CE 530 Molecular Simulation

Lecture 15

Long-range forces and Ewald sum

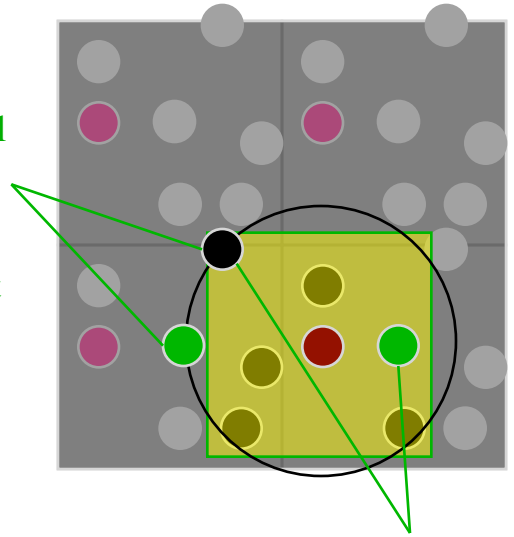
David A. Kofke
Department of Chemical Engineering
SUNY Buffalo
kofke@eng.buffalo.edu

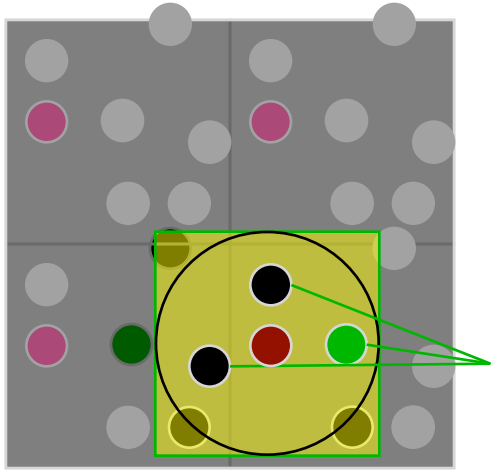
Review

- Intermolecular forces arise from quantum mechanics
  - *too complex to include in lengthy simulations of bulk phases*
- Empirical forms give simple formulas to approximate behavior
  - *intramolecular forms: bend, stretch, torsion*
  - *intermolecular: van der Waals, electrostatics, polarization*
- Unlike-atom interactions weak link in quantitative work

Truncating the Potential

- Bulk system modeled via periodic boundary condition
  - *not feasible to include interactions with all images*
  - *must truncate potential at half the box length (at most) to have all separations treated consistently*
- Contributions from distant separations may be important





Truncating the Potential

- Potential truncation introduces discontinuity
  - *Corresponds to an infinite force*
  - *Problematic for MD simulations*
    - ruins energy conservation
- Shifted potentials
  - *Removes infinite force*
  - *Still discontinuity in force*

$$u_s(r) = \begin{cases} u(r) - u(r_c) & r \le r_c \\ 0 & r > r_c \end{cases}$$

- Shifted-force potentials
  - *Routinely used in MD*

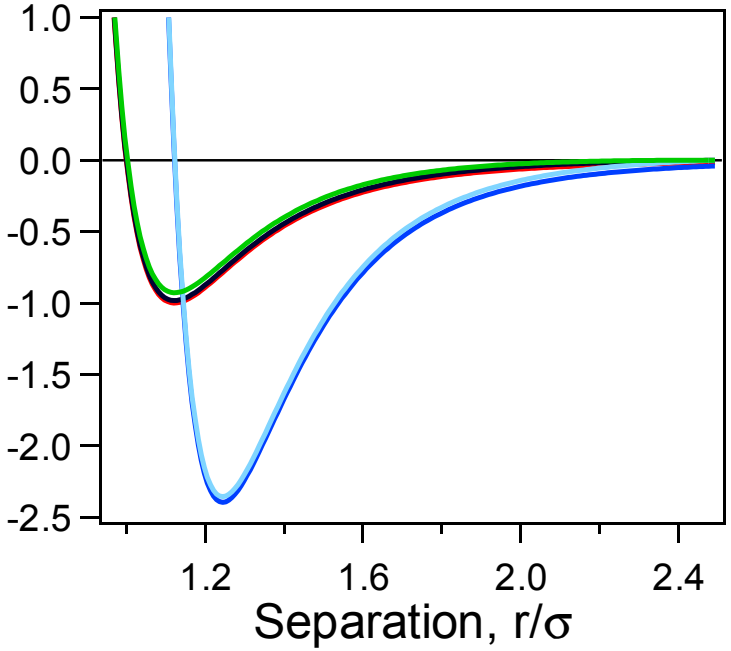
$$u_{sf}(r) = \begin{cases} u(r) - u(r_c) - \dfrac{du}{dr}(r - r_c) & r \le r_c \\ 0 & r > r_c \end{cases}$$

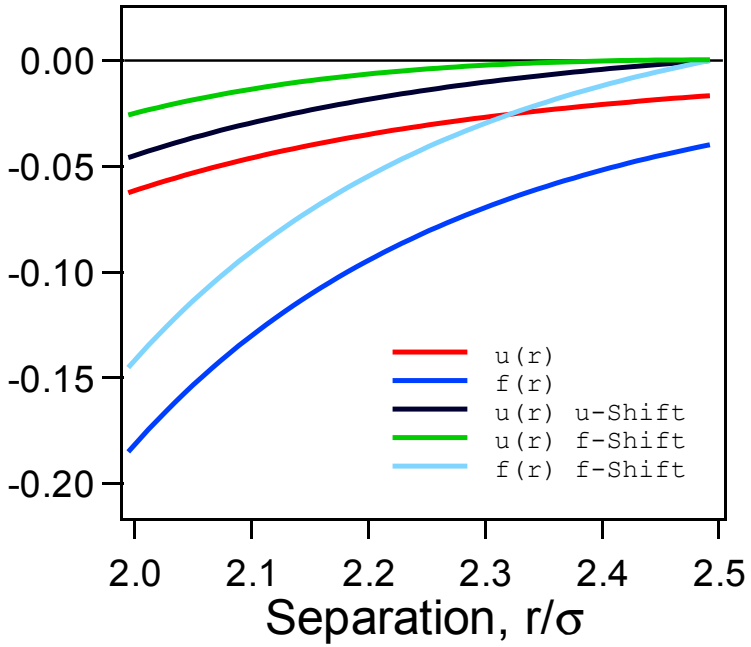
- For quantitative work need to re-introduce long-range interactions

Truncating the Potential

- Lennard-Jones example
  - $r_c = 2.5\sigma$

$$u_s(r) = \begin{cases} u(r) - u(r_c) & r \le r_c \\ 0 & r > r_c \end{cases} \qquad u_{sf}(r) = \begin{cases} u(r) - u(r_c) - \dfrac{du}{dr}(r - r_c) & r \le r_c \\ 0 & r > r_c \end{cases}$$





