Molecular Dynamics Lecture Notes

M.L. Klein
Center for Molecular Modeling
Dept. of Chemistry
University of Pennsylvania

October 2001

CMM

Outline

1. Theory
   (a) Newton's Law and Implications
   (b) Work / Conservative Force Fields
   (c) Harmonic Oscillator Example
   (d) Generalized Coordinates
   (e) Hamilton's Principle
   (f) Lagrange's Equation
   (g) Conservation Laws II
   (h) Hamilton's Equations
   (i) Phase Space
   (j) Liouville's Theorem
   (k) Time Evolution of Distribution Functions
   (l) Evolution of Phase Variables
   (m) Extended Phase Space
   (n) NVT Nosé-Hoover
   (o) NPT Andersen-Hoover

Outline

2. Practice
    (a) Integrators
        i. Verlet
        ii. Velocity Verlet
        iii. Code Structure
        iv. Reversible Integrators
    (b) Potentials of Interaction
        i. Non-bonded
        ii. Bonded
        iii. Code Structure
        iv. Truncation of Non-bonded Interactions
        v. Neighbor Lists
        vi. Ewald (after Boundary Conditions)
    (c) Boundary Conditions
        i. Bulk, Confined and Free
        ii. Periodic Boundary Conditions
        iii. Minimum Image Convention

Outline

- (d) Timescales
  - i. Time Step Selection
  - ii. Constraints
  - iii. Test of a Working Code / Suitable Timestep

3. Analysis

- (a) Normal Modes
- (b) Chemical Potential
- (c) Pressure
- (d) Transport Coefficients

Newton's Law and Its Implications

$$\begin{aligned} F &= ma && (1) \\ &= \dot{p} && (2) \end{aligned}$$

Zero Total Force →
Conservation of Linear Momentum

$$F_T = 0 = \dot{p} \qquad (3)$$

$$p = \text{constant} \qquad (4)$$

Zero Total Torque ⟶
Conservation of Angular Momentum

$$\begin{aligned} \mathbf{L} &\equiv \mathbf{r} \times \mathbf{p} && (5) \\ \mathbf{N} &\equiv \mathbf{r} \times \mathbf{F} \\ \dot{\mathbf{L}} &= \mathbf{r} \times \dot{\mathbf{p}} = \mathbf{N} \\ \mathbf{N} &= 0 \\ \mathbf{L} &= \text{constant} \end{aligned}$$

Work

$$W_{12} \equiv \int_1^2 \mathbf{F} \cdot \mathbf{dr} \tag{6}$$

$$\begin{aligned} \mathbf{F} \cdot \mathbf{dr} &= m\frac{d\mathbf{v}}{dt} \cdot \frac{d\mathbf{r}}{dt} dt \\ &= \frac{m}{2}\frac{d}{dt}\left(\mathbf{v} \cdot \mathbf{v}\right) dt \\ &= d\left(\frac{m}{2}v^2\right) \end{aligned} \tag{7}$$

$$\begin{aligned} W_{12} &= \frac{m}{2}v_2^2 - \frac{m}{2}v_1^2 \\ &= T_2 - T_1 \end{aligned} \tag{8}$$

- Now, assume a conservative force field :

$$\oint \mathbf{F} \cdot \mathbf{dr} = 0 \tag{9}$$

- Closed path have zero work
- Work done between two states independent of path
- Counter example : friction
- Under such conditions, Stokes' Law says :

$$\mathbf{F} = -\nabla V \tag{10}$$

- V scalar function called potential

$$\begin{aligned}
W_{12} &= \int_1^2 \mathbf{F} \cdot \mathbf{dr} \qquad (11) \\
&= -\int_1^2 \nabla V \cdot \mathbf{dr} \\
&= -\int_1^2 \sum_i \frac{\partial V}{\partial x_i} dx_i \\
&= -\int_1^2 dV \\
&= V_1 - V_2 \\
&= T_2 - T_1 \\
T_1 + V_1 &= T_2 + V_2
\end{aligned}$$

- Newton's Law with conservative force fields conserve total energy.

One dimensional harmonic oscillator example

$$V = \frac{1}{2}kx^2 \tag{12}$$

$$F = -kx \tag{13}$$

$$m\ddot{x} = -kx \tag{14}$$

$$\ddot{x} = -\frac{k}{m}x \tag{15}$$

$$\omega_0^2 = \frac{k}{m} \tag{16}$$

$$x(t) = A\sin\left(\omega_0 t + \delta\right) \tag{17}$$

$$\dot{x}(t) = A\omega_0\cos\left(\omega_0 t + \delta\right) \tag{18}$$

Two initial conditions completes equation

$$\{x(0), \dot{x}(0)\} \longrightarrow \{A, \delta\} \tag{19}$$

$$V = \frac{1}{2}kA^2\sin^2\left(\omega_0 t + \delta\right) \tag{20}$$

$$T = \frac{1}{2}kA^2\cos^2\left(\omega_0 t + \delta\right) \tag{21}$$

$$E = T + V = \frac{1}{2}kA^2 \tag{22}$$

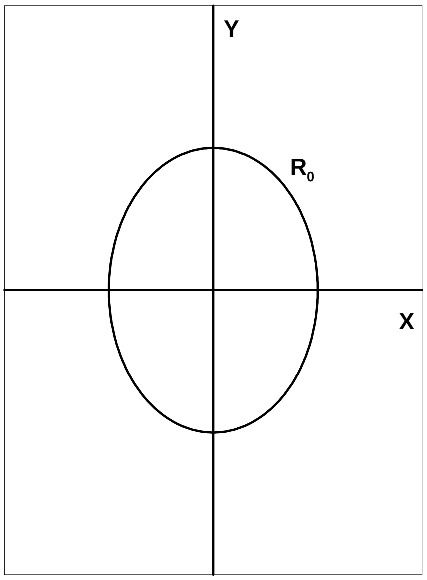
Generalized Coordinates

- Given N Free (unconstrained) Particles
  - Spherical particles
  - Point particles
  - No internal degrees of freedom
  - $3N$ degrees of freedom

- Imagine m constraints
  - Fixed bond lengths
  - Fixed bond angles
  - $3n - m$ degrees of freedom
  - $\mathrm{H}_2 = 3(2) - 1 = 5$ degrees of freedom
  - 3 Center of Mass Translations
  - 2 Rotational Degrees of Freedom

Generalized Coordinate Example

- Motion on a circle of radius r_0



1. Rectangular coordinates
    - Need equations of motion for both x and y
    - Need constantly changing constraint force such that $\sqrt{x^2+y^2}=r_0$.
2. Polar coordinates
    - Using r and θ
    - $r=r_0$ always
    - Only need constraint-free equation for θ

Generalized Coordinates

"Proper Set of Generalized Coordinates" - *a set of independent generalized coordinates that equal the number of degrees of freedom.*

- We can simplify a problem using the right set of generalized coordinates.

- Newton's Law told us how rectangular coordinate frame variables evolve.

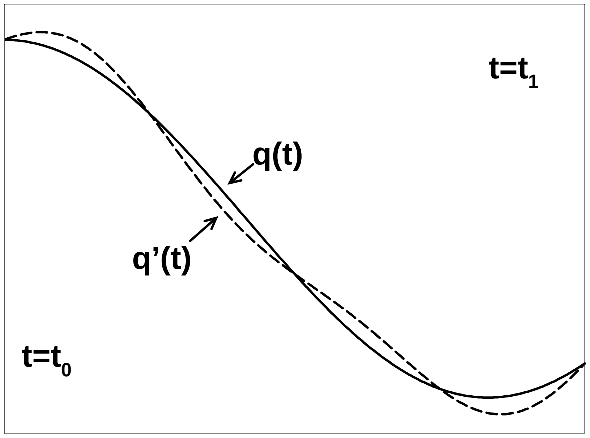
- Now need a method to tell us how a generalized set of coordinates evolve.

Hamilton's Principle

The classical path that a dynamical system follows in moving from one point in phase space to another is chosen such that the time integral of the difference between the kinetic and potential energy is minimized (extremum)

$$L = T - V \tag{23}$$

$$S = \int_{t_0}^{t_1} L(q, \dot{q}, t)dt \tag{24}$$



$$q(t) = \text{ minimum action path} \tag{25}$$

$$q'(t) = q(t) + \delta q(t) \tag{26}$$

$$\delta q(t_0) = \delta q(t_1) = 0 \tag{27}$$

Hamilton's Principle

$$\begin{aligned}
\delta S &= \int_{t_0}^{t_1} L\left(q+\delta q, \dot{q}+\delta \dot{q}, t\right) dt \qquad (28)\\
&\quad - \int_{t_0}^{t_1} L(q,\dot{q},t) dt \\
&= \int_{t_0}^{t_1} \left(\frac{\partial L}{\partial q}\delta q + \frac{\partial L}{\partial \dot{q}}\delta \dot{q}\right) dt \;\; \text{(I.B.P.)} \\
&= \frac{\partial L}{\partial \dot{q}}\delta q\Big|_{t_0}^{t_1} + \int_{t_0}^{t_1} \left[\frac{\partial L}{\partial q} - \frac{d}{dt}\left(\frac{\partial L}{\partial \dot{q}}\right)\right] \delta q \; dt
\end{aligned}$$

- Lagrange's Equation :

$$\frac{\partial L}{\partial q} - \frac{d}{dt}\left(\frac{\partial L}{\partial \dot{q}}\right) = 0 \qquad (29)$$

- We now know the way a set of generalized coordinates evolve.

Lagrange = Newton : Proof

- Rectangular coordinates and conservative system :

$$\begin{aligned} T &= T\left(\dot{x}_i\right) \\ V &= V\left(x_i\right) \\ \frac{\partial T}{\partial x_i} &= 0 \\ \frac{\partial V}{\partial \dot{x}_i} &= 0 \end{aligned} \tag{30}$$

$$\begin{aligned} \frac{\partial L}{\partial x_i} - \frac{d}{dt}\frac{\partial L}{\partial \dot{x}_i} &= 0 \\ -\frac{\partial V}{\partial x_i} - \frac{d}{dt}\frac{\partial T}{\partial \dot{x}_i} &= 0 \\ F_i - \frac{d}{dt}\frac{\partial T}{\partial \dot{x}_i} &= 0 \end{aligned} \tag{31}$$

Lagrange = Newton : Proof

$$\begin{aligned}\frac{d}{dt}\frac{\partial T}{\partial \dot{x}_i} &= \frac{d}{dt}\frac{\partial}{\partial \dot{x}_i}\left(\frac{1}{2}m\dot{x}_i^2\right) \qquad (32)\\ &= m\ddot{x}_i\end{aligned}$$

$$F = m\ddot{x} \tag{33}$$

- Another proof for Newton ⟶ Lagrange

One Dimensional Harmonic Oscillator Example

$$L = T - V \tag{34}$$

$$T = \frac{m}{2}\dot{x}^2 \tag{35}$$

$$F = -kx = -\nabla V \tag{36}$$

$$V = \frac{1}{2}kx^2 \tag{37}$$

$$\frac{\partial L}{\partial x} = -kx \tag{38}$$

$$\frac{\partial L}{\partial \dot{x}} = m\dot{x} \tag{39}$$

$$\frac{d}{dt}\frac{\partial L}{\partial \dot{x}} = m\ddot{x} \tag{40}$$

$$-kx + m\ddot{x} = 0 \tag{41}$$

Newton and Lagrange : Same Physics, Different Philosophy

- Newton
  - Outside forces acting on a body
  - Forces are vector quantities
  - Depend on coordinate system
- Lagrange
  - Energy of a body
  - Scalar quantities
  - Invariant to coordinate transformations
  - Can pick a coordinate system that simplifies problem

