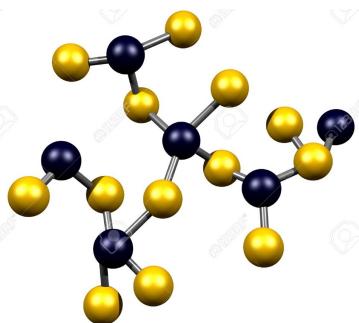
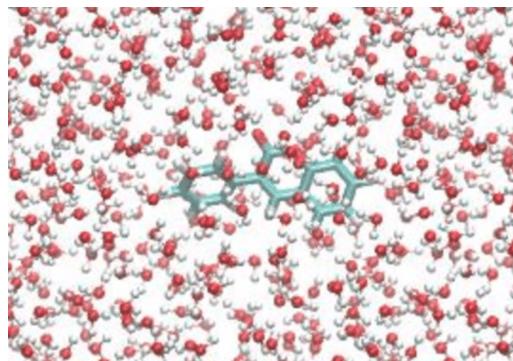


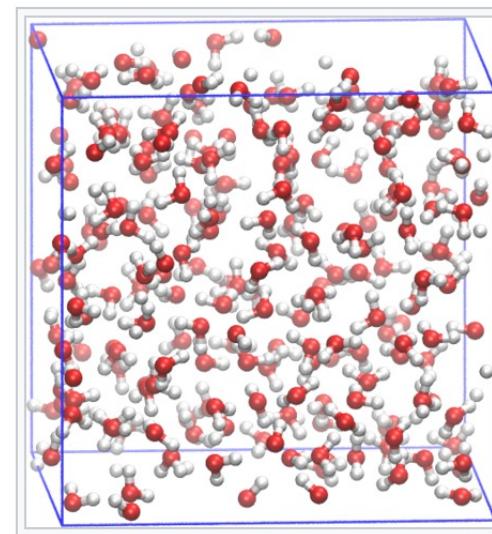
How you define the physical system: particle perspective



Isolated molecule

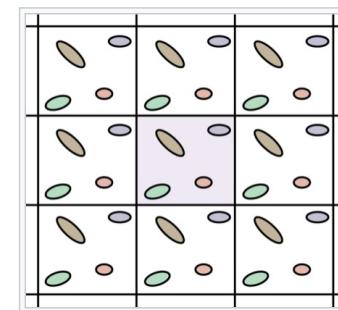


Collection of molecules



collection mimicking macroscopic behavior

Periodic boundary conditions



How you define the physical system: energy perspective

$$H_{operator} = \frac{-\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x)$$

Operator associated with kinetic energy Potential energy

01 x 165

Classical $V(x)$

$$U(R) = \sum_{bonds} k_r (r - r_{eq})^2 + \sum_{angles} k_\theta (\theta - \theta_{eq})^2 + \sum_{dihedrals} k_\phi (1 + \cos[n\phi - \gamma]) + \sum_{impropers} k_\omega (\omega - \omega_{eq})^2 + \sum_{atoms} \epsilon_{ij} \left[\left(\frac{r_m}{r_{ij}} \right)^{12} - 2 \left(\frac{r_m}{r_{ij}} \right)^6 \right] + \sum_{i < j} \frac{q_i q_j}{4\pi \epsilon_0 r_{ij}}$$

bond

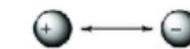
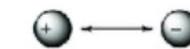
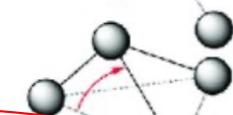
angle