Radial Distribution Function

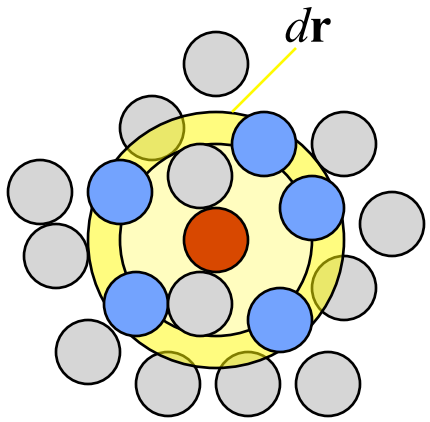
- Radial distribution function, g(r)
  - *key quantity in statistical mechanics*
  - *quantifies correlation between atom pairs*
- Definition

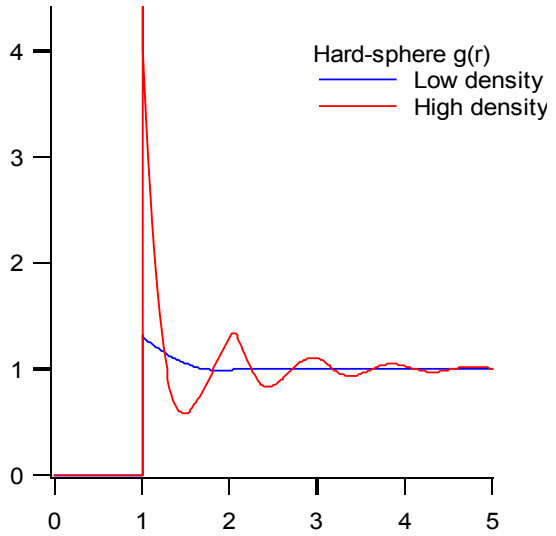
$$g(r) = \frac{\rho(r)d\mathbf{r}}{\rho^{id}(r)d\mathbf{r}}$$

Number of atoms at r in actual system

Number of atoms at r for ideal gas

$$\rho^{id}(r)d\mathbf{r} = \frac{N}{V}d\mathbf{r}$$





- Here's an applet that computes g(r)

Radial Distribution Function. Java Code

```
public class MeterRDF extends MeterFunction
```

```
/**
 * Computes RDF for the current configuration
 */
public double[] currentValue() {
    iterator.reset();                              //prepare iterator of atom pairs
    for(int i=0; i<nPoints; i++) {y[i] = 0.0;}     //zero histogram
    while(iterator.hasNext()) {                    //loop over all pairs in phase
        double r = Math.sqrt(iterator.next().r2()); //get pair separation
        if(r < xMax) {
            int index = (int)(r/delr);             //determine histogram index
            y[index]+=2;                           //add once for each atom
        }
    }
    int n = phase.atomCount();                     //compute normalization: divide by
    double norm = n*n/phase.volume();              //n, and density*(volume of shell)
    for(int i=0; i<nPoints; i++) {y[i] /= (norm*vShell[i]);}
    return y;
}
```

Simple Long-Range Correction

- Approximate distant interactions by assuming uniform distribution beyond cutoff: $g(r) = 1$ $r > r_{cut}$
- Corrections to thermodynamic properties
  - *Internal energy*

$$U_{lrc} = \frac{N}{2}\rho \int_{r_{cut}}^{\infty} u(r) 4\pi r^2 dr$$

Expression for Lennard-Jones model

$$U_{lrc}^{LJ} = \frac{8}{9}\pi N \rho \sigma^3 \varepsilon \left[\left(\frac{\sigma}{r_c} \right)^9 - 3 \left(\frac{\sigma}{r_c} \right)^3 \right]$$

  - *Virial*

$$P_{lrc} = \frac{1}{6}\rho^2 \int_{r_{cut}}^{\infty} r \frac{du}{dr} 4\pi r^2 dr$$

$$P_{lrc}^{LJ} = \frac{32}{9}\pi \rho^2 \sigma^3 \varepsilon \left[\left(\frac{\sigma}{r_c} \right)^9 - \frac{3}{2} \left(\frac{\sigma}{r_c} \right)^3 \right]$$

  - *Chemical potential*

$$\mu_{lrc} = \rho \int_{r_{cut}}^{\infty} u(r) 4\pi r^2 dr = 2\frac{U_{lrc}}{N}$$

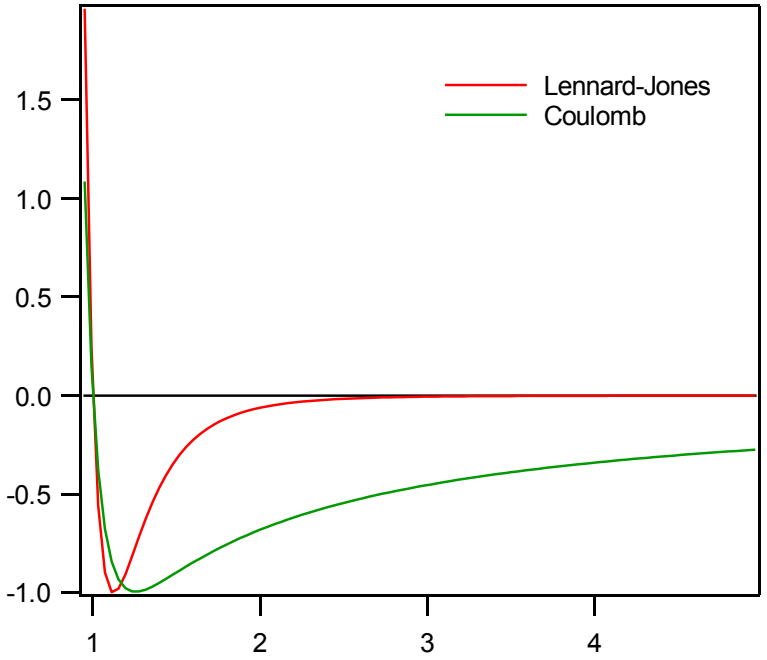
For $r_c/\sigma = 2.5$, these are about 5-10% of the total values