Conservation of Energy

Conditions

- Only assume inertial reference frame
- Newton's Laws Valid
- Closed system or
- Interacting with uniform external force field
- No explicit dependence on time $\frac{\partial L}{\partial t} = 0$

Conservation of Energy

$$\begin{aligned}
\frac{dL}{dt} &= \sum_j \frac{\partial L}{\partial q_j}\dot{q}_j + \sum_j \frac{\partial L}{\partial \dot{q}_j}\ddot{q}_j + \frac{\partial L}{\partial t} \qquad (42) \\
&= \sum_j \dot{q}_j \frac{d}{dt}\frac{\partial L}{\partial \dot{q}_j} + \sum_j \frac{\partial L}{\partial \dot{q}_j}\ddot{q}_j \\
&= \sum_j \frac{d}{dt}\left(\dot{q}_j \frac{\partial L}{\partial \dot{q}_j}\right) \\
0 &= \frac{d}{dt}\left(\sum_j \dot{q}_j \frac{\partial L}{\partial \dot{q}_j} - L\right) \\
H &\equiv \sum_j \dot{q}_j \frac{\partial L}{\partial \dot{q}_j} - L \\
&= \text{constant}
\end{aligned}$$

Conservation of Energy

- Additional condition : $\frac{\partial V}{\partial \dot{q}} = 0$

$$
\begin{aligned}
H &= \sum_j \dot{q}_j \frac{\partial L}{\partial \dot{q}_j} - L \qquad (43)\\
&= \sum_j \dot{q}_j \frac{\partial (T - V)}{\partial \dot{q}_j} - (T - V)\\
&= \sum_j \dot{q}_j \frac{\partial T}{\partial \dot{q}_j} - T + V\\
&= 2T - T + V\\
&= T + V \quad \text{conserved}
\end{aligned}
$$

Conservation of Linear Momentum

Conditions

- Inertial Frame
- Homogeneous Space
- Displace all particles by $\delta \mathbf{r} = \sum_i \delta x_i \mathbf{e_i}$

$$\delta L = \sum_i \frac{\partial L}{\partial x_i} \delta x_i = 0 \tag{44}$$

$$\begin{aligned}
\frac{\partial L}{\partial x_i} &= 0 \\
\frac{d}{dt}\frac{\partial L}{\partial \dot{x}_i} &= 0 \\
\frac{\partial L}{\partial \dot{x}_i} &= \text{constant} \\
\frac{\partial \left(T - V\right)}{\partial \dot{x}_i} &= m\dot{x}_i \\
&= \text{constant}
\end{aligned} \tag{45}$$

Hamilton's Equations

- Define a generalized momentum as

$$\begin{aligned} p_i &= \frac{\partial L}{\partial \dot{q}_i} \\ \dot{p}_i &= \frac{d}{dt} p_i \\ &= \frac{d}{dt} \frac{\partial L}{\partial \dot{q}_i} \\ &= \frac{\partial L}{\partial q_j} \end{aligned} \tag{46}$$

$$H = \sum_j p_j \dot{q}_j - L \tag{47}$$

- Using definition of momentum to express $\dot{q}$ in terms of q, p, t
- $H = H\left(q, p, t\right)$ while $L = L\left(q, \dot{q}, t\right)$

Hamilton's Equations

$$\begin{aligned} dH &= \sum_k \left(\frac{\partial H}{\partial q_k} dq_k + \frac{\partial H}{\partial p_k} dp_k \right) + \frac{\partial H}{\partial t} dt \\ &= \sum_k \left(\dot{q}_k dp_k + p_k d\dot{q}_k - \frac{\partial L}{\partial q_k} dq_k - \frac{\partial L}{\partial \dot{q}_k} d\dot{q}_k \right) \\ &\quad - \frac{\partial L}{\partial t} dt \\ &= \sum_k \left(\dot{q}_k dp_k - \dot{p}_k dq_k \right) - \frac{\partial L}{\partial t} dt \end{aligned} \tag{48}$$

- Match terms to get Hamilton's Equations

$$\begin{aligned} \frac{\partial H}{\partial q_k} &= -\dot{p}_k \\ \frac{\partial H}{\partial p_k} &= \dot{q}_k \\ \frac{\partial H}{\partial t} &= -\frac{\partial L}{\partial t} \end{aligned} \tag{49}$$

Hamilton's Equations

- Hamilton's equations 2N first order differential equations
- Lagrange equations N second order differential equations
- p and q now independent equations - equal footing
- Only time dependence comes from an explicit time dependence of the Lagrangian

Phase Space

- Phase space is a 2N dimensional space with one dimension for each of the N coordinates and N momenta.
- Any point in the space completely specifies the mechanical state of a system.
- Given a point at time t_0, $\{q^N(t_0), p^N(t_0)\}$, all points at time $t > t_0$ are completely determined.
- Time reversibility : a unique trajectory leads to $q^N(t_0), p^N(t_0)$.
- $\{q^N(t_0 + \delta t), p^N(t_0 + \delta t)\}$ is a continuous function of $\{q^N(t_0), p^N(t_0)\}$, i.e. trajectories are continuous.
- Trajectories cannot cross, merge or diverge.

Classical Ensemble

- Specify a small $(\ll 2N)$ number of state variables (N,V,T,P,E, etc ...)

- Ensemble : (infinite) collection of systems prepared to satisfy these state variables.

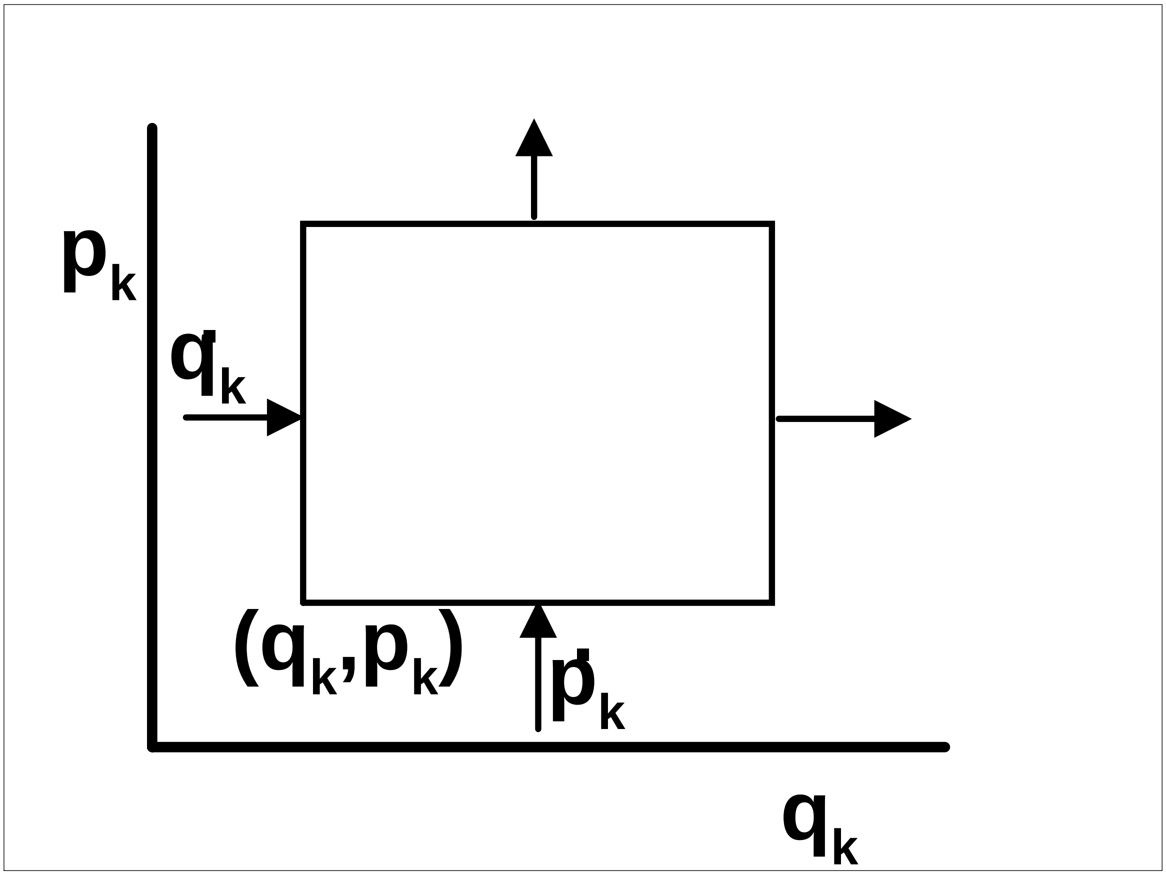
- Together, they define an almost continuous cloud of points in phase space

- Define $f\left(q^N, p^N, t\right)$ such that $f\left(q^N, p^N, t\right)\ dq^N\, dp^N$ is the fraction of states with their phase point in a volume of size $dq^N\ dp^N$ around a point q^N, p^N at time t.

- $\int f\left(q^N, p^N, t\right)\ dq^N\ dp^N = 1$

- Assume that the partial derivatives of f are continuous.

Liouville's Theorem



Liouville's Theorem

- Number of points moving across left face per unit time :

$$f\frac{dq_k}{dt}dp_k = f\dot{q}_k dp_k \tag{50}$$

- Number of points moving across bottom face per unit time :

$$f\frac{dp_k}{dt}dq_k = f\dot{p}_k dq_k \tag{51}$$

- Total moving across bottom and left per unit time:

$$f\dot{q}_k dp_k + f\dot{p}_k dq_k = f\left(\dot{q}_k dp_k + \dot{p}_k dq_k\right) \tag{52}$$

- Number of points moving across top and right face per unit time :

$$\left(f\dot{q}_k + \frac{\partial}{\partial q_k}\left(f\dot{q}_k\right)dq_k\right)dp_k + \left(f\dot{p}_k + \frac{\partial}{\partial p_k}\left(f\dot{p}_k\right)dp_k\right)dq_k \tag{53}$$

Liouville's Theorem

- Total increase per unit time :

$$\frac{\partial f}{\partial t} dq_k dp_k = -\left(\frac{\partial}{\partial q_k}\left(f \dot{q}_k\right) + \frac{\partial}{\partial p_k}\left(f \dot{p}_k\right)\right) dq_k dp_k \tag{54}$$

$$\begin{aligned}
\frac{\partial f}{\partial t} + \sum_{k=1}^{N}\left(\frac{\partial f}{\partial q_k}\dot{q}_k + f\frac{\partial \dot{q}_k}{\partial q_k} + \frac{\partial f}{\partial p_k}\dot{p}_k + f\frac{\partial \dot{p}_k}{\partial p_k}\right) &= 0 \\
\frac{\partial f}{\partial t} + \sum_{k=1}^{N}\left(\frac{\partial f}{\partial q_k}\dot{q}_k + \frac{\partial f}{\partial p_k}\dot{p}_k + f\left(\frac{\partial \dot{q}_k}{\partial q_k} + \frac{\partial \dot{p}_k}{\partial p_k}\right)\right) &= 0 \\
\frac{\partial f}{\partial t} + \sum_{k=1}^{N}\left(\frac{\partial f}{\partial q_k}\dot{q}_k + \frac{\partial f}{\partial p_k}\dot{p}_k\right) + f\Lambda\left(\Gamma\right) &= 0
\end{aligned}$$

- $\Lambda\left(\Gamma\right)$ is the phase space compression factor.

