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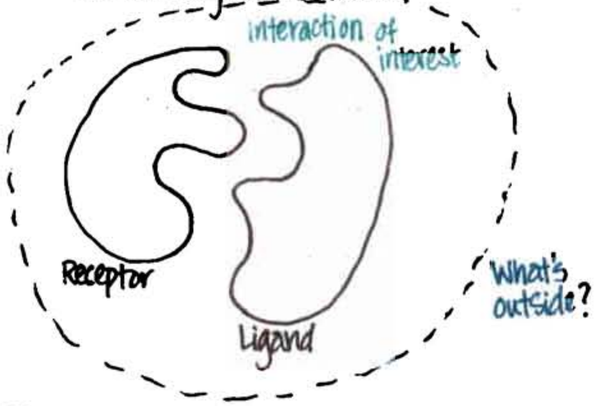
THURSDAY 2 MARCH 2006

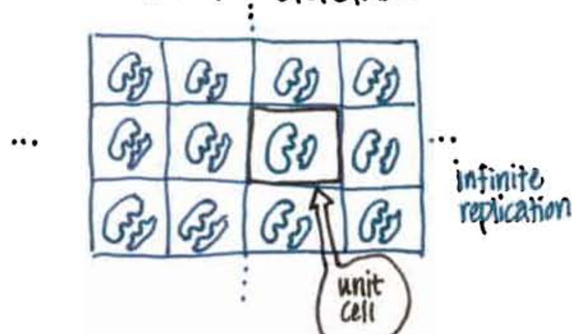
# LECTURE 7: CONTINUUM ELECTROSTATIC MODELING I

SURROUNDING ENVIRONMENT

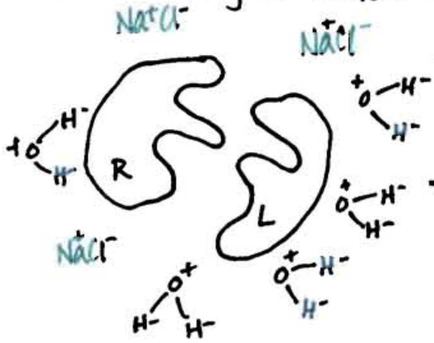



## TWO APPROACHES:

1.) PERIODIC ARRAY – "CRYSTALS"




2) SURROUNDING BY WATER OR SALT




- too many salt molecules & water molecules to track individually
- salt & ions respond rapidly to config changes

TODAY: Look at Approach 1 – infinitely periodic unit cell

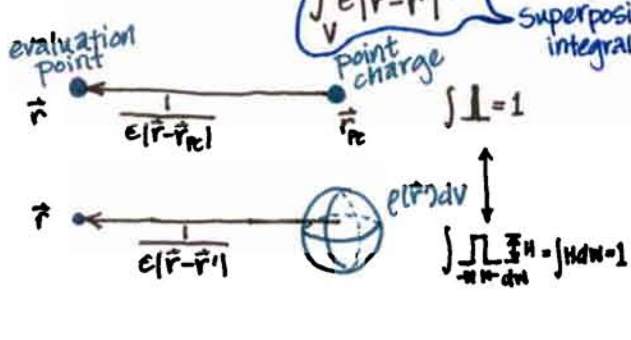
## Electrostatics

### Integral Representation

· Point Charge: $\Psi(\vec{r}) = \dfrac{q}{\epsilon|\vec{r}-\vec{r}_{pc}|}$

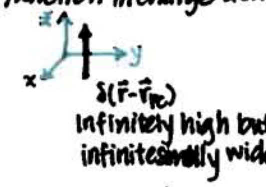
q ← charge; $\epsilon$ ← dielectric permittivity; $\vec{r}_{pc}$ ← point charge location

· Volume Charge: $\Psi(\vec{r}) = \boxed{\int_V \dfrac{\rho(\vec{r}')}{\epsilon|\vec{r}-\vec{r}'|}dV}$ ← Superposition integral




point charge is a "delta" function in charge density

$\rho(\vec{r}) = q\,\delta(\vec{r}-\vec{r}_{pc})$




KEY $\delta$ PROPERTY:

$$\int G(\vec{r})\delta(\vec{r})dV = G(0)$$

↑ smooth

$$\int \frac{q\,\delta(\vec{r}-\vec{r}')}{\epsilon|\vec{r}-\vec{r}'|}dV = \frac{q}{\epsilon|\vec{r}-\vec{r}_{pc}|}$$

### Differential Representation

Volume Charge Potential: (Poisson Equation) $\dfrac{\partial^2\Psi(\vec{r})}{\partial x^2} + \dfrac{\partial^2\Psi(\vec{r})}{\partial y^2} + \dfrac{\partial^2\Psi(\vec{r})}{\partial z^2} = -4\pi\dfrac{\rho(\vec{r})}{\epsilon}$

$\Leftrightarrow \nabla^2\Psi(\vec{r}) = -4\pi\dfrac{\rho(\vec{r})}{\epsilon}$ (Laplacian)

Point Charge Potential: $\nabla^2\Psi(\vec{r}) = -4\pi\dfrac{q\,\delta(\vec{r}-\vec{r}_{pc})}{\epsilon} = 0$ except at $\vec{r}=\vec{r}_{pc}$

try & see: $\nabla^2\left(\dfrac{q}{\epsilon|\vec{r}-\vec{r}_{pc}|}\right) = 0$ except when $\vec{r}=\vec{r}_{pc}$