Coulombic Long-Range Correction

- Coulombic interactions must be treated specially
  - *very long range*
  - *1/r form does not die off as quickly as volume grows*

$$\int_{r_c}^{\infty} \frac{1}{r} 4\pi r^2 dr = \infty$$

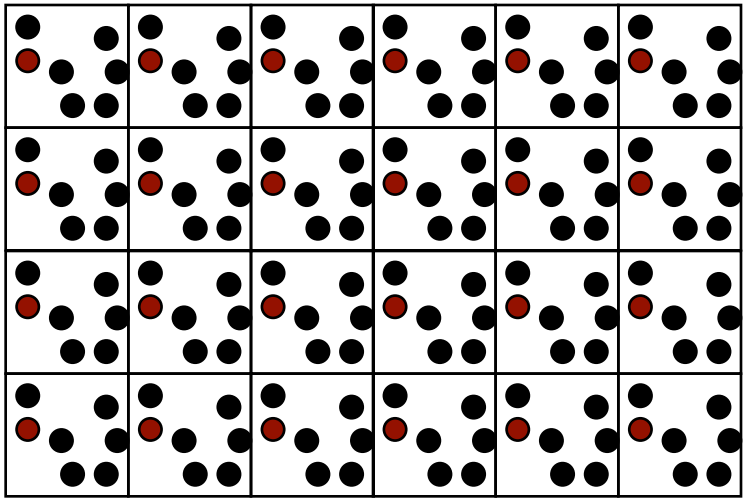
  - *finite only because + and – contributions cancel*



- Methods
  - *Full lattice sum*

    Here is an applet demonstrating direct approach

    Ewald sum
  - *Treat surroundings as dielectric continuum*



Aside: Fourier Series

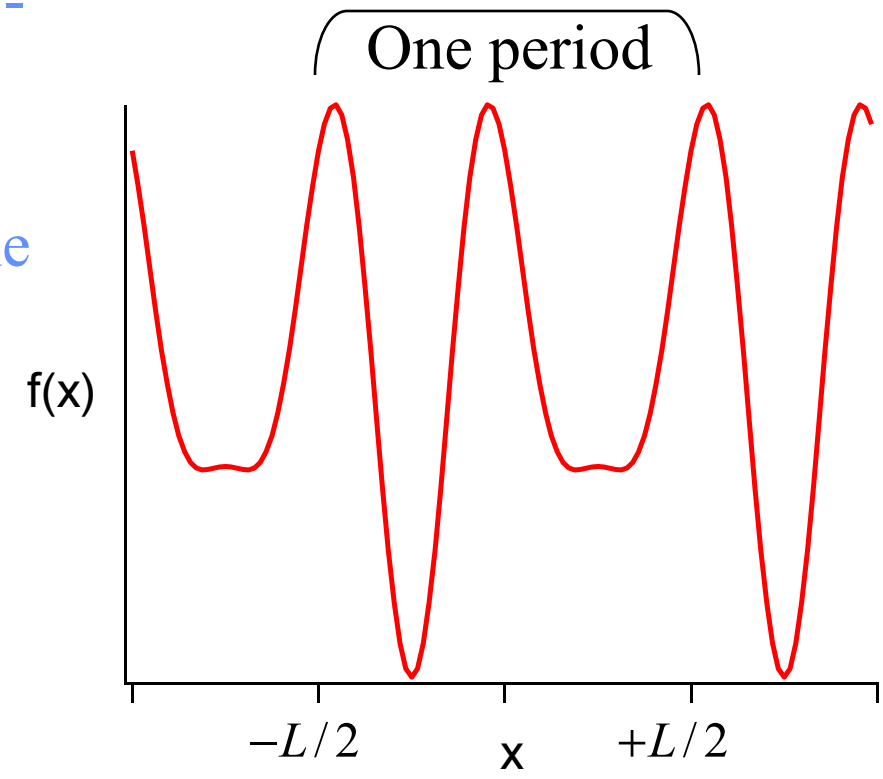
- Consider periodic function on -L/2, +L/2
- A *Fourier series* provides an equivalent representation of the function

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

- The coefficients are

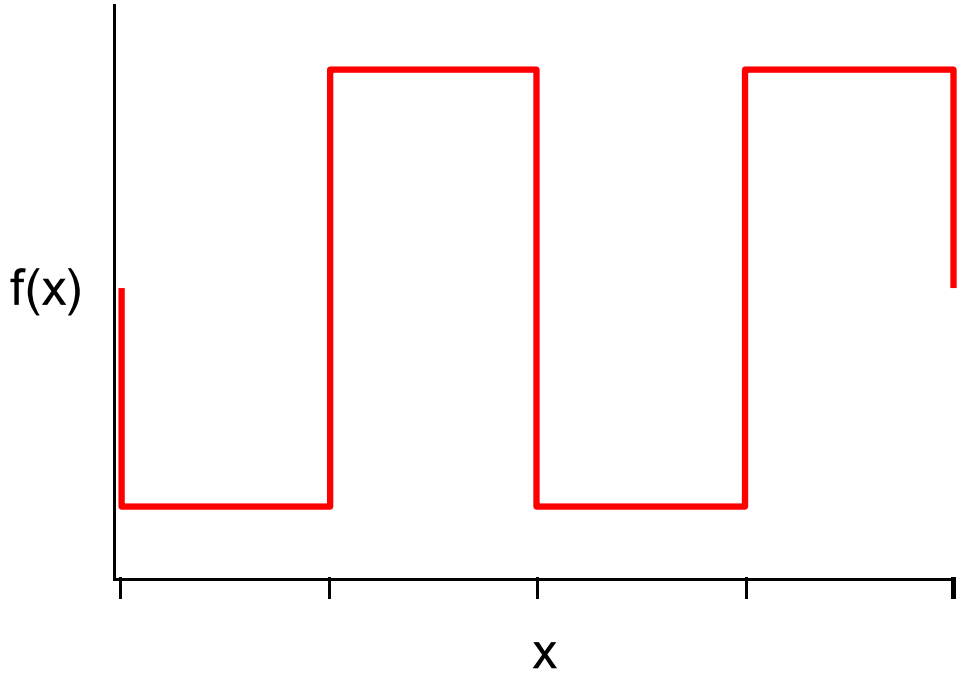
$$a_n = \frac{2}{L}\int_{-L/2}^{+L/2} f(x)\cos(2\pi nx/L)dx$$

$$b_n = \frac{2}{L}\int_{-L/2}^{+L/2} f(x)\sin(2\pi nx/L)dx$$



Fourier Series Example

- f(x) is a square wave



$$a_n = \frac{2}{L}\int_{-L/2}^{+L/2} f(x)\cos(2\pi nx/L)dx$$

$$= \frac{2}{L}\int_{-L/2}^{0} \cos(2\pi nx/L)dx - \frac{2}{L}\int_{0}^{+L/2} \cos(2\pi nx/L)dx = 0$$