Liouville's Theorem

- For Hamiltonian systems :

$$\begin{aligned}
\Lambda(\Gamma) &= \sum_{k=1}^{N}\left(\frac{\partial \dot{q}_k}{\partial q_k}+\frac{\partial \dot{p}_k}{\partial p_k}\right) \\
&= \frac{\partial}{\partial q_k}\left(\frac{\partial H}{\partial p_k}\right)+\frac{\partial}{\partial p_k}\left(-\frac{\partial H}{\partial q_k}\right) \\
&= 0
\end{aligned} \tag{55}$$

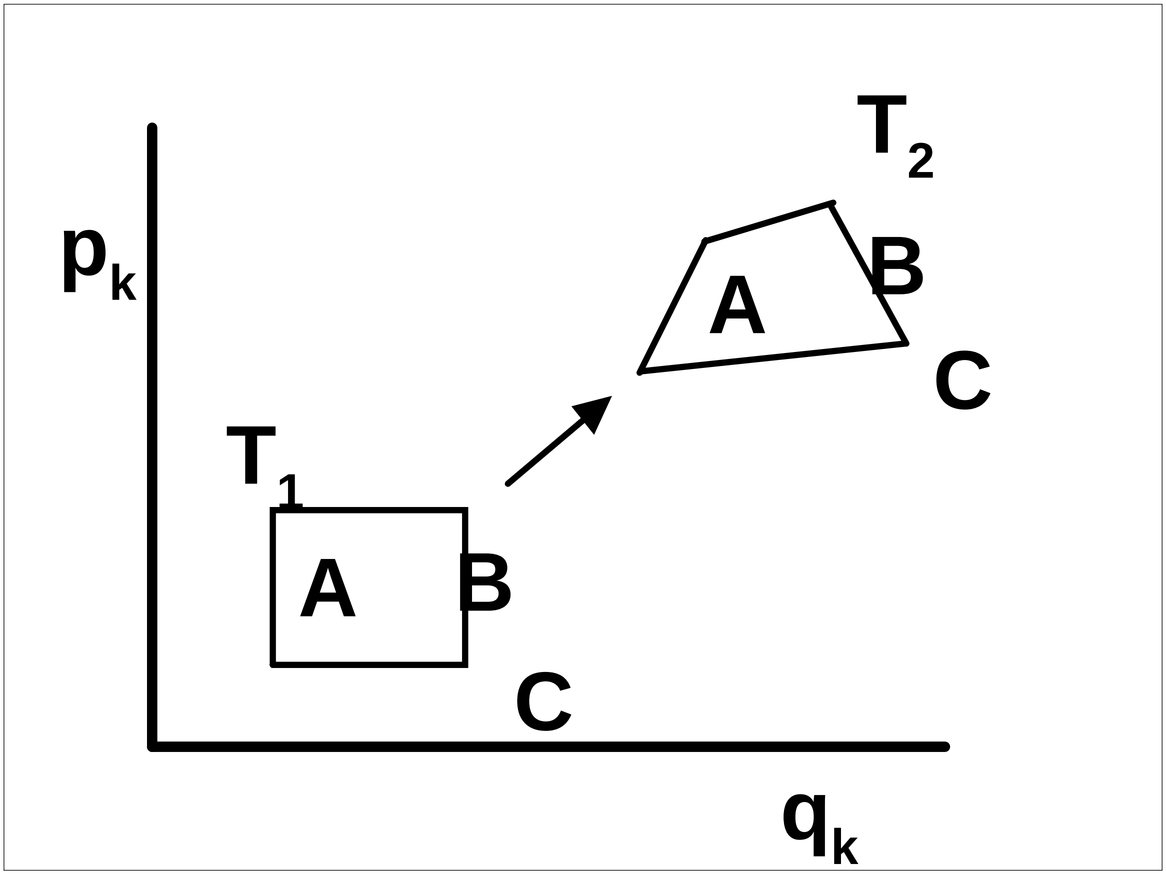
$$\begin{aligned}
\frac{\partial f}{\partial t}+\sum_{k=1}^{N}\left(\frac{\partial f}{\partial q_k}\dot{q}_k+\frac{\partial f}{\partial p_k}\dot{p}_k\right)+f\Lambda(\Gamma) &= 0 \\
\frac{\partial f}{\partial t}+\sum_{k=1}^{N}\left(\frac{\partial f}{\partial q_k}\dot{q}_k+\frac{\partial f}{\partial p_k}\dot{p}_k\right) &= 0
\end{aligned} \tag{56}$$

- Liouville's Theorem

$$\boxed{\frac{df}{dt}=0}$$

Liouville's Theorem

$$f(q,p,t) = f(q_0,p_0,t_0) \tag{57}$$



Liouville's Theorem

$$\begin{aligned} V(0) &= \int dq^N(0)dp^N(0) \qquad (58) \\ V(t) &= \int dq^N(t)dp^N(t) \\ &= \int dq^1(0)\ldots dp^N(0)\mathrm{det}\left[J(t)\right] \end{aligned}$$

$$\begin{aligned} J_{ij}(t) &= \frac{\partial q^i(t)}{\partial q^j(0)} \qquad (59) \\ \frac{dJ(t)}{dt} &= -J(t)\frac{\partial\dot{\Gamma}}{\partial\Gamma} \qquad (60) \\ \dot{J} &= 0 \\ J(t) &= \text{constant} \\ J(0) &= 1 = J(t) \end{aligned}$$

- Volume preserved

Time Evolution of a Distribution Function

$$\begin{aligned} \frac{\partial f}{\partial t} &= -\sum_{k=1}^{N}\left(\frac{\partial f}{\partial q_k}\dot{q}_k + \frac{\partial f}{\partial p_k}\dot{p}_k\right) + f\Lambda\left(\Gamma\right) \\ &= -iL_f f \end{aligned} \tag{61}$$

$$f(\Gamma, t) = \exp\left(-iL_f t\right) f(\Gamma, 0) \tag{62}$$

$$\exp\left(-iL_f t\right) = \sum_{n=0}^{\infty} \frac{-t^n}{n!}\left(iL_f\right)^n \tag{63}$$

$$f(t) = \sum_{n=0}^{\infty} \frac{-t^n}{n!}\left(iL_f\right)^n f(0) \tag{64}$$

- Taylor series expansion of the *explicit* time dependence of $f(\Gamma, t)$ about $f(\Gamma, 0)$.

Evolution of a Phase Variable $B(\Gamma)$

- Depends on Γ, implicitly on time

$$\begin{aligned} \dot{B}(\Gamma) &= \dot{\Gamma} \cdot \frac{\partial}{\partial \Gamma} B \\ &= iL_B(\Gamma) B(\Gamma) \end{aligned} \tag{65}$$

$$B(t) = \exp(iL_B t) B(0) \tag{66}$$

- Ensemble Averages :

$$< B >= \int B(\Gamma) f(\Gamma) d\Gamma \tag{67}$$

- Time Average :

$$< B >_T = \frac{1}{T} \lim_{T \to \infty} \int_t^{t+T} B(\Gamma(t')) dt' \tag{68}$$

- Ergodicity : *atleast one trajectory comes arbitrarily close to all points in phase space for which the distribution function is non-zero.*

$$< B >_T = < B > \tag{69}$$

Extended Phase Space

- Newton's Equations of Motion consistent with NVE ensemble.
- Time Average over the solution to Newton's EOM gives answers for microcanonical ensemble.
- Rare that experiments can control total energy.
- Most control temperature and/or pressure.
- Finite system sizes cause problems.
- Need EOM that generate time averages appropriate for NVT or NTP ensemble before relating to experiments.
- Andersen extended phase space beyond q, p.
- Nose and later Hoover developed a set of EOMs for NVT.

First Attempts to Control Temperature

- Natural method of conduction of heat through boundaries are difficult because of layering effects of the boundaries and strong system size dependence.

- Simple scaling of velocities will only fix first moment of the kinetic energy. Will do nothing to establish a Boltzmann distribution.

- Massive stochastic collisions- Right Ensemble, Funny Dynamics

1. Perform NVE dynamics for fixed amount of time
2. Replace all particle velocities by velocities randomly chosen from a Boltzmann's distribution
3. Go back to Step #1.

NH Example for NVT Dynamics

$$\begin{aligned}\dot{q}_i &= p_i/m &(70)\\ \dot{p}_i &= F_i - p_i\frac{p_\eta}{Q} &(71)\\ \dot{p}_\eta &= \sum_i^N p_i^2/m - N_f kT &(72)\\ \dot{\eta} &= \frac{p_\eta}{Q} &(73)\end{aligned}$$

- N_f number of degrees of freedom.
- If kinetic energy $> N_F kT$, p_η increases.
- p_η acts as a friction coefficient.
- These EOMs have the follow quantity conserved :

$$H' = \sum_i^N p_i^2/2m + V(q) + p_\eta^2/2Q + NkT\eta \quad (74)$$

NH Example for NVT Dynamics

- How do we know what f these EOMs give us?

$$\begin{aligned}
\frac{dJ(t)}{dt} &= -J(t)\frac{\partial\dot{\Gamma}}{\partial\Gamma} && (75)\\
&= -J(t)\left[\frac{\partial\dot{\eta}}{\partial\eta}+\frac{\partial\dot{p}_\eta}{\partial p_\eta}+\sum_i\frac{\partial\dot{p}}{\partial p}+\sum_i\frac{\partial\dot{q}}{\partial q}\right]\\
&= -J(t)\left[-N\frac{p_\eta}{Q}\right]\\
&= J(t)N\dot{\eta}\\
J(t) &= \exp\left(N\eta\right) && (76)
\end{aligned}$$

$$\delta\left[g(x)\right]=\frac{\delta(x-x_0)}{dg/dx} \tag{77}$$

$$H_0=\mathrm{KE}_0+V_0+p_{\eta,0}^2/2Q+NkT\eta_0 \tag{78}$$

$$\delta(H'-H_0)=\frac{\delta(\eta-\eta_0)}{NkT} \tag{79}$$

NH Example for NVT Dynamics

$$\begin{aligned} Q &= \int dq^N dp^N dp_\eta d\eta \exp\left(N\eta\right)\delta(H' - H_0) \qquad (80) \\ &= \int dq^N dp^N dp_\eta d\eta \exp\left(N\eta\right)\frac{\delta(\eta - \eta_0)}{NkT} \\ &= \frac{1}{NkT}\int dq^N dp^N dp_\eta \exp\left(N\eta_0\right) \end{aligned}$$

$$\begin{aligned} H' &= H_0 \\ NkT\eta_0 &= H_0 - \left(\sum_i^N p_i^2/2m + V(q) + p_\eta^2/2Q\right) \\ \eta_0 &= \frac{1}{NkT} \times \\ &\quad \left[H_0 - \left(\sum_i^N p_i^2/2m + V(q) + p_\eta^2/2Q\right)\right] \end{aligned}$$

NH Example for NVT Dynamics

$$\begin{aligned} Q &= \frac{1}{NkT}\exp\left(H_0/kT\right)\times \\ &\quad \int dq^N dp^N dp_\eta \\ &\quad \exp\left(-\left(\sum_i^N p_i^2/2m + V(q) + p_\eta^2/2Q\right)/kT\right) \\ Q &= \mathrm{C}\int dq^N dp^N \exp\left(-\left(\sum_i^N p_i^2/2m + V(q)\right)/kT\right) \end{aligned} \tag{81}$$

- Canonical distribution in the coordinate and momentum sub-space.
- Microcanonical distribution in extended phase space.

