Long-Range forces present extra problems

Forces that fall off slower than $\frac{1}{r^3}$ are problematic!
(this is because the number of molecules between r & $r+dr$ grows like $4\pi r^2 dr$)

If we have charge-charge $\left(\frac{1}{r}\right)$ or ion-dipole $\left(\frac{1}{r^2}\right)$ interactions, the totals of these interactions has the possibility of not converging as we add them up!

Here are some very specific issues. If we have periodic bondaries for an ionic system:

$$V = \frac{1}{2} \sum_{\vec{n}}{}' \underbrace{\sum_i \sum_j}_{\text{sum over charges in central box}} \frac{q_i q_j}{4\pi\varepsilon_0 |\vec{r}_{ij} + \vec{n}|}$$

← distance to image of other charge

sum over periodic images of the box

$$\vec{n} = (n_x L, n_y L, n_z L)$$ ← n_x, n_y, n_z are integers

This sum is of the form: $\sum_n \frac{(-1)^{n+1}}{n} = S$

these kinds of sum are conditionally convergent

The Answer we get depends on the order in which we add it up

Consider

$$S = 1 - \frac{1}{2} + \frac{1}{3} - \frac{1}{4} + \frac{1}{5} - \frac{1}{6} + \frac{1}{7} - \frac{1}{8}$$

$$\frac{1}{2} S = \frac{1}{2} - \frac{1}{4} + \frac{1}{6} - \frac{1}{8}$$

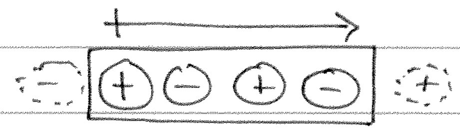
$$\frac{3}{2} S = \left(1 + \frac{1}{3} - \frac{1}{2}\right) + \left(\frac{1}{5} + \frac{1}{7} - \frac{1}{4}\right) + \left(\frac{1}{9} + \frac{1}{11} - \frac{1}{6}\right) + \ldots$$

Same as original series, but reordered!

This short proof shows that $S = \frac{3}{2} S$
(and there are other ways of proving conditional convergence)

The naïve Coulombic sum for periodic systems is also a conditionally convergent sum!

A second problem is that periodic boundaries applied to ionic solids will create crystals with a net dipole



There are a couple of ways to fix this problem:

The Ewald Sum: A numerical trick to convert 1 conditionally convergent sum into 2 absolutely convergent sums. (expensive)

Reaction field: ions within cutoff sphere are treated directly, those outside are treated as a dielectric continuum.

Wolf sum & Related Methods: New developments that are cheaper than Ewald

Fast Multipole Methods: Used for very large simulations (eg. 10^6 atoms)

The Ewald Sum

skip $i=j$ when $\vec{n}=\begin{pmatrix}0\\0\\0\end{pmatrix}$

$$V = \frac{1}{4\pi\varepsilon_0}\,\frac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{N}\sum_{\vec{n}}{}' \frac{q_i q_j}{|\vec{r}_{ij}+\vec{n}L|}$$

integer sum over copies of the box

This is the naive Coulomb sum for periodic copies of charges in a box or unit cell. The sum is <u>conditionally convergent</u> & <u>long ranged</u>.

The Basic Idea:
$$\frac{1}{r} = \frac{f(r)}{r} + \frac{1-f(r)}{r}$$
$$f(r) = \mathrm{erfc}(\alpha r)$$

<u>What this does:</u>

$$V = \underbrace{V^{(r)} + V^{(k)}}_{\text{2 absolutely convergent sums}} + \underbrace{V^{(\text{self})} + V^{(\text{dipole})}}_{\text{correction terms}}$$

$$V^{(r)} = \frac{1}{2}\sum_i\sum_j\sum_{\vec{n}}{}' q_i q_j \frac{\mathrm{erfc}(\alpha|\vec{r}_{ij}+\vec{n}L|)}{|\vec{r}_{ij}+\vec{n}L|}$$

$$V^{(k)} = \frac{1}{2L^3}\sum_{\vec{k}\neq 0}{}' \frac{4\pi}{k^2} e^{-k^2/4\alpha^2} \sum_i\sum_j q_i q_j e^{-i\vec{k}\cdot\vec{r}_{ij}}$$

$$V^{(\text{self})} = \frac{-\alpha}{\sqrt{\pi}}\sum_{i=1}^{N} q_i^2$$

$$V^{(\text{dipole})} = \frac{2\pi}{(1+2\epsilon)L^3}\left(\sum_{i=1}^{N} q_i \vec{r}_i\right)^2$$

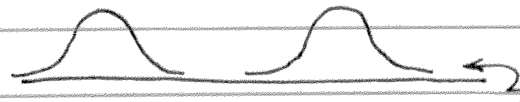
How does this all work?