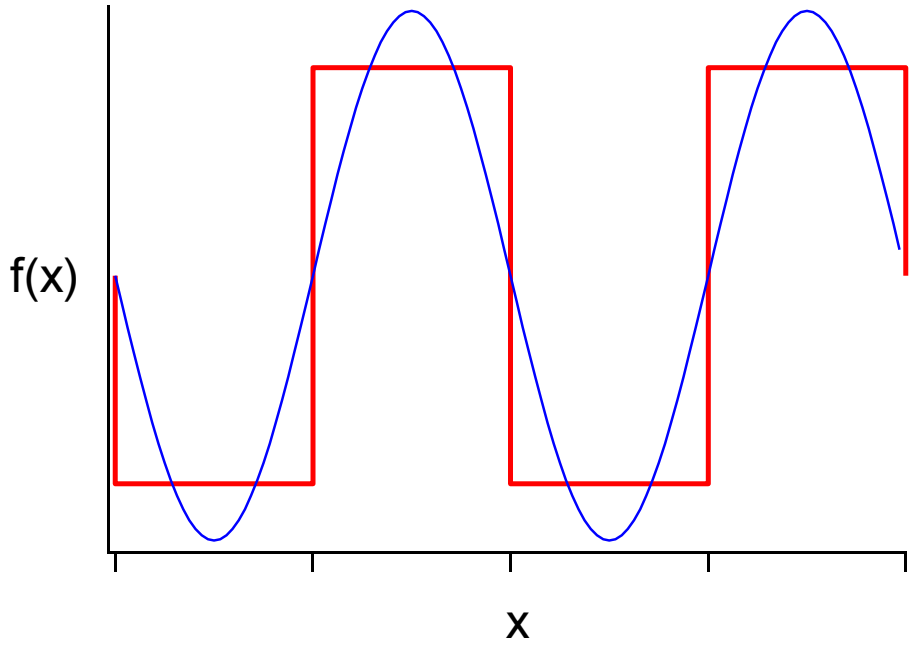
$$b_n = \frac{2}{L}\int_{-L/2}^{+L/2} f(x)\sin(2\pi nx/L)dx$$

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

Fourier Series Example

- f(x) is a square wave

n = 1



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

$$= \frac{1}{L}\int_{-L/2}^{0} \cos(2\pi nx/L)dx - \frac{1}{L}\int_{0}^{+L/2} \cos(2\pi nx/L)dx = 0$$

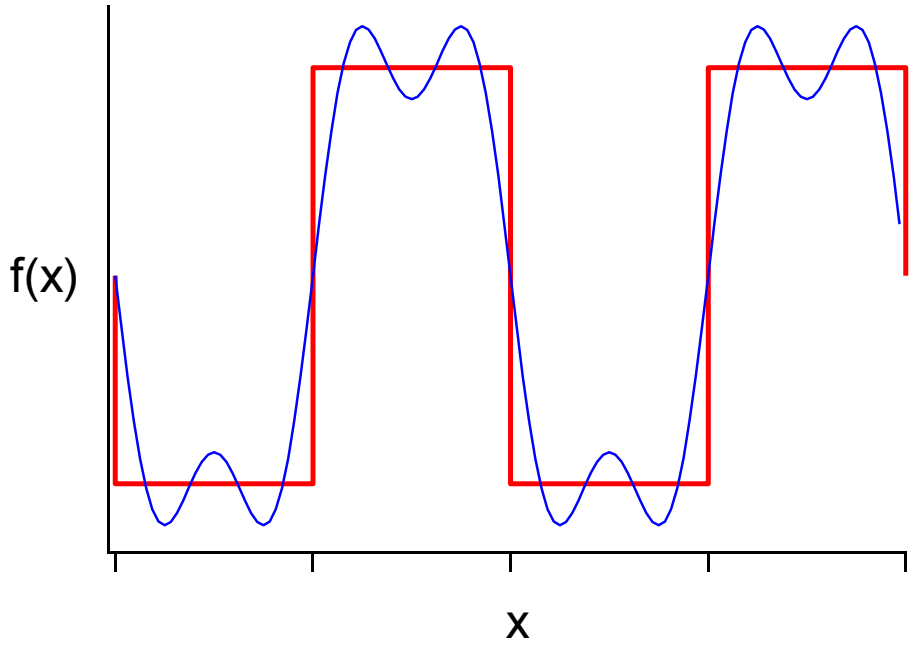
$$b_n = \frac{1}{L}\int_{-L/2}^{+L/2} f(x)\sin(2\pi nx/L)dx$$

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

Fourier Series Example

- f(x) is a square wave

n = 1, 3



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

$$= \frac{1}{L}\int_{-L/2}^{0} \cos(2\pi nx/L)dx - \frac{1}{L}\int_{0}^{+L/2} \cos(2\pi nx/L)dx = 0$$

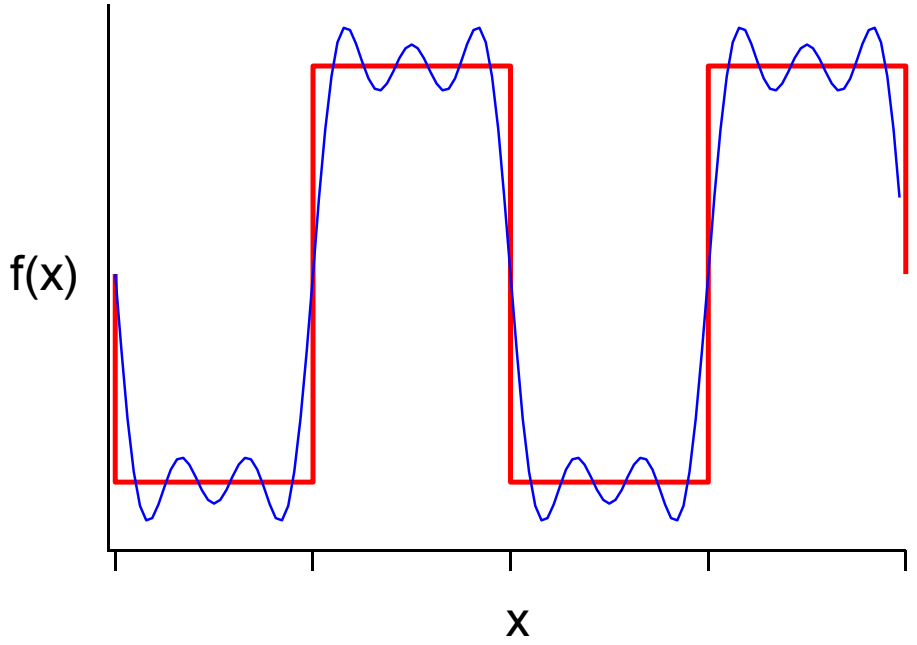
$$b_n = \frac{1}{L}\int_{-L/2}^{+L/2} f(x)\sin(2\pi nx/L)dx$$

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

Fourier Series Example

- f(x) is a square wave

n = 1, 3, 5



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

$$= \frac{1}{L}\int_{-L/2}^{0} \cos(2\pi nx/L)dx - \frac{1}{L}\int_{0}^{+L/2} \cos(2\pi nx/L)dx = 0$$