NPT Ensemble

$$\begin{aligned}
\dot{q}_i &= p_i/m + \frac{p_\epsilon}{W} q_i && (82)\\
\dot{p}_i &= F_i - p_i \frac{p_\eta}{Q} - \frac{p_\epsilon}{W} p_i && (83)\\
\dot{p}_\eta &= \sum_i^N p_i^2/m + \frac{p_\epsilon^2}{W} - (N_f + 1)kT && (84)\\
\dot{\eta} &= \frac{p_\eta}{Q} && (85)\\
\dot{p}_\epsilon &= dV\left(P_{int} - P_{ext}\right) - p_\epsilon \frac{p_\eta}{Q} && (86)\\
\dot{V} &= \frac{dV p_\epsilon}{W} && (87)
\end{aligned}$$

$$\begin{aligned}
H' = {} & \sum_i^N \frac{p_i^2}{2m_i} + V(q) + p_\eta^2/2Q + && (88)\\
& (N_f + 1)kT\eta + p_\epsilon^2/2W
\end{aligned}$$

$$
\begin{aligned}
\Delta &= \mathrm{C} \int dV \exp\left(-P_{ext}V/kT\right) \times \\
&\int dq^N dp^N \exp\left(-\left(\sum_i^N p_i^2/2m + V(q)\right)/kT\right)
\end{aligned} \tag{89}
$$

Integrators

- Force $(-\nabla V)$ generally analytic expressions.
- Differential equations generally quite complicated.
- May be solved numerical through a Taylor series expansion.

$$\begin{array}{rcll} r(t+\delta t) & = & r(t) + \delta t v(t) + \frac{1}{2}\delta t^2 a(t) + \ldots & \\ +\, r(t-\delta t) & = & r(t) - \delta t v(t) + \frac{1}{2}\delta t^2 a(t) + \ldots & \\ & \downarrow & & \\ r(t+\delta t) & = & 2r(t) - r(t-\delta t) + \delta t^2 a(t) & \text{(90)} \\ v(t) & = & \dfrac{r(t+\delta t) - r(t-\delta t)}{2\delta t} & \text{(91)} \end{array}$$

- Verlet is symmetric with respect to time.
- Requires on $3N_f$ quantities stored in memory.
- $O(\delta t^4)$ in position, $O(\delta t^2)$ in velocity.

Velocity Verlet

- Don't have velocities at time t until you have positions at time $t + \delta t$.
- Numerical problems :

$$r(t+\delta t) = \underbrace{2r(t) - r(t-\delta t)}_{\mathcal{O}\left(\delta t^0\right)} + \underbrace{\delta t^2 a(t)}_{\mathcal{O}\left(\delta t^2\right)} \tag{92}$$

$$\begin{aligned} r(t+\delta t) &= r(t) + \delta t v(t) + \frac{1}{2}\delta t^2 a(t) && (93) \\ v(t+\delta t) &= v(t) + \frac{1}{2}\delta t \left[a(t) + a(t+\delta t)\right] && (94) \end{aligned}$$

- Same storage.
- Mathematically equivalent.
- Numerically superior.
- All information at the same timestep.

Velocity Verlet Structure

$$\boxed{\text{Get initial positions, velocities and forces}}$$

$$\boxed{r\left(t\right) \rightarrow r\left(t+\delta t\right)}$$

$$\boxed{v\left(t\right) \rightarrow v\left(t+\tfrac{1}{2}\delta t\right)}$$

$$\boxed{F\left(t+\delta t\right)}$$

$$\boxed{v\left(t+\tfrac{1}{2}\delta t\right) \rightarrow v\left(t+\delta t\right)}$$

$$\boxed{\text{Analysis}}$$

- Other methods, such as predictor-corrector, Runge-Kutta, etc ... generally inferior
  - Require multiple force calculations.
  - Unstable at larger timestep.
  - Not reversible.

Reversible Integrators

$$\begin{aligned} iL &= \dot{\Gamma} \cdot \frac{\partial}{\partial \Gamma} && (95)\\ &= \sum v_i \frac{\partial}{\partial x_i} + \frac{F_i}{m}\frac{\partial}{\partial v_i} && (96)\end{aligned}$$

$$\Gamma(t) = \underbrace{\mathrm{e}^{iLt}}_{U(t)} \Gamma(0) \qquad (97)$$

$$U^{-1}(t) = U(-t) \text{ unitary operator} \qquad (98)$$

- Discrete Time Propagator - Assume $iL = iL_1 + iL_2$ and discretize time t into p sections where $\delta t = \frac{t}{p}$:

$$\begin{aligned} \mathrm{e}^{i(L_1+L_2)t} &= \left[\mathrm{e}^{i(L_1+L_2)\frac{t}{p}}\right]^p && (99)\\ &= \left[\mathrm{e}^{iL_1\frac{\delta t}{2}}\mathrm{e}^{iL_2\delta t}\mathrm{e}^{iL_1\frac{\delta t}{2}}\right]^p + \mathcal{O}\left(\frac{t^3}{p^2}\right) \end{aligned}$$

Reversible Integrators

- Trotter factorization of the Liouvillian. The error term arises because the operators do not commute.

$$\begin{aligned} G(\delta t) &= \underbrace{\mathrm{e}^{iL_1\frac{\delta t}{2}}\mathrm{e}^{iL_2\delta t}\mathrm{e}^{iL_1\frac{\delta t}{2}}}_{\text{all unitary}} && (100) \\ G^{-1}(\delta t) &= G(-\delta t) && (101) \\ & \quad\quad \text{Reversible Dynamics} && \end{aligned}$$

- To derive specific integrators, assign :

$$\begin{aligned} iL_1 &= \frac{F_i}{m}\frac{\partial}{\partial v_i} && (102) \\ iL_2 &= v_i\frac{\partial}{\partial x_i} && (103) \end{aligned}$$

- Using this result of operator mathematics :

$$\mathrm{e}^{a\frac{\partial}{\partial b}}f(b) = f(b+a) \tag{104}$$

Reversible Integrators

$$G(\delta t)\mathbf{\Gamma}(0) = U_1\left(\frac{\delta t}{2}\right)U_2\left(\delta t\right)U_1\left(\frac{\delta t}{2}\right)\mathbf{\Gamma}(0) \qquad (105)$$

$$\begin{aligned}
\mathrm{e}^{\frac{\delta t}{2}\frac{F_i}{m}\frac{\partial}{\partial v_i}}\left[\begin{array}{c} x(0) \\ v(0) \end{array}\right] &= \left[\begin{array}{c} x(0) \\ v(\frac{\delta t}{2}) = v(0) + \frac{\delta t}{2}\frac{F_i(x(0))}{m} \end{array}\right] \\
\mathrm{e}^{\delta t v_i \frac{\partial}{\partial x_i}}\left[\begin{array}{c} x(0) \\ v(\frac{\delta t}{2}) \end{array}\right] &= \left[\begin{array}{c} x(\delta t) = x(0) + \delta t v(\frac{\delta t}{2}) \\ v(\frac{\delta t}{2}) \end{array}\right] \\
\mathrm{e}^{\frac{\delta t}{2}\frac{F_i}{m}\frac{\partial}{\partial v_i}}\left[\begin{array}{c} x(\delta t) \\ v(\frac{\delta t}{2}) \end{array}\right] &= \left[\begin{array}{c} x(\delta t) \\ v(\delta t) = v(\frac{\delta t}{2}) + \frac{\delta t}{2}\frac{F_i(x(t))}{m} \end{array}\right]
\end{aligned}$$

Velocity Verlet from operators

Reversible Integrators

- Assignment of $\mathrm{iL_i}$ was arbitrary. Could have made the reverse assignments in ...

$$\begin{aligned} iL_1 &= v_i \frac{\partial}{\partial x_i} && (106) \\ iL_2 &= \frac{F_i}{m}\frac{\partial}{\partial v_i} && (107) \end{aligned}$$

$$\begin{aligned}
\mathrm{e}^{\frac{\delta t}{2} v_i \frac{\partial}{\partial x_i}} \begin{bmatrix} x(0) \\ v(0) \end{bmatrix} &= \begin{bmatrix} x(\frac{\delta t}{2}) = x(0) + \frac{\delta t}{2} v(0) \\ v(0) \end{bmatrix} \\
\mathrm{e}^{\delta t \frac{F_i}{m} \frac{\partial}{\partial v_i}} \begin{bmatrix} x(\frac{\delta t}{2}) \\ v(0) \end{bmatrix} &= \begin{bmatrix} x(\frac{\delta t}{2}) \\ v(\delta t) = v(0) + \delta t \frac{F(x(\frac{\delta t}{2}))}{m} \end{bmatrix} \\
\mathrm{e}^{\frac{\delta t}{2} v_i \frac{\partial}{\partial x_i}} \begin{bmatrix} x(\frac{\delta t}{2}) \\ v(\delta t) \end{bmatrix} &= \begin{bmatrix} x(\delta t) = x(\frac{\delta t}{2}) + \frac{\delta t}{2} v(\delta t) \\ v(\delta t) \end{bmatrix}
\end{aligned}$$

Position Verlet
Slightly worse numerically than V.V.

Potentials of Interaction

$$\begin{aligned} V(\mathbf{r}^N) &= \sum_i v_1(\mathbf{r}_i) + \sum_i \sum_{j>i} v_2(\mathbf{r}_i, \mathbf{r}_j) \\ &+ \sum_i \sum_{j>i} \sum_{k>j>i} v_3(\mathbf{r}_i, \mathbf{r}_j, \mathbf{r}_k) + \ldots \end{aligned} \tag{108}$$

- v_1 represents single particle interactions with an external field.
  - Example : ions interaction with an electric field.
  - Computation $O(N)$.

- v_2 represents pair-wise interactions.
  - Depends on magnitude of separation $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$.
  - Computation $O(N^2)$.

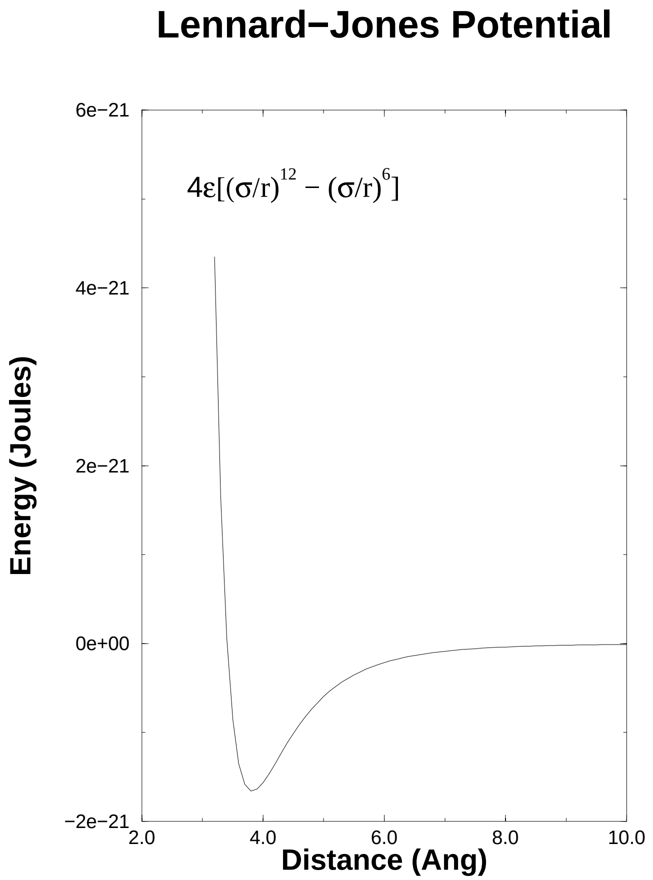
Potentials of Interaction

- v_3 represents three body interactions.
  - Interaction between A and B affected by the presence of C.
  - Example : polarizable species.
  - In *Rare Gas Solids*, (M.L. Klein editor), Jay Barker estimated that $\approx 10\%$ of lattice energy of argon non-pairwise additive.
  - Computation $O(N^3)$.