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1.) Ewald Sums Problems
2.) Algorithms for the periodic case – mixture of the differential & integral forms

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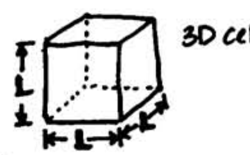
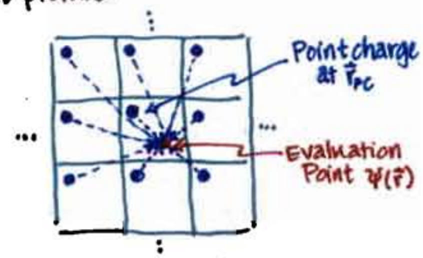
## Periodic Case:

cubic unit cell




2D picture:




Consider 1 charge in a periodic case...

$$\Psi(\vec{r}) = \sum_{n_x,n_y,n_z=-\infty}^{\infty} \frac{q}{\epsilon\left|\vec{r}-\left(\vec{r}_{pc}+n_x\begin{bmatrix}L\\0\\0\end{bmatrix}+n_y\begin{bmatrix}0\\L\\0\end{bmatrix}+n_z\begin{bmatrix}0\\0\\L\end{bmatrix}\right)\right|}$$

q ← at $\vec{r}_{pc}$; $\vec{r}_{pc}$ ← same cell

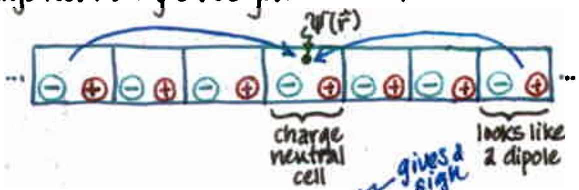
Consider 1D (along position x)...

$$\frac{1}{\epsilon|r-r_{pc}|} + \frac{1}{\epsilon|r-r_{pc}+L|} + \frac{1}{\epsilon|r-r_{pc}+2L|} + \dots$$

terms $\to \frac{1}{\epsilon L}\frac{1}{n}$ for distant cells

$\sum_{n=K}^{\infty}\frac{1}{n} \to \infty$ divergent sum

Charge Neutrality Saves you... "sort of"



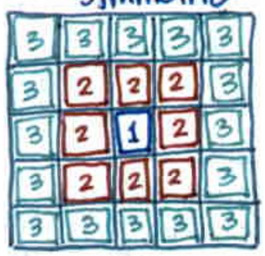

DIPOLE POTENTIAL: $\dfrac{(\vec{r}-\vec{r}_{dipole})\cdot\vec{P}}{\epsilon\,|\vec{r}-\vec{r}_{dipole}|^3}$ ← gives a sign ← dipole moment

decays like $\frac{1}{R^2}$ ⇒ not fast enough in 3D

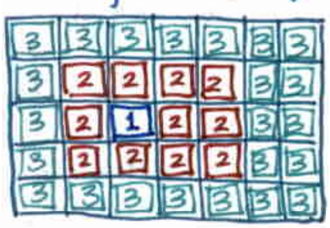
Symmetry ensures cancellation
left & right dipoles nearly cancel
difference dies like $\frac{1}{R^3}$ ⇒ fast enough

Computed Sum depends on ORDER

symmetric

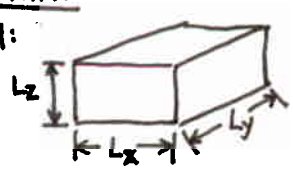



"shell" ordering
⇓
vs. asymmetric (diverges)




## EWALD SUM ALGORITHMS

Consider a 3-D cell: has N charges $\vec{q}_1, \dots, \vec{q}_N$ at $\vec{r}_1, \dots, \vec{r}_N$




Only finite potential if $\sum \vec{q}_i = 0$ — charge neutral

finite potential ← must be periodic

[Periodic Series are described by Fourier Series:]

potential

$$u(\vec{r}) = \sum_{m_{x,y,z}=-\infty}^{+\infty} \underbrace{\bar{U}[m_x,m_y,m_z]}_{\text{determine}} e^{j2\pi m_x \frac{x}{L_x}} \cdot e^{j2\pi m_y \frac{y}{L_y}} \cdot e^{j2\pi m_z \frac{z}{L_z}}$$

periodic

charge density is also periodic:

$$\rho(\vec{r}) = \sum \underset{\text{charge density}}{\bar{\rho}}[m_x,m_y,m_z]\, e^{j2\pi \overbrace{\left(\frac{m_x}{L_x}x + \frac{m_y}{L_y}y + \frac{m_z}{L_z}z\right)}}$$

$$\vec{m}_L \cdot \vec{r} = \begin{bmatrix} \frac{m_x}{L_x} & \frac{m_y}{L_y} & \frac{m_z}{L_z} \end{bmatrix} \cdot \begin{bmatrix} x \\ y \\ z \end{bmatrix}$$

Poisson Eqn: $\nabla^2 u = -4\pi\rho$

- plug in the Fourier Representation on both sides
- match Fourier terms...

$$\bar{U}[m_x,m_y,m_z] = \underbrace{\boxed{\frac{-4\pi}{(2\pi)^2 \vec{m}_L^2}}}_{\text{(scalar)}} \bar{\rho}[m_x,m_y,m_z]$$

(same Fourier components)

to solve periodic problem:

- take charge density, compute Fourier Series ← hard due to point charges
- easily compute Fourier Series for periodic potential