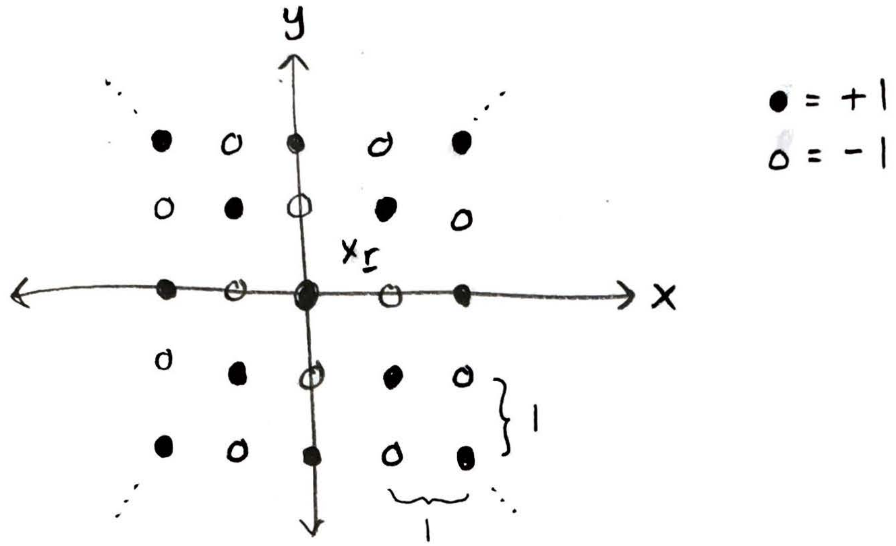
Ewald summation

DF, 2018

Suppose we want to calculate the electrostatic potential Φ in a 2D ionic solid:



At a point $\underline{r} = (x,y)$, the potential is

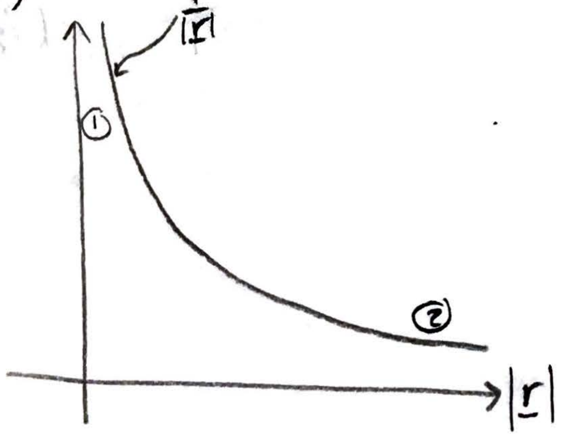
Converges slowly!

$$\Phi(\underline{r}) = \Phi(x,y) = \sum_{n_x=-\infty}^{\infty} \sum_{n_y=-\infty}^{\infty} (-1)^{n_x+n_y} \underbrace{\frac{1}{\sqrt{(x-n_x)^2+(y-n_y)^2}}} \quad \circledast$$

$\phi(x-n_x, y-n_y)$ is the Coulomb potential due to a single +1 ion.

i.e. $\phi(\underline{r}) = \frac{1}{|\underline{r}|}$

(in 1D:)



$\phi(\underline{r})$ is: ① Rapidly varying for small $|\underline{r}|$

② Slowly varying for large $|\underline{r}|$

Ewald idea: Break up $\phi(\underline{r})$ into two pieces:

- A <u>short-range</u> piece that captures the rapid variation for small $|\underline{r}|$ but decays rapidly for large $|\underline{r}|$ } ϕ_{short}
- A <u>long-range</u> piece that captures the tail but is nonsingular for small $|\underline{r}|$. } ϕ_{long}

$$\phi(\underline{r}) = \phi_{short}(\underline{r}) + \phi_{long}(\underline{r})$$

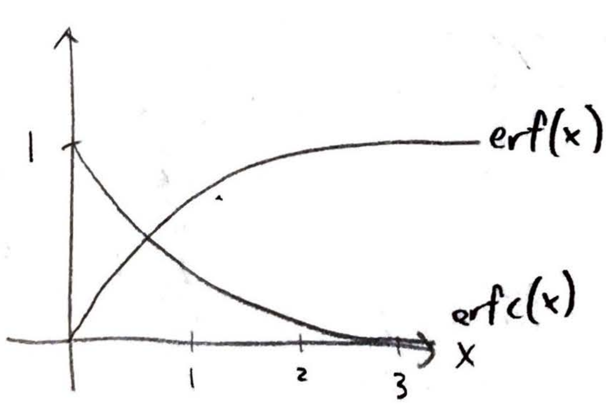
To construct ϕ_{short} & ϕ_{long}, we can use the <u>windowing trick</u>. Given a window $w(\underline{r})$ that is 1 for small $|\underline{r}|$ but falls to 0 rapidly for large $|\underline{r}|$, we can write:

$$\phi(\underline{r}) = \underbrace{w(\underline{r})\,\phi(\underline{r})}_{\phi_{short}} + \underbrace{(1-w(\underline{r}))\,\phi(\underline{r})}_{\phi_{long}}$$