dihedral

improper

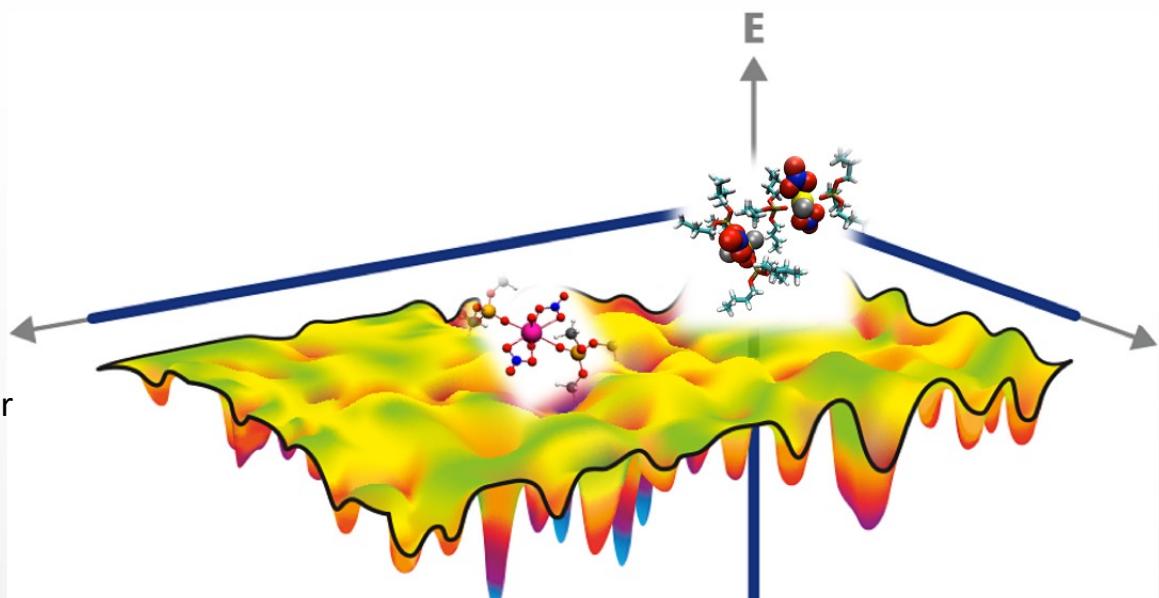
van der Waals

electrostatic



Creating the equilibrium ensemble – exploring the energy landscape

- The ensemble is all configurations that should be populated (or observed) under a given set of conditions
- This requires SAMPLING the energy landscape (finding the structures in different minima, etc)
- Two approaches to sampling:
Deterministic – letting molecules move under the forces defined by the potential energy (molecular dynamics), Non-deterministic – randomly moving molecules to see how the energy changes (Monte Carlo)



Equations of motion

- Newton's second law: $F = ma$
 - where F is force on an atom, m is mass of the atom, and a is the atom's acceleration
- Recall that: $F(x) = -\nabla U(x)$
 - where x represents coordinates of all atoms, and U is the potential energy function
- Velocity is the derivative of position, and acceleration is the derivative of velocity.
- We can thus write the equations of motion as:

$$\frac{dx}{dt} = v$$

$$\frac{dv}{dt} = \frac{F(x)}{m}$$

Solving the equations of motion

$$\frac{dx}{dt} = v$$

$$\frac{dv}{dt} = \frac{F(x)}{m}$$

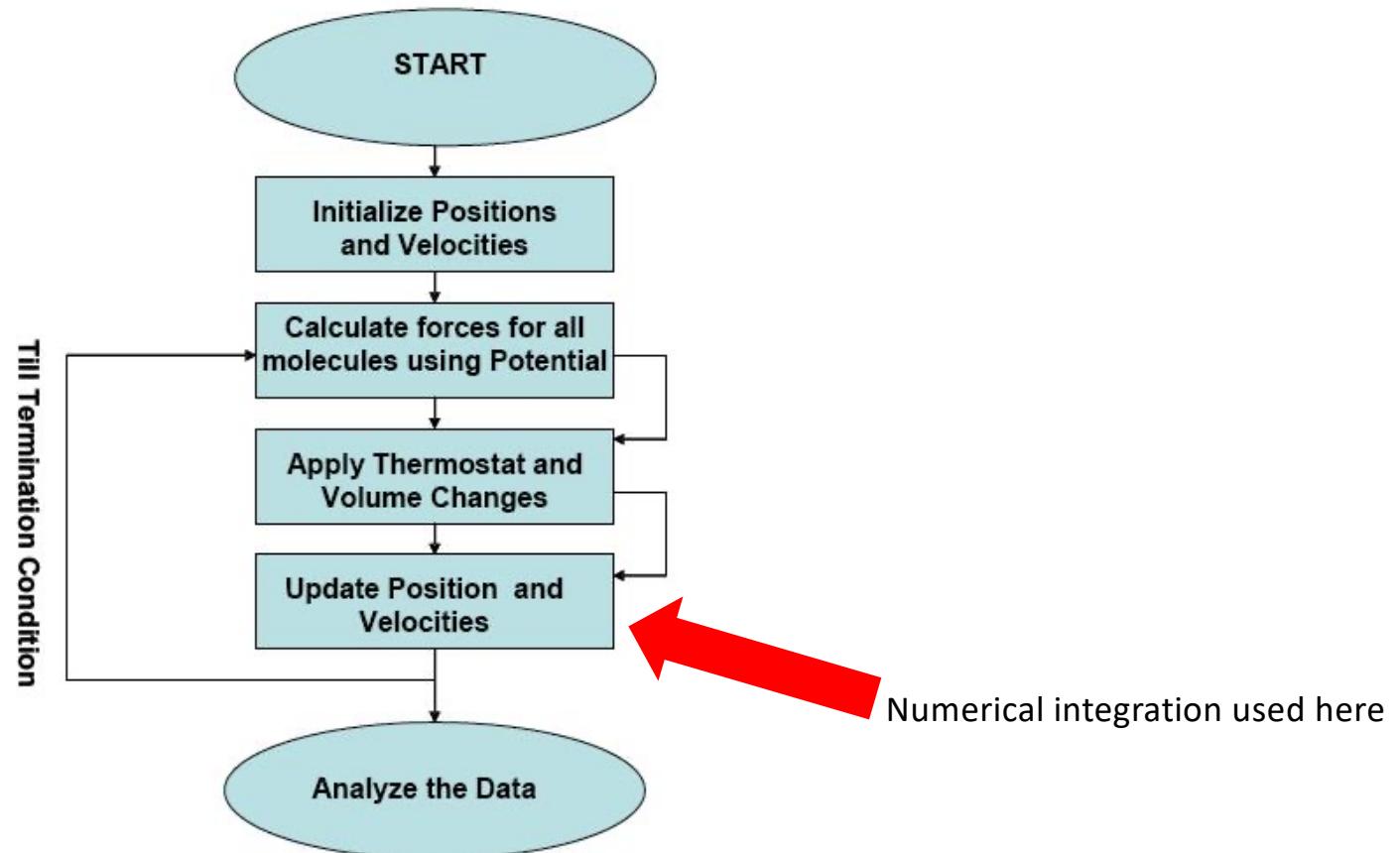
- This is a system of ordinary differential equations
 - For n atoms, we have $3n$ position coordinates and $3n$ velocity coordinates
- “Analytical” (algebraic) solution is impossible
- Numerical solution is straightforward

$$v_{i+1} = v_i + \delta_t F(x_i)/m$$

$$x_{i+1} = x_i + \delta_t v_i$$

- where δ_t is the time step

MD Flow Chart



Newton's Equations of Motion in MD

- Forces obtained from potential energy description of interparticle interactions
 - Itself a summation over all (interacting) pairs of particles
- Sum over N particles in system, calculate force, adjust q_i and p_i
 - Using i as index for particles on this slide only, not generalized coordinates of which there are 3N
- Dot notation for time derivatives

$$\sum_i^N \mathbf{F}_i = -\nabla V_i = m_i \ddot{\mathbf{q}}_i$$

Hamiltonian Formulation

- For i generalized coordinates, q , and corresponding momenta, p

$$\mathcal{H} = T + V$$

$$\frac{\partial q_i}{\partial t} = \dot{q}_i = \frac{\partial \mathcal{H}}{\partial p_i}$$

$$\frac{\partial p_i}{\partial t} = \dot{p}_i = -\frac{\partial \mathcal{H}}{\partial q_i}$$

- Results applicable to high dimensionality ($3N$), but derivation for low dimensionality in this talk for clarity

Trajectories in Phase Space

- Can consider points in phase space, \mathbf{z} , as trajectories
- Defined by values for all p and q
- Trajectory uniquely described by point in phase space!

$$\mathbf{v} = \dot{\mathbf{z}} = (\dot{q}, \dot{p}) = \left(\frac{\partial \mathcal{H}}{\partial p}, -\frac{\partial \mathcal{H}}{\partial q} \right)$$

Numerical Integration Schemes

- How to propagate the trajectory* defined by the set of q_i and p_i in time?
- Given that we know

$$q_i, \dot{q}_i, \ddot{q}_i \text{ and } m_i$$

for all i at time t_0 .

