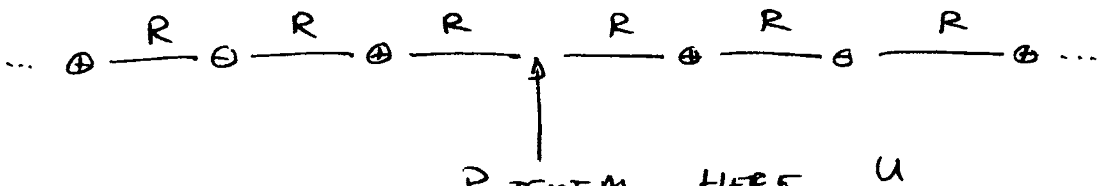
Continuation of JRC note...

Consider ionic solid (NaCl)

Born-Mayer potential

$$u_{ij} = \begin{cases} \lambda \, \mathrm{EXP}\left[-R/\rho\right] - q^2/R & \text{: neighbor} \\ \pm \, q^2/R & \text{: else} \end{cases}$$

Problems with $1/r$ potentials.



$$u = \frac{2q^2}{R} + \frac{-2q^2}{2R} + \frac{2q^2}{3R} + \frac{-2q^2}{4R} + \cdots$$

$$= \frac{+2q^2}{R} \underbrace{\left[1 - \frac{1}{2} + \frac{1}{3} - \cdots\right]}_{\text{Slowly converging.}}$$

Can be solved by series for special geometries.

$$\ln(1+x) = x - \frac{x^2}{2} + \frac{x^3}{3} + \cdots$$

Case $x = 1$

$$\ln(2) = 1 - \frac{1}{2} + \frac{1}{3} - \frac{1}{4} \cdots$$

$$u = \frac{+2q^2}{R}\ln(2) = \frac{q^2}{R}\alpha$$

$\alpha \equiv$ Madelung constant.

$= (\pm) 2\ln(2)$ for $+ \text{—} - \text{—} + \text{—} - \text{—}$

SIGN DEPENDS IF REFERENCE SIGHT IS $+q$ OR $-q$.

$= (\pm) 1.7475$ FOR NaCl

$(\pm) 1.7627$ FOR CsCl

$(\pm) 1.6381$ FOR ZnS

GEOMETRY DEPENDENT.

WE want a more general solution.

<u>Ewald Method</u>

Appendix B OF childrens' KITTLE.

OVERVIEW:

TAKE "CONDITIONALLY CONVERGENT" SUMMATION AND BREAK INTO 2 PARTS.

1 PART REAL SPACE

1 PART FOURIER SPACE

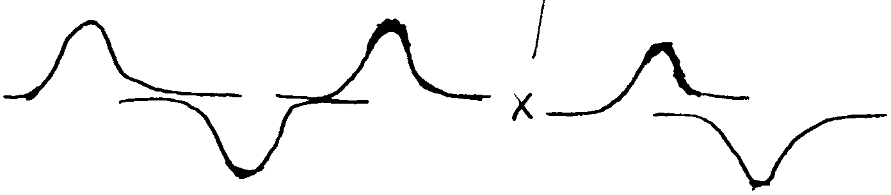
APPLY SIMPLIFYING BACKGROUND CHARGE THAT ALLOWS FOR EASIER MANIPULATION OF PROBLEM, BUT WHICH CAN BE SUBTRACTED FROM FINAL SOLUTION.

GAUSSIAN: WIDTH $\propto \left(\frac{1}{\eta}\right)$ IS

CONVERGENCE PARAMETER WHICH AFFECTS THE RATE OF SUMMATION CONVERGENCE BUT NOT THE FINAL, FULLY CONVERGED VALUE.

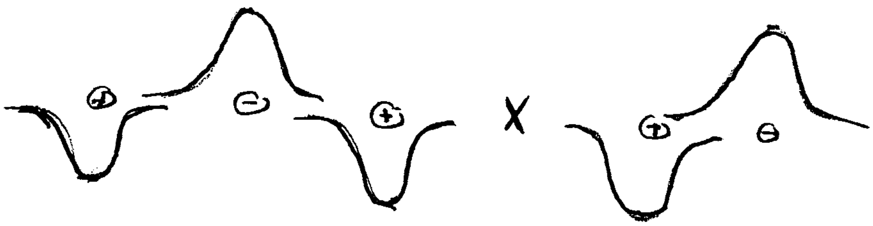
BASIC IDEA

REFERENCE SIGHT



$\equiv \phi_1$

SERIES OF CHARGED GAUSSIANS AT EACH SIGHT EXCEPT REFERENCE SIGHT, X.



$\equiv \phi_2$

SERIES OF CHARGED GAUSSIANS PLUS POINT CHARGES EXCEPT AT X.