- Higher order terms $v_4, v_5, \ldots$ generally quite small.

- Despite magnitude, generally do not include v_3
  - $O(N)$ worse computation to get remaining $\approx 10\%$.
  - Modify v_2 to include average effects of v_3
  - $v_2^{eff} \equiv v_2 + < v_3 >$

Potential of Interaction



(Pseudo−)atom	σ ($\AA$)	ϵ (K)
Argon	3.405	119.3
CH_3	3.9057	88.064

- Power law repulsion term (r^{-12}) not accurate for close interactions. Williams potential uses exponential repulsion in:

$$V_{\mathrm{williams}} = A\mathrm{e}^{-Br} + Cr^{-6} \tag{109}$$

Bonded Interactions

- Bonds
  - Assume harmonic bonds
  - $\sum_i^{N_{bonds}} \frac{1}{2} K_i^b \left(b_i - b_i^0\right)^2$
- Angles
  - Assume harmonic angle
  - $\sum_i^{N_{angles}} \frac{1}{2} K_i^\theta \left(\theta_i - \theta_i^0\right)^2$
- Torsions ("1-4" interactions)
  - $\sum_i^{N_{dihedral}} K_i^\phi \left[1 + \cos n_i \phi_i - \delta_i\right]$
- Bonded Non-Bonded corrections

Potential of Interaction

- Example Code : given function pot(r) and force(r) that calculates pairwise potential and force ...

```
V=0.0

F(i=1,N)=0.0

do i=1, N-1

   do j=i+1,N
      rij=r(j) - r(i)
      rijsq=rij*rij
      rij=sqrt(rijsq)
      v=v+pot(rij)
      f(i)=f(i) - force(rij)
      f(j)=f(j) + force(rij)
   end j loop

end i loop
```

Truncation of the Non-Bonded Interactions

- If **r** is large, $v(\mathbf{r}) \approx 0$.

- Example : SPC/E model of water, oxygen-oxygen $v_{LJ}\left(10\mathring{A}\right) \approx .001kT$

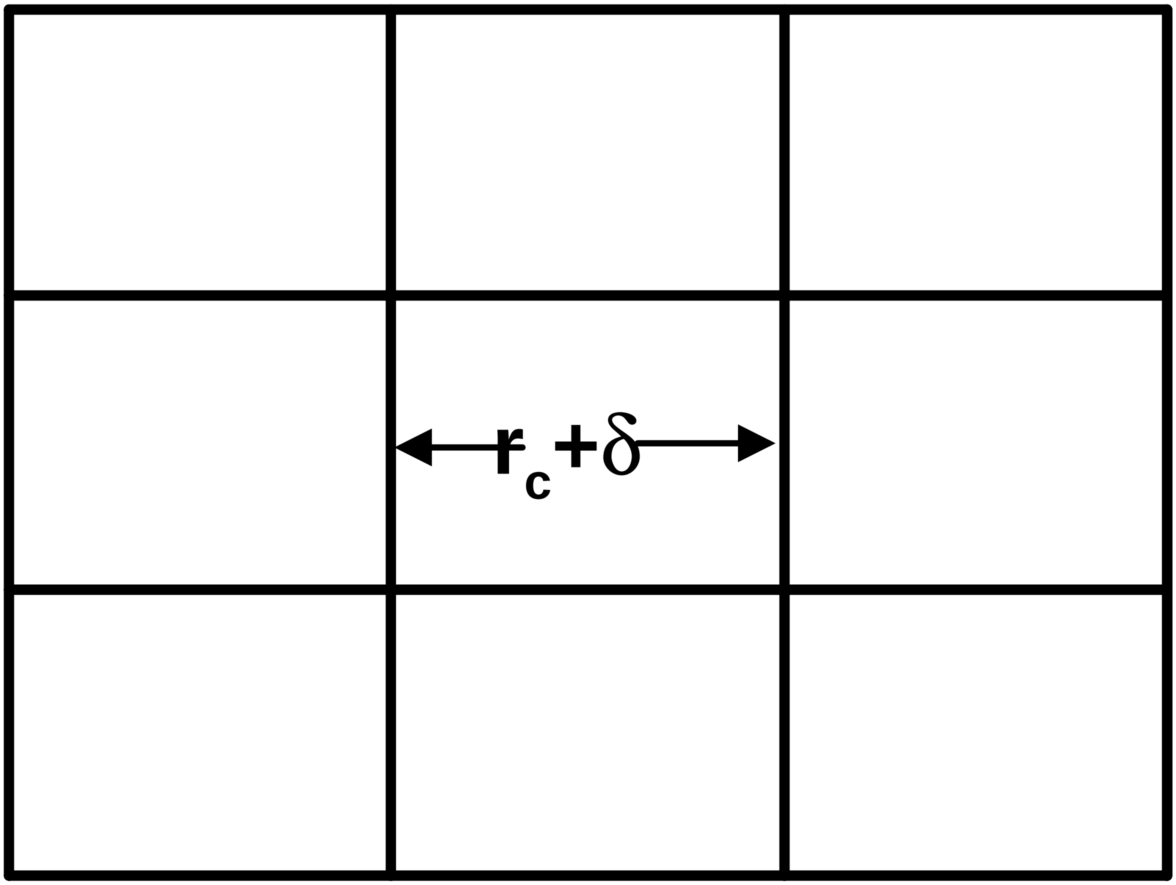
- Assume $V(r) = 0$ for $r > r_c$.
  - Simple truncation
  - Shift
  - Switch

- Turns computation from $N(N-1)/2$ to $\approx \frac{4\pi r_c^3}{3}\rho N$.
  - For $10,000$ SPC/E water molecules, LJ interactions drop by a factor of 30 at $\rho = 1\mathrm{g/cm}$.
  - Benefit increases as $r_c \ll L_{box}$.

- Long range interactions need special treatment (see Ewald slide)