$q_i \quad r_{ij} \quad q_j$

← delta function or point charges

$$V_{ij} = \frac{q_i q_j}{r_{ij}}$$

← smeared charges

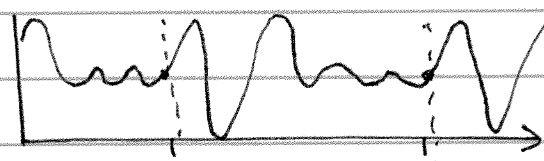


$$\rho_i = q_i e^{-\alpha(r-r_i)^2} \qquad \rho_j = q_j e^{-\alpha(r-r_j)^2}$$

$$V_{ij} = \int_{\substack{\text{all} \\ \text{space}}} \frac{\rho_i(r)\rho_j(r)}{r}\, dr = \sqrt{\frac{\pi}{2\alpha}}\; q_i q_j\, e^{-\alpha(r_i - r_j)^2/2}$$

To show the various parts, we need a brief refresher on Fourier Series:

Suppose we have a function with periodicity L on the interval $(-L/2, L/2)$



A Fourier series provides an equivalent representation:

$$f(x) = \frac{1}{2} a_0 + \sum_{n=1}^{\infty} \left[a_n \cos(nx) + b_n \sin(nx) \right]$$

The Fourier coefficients:

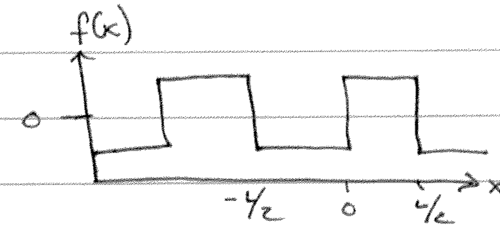
$$a_n = \frac{1}{L} \int_{-L/2}^{L/2} f(x) \cos\left(\frac{2\pi n x}{L}\right) dx$$

$$b_n = \frac{1}{L} \int_{-L/2}^{L/2} f(x) \sin\left(\frac{2\pi n x}{L}\right) dx$$

If you want to think quantum mechanically,
This is expansion in a cos & sin basis set

An Example

Suppose $f(x)$ is a square wave



$$a_n = \frac{1}{L}\int_{-L/2}^{L/2} f(x)\cos\left(\frac{2\pi n x}{L}\right)dx$$

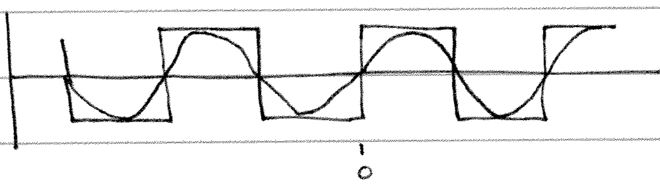
$$= \frac{1}{L}\left[-\int_{-L/2}^{0}\cos\left(\frac{2\pi n x}{L}\right)dx + \int_{0}^{L/2}\cos\left(\frac{2\pi n x}{L}\right)dx\right] = 0$$

cos is an <u>even</u> function

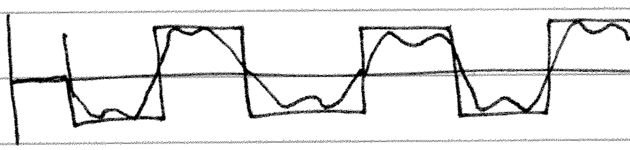
$$b_n = \frac{1}{L}\int_{-L/2}^{L/2} f(x)\sin\left(\frac{2\pi n x}{L}\right)dx$$

$$b_n = \begin{cases} 4/n\pi & n = \text{odd} \\ 0 & n = \text{even} \end{cases}$$

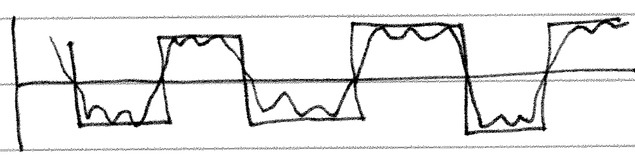
n=1



n=1,3



n=1,3,5



<u>A Fourier representation</u>:

- The set of fourier coefficients, a_n, b_n contain complete information about the function
- Although $f(x)$ is periodic to ∞, b_n is <u>very</u> small after a short range:

In[13]:=
```
sines = Table[Sin[2 n Pi x / l], {n, 1, 10}]
```

Out[13]= {Sin[2 π x], Sin[4 π x], Sin[6 π x], Sin[8 π x], Sin[10 π x], Sin[12 π x], Sin[14 π x], Sin[16 π x], Sin[18 π x], Sin[20 π x]}

In[2]:=
```
cosines = Table[Cos[2 n Pi x / l], {n, 1, 10}]
```

Out[2]= $\left\{\text{Cos}\left[\frac{2\pi x}{l}\right], \text{Cos}\left[\frac{4\pi x}{l}\right], \text{Cos}\left[\frac{6\pi x}{l}\right], \text{Cos}\left[\frac{8\pi x}{l}\right], \text{Cos}\left[\frac{10\pi x}{l}\right], \text{Cos}\left[\frac{12\pi x}{l}\right], \text{Cos}\left[\frac{14\pi x}{l}\right], \text{Cos}\left[\frac{16\pi x}{l}\right], \text{Cos}\left[\frac{18\pi x}{l}\right], \text{Cos}\left[\frac{20\pi x}{l}\right]\right\}$

In[14]:=
```
bs = Table[If[OddQ[n], 4/(n Pi), 0], {n, 1, 10}]
```

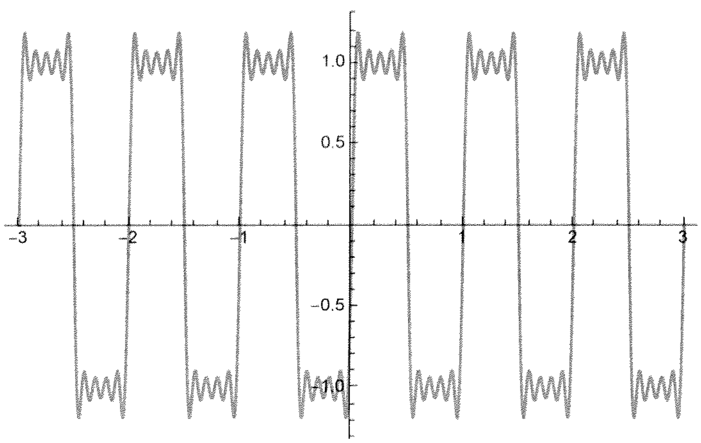
Out[14]= $\left\{\frac{4}{\pi}, 0, \frac{4}{3\pi}, 0, \frac{4}{5\pi}, 0, \frac{4}{7\pi}, 0, \frac{4}{9\pi}, 0\right\}$

In[4]:=
```
l = 1
```

Out[4]= 1

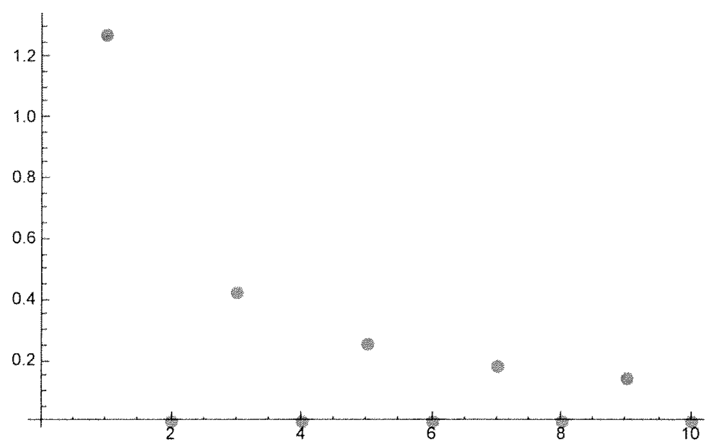
In[15]:=
```
Plot[bs.sines, {x, -3, 3}]
```