GAUSSIANS IN ϕ_1 ϕ_2 OPPOSITE CHARGE SO

$\phi_1 + \phi_2$

... ⊕ ⊖ ⊕ X ⊕ ⊖ ...

REFERENCE

WILL WORK IN RECIPROCAL SPACE.

$$\underset{\sim}{R} = n_1 \underset{\sim}{a}_1 + n_2 \underset{\sim}{a}_2 + n_3 \underset{\sim}{a}_3$$

$\underset{\sim}{a}_i$ lattice vectors in Real space

$$\underset{\sim}{G} = m_1 \underset{\sim}{b}_1 + m_2 \underset{\sim}{b}_2 + m_3 \underset{\sim}{b}_3$$

$\underset{\sim}{b}_i$ reciprocal lattice vectors

$$\underset{\sim}{b}_i = \frac{2\pi}{V_{cell}} \left(\underset{\sim}{a}_j \times \underset{\sim}{a}_k \right) \qquad i, j, k \text{ cyclic}$$

$$V_{cell} = \left| \underset{\sim}{a}_1 \cdot \left(\underset{\sim}{a}_2 \times \underset{\sim}{a}_3 \right) \right|$$

PROPERTIES

$$f(\underset{\sim}{r}) = \sum_G C_G \exp\left[i \underset{\sim}{G} \cdot \underset{\sim}{r} \right]$$

THEN

$$f(\underset{\sim}{r} + \underset{\sim}{R}) = \sum_G C_G \exp\left[i G \cdot (r + R) \right]$$

$$= \underline{\underline{\sum C_G \; e^{iGr}}} \; \underbrace{e^{iGR}}_{=1} = f(\underset{\sim}{r})$$

$$\underset{\sim}{a}_i \cdot \underset{\sim}{b}_j = 2\pi \, \delta_{ij}$$

BEGIN WITH ϕ_1

SAY $\phi_1 = \phi_a - \phi_b$

$\phi_a =$ 

$\phi_b =$ 

WRITE POTENTIAL $\phi_a = \sum_G C_G e^{iG\cdot r}$

CHARGE DENSITY

$$\rho = \sum_G \rho_G e^{+iG\cdot r}$$

POISSON EQUATION

$$\nabla^2 \phi_a = -4\pi\rho$$

SUBSTITUTE + SOLVE

$$\sum_G G^2 c_G e^{+i\underset{\sim}{G}\cdot\underset{\sim}{r}} = -4\pi \sum_G \rho_G e^{+i\underset{\sim}{G}\cdot\underset{\sim}{r}}$$

SO

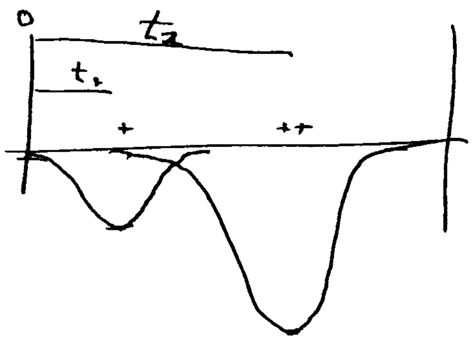
$$\boxed{C_G = \frac{4\pi \rho_G}{G^2}}$$

Now solve for ρ_G.

Define Gaussian charge distribution

$$\rho(r) = q\left(\frac{\eta}{\pi}\right)^{3/2} \mathrm{EXP}\left[-\eta r^2\right]$$

One could in principle have multiple charges (gaussian) in one cell so (1D EXAMPLE)



$$q_{t_1}\left(\frac{\eta}{\pi}\right)^{3/2} \mathrm{EXP}\left(-\eta\left(r-r_{t_1}\right)^2\right)$$
$$+\, q_{t_2}\left(\frac{\eta}{\pi}\right)^{3/2} \mathrm{EXP}\left[-\eta\left(r-r_{t_2}\right)^2\right]$$

STANDARD SOLUTION FOR ρ_G

$$\rho = \sum_G \rho_G e^{iG\cdot r}$$

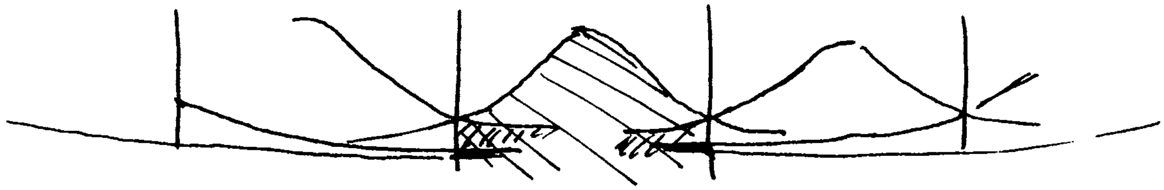
Charge inside 1 cell

MULTIPLY BY $e^{-iG\cdot r}$

AND $\int_{\text{cell}} dr$

THE CHARGE IN 1 UNIT CELL

IS



central region
+ tails from <u>all</u>
surrounding cells.

$$\int_{\text{cell}} \text{CHARGE INSIDE CELL} = \int_{\text{all SPACE}} \text{GAUSSIAN FROM 1 cell.}$$

YOU CAN SEE THIS BY UNFOLDING GAUSSIANS into neighboring cells.

