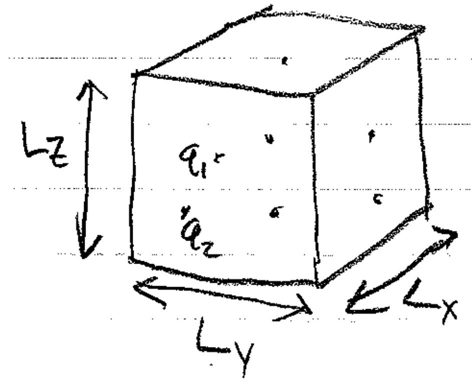
An Alternative derivation of Ewald Sums

Consider a cubic unit cell (Generalized later)



with N charges $q_1, \ldots q_N$ at positions $\vec{r}_1, \ldots \vec{r}_N$.

In an infinite three dimensional array of such cubes, the potential can only be finite if

$$\sum_{i=1}^{N} q_i = 0$$

Presuming a finite potential, the array must generate a periodically varying potential describable by Fourier Series

$$U(x) = \sum_{m_{x,y,z}=-\infty}^{\infty} \tilde{U}[m_x, m_y, m_z] e^{j2\pi m_x \frac{x}{L_x}} e^{j2\pi m_y \frac{y}{L_y}} e^{j2\pi m_z \frac{z}{L_z}}$$

Given that the potential must satisfy the poisson equation ($\epsilon = 1$)

$$\frac{\partial^2 U(\vec{r})}{\partial x^2} + \frac{\partial^2 U(\vec{r})}{\partial y^2} + \frac{\partial^2 U(\vec{r})}{\partial z^2} = -4\pi\sigma(\vec{r}) = \nabla^2 U(\vec{r})$$

The Fourier series for the potential can be related to a Fourier series for the periodic charge through Poisson's equation by

$$\nabla^2\left(\sum \bar{\Phi}[m_x, m_y, m_z]\, e^{j2\pi\left(\frac{m_x}{L_x}x + \frac{m_y}{L_y}y + \frac{m_z}{L_z}z\right)}\right)$$

$$= -\sum_{\substack{m_x, m_y, m_z \\ m_z \neq m_x \neq m_y \neq 0}} \bar{\Phi}[m_x, m_y, m_z]\left(\left(\frac{2\pi m_x}{L_x}\right)^2 + \left(\frac{2\pi m_y}{L_y}\right)^2 + \left(\frac{2\pi m_z}{L_z}\right)^2\right) \cdot e^{j2\pi\left(\frac{m_x}{L_x}x + \frac{m_y}{L_y}y + \frac{m_z}{L_z}z\right)}$$

Leave out constant term. Can make no difference in forces, or help match charge.

$$= -4\pi \sum \bar{\sigma}[m_x, m_y, m_z] \cdot e^{j2\pi \underbrace{\left(\frac{m_x}{L_x}x + \frac{m_y}{L_y}y + \frac{m_z}{L_z}z\right)}_{= \vec{m}_L \cdot \vec{r}}}$$

Matching terms (using orthogonality of complex exps)

$$\bar{\Phi}[m_x, m_y, m_z] = \frac{4\pi}{(2\pi)^2\, \vec{m}_L^2} \cdot \bar{\sigma}[m_x, m_y, m_z]$$

Using the Fourier synthesis formula

$$\bar{\sigma}[\vec{m}] = \frac{1}{\underbrace{L_x L_y L_z}_{V}} \int \sigma(\vec{r})\, e^{j2\pi(\vec{m}_L \cdot \vec{r})}\, dV$$

If $\sigma(\vec{r})$ is made of point charges

$$\sigma(\vec{r}) = \sum_{i=1}^{N} q_i \delta(\vec{r} - \vec{r}_i)$$

The Fourier synthesis formula yields

$$\bar{\sigma}[m] = \frac{1}{V}\sum_{i=1}^{N}\int q_i\delta(r-r_i)\, e^{j2\pi(\vec{m}_L\cdot\vec{r})}dV$$

$$= \frac{1}{V}\sum_{i=1}^{N} q_i\, e^{j2\pi\vec{m}_L\cdot\vec{r}_i}$$

From matching

$$\bar{u}[\vec{m}] = \frac{1}{\pi V}\sum_{i=1}^{N} q_i \frac{e^{j2\pi m_L \vec{r}_i}}{m^2}$$

Note that $|\bar{u}[\vec{m}]| \propto \frac{1}{m^2}$ (slow decay)

Now suppose the charge density is smoothed

$$\sigma(\vec{r}) = \sum q_i\left(\frac{\beta}{\sqrt{\pi}}\right)^3 e^{-\beta^2(\vec{r}-\vec{r}_i)^2}$$

