

Molecular Dynamics

Day 1

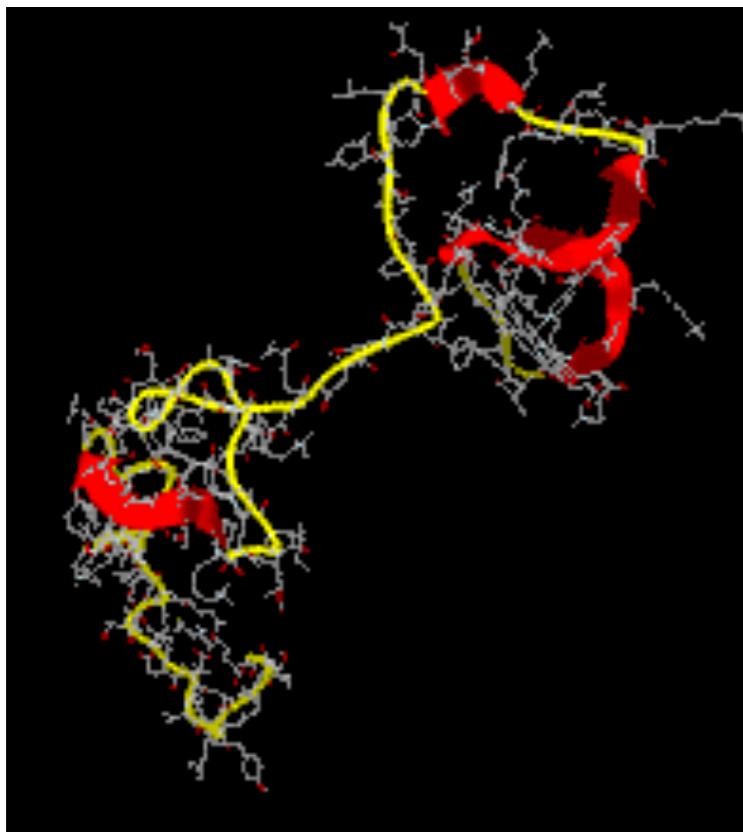
Ben Leimkuhler

**models, goals and purposes,
equations of motion,
deterministic numerical
methods by splitting**

Peking 2018

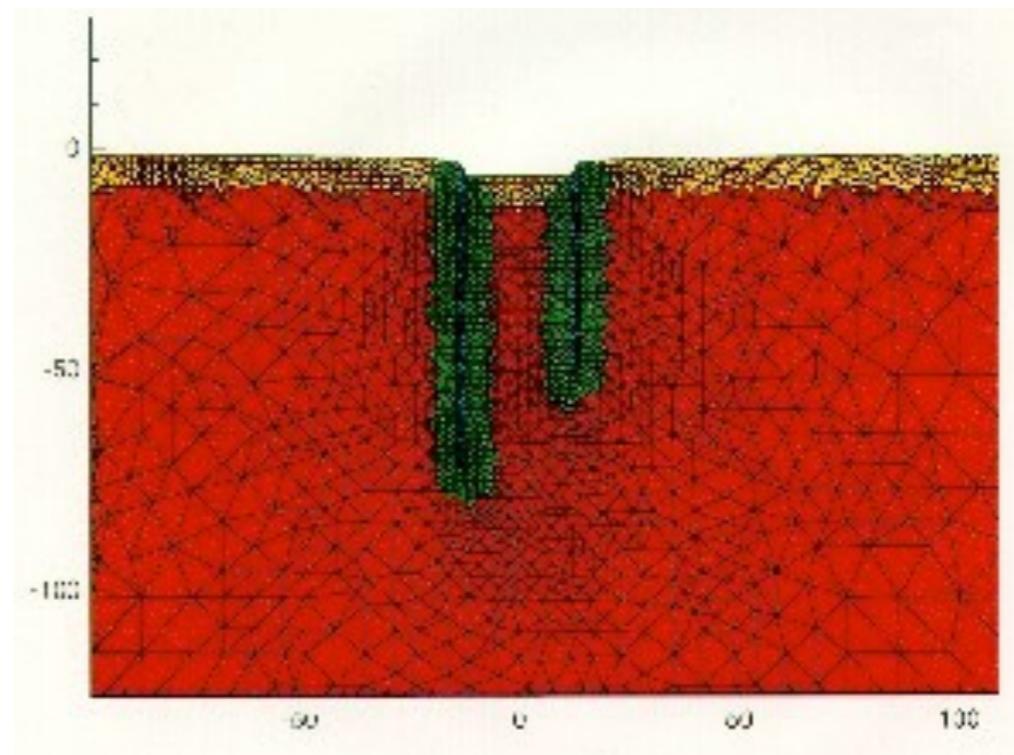
Molecular Dynamics (MD)

