Ewald Sum

Notes:

- Large α makes first term converge faster
- Small α makes second term to need fewer terms (big α make sharp charge dist.)

Need a middle ground.

- Want α large enough to converge with only |n| =0 (within the original box)
- Typically, α = 5/L and need 100-200 terms in reciprocal space.

Ewald Sum

Caveats:

- Straighforward implementations of Ewald Sum scales as N^2

Solution via other methods (modern techniques):

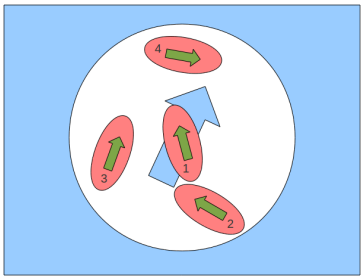
- Particle Mesh algorithm (to sum the long range part)
  - Layout a 3D grid in the box and approximate charge density in the fluid by assigning charges to the finely-spaced mesh points
  - Use FFT to solve Poisson's equation for potential at grid points
  - Calculate field at arbitrary points in the box by interpolation
  - Scales as *O*(*N* ln *N*)

Dipolar Liquids

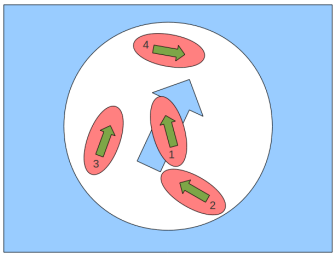
- Interaction is of order $1/r^3$
- Long ranged

Solution:

- Interact directly with nn in cavity
- Take the "rest" as a continuum with dielectric constant ε_s



Dipolar Liquids



- The outside continuum creates a "reaction" field back inside center

$$E_i = \frac{2(\varepsilon_s - 1)}{2\varepsilon_s + 1} \frac{1}{r_c^3} \sum_{j \in E} \mu_j$$

- r_c radius of cavity
- μ_i - particle dipole moments

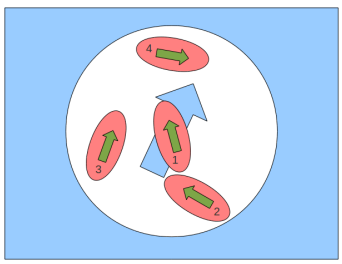
Dipolar Liquids

- Reaction field contributes to the energy

$$-\frac{1}{2}\mu_i \cdot E_i$$

- Torque on particle i

$$\mu_i \times E_i$$



Dipolar Liquids

- To avoid the "jumps" in energy due to particles going in and out of the cavity, use tapering function
- Linear tapering: multiply interaction between particles i and j by:

$$f(r_{ij}) = \begin{cases} 1.0 & r_{ij} < r_t \\ (r_c - r_{ij})/(r_c - r_t) & r_t \le r_{ij} \le r_c \\ 0.0 & r_c < r_{ij} \end{cases}$$

$r_t \sim 0.95\, r_c$

Dipolar Liquids

- Pros:
  - Straightforward calculation in MD
  - Modest increase in execution time
- Cons:
  - The need for an *a priori* knowledge of ε_s

    (however, there is a certain freedom of choice since the thermodynamics of dipolar fluids is rather insensitive to the value of ε_s)

Dimensionless Units

- Offer convenience and simplicity of expressions
- Numerical values are close to unity
  - removes the risk of under or overflows dictated by computer hardware
- No parameters in equations of motion
- Offers the concept of *scaling* where a single model can describe a whole class of problems

Dimensionless Units

- e.g. in LJ choose units of length (σ), mass (m), energy (ε) by:
  - length : $r \rightarrow r\sigma$
  - energy : $e \rightarrow e\varepsilon$
  - time : $t \rightarrow t\sqrt{(m\sigma^2/\varepsilon)}$
- Potential Energy:

$$V(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] \rightarrow V(r) = 4\left[\left(\frac{1}{r}\right)^{12} - \left(\frac{1}{r}\right)^{6}\right]$$

Dimensionless Units

- Kinetic Energy per particle:

$$E_k = \frac{1}{2N}\sum_{i=1}^{N} m_i v_i^2 \rightarrow E_k = \frac{1}{2N}\sum_{i=1}^{N} v_i^2$$

- Temperature in units of ε/k_B ($T \rightarrow T\cdot\varepsilon/k_B$)

$$T = \frac{1}{dk_B N}\sum_{i} m_i \mathbf{v}_i^2 \rightarrow T = \frac{1}{dN}\sum_{i} \mathbf{v}_i^2$$

equipartition $d \cdot \frac{k_B T}{2} = \frac{1}{2} m v^2$

Dimensionless Units

- Force:

$$\mathbf{F}(r_{ij}) = \frac{48\varepsilon}{\sigma^2}\left[\left(\frac{\sigma}{r_{ij}}\right)^{14} - \frac{1}{2}\left(\frac{\sigma}{r_{ij}}\right)^{8}\right]\mathbf{r}_{ij}$$

$$\rightarrow \ddot{\mathbf{r}}(r_{ij}) = 48\left[\left(\frac{1}{r_{ij}}\right)^{14} - \frac{1}{2}\left(\frac{1}{r_{ij}}\right)^{8}\right]\mathbf{r}_{ij}$$