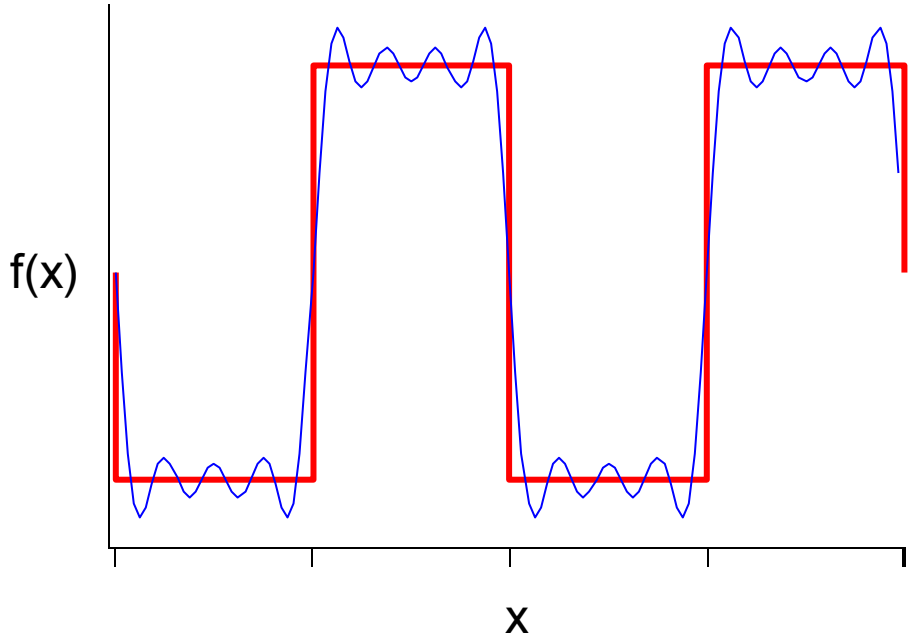
$$b_n = \frac{1}{L}\int_{-L/2}^{+L/2} f(x)\sin(2\pi nx/L)dx$$

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

Fourier Series Example

- f(x) is a square wave

n = 1, 3, 5, 7



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

$$= \frac{1}{L}\int_{-L/2}^{0} \cos(2\pi nx/L)dx - \frac{1}{L}\int_{0}^{+L/2} \cos(2\pi nx/L)dx = 0$$

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

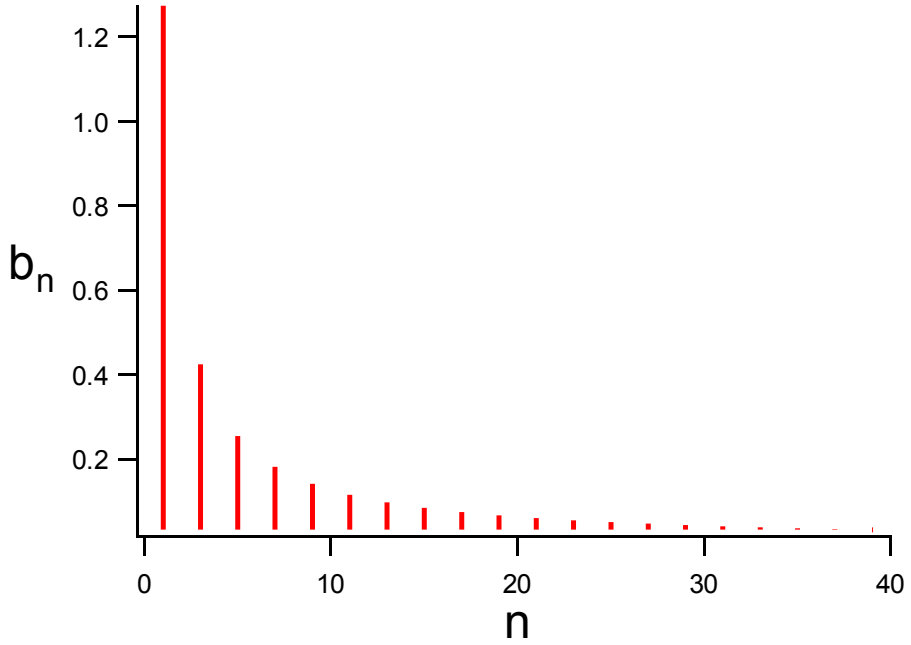
$$= \begin{cases} \frac{4}{n\pi} & \text{n odd} \\ 0 & \text{n even} \end{cases}$$

Fourier Representation

- The set of Fourier-space coefficients b_n contain complete information about the function

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

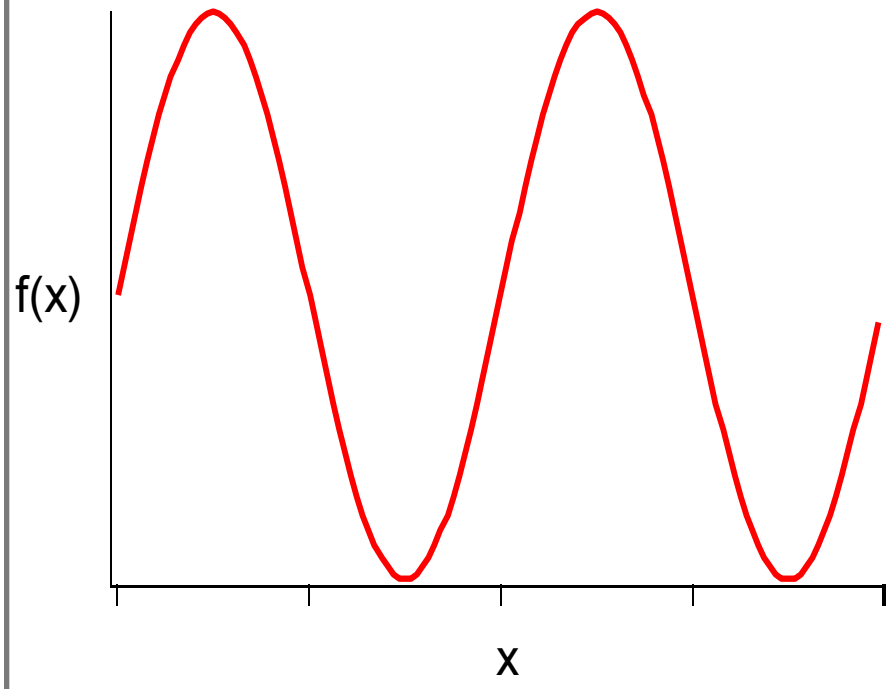
- Although f(x) is periodic to infinity, b_n is non-negligible over only a finite range
- Sometimes the Fourier representation is more convenient to use