Transform Identity

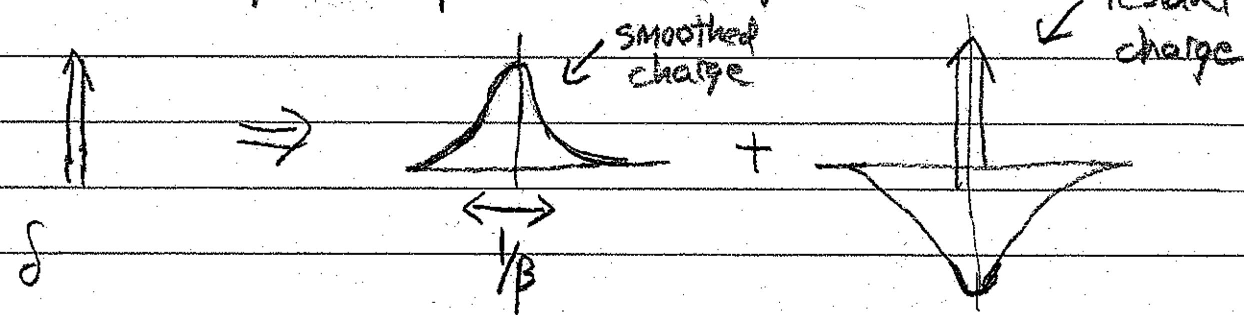
$$\frac{1}{V}\int \underbrace{\left(\frac{\beta}{\sqrt{\pi}}\right)^3 e^{-\beta^2\vec{r}^2}}_{\text{Unit charge at origin}} e^{j2\pi(\vec{m}_L\cdot\vec{r})}\, dV$$

$$= \frac{1}{V}e^{-\pi^2\vec{m}_L^2/\beta^2}$$

Key Idea

1) Determine Fourier Series representation of potential due to a point charge. Note slow decay of Fourier coefficients with frequency

2) Decompose point charge



Fourier Series for potential Decays exponentially — Terms can be truncated!

potential dies exponentially fast in Space — Interactions can be truncated

3) Compute Potential from smoothed charge plus contribution from nearby residual charges, but subtract self charge contribution

4) Use a fast algorithm to compute smoothed charge potentials

Using Identity for charge at $\vec{r}_i$

$$\frac{1}{V}\int\left(\frac{\beta}{\sqrt{\pi}}\right)^3 e^{-\beta^2(\vec{r}-\vec{r}_i)^2} e^{-j2\pi(\vec{m}_L\cdot\vec{r})}\,dV$$

$\hat{r} = r - r_i \qquad r = \hat{r} + r_i$

$$\frac{1}{V}\int\left(\frac{\beta}{\sqrt{\pi}}\right)^3 e^{-\beta^2(\hat{r})^2} e^{-j2\pi\,\vec{m}_L\cdot(\hat{r}+\vec{r}_i)}\,dV$$

$$= \frac{1}{V} e^{-\pi^2 m_L^2/\beta^2} e^{-j2\pi\,\vec{m}_L\cdot\vec{r}_i}$$

Transforming $\sigma(\vec{r})$ using identity

$$\sigma[\vec{m}] = \frac{1}{V} e^{-\pi^2 m_L^2/\beta^2}\sum q_i\, e^{-j2\pi\vec{m}_L\cdot\vec{r}_i}$$

$$\vec{u}(\vec{r}) = \frac{1}{\pi V}\sum_{m=-\infty}^{\infty}\underbrace{\left(\underbrace{\frac{e^{-\pi^2 m_L^2/\beta^2}}{m_L^2}}_{\text{exponentially fast decay}}\sum_{i=1}^{N} q_i\, e^{-j2\pi(\vec{m}_L\cdot\vec{r}_i)}\right)}_{\text{Fourier series coefficients}} e^{j2\pi\vec{m}_L\cdot\vec{r}}$$

Energy

$$E = \frac{1}{2}\sum_{j=1}^{N} q_j\,\vec{u}(\vec{r}_j) - \text{correction (self term)}$$

$$E = \frac{1}{2\pi V} \sum_{\vec{m}=-\infty}^{\infty} \frac{e^{-\pi m_L^2/\beta^2}}{m_L^2} \sum_{i,j=1}^{N} q_i q_j e^{j2\pi(\vec{r}_j - \vec{r}_i)}$$

$$- \text{correction (self term)}$$

Self term

$$\frac{1}{2}\left(\text{Potential due to } q_j \text{ at } x_j\right) \cdot q_j$$

Potential due to q_j at x_j

$$u_{q_j}(x_j) = \frac{1}{\pi V} \sum_{\vec{m}=-\infty}^{\infty} \frac{e^{-\pi^2 m_L^2/\beta^2}}{m_L^2} \cdot q_j \underbrace{e^{j2\pi(\cancel{\vec{r}_j - \vec{r}_j})}}_{=1}$$

$$= \underbrace{\frac{q_j}{\pi V} \sum_{\vec{m}=-\infty}^{\infty} \frac{e^{-\pi^2 m_L^2/\beta^2}}{m_L^2}}_{2 q_j \frac{\beta}{\sqrt{\pi}} ?}$$

Easier to show directly

Potential Due to $\sigma(x,y,z) = \left(\frac{\beta}{\sqrt{\pi}}\right)^3 e^{-\beta^2 \overbrace{(x^2+y^2+z^2)}^{r^2}}$

at $0,0,0$

$$\Phi(0,0,0) = \left.\frac{\operatorname{erf}(\beta r)}{r}\right|_{r=0} \Bigg\} \text{ Prove this is true}$$