Other Dynamical Systems

- Hard Spheres
  - Particles interact via “hard” potentials
- Langevin's Dynamics
  - Forces are not computed explicitly but are replaced by stochastic quantities

Hard Spheres

- Hard sphere potential

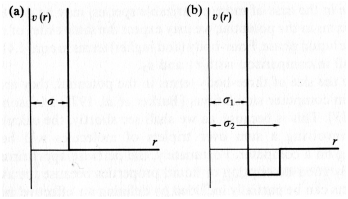
$$v^{HS}(r) = \begin{cases} \infty & (r < \sigma) \\ 0 & (\sigma \leq r) \end{cases}$$

- Square well potential

$$v^{SW}(r) = \begin{cases} \infty & (r < \sigma_1) \\ -\epsilon & (\sigma_1 \leq r < \sigma_2) \\ 0 & (\sigma_2 \leq r) \end{cases}$$

Step-wise Potentials

$$v^{HS}(r) = \begin{cases} \infty & (r < \sigma) \\ 0 & (\sigma \leq r) \end{cases}$$



Can be generalized to any number of steps!

$$v^{SW}(r) = \begin{cases} \infty & (r < \sigma_1) \\ -\epsilon & (\sigma_1 \leq r < \sigma_2) \\ 0 & (\sigma_2 \leq r) \end{cases}$$

Step-wise Potentials

- Dynamics are fundamentally different from continuous potentials:
  - There is no interaction when particles are separated by more than one diameter
  - In the case of steps, there is no interaction (or constant potential) when in one of the steps
- → force = 0
- Thus, free motion until there is a discontinuity.
- At discontinuity there is a *collision.* Treat them as billiard balls.
- Can be simulated as an event-driven system.

Step-wise Potentials

General Scheme:

- Find collision times
- Move particles up to that collision time
- Do collision dynamics
- Calculate properties
- GOTO 1

Step-wise Potentials

General Scheme:

- **Find collision times (most time consuming)**
  - Start by tabulating all collision times for all possible N^2 pairs
  - Sort in ascending order of time
  - Choose the shortest collision time
- Move particles up to that collision time
- Do collision dynamics
- Calculate properties
- GOTO 1

Step-wise Potentials

General Scheme:

- Find collision times
- **Move particles up to that collision time**
  - Advance positions of all particles following a rectilinear path (free motion) for a length of time corresponding to the shortest collision time
- Do collision dynamics
- Calculate properties
- GOTO 1

Step-wise Potentials

General Scheme:

- Find collision times
- Move particles up to that collision time
- **Do collision dynamics**
  - Conservation of momentum, energy
- Calculate properties
- GOTO 1

Step-wise Potentials

General Scheme:

- Find collision times
- Move particles up to that collision time
- Do collision dynamics
- **Calculate properties**
  - Energy, temperature, pressure, ...
- GOTO 1

Step-wise Potentials

<u>Collision time.</u> For two particles to collide,

$$|\mathbf{r}_{ij}(t+t_{ij})| = |\mathbf{r}_{ij} + \mathbf{v}_{ij}t_{ij}| = \sigma$$

where $\boldsymbol{r}_{ij} = \boldsymbol{r}_i - \boldsymbol{r}_j$ and $\boldsymbol{v}_{ij} = \boldsymbol{v}_i - \boldsymbol{v}_j$. If we define $b_{ij} = \boldsymbol{r}_{ij} \cdot \boldsymbol{v}_{ij}$

$$v_{ij}^2 t_{ij}^2 + 2b_{ij}t_{ij} + r_{ij}^2 - \sigma^2 = 0$$

Step-wise Potentials

$$v_{ij}^2 t_{ij}^2 + 2b_{ij}t_{ij} + r_{ij}^2 - \sigma^2 = 0$$

- Cases:
  - $b_{ij} > 0$ molecules are going away from each other, no collision
  - $b_{ij} < 0$ but only complex roots, then no collision
  - $b_{ij} < 0$ two real roots where smallest is time of impact

$$t_{ij} = \frac{-b_{ij} - (b_{ij}^2 - v_{ij}^2(r_{ij}^2 - \sigma^2))^{1/2}}{v_{ij}^2}$$

Step-wise Potentials

<u>Collision Dynamics.</u> From conservation of energy and linear momentum:

$$\begin{aligned} \mathbf{v}_i(after) &= \mathbf{v}_i(before) + \delta\mathbf{v}_i \\ \mathbf{v}_j(after) &= \mathbf{v}_j(before) - \delta\mathbf{v}_i \end{aligned}$$

where

$$\delta\mathbf{v}_i = -(b_{ij}/\sigma^2)\mathbf{r}_{ij}$$