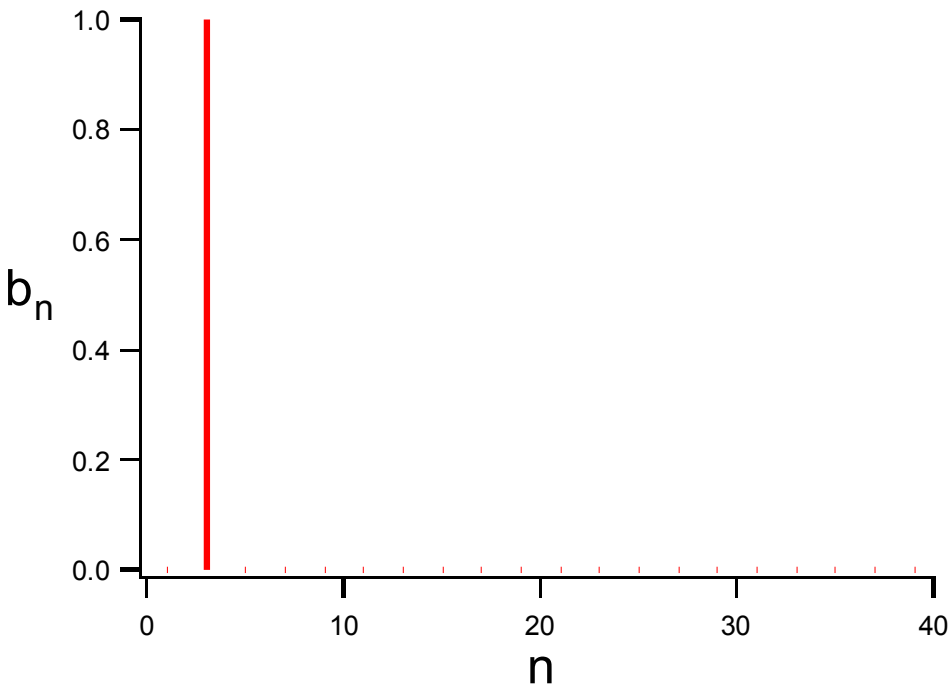


Convergence of Fourier Sum

- If f(x) = sin(2πkx/L), transform is simple
  - $b_n = 1$ *for* $n = k$
  - $b_n = 0$ *otherwise*

Converges very quickly!





Observations on Fourier Sum

- Smooth functions f(x) require few coefficients b_n
- Sharp functions (square wave) require more coefficients
- Large-n coefficients describe high-frequency behavior of f(x)
  - *large n = short wavelength*
- Small-n coefficients describe low-frequency behavior
  - *small n = long wavelength*
  - *e.g., n = 0 coefficient is simple average of f(x)*

Fourier Transform

- As L increases, f(x) becomes less periodic
- Fourier transform arrives in limit of L → ∞
- Compact form obtained with exponential form of cos/sin

$$e^{i\theta} = \cos\theta + i\sin\theta$$

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

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

$$a_n = \frac{1}{\pi}\int_{-L/2}^{+L/2} f(x)\cos(2\pi nx/L)\,dx$$

$$b_n = \frac{1}{\pi}\int_{-L/2}^{+L/2} f(x)\sin(2\pi nx/L)\,dx$$

forward $$\hat{f}(k) = \int_{-\infty}^{+\infty} f(x) e^{2\pi ikx} dx$$

a_n = real part of transform

b_n = imaginary part

- Useful relations
  - *derivative* $$\left[f^{(m)}(x)\right](k) = (-2\pi ik)^m \hat{f}(k)$$
  - *convolution* $$\left[\int f(t)g(x-t)dt\right](k) = \hat{f}(k)\hat{g}(k)$$

Fourier Transform Example

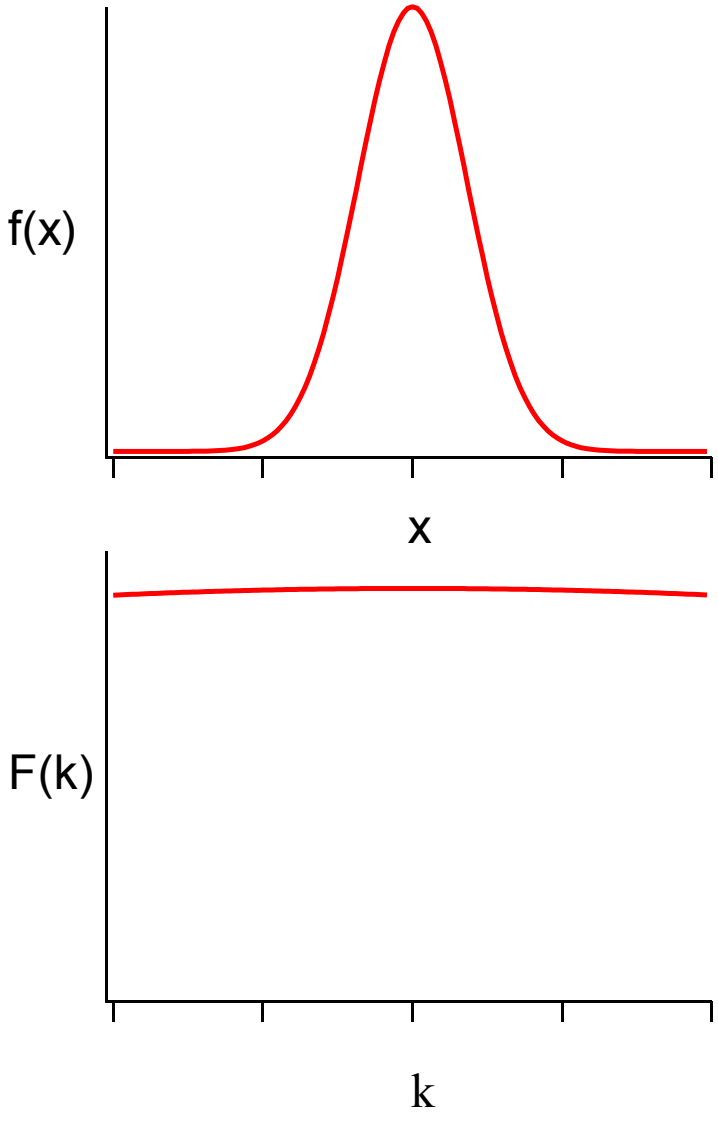
- Gaussian

$$f(x) = \frac{\alpha}{2\pi} \exp\left[-\alpha \frac{x^2}{2}\right]$$

- Transform is also a Gaussian!