Neighbor Lists

Cells

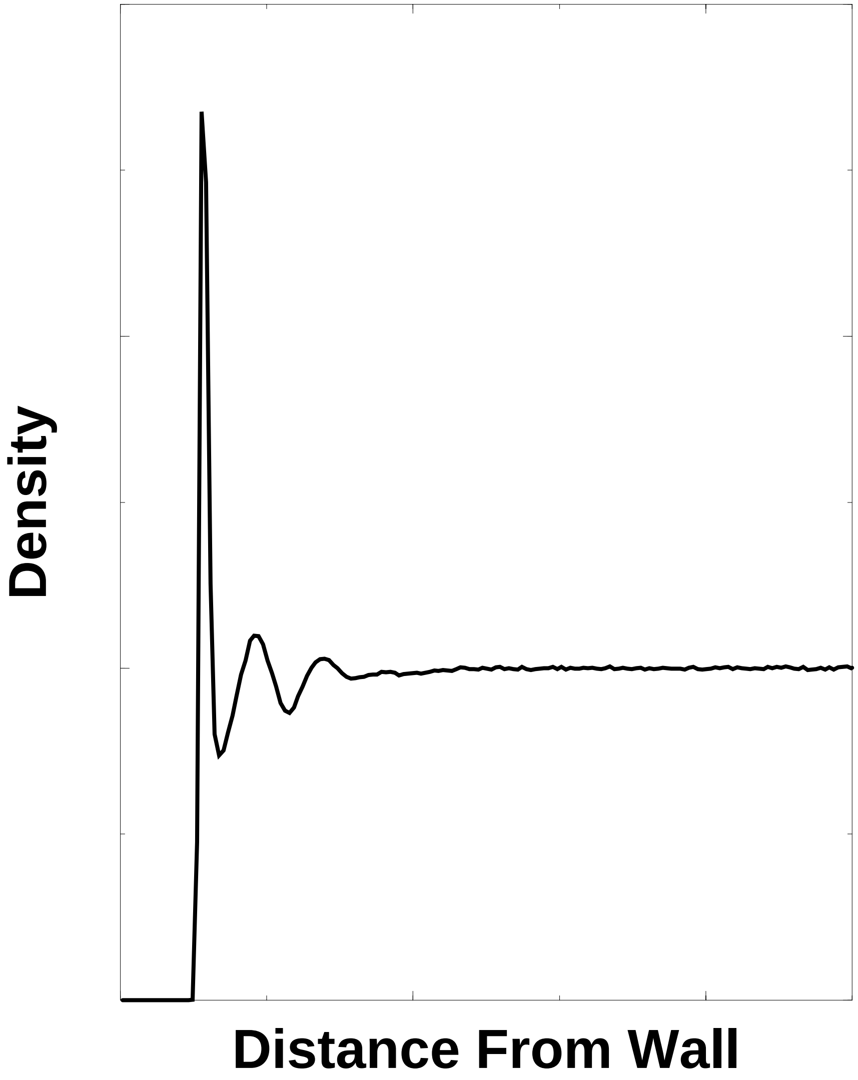


Boundary Conditions

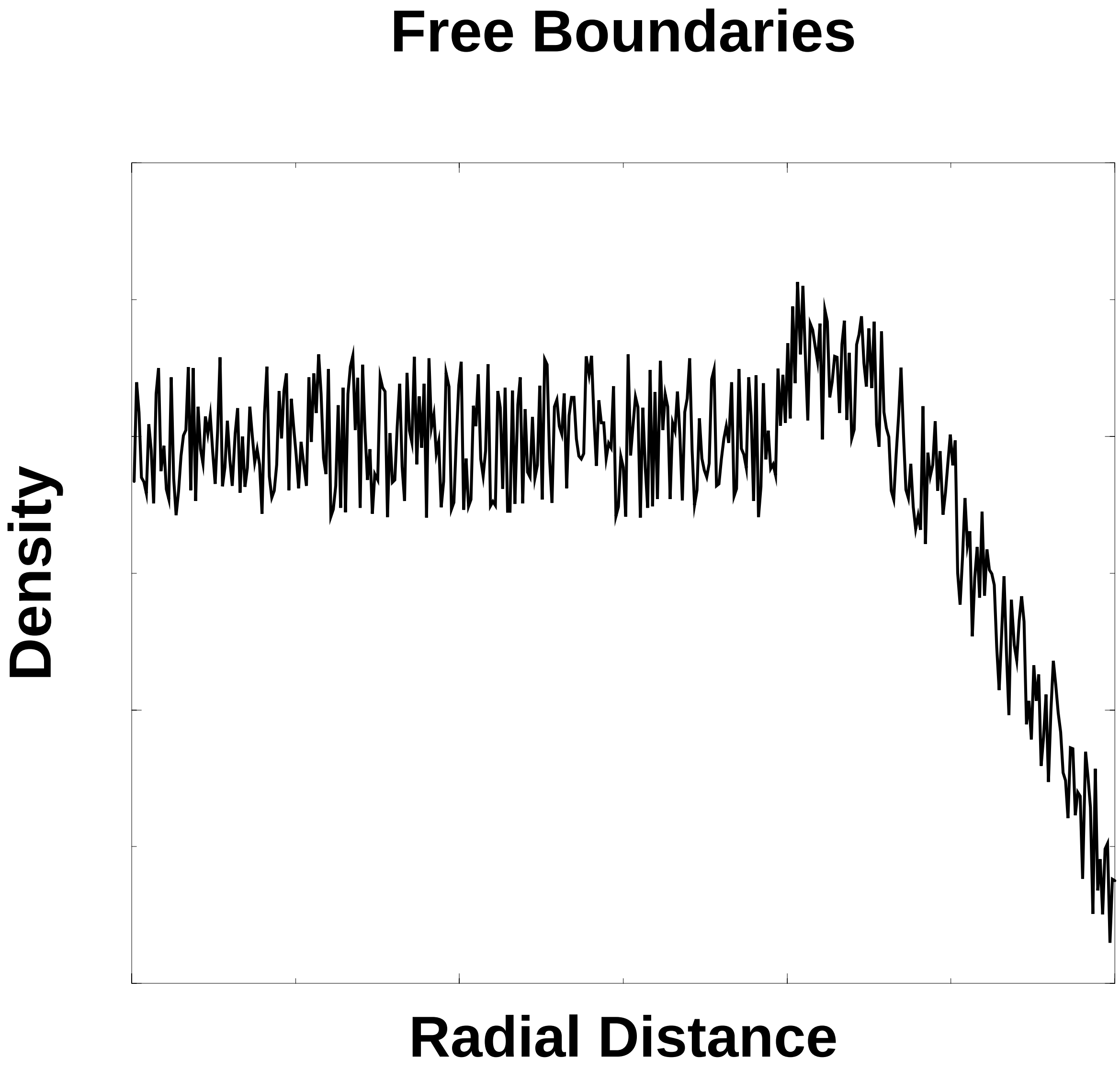
- MD system sizes small compared to 10^{23}
- Surface to volume ratio large
- Surface effects too large (i.e. layering, etc ...)
- Can still be used for isolated systems like clusters

Boundary Conditions

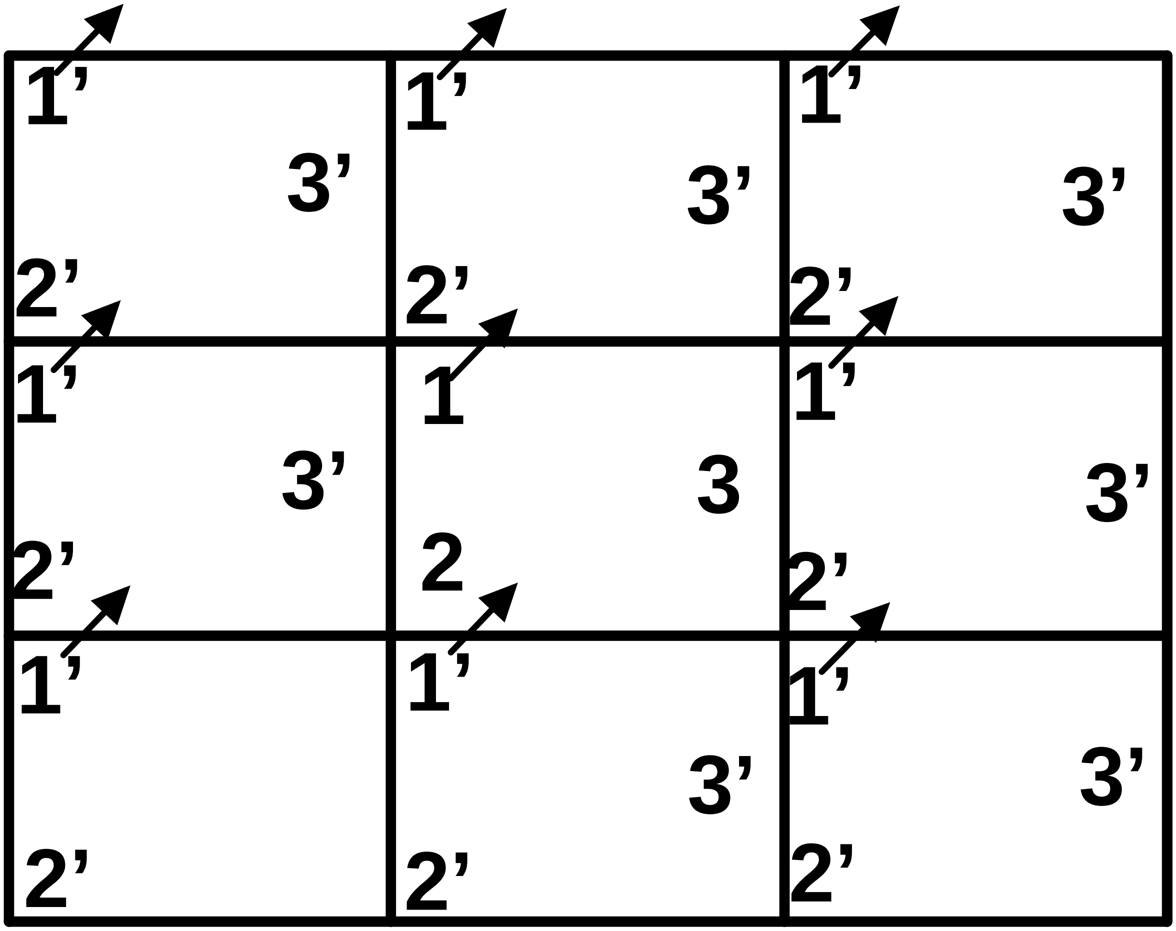
Effect of Walls on Density



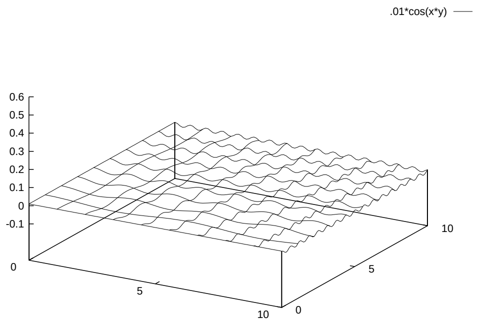
Boundary Conditions

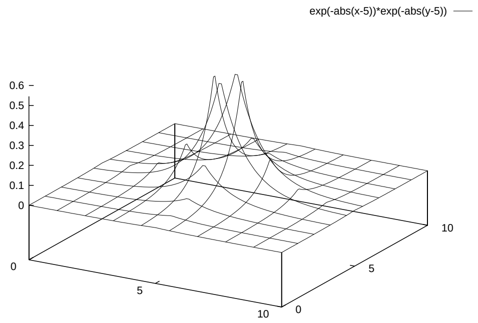


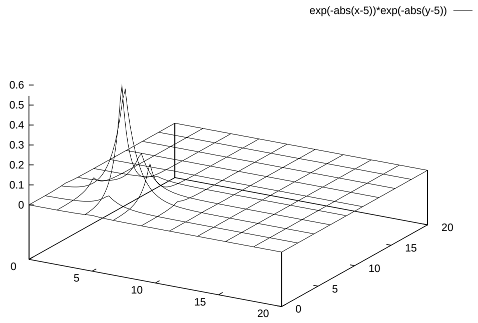
Periodic boundary conditions

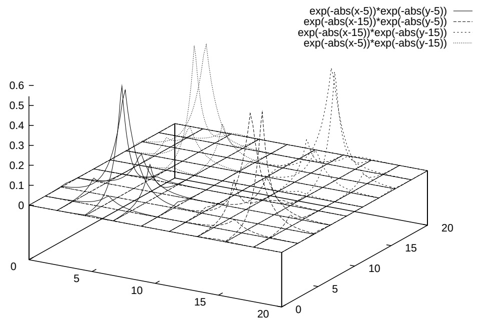


PBC: System Size artifacts

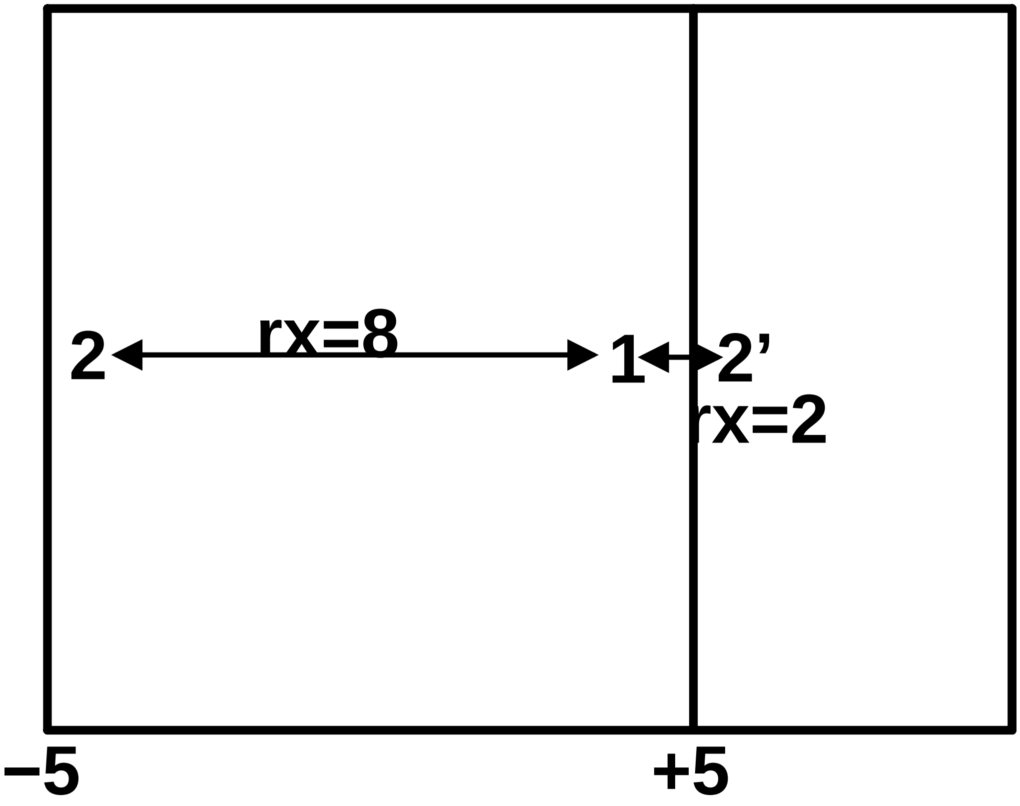








Minimum Image Convention



$$
\begin{aligned}
\mathrm{rxij} &= \mathrm{rxij} - \mathrm{L_x} \times \mathrm{NINT}\,(\mathrm{rxij}/\mathrm{L_x}) \\
&= -8 - 10 \times \mathrm{NINT}\,(-8/10) \\
&= -8 + 10 \\
&= 2
\end{aligned}
$$

Potentials Revisited : Long Ranged Interactions

Long ranged interactions ($e.g.$ potential decaying slower than r^{-d}, where d is the dimensionality) can not be simply truncated without missing significant contributions. If we have charges on our atoms, we have point charge interactions of the form :

$$V_{\mathrm{electrostatic}} = \frac{q_i q_j}{4\pi\epsilon r_{ij}} \tag{110}$$

To solve this problem, we add an oppositely charged Gaussian distributed counter-ion cloud around the point charge. If q_i is the charge on an atom located at r_i, this cloud has a charge density given by :

$$\rho\left(r_i'\right) = -\frac{(q_i)\alpha^3}{\pi^{3/2}}\mathrm{e}^{-\alpha^2 (r_i')^2} \tag{111}$$

where $r' = r - r_i$ and α is a parameter that controls the width of the counter-ion cloud.