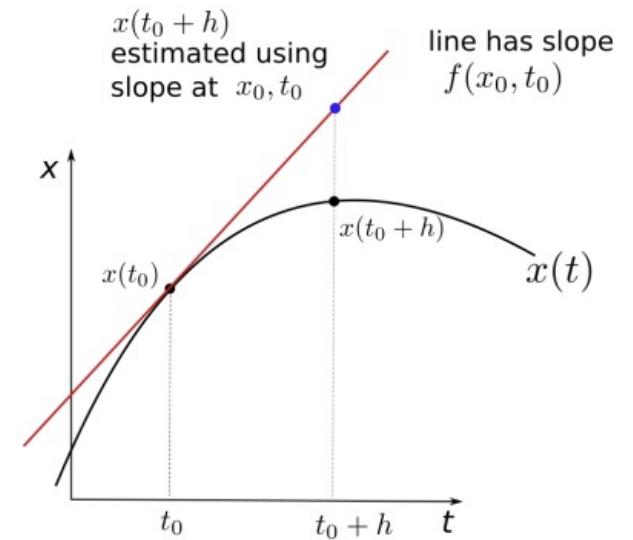
*estimation of “true” trajectory, even if interparticle potentials are exact

Euler's Method

- Obvious approach: use truncated Taylor expansion to get new q for $t=t_0+h$
- This is second order Euler:

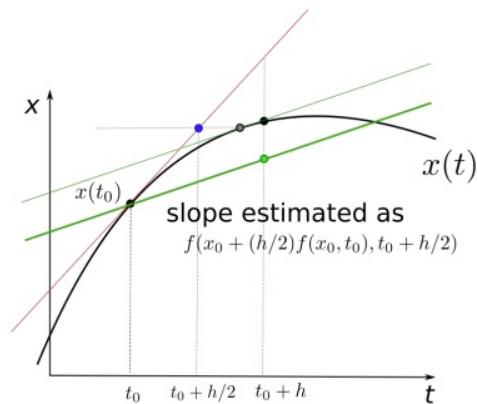
$$q(t_0 + h) = q(t_0) + h\dot{q}(t_0) + \frac{1}{2}h^2\ddot{q}(t_0),$$

$$\dot{q}(t_0 + h) = \dot{q}(t_0) + h\frac{\ddot{q}(t_0 + h) + \ddot{q}(t_0)}{2}.$$



Runge-Kutta Methods

- More accurate estimation than Euler's method using midpoint(s) of interval h
- Expandable to different orders (more midpoint estimates, which can be weighted differently)



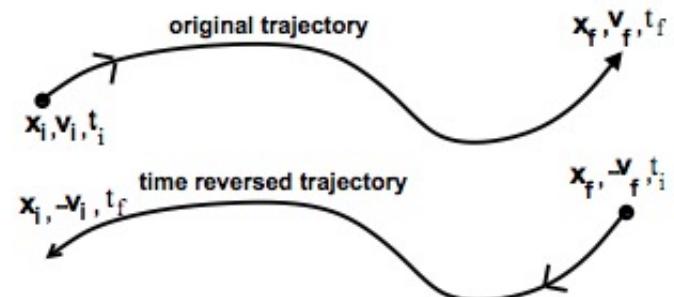
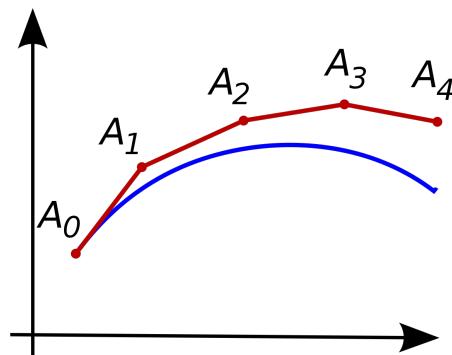
$$q(t_0 + h) = q(t_0) + \frac{k_1 + k_2}{2} h$$

$$k_1 = \dot{q}_i(t_0)$$

$$k_2 = \dot{q}_i(t_0 + h)$$

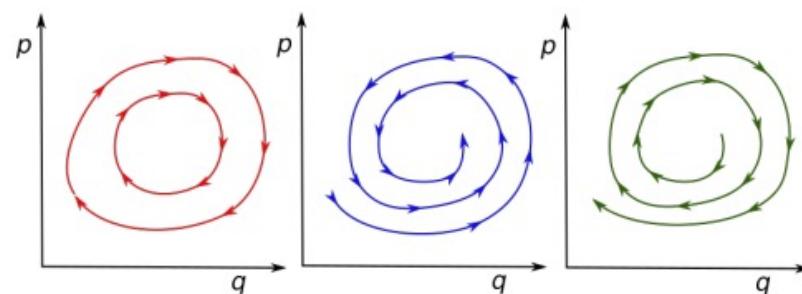
Time Reversibility

- An integration algorithm is not necessarily time reversible
 - Does not contain that symmetry inherent in Newton's equations of motion