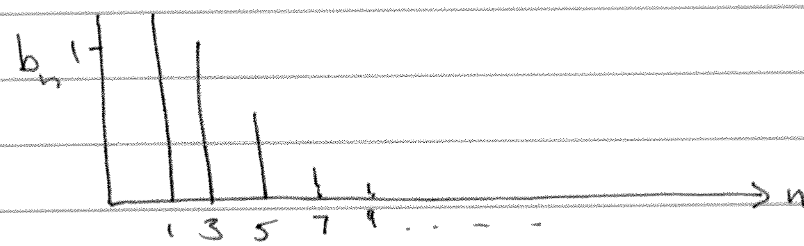
Out[15]=



In[16]:=
```
ListPlot[bs, PlotRange → Full]
```

Out[16]=

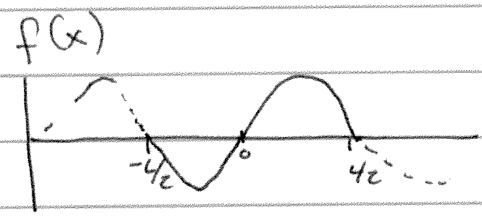


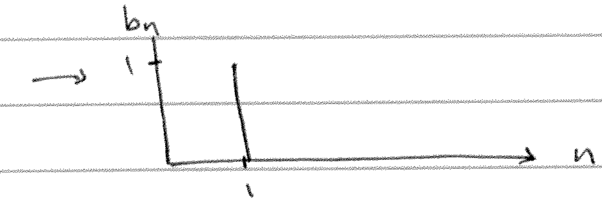


Convergence: If $f(x) = \sin\left(\frac{2\pi kx}{L}\right)$, then

$b_n = 1$ for $n = k$

$b_n = 0$ for all other values!





Smooth functions in x require few coefficients b_n

Sharp functions require more

- Large n = high frequency = short wavelength
- Small n = low frequency = Long wavelength
- $n = 0$ = average of $f(x)$ over $(-L/2, L/2)$

Fourier Transforms : When $L \to \infty$, $f(x)$ may be less periodic

- Also, we can combine a_n & b_n using Euler's relation $e^{i\theta} = \cos\theta + i\sin\theta$

What we had before:

$$f(x) = \frac{1}{2} a_0 + \sum_{n=1}^{\infty} a_n \cos\left(\frac{2\pi n x}{L}\right) + b_n \sin\left(\frac{2\pi n x}{L}\right)$$

$k = \frac{n}{L}$

$$f(x) = \int_{-\infty}^{\infty} \hat{f}(k)\, e^{-2\pi i k x}\, dk$$

This is sometimes called an inverse Fourier transform

Also: what we had before: $a_n = \frac{1}{\pi} \int_{-L/2}^{L/2} f(x) \cos\left(\frac{2\pi n x}{L}\right) dx$

$$b_n = \frac{1}{\pi} \int_{-L/2}^{L/2} f(x) \sin\left(\frac{2\pi n x}{L}\right) dx$$

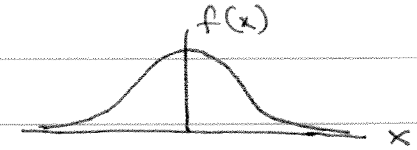
These become $\quad \hat{f}(k) = \frac{1}{2\pi} \int_{-\infty}^{\infty} f(x)\, e^{2\pi i k x}\, dx$

a_n = real part of $\hat{f}(k)$

b_n = imaginary part of $\hat{f}(k)$

One very important Fourier transform:

Gaussian: $\quad f(x) = \frac{\alpha}{2\pi}\, e^{-\alpha x^2/2}$



The Fourier transform is <u>also</u> Gaussian:

$$\hat{f}(k) = \left(\frac{2\alpha}{\pi}\right)^{1/2} e^{-k^2/2\alpha}$$

The <u>width</u> of the tranform is <u>reciprocal</u> to the width in real space.

Fourier space is sometimes called k-space or "reciprocal"-space.

<u>Derivatives:</u> Consider $f(x) = \int_{-\infty}^{\infty} \hat{f}(k)\, e^{-2\pi i k x}\, dk$

$$f'(x) = +\int_{-\infty}^{\infty} \hat{f}(k)\,(-2\pi i k)\, e^{-2\pi i k x}\, dk$$

$$f''(x) = \int_{-\infty}^{\infty} \hat{f}(x)\,(4\pi^2 i^2 k^2)\, e^{-2\pi i k x}\, dk = -\int_{-\infty}^{\infty} 4\pi^2 k^2 \hat{f}(k) e^{-2\pi i k}$$

A quick review of some electrostatics

Force between two charges: $\vec{F} = \frac{q_i q_j}{|r_{ij}|^2} \hat{r}_{ij}$ ← unit vector

← $\frac{1}{4\pi\varepsilon_0}$ is implied

Force on a charge in a field: $\vec{F}(\vec{r}) = q_i \vec{E}(\vec{r})$

A static electric field satisfies:

$$\vec{\nabla} \cdot \vec{E}(\vec{r}) = 4\pi\rho(\vec{r})$$ ← charge density

divergence operator

(Sometimes: $\nabla \cdot E = \frac{\rho}{\varepsilon_0}$)