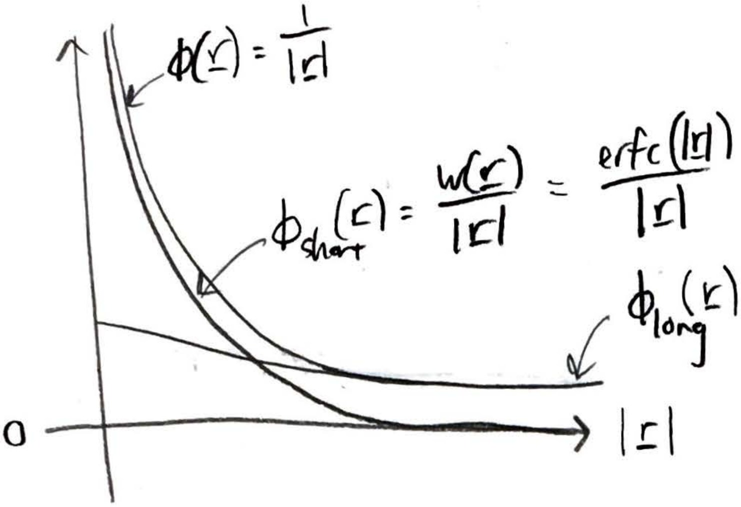
Typical choice: $w(\underline{r}) = \mathrm{erfc}(|\underline{r}|) = 1 - \mathrm{erf}(|\underline{r}|)$

where $\mathrm{erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-t^2}\,dt$ and $\mathrm{erfc}(x) = \frac{2}{\sqrt{\pi}} \int_x^\infty e^{-t^2}\,dt$

$$= \frac{2x}{\sqrt{\pi}} \int_0^1 e^{-x^2u^2}\,du$$



Using $w(\underline{r}) = \operatorname{erfc}(|\underline{r}|)$ as the window, the short and long range functions look like



(*) **Ewald idea**: Break up the sum $\Phi(\underline{r})$ into two pieces:

- A short-range sum containing contributions of nearby ions
- A long-range sum for distant ions.

$$\Phi(\underline{r}) = \Phi_{short}(\underline{r}) + \Phi_{long}(\underline{r})$$

- The sum Φ_{short} converges rapidly.
- The sum Φ_{long} converges slowly, but the function $\Phi_{long}(\underline{r})$ is slowly varying $\Rightarrow$ its Fourier transform decays rapidly in Fourier space. Using Poisson summation*, the sum Φ_{long} can be rewritten as a sum of Fourier coeffs. that converges rapidly.

$\left(* \sum_{n=-\infty}^{\infty} f(n) = \sum_{k=-\infty}^{\infty} \hat{f}(k), \quad \hat{f}(k) = \int_{-\infty}^{\infty} f(x) e^{-ikx} dx \right)$

The sum $\Phi(\underline{r})$ then decomposes:

$$\Phi(\underline{r}) = \Phi_{short}(\underline{r}) + \Phi_{long}(\underline{r})$$

$$\left.\Phi_{short}(\underline{r}) = \sum_{n_x}\sum_{n_y} (-1)^{n_x+n_y} \phi_{short}(x-n_x, y-n_y) \right\} \text{Converges rapidly}$$

$$\Phi_{long}(\underline{r}) = \sum_{n_x}\sum_{n_y} (-1)^{n_x+n_y} \phi_{long}(x-n_x, y-n_y)$$

Now let's convert the sum Φ_{long} into a sum in Fourier space:

$$\Phi_{long}(\underline{r}) = \sum_{n_x}\sum_{n_y} (-1)^{n_x+n_y} \phi_{long}(x-n_x, y-n_y)$$

$$\overset{\text{(Poisson summation)} + \text{(algebra)}}{=} 4\pi^2 \sum_{\substack{k_x \\ \text{odd}}} \sum_{\substack{k_y \\ \text{odd}}} e^{-i\pi(k_x x + k_y y)} \hat{\phi}_{long}(-\pi k_x, -\pi k_y)$$

where $\hat{\phi}_{long}$ is the Fourier transform of ϕ_{long}:

$$\hat{\phi}_{long}(k_x, k_y) = \frac{1}{(2\pi)^2} \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \underbrace{\phi_{long}(x,y)}_{\text{"}erf(|r|)/|r|} e^{-i(k_x x + k_y y)} dx\, dy$$

$$= \frac{1}{2\pi^{5/2}} \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{0}^{1} e^{-(x^2+y^2)u^2 - i(k_x x + k_y y)} du\, dx\, dy$$

$$\overset{\text{(... algebra ...)}}{=} \frac{1}{2\pi|\underline{k}|} \operatorname{erfc}\left(\frac{|k|}{2}\right)$$

So, $$\Phi_{long}(x,y) = 2 \sum_{k_x \text{ odd}} \sum_{k_y \text{ odd}} e^{-i\pi(k_x x + k_y y)} \frac{\text{erfc}\left(\frac{\pi |\underline{k}|}{2}\right)}{|\underline{k}|}$$

(algebra...)

$$= 8 \sum_{\substack{k_x=1 \\ \text{odd}}}^{\infty} \sum_{\substack{k_y=1 \\ \text{odd}}}^{\infty} \cos(\pi k_x x) \cos(\pi k_y y) \frac{\text{erfc}\left(\frac{\pi |\underline{k}|}{2}\right)}{|\underline{k}|}$$

In total:

$$\underbrace{\sum_{n_x} \sum_{n_y} \frac{(-1)^{n_x+n_y}}{|\underline{r}-\underline{n}|}}_{\substack{\Phi(\underline{r}) \\ \text{(slow)}}} = \overbrace{\sum_{n_x} \sum_{n_y} \frac{(-1)^{n_x+n_y} \text{erfc}(|\underline{r}-\underline{n}|)}{|\underline{r}-\underline{n}|}}^{\Phi_{short} \text{ (fast)}}$$

$$+ \underbrace{8 \sum_{\substack{k_x=1 \\ \text{odd}}}^{\infty} \sum_{\substack{k_x=1 \\ \text{odd}}}^{\infty} \cos(\pi k_x x) \cos(\pi k_y y) \frac{\text{erfc}\left(\frac{\pi |\underline{k}|}{2}\right)}{|\underline{k}|}}_{\substack{\Phi_{long} \\ \text{(fast)}}}$$