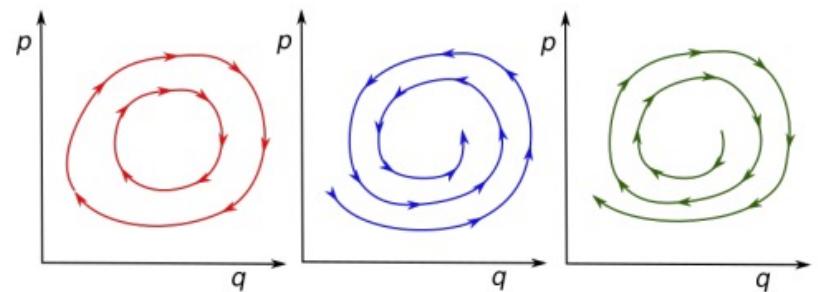
Integrators and Energy Conservation

- The real problem with non-time reversible methods is that they don't conserve the Hamiltonian
- Short term and long term energy conservation (accuracy)... not the same
 - MD relies on long-term accuracy to estimate an ensemble with ergodicity



Importance for Molecular Dynamics

- Changes to phase space volume of system results in long-term energy drift of that system... the Hamiltonian is not conserved
 - Problem for systems with long time evolution
- For classical Hamiltonian mechanics, density of trajectories in phase space is constant (Liouville's theorem)
 - For a time-independent Hamiltonian and conservative forces
 - This applies to description of energy in NVE ensemble molecular dynamics simulations



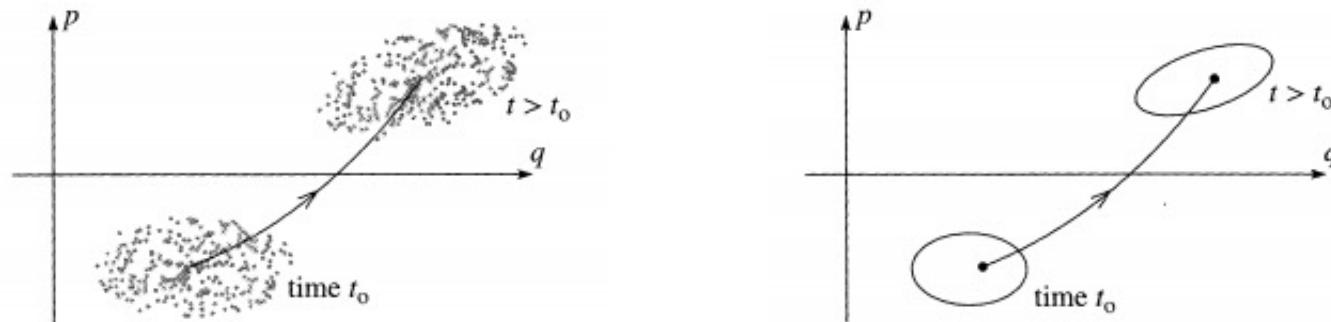
Liouville's Theorem

- Density of trajectories in phase space is constant for NVE molecular dynamics
- Essential to ensure energy conservation
- Derivation to follow!

Time Evolution of Trajectories

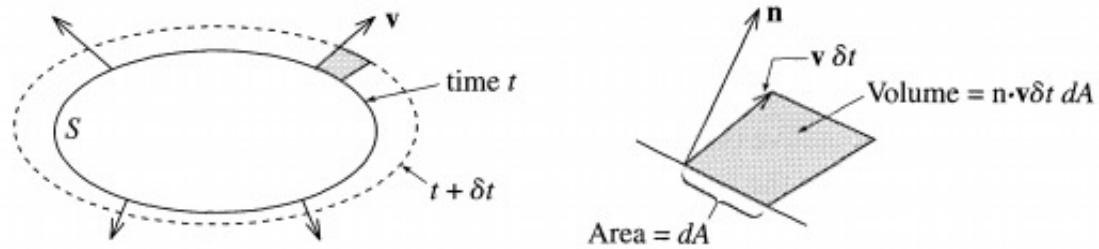
- Time evolution of trajectories near each other in phase space and the evolution of their enclosing hypervolume in time

$$\mathbf{v} = \dot{\mathbf{z}} = (\dot{q}, \dot{p}) = \left(\frac{\partial \mathcal{H}}{\partial p}, -\frac{\partial \mathcal{H}}{\partial q} \right)$$