Also $\underbrace{\vec{\nabla} \times}_{\text{curl operator}} \vec{E}(\vec{r}) = 0$

The Charge Density $\rho(\vec{r})$

For a point charge: $\rho(\vec{r}) = q_j \delta(\vec{r} - \vec{r}_j)$

The Electrostatic Potential

Zero curl implies $\vec{E}(\vec{r}) = -\nabla\phi(\vec{r})$ ← that is that the electrostatic potential is a scalar quantity

This also means that the potential energy of charge q_i @ $\vec{r}_i$ relative to a location @ ∞ is

$$U(\vec{r}_i) = q_i \phi(\vec{r}_i)$$

All of this also leads to

$$\vec{\nabla} \cdot \vec{E}(\vec{r}) = \vec{\nabla}(-\vec{\nabla}\phi(\vec{r})) = 4\pi\rho(\vec{r})$$

Poisson's Equation $\underbrace{\nabla^2}_{\text{Laplacian}} \phi(\vec{r}) = -4\pi\rho(\vec{r})$

If there are no charges, we get Laplace's equation:

$$\nabla^2 \phi(\vec{r}) = 0$$

Now, Back to the Ewald sum

We want to sum up the interaction energy of each charge with all the images of the other charges. If we can find the potential in the box:

$$V = \frac{1}{2} \sum_{\substack{\text{charges} \\ \text{in central} \\ \text{box}}} q_i \overbrace{\phi(\vec{r}_i)}$$

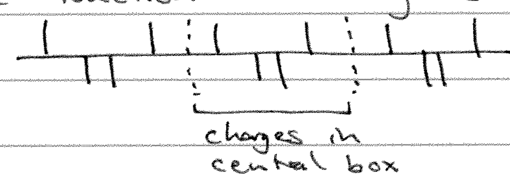
Now how do we get this?

The charge density creating the potential is known:

$$\rho(\vec{r}) = \sum_{\vec{n}}{}' \sum_{j \text{ in } \vec{n}} q_i \, \delta(\vec{r} - (\vec{r}_j + \vec{n}L))$$

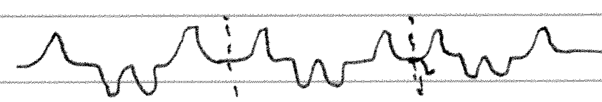
= a periodic function with very sharp features

<u>Ewald's Big Idea</u>



$= \rho(\vec{r})$

Compute the <u>field</u> by smearing out the <u>charges</u>:



$$\rho(\vec{r}) = \sum_{\vec{n}} \sum_{j} \left(\frac{\alpha}{\pi}\right)^{3/2} e^{-\alpha|\vec{r} - (\vec{r}_j + \vec{n}L)|^2}$$

large α reverts back to δ functions

Get to the electrostatic <u>potential</u> by way of Poisson's equation

direct-space form $\quad \nabla^2 \phi(\vec{r}) = -4\pi \rho(\vec{r})$

<u>reciprocal</u>-space form $\quad k^2 \hat{\phi}(\vec{k}) = -4\pi \hat{\rho}(\vec{k})$

3 spatial variables give us magnitude^2 of $\vec{k}$

So we need to Fourier transform the charge density

$$\hat{\rho}(\vec{k}) = \frac{1}{V}\int_V d\vec{r}\, e^{-i\vec{k}\cdot\vec{r}}\, \rho(\vec{r})$$

this is a sum of Gaussians, so the FT is just a sum of Gaussians!

$$= \frac{1}{V}\sum_j q_j\, e^{-i\vec{k}\cdot\vec{r}_j}\, e^{-k^2/4\alpha}$$

Now we can use Poisson's Equation for the electrostatic potential:

$$\hat{\phi}(\vec{k}) = \frac{-4\pi}{k^2}\,\hat{\rho}(\vec{k})$$

Next: we can invert the Fourier transform to recover the potential in real space:

$$\phi(\vec{r}) = \sum_{k\neq 0} \hat{\phi}(\vec{k})\, e^{i\vec{k}\cdot\vec{r}}$$

$$= \frac{1}{V}\underbrace{\sum_{\vec{k}\neq 0}}_{\text{in principle this is a sum over infinite k}}\sum_j \frac{4\pi q_j}{k^2}\, e^{i\vec{k}\cdot(\vec{r}-\vec{r}_j)}\, \underbrace{e^{-k^2/4\alpha}}_{\text{This damps to 0 quickly if } \alpha \text{ is small}}$$