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

- Width of transform is reciprocal of width of function
  - *k-space is "reciprocal" space*
  - *sharp f(x) requires more values of F(k) for good representation*
  - *$\delta(x-x_o)$ transforms into a sine/cosine wave of frequency x_o:* $\hat{\delta}(k) = e^{2\pi i k x_o}$



Fourier Transform Relevance

- Many features of statistical-mechanical systems are described in k-space
  - *structure*
  - *transport behavior*
  - *electrostatics*
- This description focuses on the correlations shown over a particular length scale (depending on k)
- Macroscopic observables are recovered in the k → 0 limit
- Corresponding treatment is applied in the time/frequency domains

Review of Basic Electrostatics

- Force between charges $\mathbf{F} = \frac{q_1 q_2}{r^2}\hat{\mathbf{r}}$
- In terms of electric field $\mathbf{F}(\mathbf{r}) = q_1 \mathbf{E}(\mathbf{r})$
- Static electric field satisfies

$$\nabla \cdot \mathbf{E}(\mathbf{r}) = 4\pi\rho(\mathbf{r})$$
$$\nabla \times \mathbf{E}(\mathbf{r}) = 0$$

- Charge density $\rho(\mathbf{r})$
  - *for point charge* q_2: $\rho(\mathbf{r}) = q_2\delta(\mathbf{r})$
- Electrostatic potential
  - *zero curl implies* ***E*** can be written $\mathbf{E}(\mathbf{r}) = -\nabla\phi(\mathbf{r})$
  - *potential energy of charge* q_1 *at* $\mathbf{r}$, *relative to position at infinity*

$$u(\mathbf{r}) = q_1\phi(\mathbf{r})$$

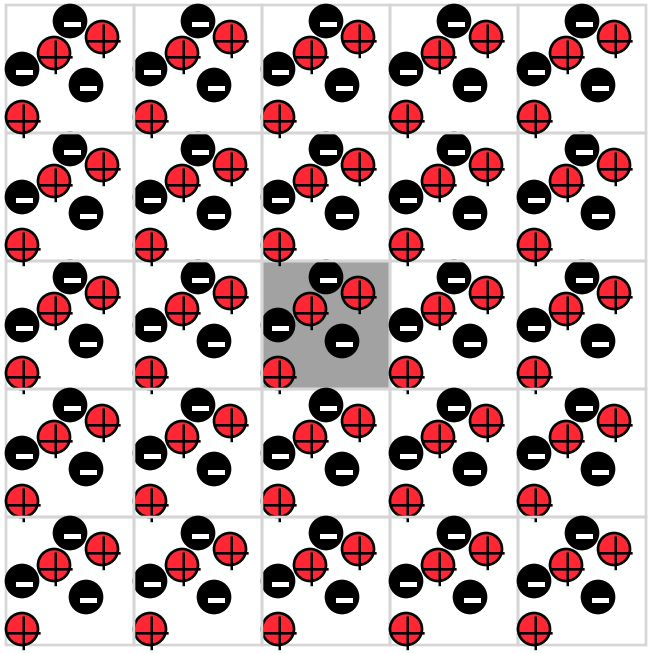
Mass analogy: $u(z) = m \times gz = m\phi(z)$

- Poisson's equation
  - $\nabla^2\phi = -4\pi\rho$

Ewald Sum

- We want to sum the interaction energy of each charge in the central volume with all images of the other charges
  - *express in terms of electostatic potential*

$$U_q = \frac{1}{2} \sum_{\substack{\text{charge i} \\ \text{in central} \\ \text{volume}}} q_i \phi(\mathbf{r}_i)$$



  - *the charge density creating the potential is*

$$\rho(\mathbf{r}) = \sum_{\substack{\mathbf{n}, \text{image } j \text{ in } \mathbf{n} \\ \text{vectors}}} \sum q_j \delta(\mathbf{r} - \mathbf{r}_j)$$

$$= \sum_{\mathbf{n}} \sum_{j} q_j \delta\left(\left|\mathbf{r} - (\mathbf{r}_j + \mathbf{n}L)\right|\right)$$

  - *this is a periodic function (of period L), but it is very sharp*

    Fourier representation would never converge

Ewald Sum: Fourier 1.

- Compute field instead by smearing all the charges

$$\rho(\mathbf{r}) = \sum_{\mathbf{n}} \sum_{j} q_j (\alpha/\pi)^{3/2} \exp\left[-\alpha \left| \mathbf{r} - (\mathbf{r}_j + \mathbf{n}L) \right|^2 \right]$$

include $\mathbf{n} = 0$

Large α takes ρ back to δ function

- Electrostatic potential via Poisson equation
  - *direct space form* $\nabla^2 \phi(\mathbf{r}) = -4\pi\rho(\mathbf{r})$
  - *reciprocal space* $k^2 \phi(\mathbf{k}) = -4\pi\rho(\mathbf{k})$
- Discrete Fourier transform the charge density

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

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

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

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

Ewald Sum. Fourier 2.

- Use Poisson's equation for electrostatic potential

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

- Invert transform to recover real-space potential

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

$$= \frac{1}{V}\sum_{k\neq 0}\sum_{j}\frac{4\pi q_j}{k^2}e^{i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}_j)}e^{-k^2/4\alpha}$$

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

- *in principle requires sum over infinite number of wave vectors* **k**
- *but reciprocal Gaussian goes to zero quickly if* α *is small (broad Gaussian, large smearing of charge)*

Ewald Sum. Fourier 3.

- The electrostatic energy can now be obtained
  - *for point charges in potential of smeared charges*

$$U_q = \tfrac{1}{2}\sum_i q_i \phi(\mathbf{r}_i)$$

$$= \tfrac{1}{2}\sum_{\mathbf{k}\neq 0} \frac{4\pi V}{k^2} e^{-k^2/4\alpha} \sum_{i,j} \frac{q_i q_j}{V^2} e^{i\mathbf{k}\cdot(\mathbf{r}_i - \mathbf{r}_j)}$$