Time Evolution of Trajectory Volume

- Change in phase space volume* during progression in time

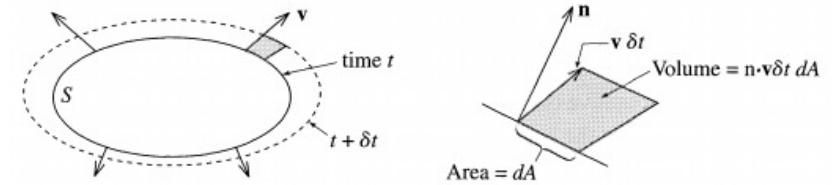


$$\delta V = \int_S \mathbf{n} \cdot \mathbf{v} \, \delta t \, dA$$

$$\frac{dV}{dt} = \int_S \mathbf{n} \cdot \mathbf{v} \, dA$$

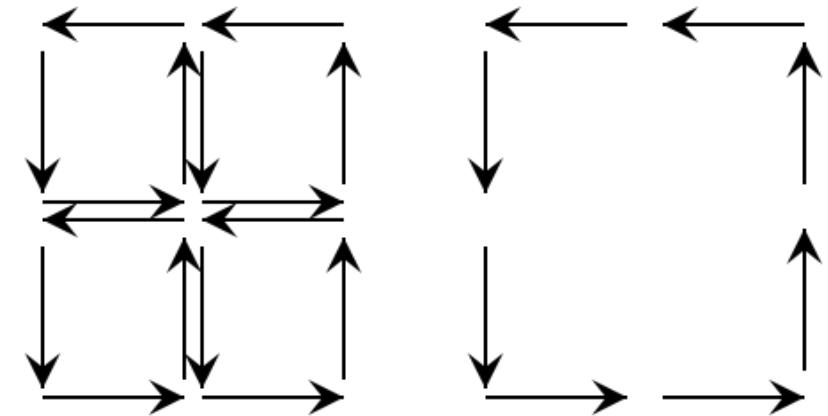
*works for arbitrary coordinate dimensionality

Divergence Theorem

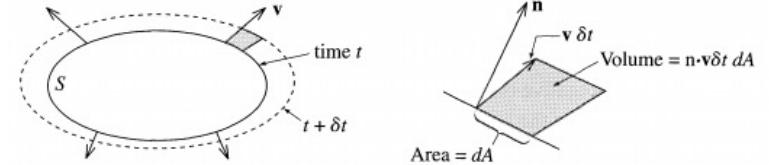


- Divergence: sum of diagonal elements of the Jacobian of a vector
- Surface integral transformed into volume integral

$$\frac{dV}{dt} = \int_S \mathbf{n} \cdot \mathbf{v} dA = \int_V \nabla \cdot \mathbf{v} dV$$



Small Volume Approximation



$$\frac{dV}{dt} = \int_S \mathbf{n} \cdot \mathbf{v} \, dA = \int_V \nabla \cdot \mathbf{v} \, dV$$

- If V is small enough that the divergence of \mathbf{v} is constant throughout V

$$\nabla \cdot \mathbf{v} = \frac{1}{V} \frac{dV}{dt}$$

- Outward flow of trajectories per volume

Liouville's Theorem

$$\nabla \cdot \mathbf{v} = \frac{1}{V} \frac{dV}{dt}$$

- Change in volume* of trajectories (and therefore density) is zero!
- “Incompressible flow”

$$\mathbf{v} = \dot{\mathbf{z}} = (\dot{q}, \dot{p}) = \left(\frac{\partial \mathcal{H}}{\partial p}, -\frac{\partial \mathcal{H}}{\partial q} \right)$$

$$\begin{aligned}\nabla \cdot \mathbf{v} &= \frac{\partial \dot{q}}{\partial q} + \frac{\partial \dot{p}}{\partial p} = \frac{\partial}{\partial q} \left(\frac{\partial \mathcal{H}}{\partial p} \right) - \frac{\partial}{\partial p} \left(\frac{\partial \mathcal{H}}{\partial q} \right) \\ &\therefore \frac{dV}{dt} = 0\end{aligned}$$

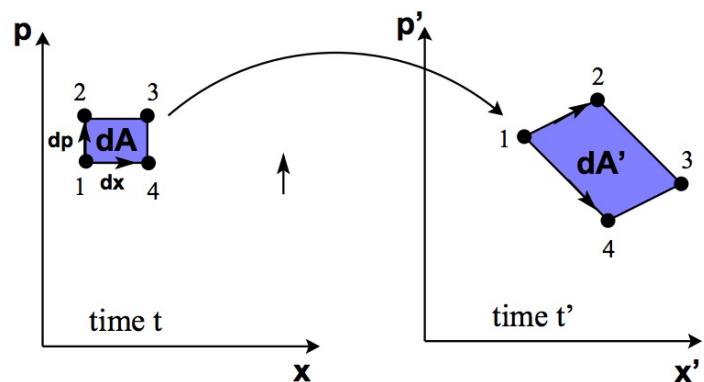
*although not shape

Transformations and Symplecticity

- Application to coordinate and momenta transformations... as in integrators
- Is a condition which, among other properties, describes a canonical transformation in phase space which is area-preserving... which propagation of true NVE trajectories is!
- Now providing mathematical description of the symplectic condition