Demonstrating $u = \frac{\mathrm{erf}(\beta r)}{r}$ if $\sigma = \left(\frac{\beta}{\sqrt{\pi}}\right)^3 e^{-\beta^2 r^2}$

Poission in spherical coordinates

$$\nabla^2 u = \frac{\partial^2 u}{\partial r^2} + \frac{1}{r^2}\frac{\partial^2 u}{\partial \theta^2} + \frac{1}{r^2 \sin^2\theta}\frac{\partial^2 u}{\partial \phi^2} + \frac{2}{r}\frac{\partial u}{\partial r} + \frac{\cot\theta}{r^2}\frac{\partial u}{\partial \theta}$$

$$= -4\pi \left(\frac{\beta}{\sqrt{\pi}}\right)^3 e^{-\beta^2 r^2}$$

$$\frac{\partial u}{\partial \theta} = 0 \quad \frac{\partial u}{\partial \phi} = 0$$ (radially symmetric charge)

$$\frac{\partial^2 u}{\partial r^2} + \frac{2}{r}\frac{\partial u}{\partial r} = -4\pi \left(\frac{\beta}{\sqrt{\pi}}\right)^3 e^{-\beta^2 r^2}$$

If $u = \frac{\mathrm{erf}(\beta r)}{r}$ satisfies equation

$$\frac{2}{r}\frac{\partial u}{\partial r} = \left(\frac{2\beta}{\sqrt{\pi}} \frac{e^{-\beta^2 r^2}}{r} - \mathrm{erf}(\beta r)\, r^{-2}\right)\frac{2}{r}$$

$$\frac{\partial^2 u}{\partial r^2} = -\frac{4\beta^3 \cancel{r}}{\sqrt{\pi}} \frac{e^{-\beta^2 r^2}}{\cancel{r}}$$

$$- \frac{2\beta}{\sqrt{\pi}} e^{-(\beta^2 r^2)}\, r^{-2}$$

$$- \frac{2\beta}{\sqrt{\pi}} e^{-\beta^2 r^2}\, r^{-2}$$

$$+ 2\, \mathrm{erf}(\beta r)\, r^{-3}$$

$$\cancel{\frac{\frac{4\beta}{\sqrt{\pi}} e^{-\beta^2 r^2}}{r^2}} - \cancel{\frac{2\,\mathrm{erf}(\beta r)}{r^3}}$$

$$= \frac{4\beta^3}{\sqrt{\pi}} e^{-(\beta^2 r^2)}$$

$$- \cancel{\frac{2\beta}{\sqrt{\pi}} e^{-(\beta^2 r^2)} r^{-2}}$$

$$- \cancel{\frac{2\beta}{\sqrt{\pi}} e^{-\beta^2 r^2} r^{-2}}$$

$$+ \cancel{\frac{2\,\mathrm{erf}(\beta r)}{r^3}}$$

$$= -4 \frac{\beta^3}{\sqrt{\pi}} e^{-(\beta^2 r^2)}$$ works!

$$= -4\pi \left(\frac{\beta^3}{\sqrt{\pi}}\right) e^{-(\beta^2 r^2)}$$

Finally

$$\Phi(0,0,0) = \left.\frac{\mathrm{erf}(\beta r)}{r}\right|_{r=0} \xrightarrow{\text{l'hopital's}} = \left.\frac{\frac{2\beta}{\sqrt{\pi}} e^{-\beta^2 r^2}}{1}\right|_{r=0}$$

$$= \frac{2\beta}{\sqrt{\pi}}$$

Potential due to q_j at x_j

$$q_j \frac{2\beta}{\sqrt{\pi}}$$

Energy Correction for self term

$$\sum_{j=1}^{N} q_j^2 \frac{\beta}{\sqrt{\pi}}$$

Next the potential due to residual chg

$$\sigma(\vec{r}) = \delta(\vec{r}) - \left(\frac{\beta}{\sqrt{\pi}}\right)^3 e^{-(\beta^2 \vec{r}^2)}$$

$$\nabla^2 u = -4\pi\left(\delta(\vec{r}) - \left(\frac{\beta}{\sqrt{\pi}}\right)^3 e^{-(\beta^2 \vec{r}^2)}\right)$$

$$\underbrace{u(\vec{r}) = \frac{1}{|\vec{r}|} - \frac{\mathrm{erf}(\beta|r|)}{|\vec{r}|}}_{} = \frac{1 - \mathrm{erf}(\beta|r|)}{|\vec{r}|}$$

Does not satisfy periodicity conditions unless

$$1 - \mathrm{erf}(\beta|r|) \simeq 0 \qquad r \geq L/2$$

For $(\beta L/2)$ $\qquad 1 - \mathrm{erf}(\underbrace{\beta \tfrac{L}{2}}_{4}) \simeq 1.5 \cdot 10^{-8}$

$$\beta \geq \frac{8}{L}$$