Potentials Revisited : Long Ranged Interactions

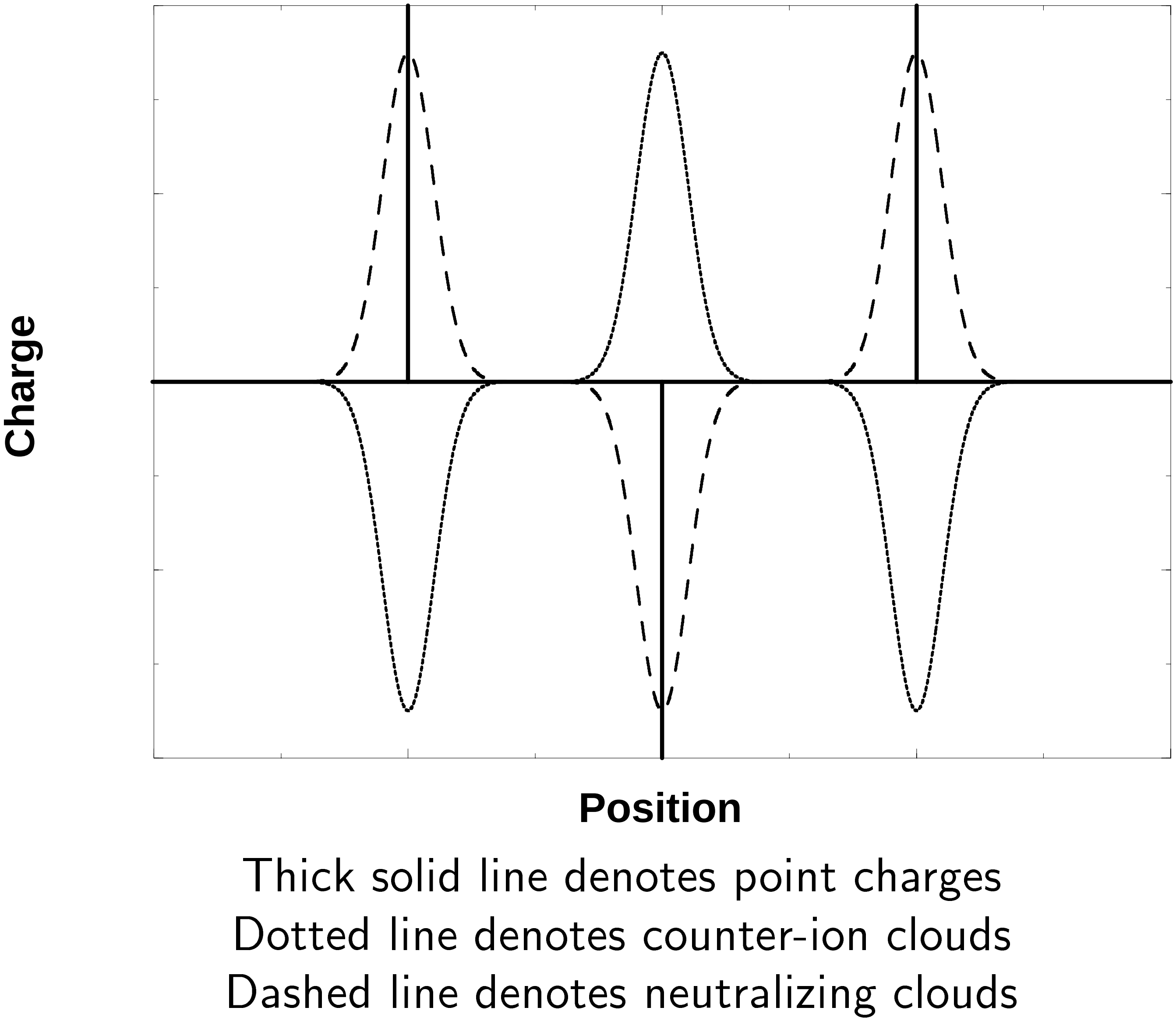
Now, the interactions between the atoms are screened by the counter-ion clouds and hence they become "short-ranged" in the form of :

$$V_{\text{screened}} = \frac{q_i q_j}{4\pi\epsilon r_{ij}} \operatorname{erfc}\left(\|\alpha r_{ij}\|\right) \qquad (112)$$

and hence can be safely truncated. To balance the effect of adding the counter-ion clouds, we add neutralizing Gaussian clouds of opposite sign. Since these neutralizing charges are of a simple form (Gaussian) and they are periodic in real space, their energy can be easy handled in Fourier space.

Potentials Revisited : Long Ranged Interactions

Ewald Summation



Thick solid line denotes point charges
Dotted line denotes counter-ion clouds
Dashed line denotes neutralizing clouds

Time Step

- Time step size selection a question of balance.
  - Want a small enough timestep to accurately integrate EOMs.
  - Want a big enough timestep to see interesting behavior in a tractable amount of computer time.
  - Timesteps typically on the order of femtoseconds for common molecular systems.
  - Many processes of interest happen on timescales of nano/picoseconds.

- Time step determined by curvature of the potential.
  - $r(t+\delta t) = r(t) + \delta t v(t) + \frac{1}{2}\delta t^2 a(t)$
  - Hoping that F remains fairly constant between $r(t)$ and $r(t+\delta t)$.
  - $\frac{dF}{dr} = \frac{d}{dr}\left(-\frac{dV}{dr}\right)$.
  - Essence of protein folding problem.

- Time Steps typical for flexible high frequency bonds (such as O-H in water) around 0.5 fs.

Constraints

- Some high frequency vibrations not of interest.

- If they couple weakly to the dynamics of interest, they can safely be ignored.

- Imagine replacing the stiff $N \equiv N$ bond with a fixed constraint of $|\mathbf{r}_{12}| = d_{12}$.

$$
\begin{aligned}
m\ddot{r}_1 &= f_{u,1} + f_{c,1} && (113) \\
m\ddot{r}_2 &= f_{u,2} + f_{c,2} && (114) \\
f_{c,1} &= \lambda_{12}\mathbf{r}_{12} && (115) \\
f_{c,2} &= -\lambda_{12}\mathbf{r}_{12} && (116)
\end{aligned}
$$

$$
\begin{aligned}
\mathbf{r}_1 &= \mathbf{r}_{u,1} + \frac{\delta t^2}{2m}\lambda_{12}\mathbf{r}_{12} && (117) \\
\mathbf{r}_2 &= \mathbf{r}_{u,2} - \frac{\delta t^2}{2m}\lambda_{12}\mathbf{r}_{12} && (118) \\
\mathbf{r}_{12} &= \mathbf{r}_{u,12} + \frac{\delta t^2}{m}\lambda_{12}\mathbf{r}_{12} && (119)
\end{aligned}
$$

Constraints

$$\begin{aligned} d_{12} &= |\mathbf{r}_{12}| \qquad (120) \\ d_{12}^2 &= \mathbf{r}_{u,12}^2 \qquad (121) \\ &+2\left(\frac{\delta t^2}{m}\right)(\lambda_{12})(\mathbf{r}_{12})\,\mathbf{r}_{u,12} \\ &+\left(\frac{\delta t^4}{m^2}\right)(\lambda_{12}^2)\,\mathbf{r}_{12}^2 \end{aligned}$$

• Since quadratic term for λ_{12} is $O(\delta t^4)$, make linear approximation.

$$\lambda_{12} = \frac{d_{12}^2 - \mathbf{r}_{u,12}^2}{2\left(\frac{\delta t^2}{m}\right)(\mathbf{r}_{12})\,\mathbf{r}_{u,12}} \tag{122}$$

• Update **r** and iterate to convergence.

• Cyclic updating of all constraints until some tolerance is reached : SHAKE.

Constraints

Velocities have their own constraint to satisfy :

$$\begin{aligned} r_{12}^2 &= \mathbf{r}_{12} \cdot \mathbf{r}_{12} && (123) \\ \frac{dr_{12}^2}{dt} &= 2\mathbf{r}_{12} \cdot \dot{\mathbf{r}}_{12} && (124) \\ &= 0 \end{aligned}$$

$$\begin{aligned} \mathbf{v}_{12} &= \mathbf{v}_{12}^u + \frac{\delta t}{m}\lambda_{12}\mathbf{r}_{12} && (125) \\ \mathbf{r}_{12} \cdot \mathbf{v}_{12} &= \mathbf{r}_{12} \cdot \mathbf{v}_{12}^u + \frac{\delta t}{m}\lambda_{12}\mathbf{r}_{12} \cdot \mathbf{r}_{12} && (126) \\ 0 &= \mathbf{r}_{12} \cdot \mathbf{v}_{12}^u + \frac{\delta t}{m}\lambda_{12}\mathbf{r}_{12} \cdot \mathbf{r}_{12} && (127) \end{aligned}$$

Solve for λ_{12}
RATTLE

Tests of Suitable Timestep / Working Code

- Conserved quantities
  - Total energy in NVE simulations
  - H' for Nosé-Hoover NVT simulations.
  - $E_{cons}(t) = \frac{E(t)-E(0)}{E(0)}$.
  - $E_{cons} \approx 10^{-4}$ typical.
  - Linear momentum conservation (machine precision).

- Velocity Verlet
  - RMS fluctuations in energy grow as timestep squared in linear regime.

- Numerical derivatives of potential versus force.

Analysis Techniques : Normal Modes

For a simple scalar function, we write the Taylor Series expansion as :

$$V(\delta r) = V(0) + \frac{\partial V}{\partial r}\delta r + \frac{1}{2}\frac{\partial^2 V}{\partial r^2}\delta r^2 + \ldots \qquad (128)$$

where the last term represents the harmonic component of V. Since the potential energy actually depends all the atomic positions, we can analogously write:

$$V\left(r(\vec{t})\right) = V\left(r(\vec{0})\right) + \left(-F \cdot \vec{\Delta r}\right) + \left(\frac{1}{2}\vec{\Delta r}^{\,T} \cdot D \cdot \vec{\Delta r}\right) + \ldots \qquad (129)$$

where $\vec{\Delta r} = r(\vec{t}) - r(\vec{0})$, $F = -\frac{\partial V}{\partial r_i}$ and the Hessian $D = \frac{\partial^2 V}{\partial r_i \partial r_j}$. This last term now represents the harmonic components of the potential energy. Normal modes of a system, however, are independent harmonic components. Hence, we apply a unitary matrix U that diagonalized the Hessian D.