Canonical Transformations

- Canonical transformation of p and q in phase space into P and Q preserves equations of motion and is therefore area preserving (from Liouville's theorem)
- A transformation is canonical if the Jacobian matrix of the transformation satisfies the symplectic condition



$$Q = Q(p, q)$$
$$P = P(q, p)$$
$$\mathbf{M} \boldsymbol{\omega} \tilde{\mathbf{M}} = \boldsymbol{\omega}$$

Symplectic Condition

- Preservation of equations of motion

$$\mathbf{v} = \dot{\mathbf{z}} = (\dot{q}, \dot{p}) = \left(\frac{\partial \mathcal{H}}{\partial p}, -\frac{\partial \mathcal{H}}{\partial q} \right)$$

$$\dot{\eta} = \begin{bmatrix} \dot{\mathbf{q}} \\ \dot{\mathbf{p}} \end{bmatrix} = \begin{bmatrix} 0 & I \\ -I & 0 \end{bmatrix} \begin{bmatrix} \frac{\partial \mathcal{H}}{\partial \mathbf{q}} \\ \frac{\partial \mathcal{H}}{\partial \mathbf{p}} \end{bmatrix} = \omega \frac{\partial \mathcal{H}}{\partial \eta}$$

Symplectic Condition

- Coordinate transformation and transformed equations of motion

$$Q = Q(p, q)$$

$$P = P(q, p)$$

$$\dot{\xi} = \begin{bmatrix} \dot{\mathbf{Q}} \\ \dot{\mathbf{P}} \end{bmatrix}$$

$$\dot{\xi} = \mathbf{M}\dot{\eta}$$

- Jacobian of transformation matrix, \mathbf{M}

$$M_{ij} = \frac{\partial \xi_i}{\partial \eta_j}$$

Symplectic Condition

$$M_{ij} = \frac{\partial \xi_i}{\partial \eta_j}$$

- If new coordinates ξ have canonical form, \mathbf{M} will satisfy symplectic condition

$$\dot{\xi} = \mathbf{M}\dot{\eta}$$

$$\dot{\eta} = \omega \frac{\partial \mathcal{H}}{\partial \eta}, \quad \dot{\xi} = \omega \frac{\partial \mathcal{H}}{\partial \xi}$$

$$\dot{\xi} = \mathbf{M}\omega \frac{\partial \mathcal{H}}{\partial \eta}$$

$$\frac{\partial \mathcal{H}}{\partial \eta} = \tilde{\mathbf{M}} \frac{\partial \mathcal{H}}{\partial \xi}$$

$$\dot{\xi} = \mathbf{M}\omega \tilde{\mathbf{M}} \frac{\partial \mathcal{H}}{\partial \xi}$$

$$\omega = \mathbf{M}\omega \tilde{\mathbf{M}}$$

Time Evolution is Symplectic

- We showed this earlier, it can also be resolved with the symplectic criterion just defined

$$\mathbf{M}\omega\tilde{\mathbf{M}} = \left(\mathbf{I} + \delta t\omega \frac{\partial^2 \mathcal{H}}{\partial \eta \partial \eta}\right)\omega\left(\mathbf{I} - \delta t\omega \frac{\partial^2 \mathcal{H}}{\partial \eta \partial \eta}\right)$$
$$\mathbf{M}\omega\tilde{\mathbf{M}} \approx \omega$$

- For sufficiently small δt

Symplectic Integrators

- If actual time evolution of a trajectory is symplectic, a time-evolving numerical integrator should be symplectic as well to preserve this feature of the transformation
- Area of phase space between coordinates differs by factor of $\det \omega$, which must be unity for symplectic integrator to preserve area
- This is true for Verlet propagation

Verlet Algorithm

- Order three derivatives cancel, error in order 4

$$q(t_0 + h) = q(t_0) + \dot{q}(t_0)h + \ddot{q}(t_0)\frac{h^2}{2} + \dddot{q}(t_0)\frac{h^3}{3!} + \dots$$