So, the electrostatic energy is now:

$$V = \frac{1}{2}\sum_i q_i\, \phi(\vec{r}_i)$$

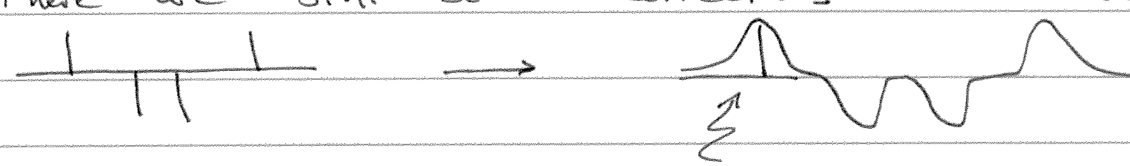
$$= \frac{1}{2}\sum_{\vec{k}\neq 0} \frac{4\pi V}{k^2}\, e^{-k^2/4\alpha}\, \underbrace{\sum_{i,j}\frac{q_i q_j}{V^2}\, e^{i\vec{k}\cdot(\vec{r}_i-\vec{r}_j)}}_{\text{A product of identical sums}}$$

$$V = \frac{1}{2} \sum_{k \neq 0} \frac{4\pi V}{k^2} e^{-k^2/4\alpha} \left| \hat{\rho}(\vec{k}) \right|^2$$

$$\hat{\rho}(\vec{k}) = \frac{1}{V} \sum_j q_j e^{-i\vec{k}\cdot\vec{r}_j}$$ ← Fourier representatio of charge density

Note that this recognition of $\sum_{i,j}$ as a product of identical single sums is what makes the Ewald sum remotely tractable!

There are still some corrections to be made:



we had the point charges interacting with the smeared copy of itself. We need to subtract this!

We work in real space to deal with the self term

$$\nabla^2 \phi(\vec{r}) = -4\pi \rho(\vec{r})$$ where $\rho(\vec{r}) = q_j \left(\frac{\alpha}{\pi}\right)^{3/2} e^{-\alpha|\vec{r}-\vec{r}_j|^2}$

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial}{\partial r}\right)$$ ← no angular behavior for charges

The solution to this diff EQ:

$$\phi(r) = \frac{q_j}{r}\, \mathrm{erf}(\sqrt{\alpha}\, r)$$ ← radial potential due to smearing

at $r=0$,

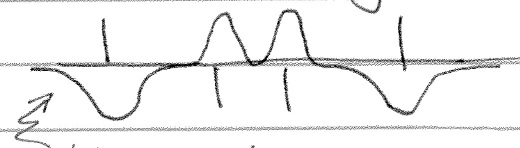
$$\phi(0) = 2 q_j \left(\frac{\alpha}{\pi}\right)^{1/2}$$

The "Self" correction subtracts this for all charges

$$V^{(self)} = \frac{1}{2} \sum_j q_j \, \phi(0)$$

$$V^{(self)} = \sqrt{\frac{\alpha}{\pi}} \sum_j q_j^2$$

We also need a correction for smearing all of the other charges



this is the reverse of the smearing we did before!

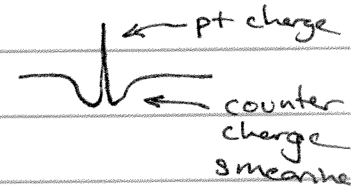
We're basically adding the correct field and subtracting the smeared field

$$\Delta \phi_j(\vec{r}) = \underbrace{\phi_j^P(\vec{r})}_{\text{point charges}} - \underbrace{\phi_j^G(\vec{r})}_{\text{Gaussian smears}}$$

$$= \frac{q_j}{|\vec{r} - \vec{r}_j|} - \frac{q_j}{|\vec{r} - \vec{r}_j|} \operatorname{erf}\left(\sqrt{\alpha}\,|\vec{r} - \vec{r}_j|\right)$$

$$\Delta \phi_j(\vec{r}) = \frac{q_j}{|\vec{r} - \vec{r}_j|} \operatorname{erfc}\left(\sqrt{\alpha}\,|\vec{r} - \vec{r}_j|\right)$$

short ranged for large α



We sum all$^{(i,j)}$ of these up for the smearing (real-space) correction

$$V^{(r)} = \frac{1}{2} \sum_{\vec{n}} \sum_{i \neq j} q_i \, \Delta \phi_j(r_{ij})$$

$$\Delta V = \frac{1}{2} \sum_{\vec{n}} \sum_{i \neq j} \frac{q_i q_j}{r_{ij}} \operatorname{erfc}(\sqrt{\alpha}\, r_{ij})$$