product of identical sums

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

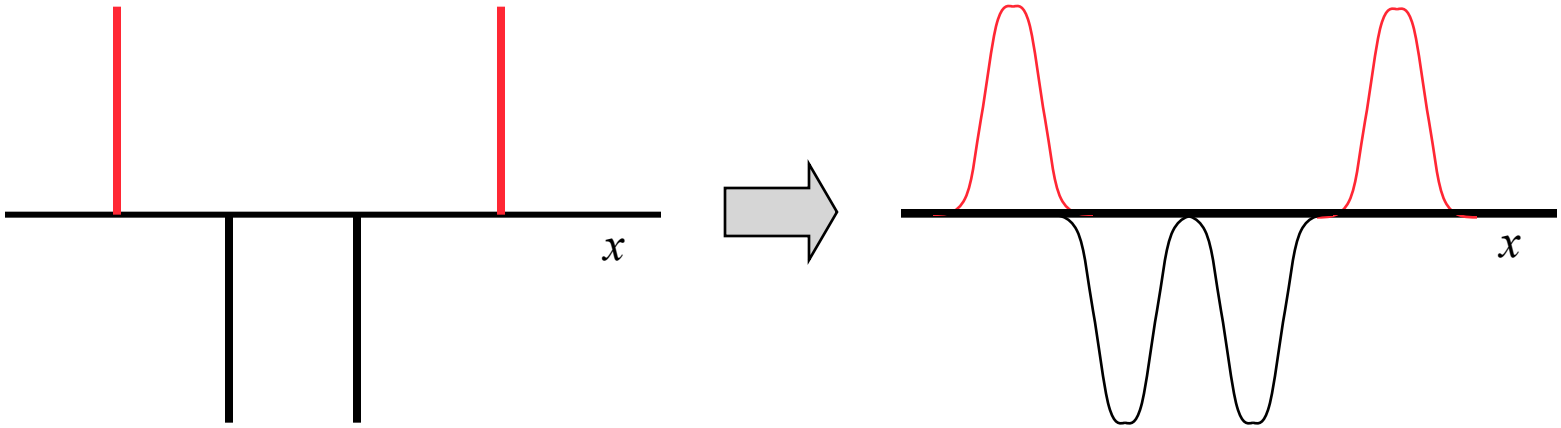
$$\phi(\mathbf{r}) = \frac{1}{V}\sum_{k\neq 0}\sum_j \frac{4\pi q_j}{k^2} e^{i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}_j)} e^{-k^2/4\alpha}$$

$$\rho(\mathbf{k}) = \frac{1}{V}\sum_j q_j e^{-i\mathbf{k}\cdot\mathbf{r}_j}$$

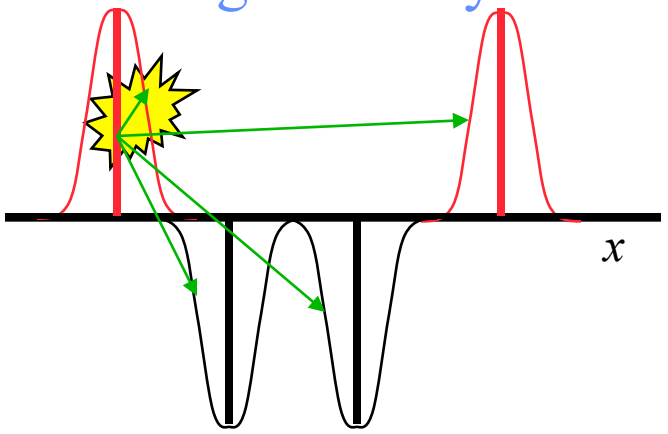
- Two corrections are needed
  - *self interaction*
  - *correct for smearing*

Ewald Sum. Self Interaction 1.

- In Ewald sum, each point charge is replaced by smeared Gaussian centered on that charge
  - *this is done to estimate the electrostatic potential field*



- All point charges interact with the resulting field to yield the potential energy
  - *This means that the point charge interacts with its smeared representation*
  - *We need to subtract this*



Ewald Sum. Self Interaction 2.

- We work in real space to deal with the self term
  - *Poisson's equation for the electrostatic potential due to a single smeared charge*

$$\nabla^2\phi(\mathbf{r}) = -4\pi\rho(\mathbf{r}) \qquad \rho(\mathbf{r}) = q_j(\alpha/\pi)^{3/2}\exp\left[-\alpha\left|\mathbf{r}-\mathbf{r}_j\right|^2\right]$$

  - *The solution is*

$$\phi(r) = \frac{q_j}{r}erf\left(\sqrt{\alpha}\,r\right)$$

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)$$

  - *In particular, at r = 0*

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

  - *The self-correction subtracts this for each charge*

$$U_{self} = \tfrac{1}{2}\sum_j q_j\phi(0)$$

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

independent of configuration

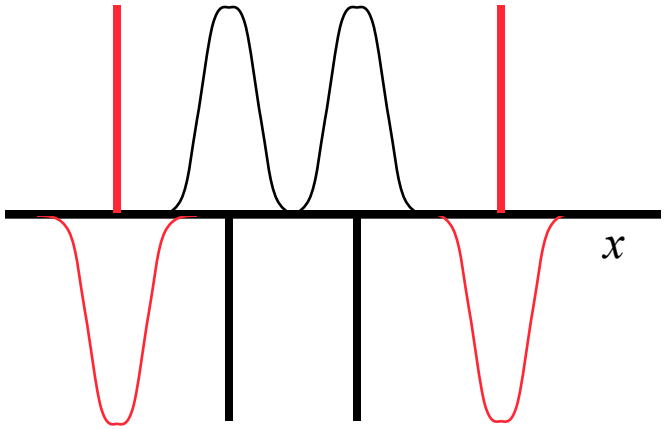
Ewald Sum. Smearing Correction 1.

- We add the correct field and subtract the approximate one to correct for the smearing

$$\Delta\phi_j(\mathbf{r}) = \phi_j^p(\mathbf{r}) - \phi_j^G(\mathbf{r})$$

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

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



- This field is short ranged for large α (narrow Gaussians)
  - *can view as point charges surrounded by shielding countercharge distribution*

Ewald Sum. Smearing Correction 2.

- Sum interaction of all charges with field correction
  - *convenient to stay in real space*
  - *Usually α is chosen so that sum converges within central image*

$$\Delta U = \frac{1}{2}\sum_{\mathbf{n}}\sum_{i\neq j} q_i \Delta\phi_j(r_{ij})$$

$$= \frac{1}{2}\sum_{\mathbf{n}}\sum_{i\neq j} \frac{q_i q_j}{r_{ij}} erfc\left(\sqrt{\alpha}\, r_{ij}\right)$$

- Total Coulomb energy

$$U_c = U_q(\alpha) - U_{self}(\alpha) + \Delta U(\alpha)$$

  - *each term depends on α, but the sum is independent of it*

    if enough lattice vectors are used in the reciprocal- and real-space sums

- Here is an applet that demonstrate the Ewald method

Ewald Method. Comments

- Basic form requires an $O(N^2)$ calculation
  - *efficiency can be introduced to reduce to* $O(N^{3/2})$
  - *good value of* α *is 5L, but should check for given application*
  - *can be extended to sum point dipoles*
- Other methods are in common use
  - *reaction field*
  - *particle-particle/particle mesh*
  - *fast multipole*

Summary

- Contributions from distant interactions cannot be neglected
  - *potential truncated at no more than half box length*
  - *treat long-range assuming uniform radial distribution function*
- Coulombic interactions require explicit summing of images
  - *too costly to perform direct sum*
  - *Ewald method is more efficient*
    - smear charges to approximate electrostatic field
    - simple correction for self interaction
    - real-space correction for smearing