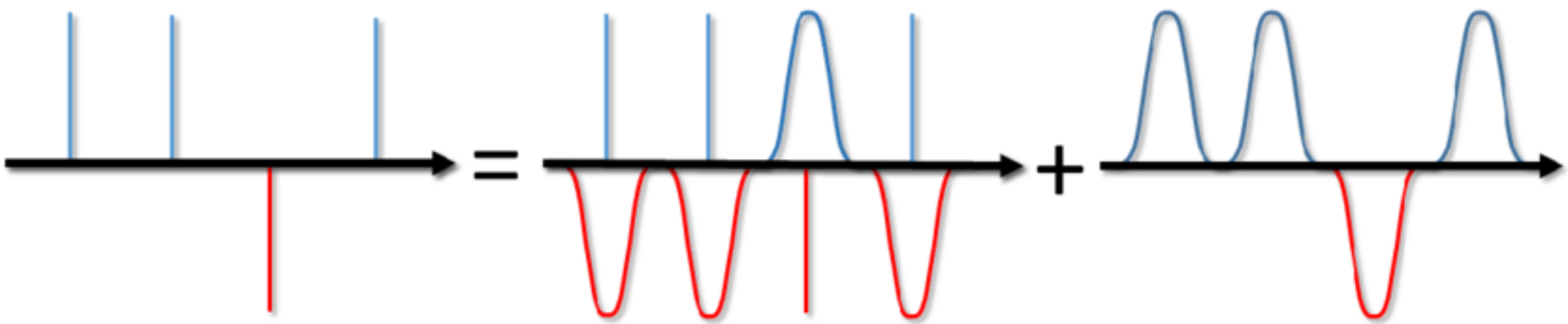
Real space



Fourier space



General idea



positive and negative point charges

every point charge is screened by Gaussian charge of opposite sign

Gaussian screening charges

neutral entities with short-ranged interactions in real space

soft charge distributions converging fast in Fourier space

The width of the Gaussian determines how the weight of the calculation is distributed between real space and Fourier space.

Decomposition of the energy

$$U_c = \frac{1}{2} \sum_{\substack{l,\, \boldsymbol{n}J \\ l \neq \boldsymbol{0}J}} q_l\, \Phi^{P}{}_{\boldsymbol{n}J}(\vec{R}_l)$$

potential from a Gaussian charge

$$= \frac{1}{2} \sum_{\substack{l,\, \boldsymbol{n}J \\ l \neq \boldsymbol{0}J}} q_l\, \Phi^{G}{}_{\boldsymbol{n}J}(\vec{R}_l) \quad + \quad \frac{1}{2} \sum_{\substack{l,\, \boldsymbol{n}J \\ l \neq \boldsymbol{0}J}} q_l \left[\underbrace{\Phi^{P}{}_{\boldsymbol{n}J}(\vec{R}_l) - \Phi^{G}{}_{\boldsymbol{n}J}(\vec{R}_l)}_{\text{potential from a screened charge}} \right]$$

$$= \frac{1}{2} \sum_{\substack{l,\, \boldsymbol{n}J \\ \text{all}}} q_l\, \Phi^{G}{}_{\boldsymbol{n}J}(\vec{R}_l) \; - \; \frac{1}{2} \sum_{l} q_l\, \Phi^{G}{}_{\boldsymbol{0}l}(\vec{R}_l) \; + \; \frac{1}{2} \sum_{\substack{l,\, \boldsymbol{n}J \\ l \neq \boldsymbol{0}J}} q_l \left[\Phi^{P}{}_{\boldsymbol{n}J}(\vec{R}_l) - \Phi^{G}{}_{\boldsymbol{n}J}(\vec{R}_l) \right]$$

soft long-range interaction

$E_c^{(1)}$

self-interaction correction

$E_c^{(2)}$

short-range interaction

$E_c^{(3)}$

Course 13/1

Ewald summation (1/2)

- Electrostatic Coulomb energy
- Problem
- General idea
- Decomposition of the energy