So far we have:

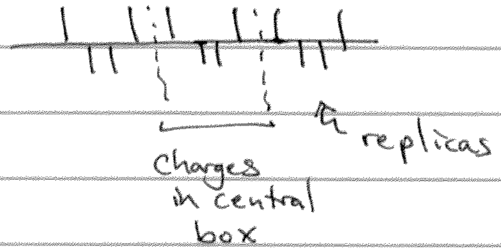
$$V = \underbrace{V^{(k)}(\alpha)}_{\text{reciprocal space}} + \underbrace{\underbrace{V^{(\text{self})}(\alpha)}_{\text{self correction}} + \underbrace{\Delta V^{(r)}(\alpha)}_{\text{correcting for smearing}}}_{\text{actually contains } \underline{\text{most}} \text{ of the total potential!}}$$

<u>Efficiency</u>:

$$O(N^2) \longrightarrow O(N^{3/2}) \longrightarrow O(N \ln N)$$

naive sum — fourier transform — other techniques (FFT, grids, etc

Ewald Review



$= \rho(\vec{r}) \longleftarrow$ charge density

electrostatic potential @ $\vec{r}_i$

The total potential is $\sum_i q_i \phi(\vec{r}_i)$

Basic electrostatics (that is Poisson's equation) gets us from $\rho(\vec{r})$ to $\phi(\vec{r})$:

$$\nabla^2 \phi(\vec{r}) = -4\pi \rho(\vec{r}) \longleftarrow \text{real space form}$$

$$\hat{\phi}(\vec{k}) = \frac{-4\pi}{k^2} \hat{\rho}(\vec{k}) \longleftarrow \text{reciprocal space form}$$

Road Map:

$$\rho(\vec{r}) \xrightarrow[\text{Fourier Transform}]{} \hat{\rho}(\vec{k}) \xrightarrow[\text{Poisson}]{} \hat{\phi}(\vec{k}) \xrightarrow[\text{Inverse FT}]{} \phi(\vec{r})$$

δ functions are hard to Fourier Transform, so

$$\rho(\vec{r}) \approx \sum_{\vec{n}} \sum_j q_j \left(\frac{\alpha}{\pi}\right)^{3/2} e^{-\alpha(\vec{r} - \vec{r}_j + \vec{n}L)^2} \longleftarrow \text{Gaussian Approximation}$$

$$\hat{\rho}(\vec{k}) = \frac{1}{V} \sum_j q_j e^{-i\vec{k}\cdot\vec{r}_j} e^{-k^2/4\alpha}$$

$$\hat{\phi}(k) = \frac{-4\pi}{Vk^2} \sum_j q_j e^{-i\vec{k}\cdot\vec{r}_j} e^{-k^2/4\alpha}$$

$$\phi(\vec{r}) = \frac{1}{V} \sum_{k \neq 0} \sum_j \frac{4\pi q_j}{k^2} e^{ik(\vec{r} - \vec{r}_j)} e^{-k^2/4\alpha}$$

Reciprocal space interaction potential:

$$V^{(k)} = \frac{1}{2} \sum_{k \neq 0} \frac{4\pi V}{k^2} e^{-k^2/4\alpha} \left| \hat{\rho}(\vec{k}) \right|^2$$

$$\rho(\vec{k}) = \frac{1}{V} \sum_j q_j e^{-i\vec{k}\cdot\vec{r}_j}$$ ← most expensive part of reciprocal space sum

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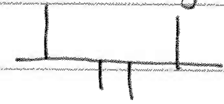
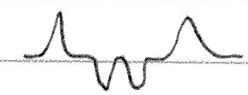
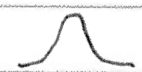
This was: point charges  interacting with smeared $\rho(\vec{r})$ 

We need 2 corrections:  interacts with  in the <u>same</u> box (self correction)

$$V^{(self)} = \sqrt{\frac{\alpha}{\pi}} \sum_j q_j^2$$ ← solved by real-space integration of $\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial}{\partial r}\right)$ on ρ to give ϕ