Analysis Techniques : Normal Modes

$$V\left(r(\vec{t})\right) = V\left(r(\vec{0})\right) + \sum_{\alpha} \left[-f_\alpha q_\alpha\left(t\right) + \frac{1}{2}\omega_\alpha^2 q_\alpha\left(t\right)\right] \tag{130}$$

where

$$\begin{aligned} q_\alpha\left(t\right) &= \left[U \cdot \vec{\Delta} r\left(t\right)\right]_\alpha \\ f_\alpha &= \left[U \cdot F\right]_\alpha \\ \omega_\alpha^2 &= \left[U^T \cdot D \cdot U\right]_{\alpha\alpha} \end{aligned}$$

The vector q_α represents an independent harmonic mode with corresponding frequency ω_α. Hence, it is now possible to match peaks in an I.R. or Raman spectra with the molecular motion that generates that peak.

Chemical Potential

- Remember that the average of a quantity B over a distribution f is given by:

$$\langle B \rangle_f = \int B f(\Gamma)\, d\Gamma \tag{131}$$

- The chemical potential is defined by :

$$\mu \equiv \left(\frac{\partial A}{\partial N} \right)_{T,V} \tag{132}$$

- In the limit of large N, it could be approximated by :

$$\mu \approx A(N+1, V, T) - A(N, V, T) \tag{133}$$

Chemical Potential

- Remember that the Helmholtz Free Energy can be expressed as

$$A(N,V,T) = -KT \ln Q(N,V,T) \tag{134}$$

where Q is the canonical partition function. We can then write :

$$\begin{aligned}
\mu &= -KT \ln \frac{Q_{N+1}}{Q_N} && (135)\\
Q_N &= \frac{Z_N}{N!\Lambda^{3N}} && (136)\\
\beta\mu &= \beta\mu_{ideal} + \beta\mu_{residual} && (137)\\
&= \ln \frac{(N+1)\Lambda^3}{V} - \ln \frac{Z_{N+1}}{V Z_N}
\end{aligned}$$

- Two components : ideal gas chemical potential and residual chemical potential.

Chemical Potential

$$e^{\beta \mu_r} = \frac{Z_{N+1}}{V Z_N} = \frac{\int e^{-\beta U(N+1)} dr^{N+1}}{\int dr_{N+1} \int e^{-\beta U(N)} dr^N} \tag{138}$$

- Rewrite the N+1 particle potential in the form of :

$$U(N+1) \equiv U(N) + \phi(r^N, r_{N+1}) \tag{139}$$

- where the last term represents the interaction of the (N+1)th particle with the remaining N particles.

$$\begin{aligned} \frac{Z_{N+1}}{V Z_N} &= \frac{\int dr_{N+1} \int e^{-\beta U(N)} e^{-\beta \phi}}{V \int e^{-\beta U(N)} dr^N} \\ &= \frac{\int dr_{N+1} < e^{-\beta \phi} >_N}{\int dr_{N+1}} \\ &= \left\langle \left\langle e^{-\beta \phi} \right\rangle_N \right\rangle_{r_{N+1}} \end{aligned} \tag{140}$$

Chemical Potential

- Widom's Test Particle Method
  - Compatible with either MC or MD.
  - After a certain number of steps (moves), freeze configuration.
  - Randomly insert "test" (N+1) particles.
  - Measure increase in potential energy ϕ.
  - Average over many insertions and configurations.
  - Non-destructive.
- For dense systems, $\phi \gg kT \rightarrow e^{-\beta\phi} \approx 0$.
- Poor statistics.
- Can improve sampling through Umbrella Sampling.

Pressure

$$\overset{\leftrightarrow}{\mathbf{P}} = \frac{1}{3V}\left[\sum_{i=1}^{N}\frac{\mathbf{p}_i^2}{m_i} + \sum_{i=1}^{N}\mathbf{r_i}\cdot\mathbf{F_i}\right] \tag{141}$$

$$P_{\alpha\beta} = \frac{1}{V}\left[\sum_{i=1}^{N}\frac{P_{i,\alpha}P_{i,\beta}}{m_i} + \sum_{i=1}^{N}r_{i,\alpha}F_{i,\beta}\right] \tag{142}$$

- At equilibrium,

$$\langle P_{\alpha\beta}\rangle = 0 \text{ if } \alpha \neq \beta \tag{143}$$

$$\begin{aligned} P &= \frac{1}{3}\mathrm{Tr}\left(\overset{\leftrightarrow}{\mathbf{P}}\right) \qquad (144) \\ &= \frac{1}{3}\sum_{\alpha=x,y,z}P_{\alpha\alpha} \end{aligned}$$

Transport Coefficients

• Using continuity equations (Fick's Law) for density, Einstein presented his expression for the diffusion coefficient in terms of the mean square displacement of a particle at long times :

$$D = \lim_{t \to \infty} \frac{1}{6t} \left\langle \left| \mathbf{r}\left(t\right) - \mathbf{r}\left(0\right) \right|^2 \right\rangle \tag{145}$$

• We can rewrite a particle's displacement using a velocity expression:

$$\mathbf{r}(t) - \mathbf{r}(0) = \int_0^t \mathbf{v}\left(t'\right) dt' \tag{146}$$

• For small t, the particle velocity remains the constant, i.e. $\mathbf{v}(t) \approx \mathbf{v}(0) \equiv \mathbf{v}_0$. Under such "ballistic" conditions :

$$\begin{aligned} r(t) - r(0) &= v_0 t && (147) \\ |r(t) - r(0)|^2 &= |v_0|^2 t^2 && (148) \end{aligned}$$

Transport Coefficients

- For a general time t :

$$\begin{aligned} \left[r(t) - r(0)\right]^2 &= \int_0^t dt' \int_0^t dt'' \mathbf{v}\left(t'\right) \cdot \mathbf{v}\left(t''\right) \qquad (149) \\ \left\langle \left[r(t) - r(0)\right]^2 \right\rangle &= \int_0^t dt' \int_0^t dt'' \left\langle \mathbf{v}\left(t'\right) \cdot \mathbf{v}\left(t''\right) \right\rangle \end{aligned}$$

- Stationarity and time reversibility gives us:

$$\left\langle \mathbf{v}\left(t'\right) \cdot \mathbf{v}\left(t''\right) \right\rangle = \left\langle \mathbf{v}\left(0\right) \cdot \mathbf{v}\left(t'' - t'\right) \right\rangle \qquad (150)$$

- Now, we change variables to $\tau = t'' - t'$ and perform the first integration:

$$\left\langle \left[r(t) - r(0)\right]^2 \right\rangle = 2t \int_0^t \left(1 - \frac{\tau}{t}\right) \left\langle \mathbf{v}\left(0\right) \cdot \mathbf{v}\left(\tau\right) \right\rangle d\tau \qquad (151)$$

Transport Coefficients

- If τ' is the time is takes for the particle to suffer multiple collisions, the velocity of a particle will become completely uncorrelated to its initial velocity, i.e.

$$\langle \mathbf{v}(0) \cdot \mathbf{v}(\tau) \rangle \approx 0 \quad \text{for} \quad \tau > \tau' \tag{152}$$

- If the time $t \gg \tau'$, then we can safely ignore the $\frac{\tau}{t}$ term.

$$\left\langle [r(t) - r(0)]^2 \right\rangle = 2t \int_0^t \langle \mathbf{v}(0) \cdot \mathbf{v}(\tau) \rangle \, d\tau \tag{153}$$

$$D = \frac{1}{3} \int_0^\infty \langle \mathbf{v}(0) \cdot \mathbf{v}(\tau) \rangle \, d\tau \tag{154}$$

- In the last line, we can safely extend the integral to ∞ because $\langle \mathbf{v}(0) \cdot \mathbf{v}(\tau) \rangle \approx 0$ for large τ.

Transport Coefficients

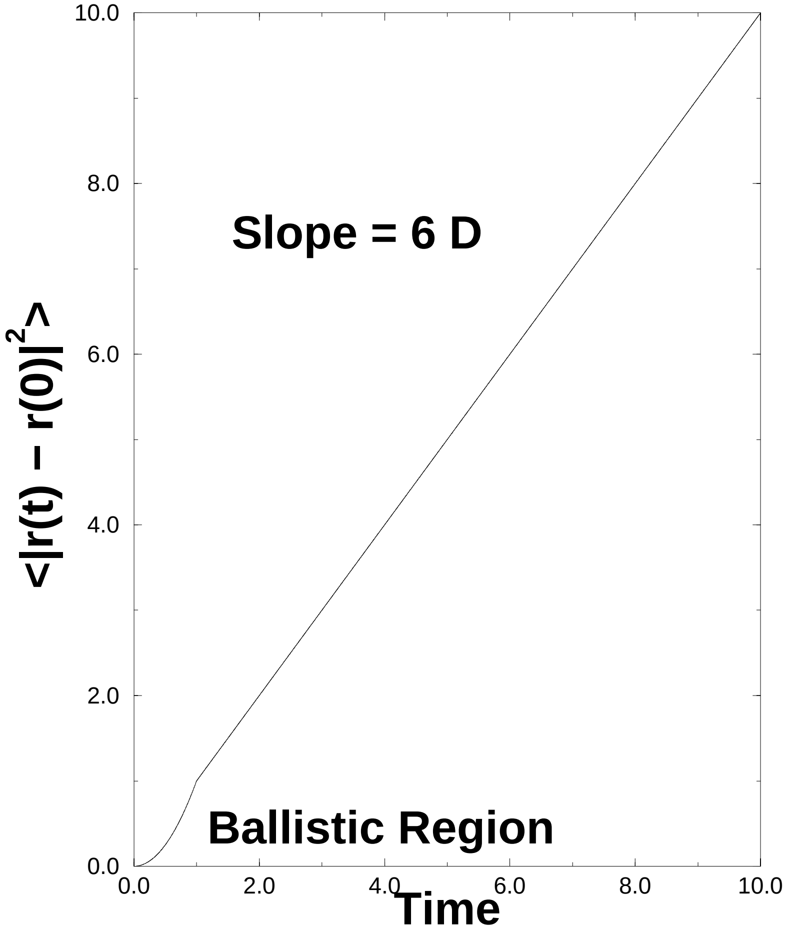
- The integral is writen using the “unnormalized” autocorrelation function. We often used a normalized version written :

$$C(\tau) = \frac{\langle \mathbf{v}\,(0) \cdot \mathbf{v}\,(\tau) \rangle}{\langle \mathbf{v}\,(0) \cdot \mathbf{v}\,(0) \rangle} \tag{155}$$

- Since $\langle \mathbf{v}\,(0) \cdot \mathbf{v}\,(0) \rangle = 3kT/m$,

$$D = \frac{kT}{m} \int_0^\infty C\,(\tau)\,d\tau \tag{156}$$

Transport Coefficients



Green-Kubo relations for Transport Coefficients

- Self-Diffusion :

$$D = \frac{1}{3}\int_0^\infty \langle \mathbf{v}\,(0) \cdot \mathbf{v}\,(\tau)\rangle \, d\tau \tag{157}$$

- Shear Viscosity :

$$\eta = \frac{V}{kT}\int_0^\infty \langle P_{xy}(0) P_{xy}(t)\rangle \tag{158}$$

where P_{xy} is the xy component of the pressure tensor.

- Thermal conducivity :

$$\lambda = \frac{V}{3kT^2}\int_0^\infty \langle \mathbf{J}_Q(t) \cdot \mathbf{J}_Q(0)\rangle \, dt \tag{159}$$

where $\mathbf{J}_Q$ is the energy flux.