RETURNING TO PROBLEM OF FINDING ρ_G.

$$\rho = \sum_G \rho_G e^{iG\cdot r}$$

charge inside 1 cell.

STANDARD SOLUTION FOR ρ_G

MULTIPLY BY $\underline{e^{-iG\cdot r}}$

$$\int_{\text{cell}} dr$$

FROM P. 7

$$\int_{\substack{\text{all}\\\text{space}}} \sum_t q_t \left(\frac{\eta}{\pi}\right)^{3/2} \mathrm{EXP}\left[-\eta\,(r-r_t)^2\right] \mathrm{EXP}\left[-i\,\underset{\sim}{G}\cdot\underset{\sim}{r}\right] dr$$

SUM OVER ALL GAUSSIAN IN UNIT CELL

$$\underbrace{\int e^{iG\cdot r} e^{-iG\cdot r} dr = V_{cell}}.$$

$$\rho_G V_{cell}.$$

$$\rho_G V_{cell} = \sum_t q_t \, \mathrm{EXP}\left[-i\,\underset{\sim}{G}\cdot\underset{\sim}{r}_t\right]\left(\frac{\eta}{\pi}\right)^{3/2}\int_{\substack{\text{ALL}\\ \text{SPACE}}} e^{-(iG\cdot\rho+\eta\rho^2)}\, d\rho$$

$$\underset{\sim}{\rho} = \underset{\sim}{r} - \underset{\sim}{r}_t$$

The Structure Factor $S(\underset{\sim}{G})$ is defined

$$\sum_t q_t \, \mathrm{EXP}\left[-i\,\underset{\sim}{G}\cdot\underset{\sim}{r}_t\right]$$

$$\boxed{\rho_G V_{cell} = S(\underset{\sim}{G})\, \mathrm{EXP}\left[-G^2/4\eta\right]}$$

Using C_G from page 5

$$\boxed{\phi_a = \frac{4\pi}{V_{cell}} \sum_G S(G)\, G^{-2}\, \mathrm{EXP}\left[\frac{-G^2}{4\eta}\right]}$$

For ϕ_b ~~the~~ the solution to Poisson's Equation for GAUSSIAN ρ is "well known"

$$\nabla^2 \Phi = -4\pi \rho(r)$$

$$\rho(r) = \frac{Q}{\sigma^3 \sqrt{2\pi}^3} e^{\frac{-r^2}{2\sigma^2}}$$

SOLUTION:

$$\Phi = \frac{Q}{r} \, \mathrm{ERF}\left[\frac{r}{\sqrt{2}\,\sigma}\right]$$

Making appropriate substitutions (i.e. $\eta = \frac{1}{2\sigma^2}$) and taking limit as $r \to 0$

$$\phi_b = 2 q_i \left(\frac{\eta}{\pi}\right)^{1/2}$$

So

$$\phi_1 = \frac{4\pi}{V_{cell}} \sum_{G} S(\underset{\sim}{G})\, G^{-2} \, \mathrm{EXP}\left[\frac{-G^2}{4\eta}\right] - 2 q_i \left(\frac{\eta}{\pi}\right)^{1/2}$$

It is left as an exercise for the reader to show that

$$\phi_2 = \sum_{\ell} \frac{q_\ell}{r_\ell} \, \mathrm{ERFC}\left[\eta^{1/2} r_\ell\right]$$

$$\boxed{\phi(i) = \frac{4\pi}{V_{cell}} \sum_{G} S(G)\, G^{-2} \, \mathrm{EXP}\left[\frac{-G^2}{4\eta}\right] - 2 q_i \left(\frac{\eta}{\pi}\right)^{1/2} + \sum_{\ell} \frac{q_\ell}{r_\ell} \, \mathrm{ERFC}\left(\eta^{1/2} r_\ell\right)}$$

"TADA"

η "CONVERGENCE PARAMETER."

Check class status at

www.ices.utexas.edu/~sbeckman/che384.html

ANNOUNCEMENT BY 5:00 4/18/2006

~~ERFC~~

$$ERFC(z) = \frac{2}{\sqrt{\pi}} \int_{z}^{\infty} e^{-t^2}\, dt$$

$$ERF(z) = \frac{2}{\sqrt{\pi}} \int_{0}^{z} e^{-t^2}\, dt$$