That is, if $\rho(\vec{r}) = q_j \left(\frac{\alpha}{\pi}\right)^{3/2} e^{-\alpha(\vec{r}-\vec{r}_j)^2}$ ← <u>non-periodic</u>

then $\phi(\vec{r}) = \frac{q_j}{r} \operatorname{erf}(\sqrt{\alpha}\, r)$

and the <u>self</u> interaction is $q_j \phi(0) = q_j \lim_{r \to 0} \frac{\operatorname{erf}(\sqrt{\alpha}\, r)}{r}$

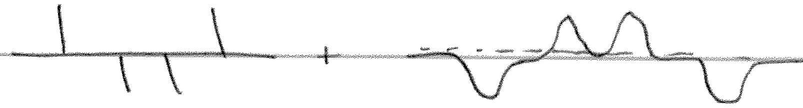
<u>The Smearing correction</u>

- We add the <u>correct</u> potential and subtract the approximate one to correct for smearing:

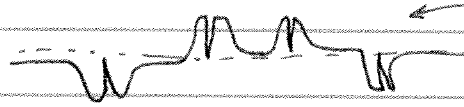
$$\Delta\phi_j(\vec{r}) = \phi_j^{P}(\vec{r}) - \phi_j^{G}(\vec{r})$$

↑ point charges ↑ Gaussian smear

$$\Delta\phi_j(\vec{r}) = $$



$$\|$$



← essentially neutral and short ranged!

$$\Delta\phi_j(\vec{r}) = \frac{q_j}{|\vec{r}-\vec{r}_j|} - \frac{q_j}{|\vec{r}-\vec{r}_j|}\,\mathrm{erf}\left(\sqrt{\alpha}\,|\vec{r}-\vec{r}_j|\right)$$

$$= \frac{q_j}{|\vec{r}-\vec{r}_j|}\,\mathrm{erfc}\left(\sqrt{\alpha}\,|\vec{r}-\vec{r}_j|\right)$$

← short ranged for large α (narrow gaussians)

Now we just sum up all the smearing corrections:

$$V^{(r)} = \frac{1}{2}\sum_{\vec{n}}\sum_{i}\sum_{j} q_i\,\Delta\phi_j(r_{ij})$$

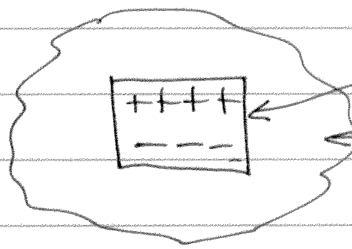
$$V^{(r)} = \frac{1}{2}\sum_{\vec{n}}\sum_{i\neq j}\frac{q_i q_j}{|\vec{r}_{ij}+\vec{n}L|}\,\mathrm{erfc}\left(\sqrt{\alpha}\,|\vec{r}_{ij}+\vec{n}L|\right)$$

= "real space sum"

$$V^{(k)} = \frac{1}{2}\sum_{k\neq 0}\sum_{i,j}\frac{1}{\pi L^3}\,\frac{q_i q_j\,4\pi^2}{k^2}\,e^{-k^2/4\alpha}\cos(\vec{k}\cdot\vec{r}_{ij})$$

$$V^{(self)} = \frac{-\alpha}{\sqrt{\pi}}\sum_j q_j^2$$

Dipolar corrections



net dipole

polarizable medium (ϵ = dielectric constant)

If $\epsilon = \infty$: "tin foil" boundary conditions, then no correction is required

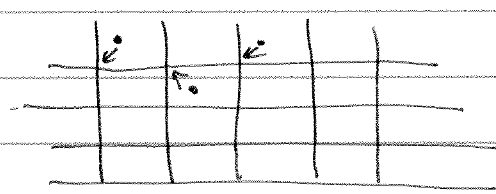
If $\epsilon \neq \infty$

$$V^{(\text{dipole})} = \underbrace{\frac{2\pi}{(2\epsilon+1)V}}_{\text{polarization of dielectric}} \Big| \overbrace{\sum_{i=1}^{N} \vec{r}_i q_i}^{\text{net dipole}} \Big|^2$$

The most costly part of the Ewald sum is the fourier transform. We can't use FFTs (which are grid based : $\cos(\vec{k}\cdot\vec{r}_j)$

$\vec{r}_j$ ← not on a grid!

1) Particle-Particle / Particle-Mesh (P^3M)
2) Particle Mesh Ewald (PME)
3) Smooth particle Mesh Ewald (SPME)



$$W(\vec{r}) = W(\vec{r}_p - \vec{r})$$

$\vec{r}_p$ ← mesh point $\vec{p}$

$W(\vec{r})$ ← weight at location $\vec{r}$