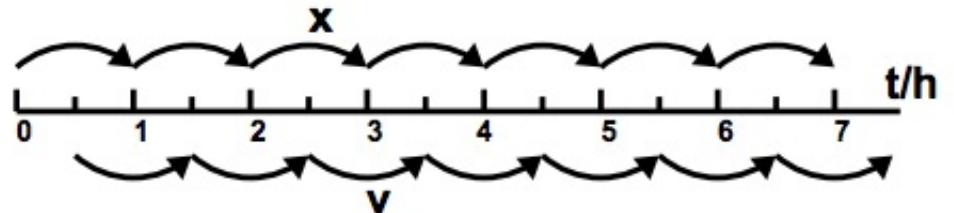
$$q(t_0 - h) = q(t_0) - \dot{q}(t_0)h + \ddot{q}(t_0)\frac{h^2}{2} - \dddot{q}(t_0)\frac{h^3}{3!} + \dots$$

$$q(t_0 + h) = 2q(t_0) - q(t_0 - h) + \ddot{q}(t_0)h^2$$

- Velocities not used! Calculated separately from change in position.

Leap-Frog Verlet Algorithm

- Variant of Verlet which is more efficient to implement, velocities and positions not computed for the same time step at the same time

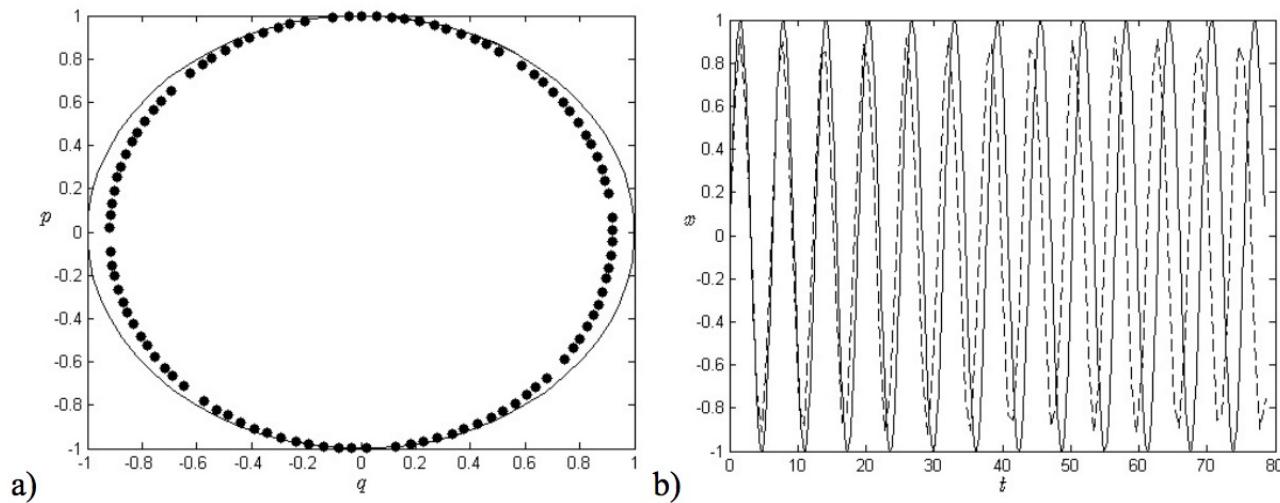


$$\dot{q}(t_0 + \frac{h}{2}) = \dot{q}(t_0 - \frac{h}{2}) + \ddot{q}(t_0)h$$

$$q(t_0 + h) = q(t_0) + \dot{q}(t_0 + \frac{h}{2})h$$

Well... Pseudo-Hamiltonian

- Simulation trajectory follows actual trajectory closely
- Conserved pseudo-Hamiltonian slightly different than actual Hamiltonian



Notes on Accuracy

- Truncation error from using computer unavoidable
- Possible to implement higher accuracy
 - Symplectic Runge-Kutta
 - Predictor-corrector schemes
- Generally better served by decreasing h
- Actually trying to statistically generate ensemble of configurations for given NVE macrostate
 - Propagating the “true” trajectory not necessary for MD
 - Is necessary for other applications!

Conclusions

- Propagation of Newton's equations of motion for molecular dynamics requires care: stepwise accuracy is not sufficient
- The property that phase space density for time evolution canonical transformations is called symplecticity... and is required for good MD integrators
- Accurate MD integrators should satisfy the symplectic condition