cytochrome C folding: Elber and Cardenas

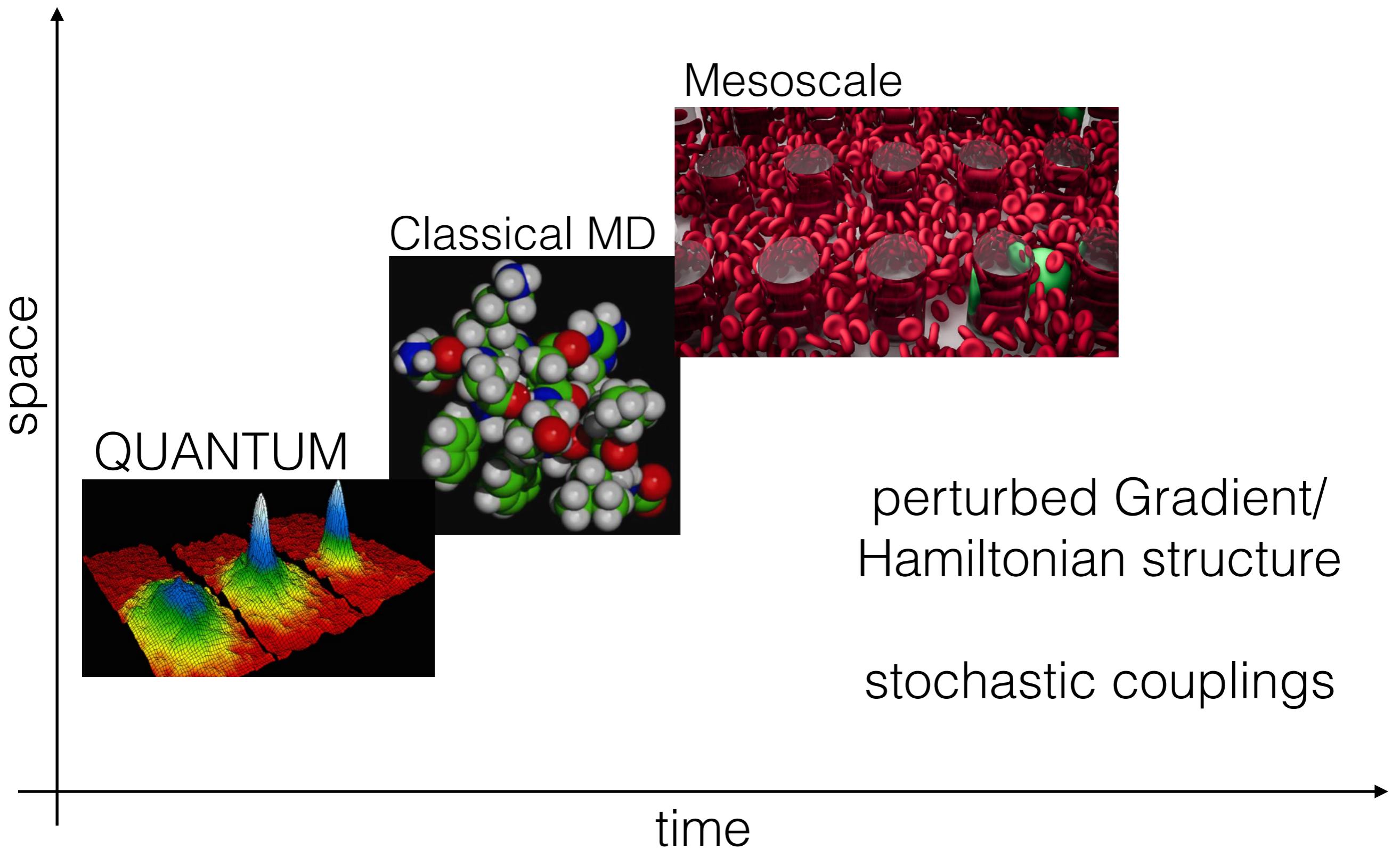


Biomolecules

Materials



Quasi-continuum method: molecular dynamics
with coarse-graining for indentation studies.
Ortiz, Phillips and Tadmor

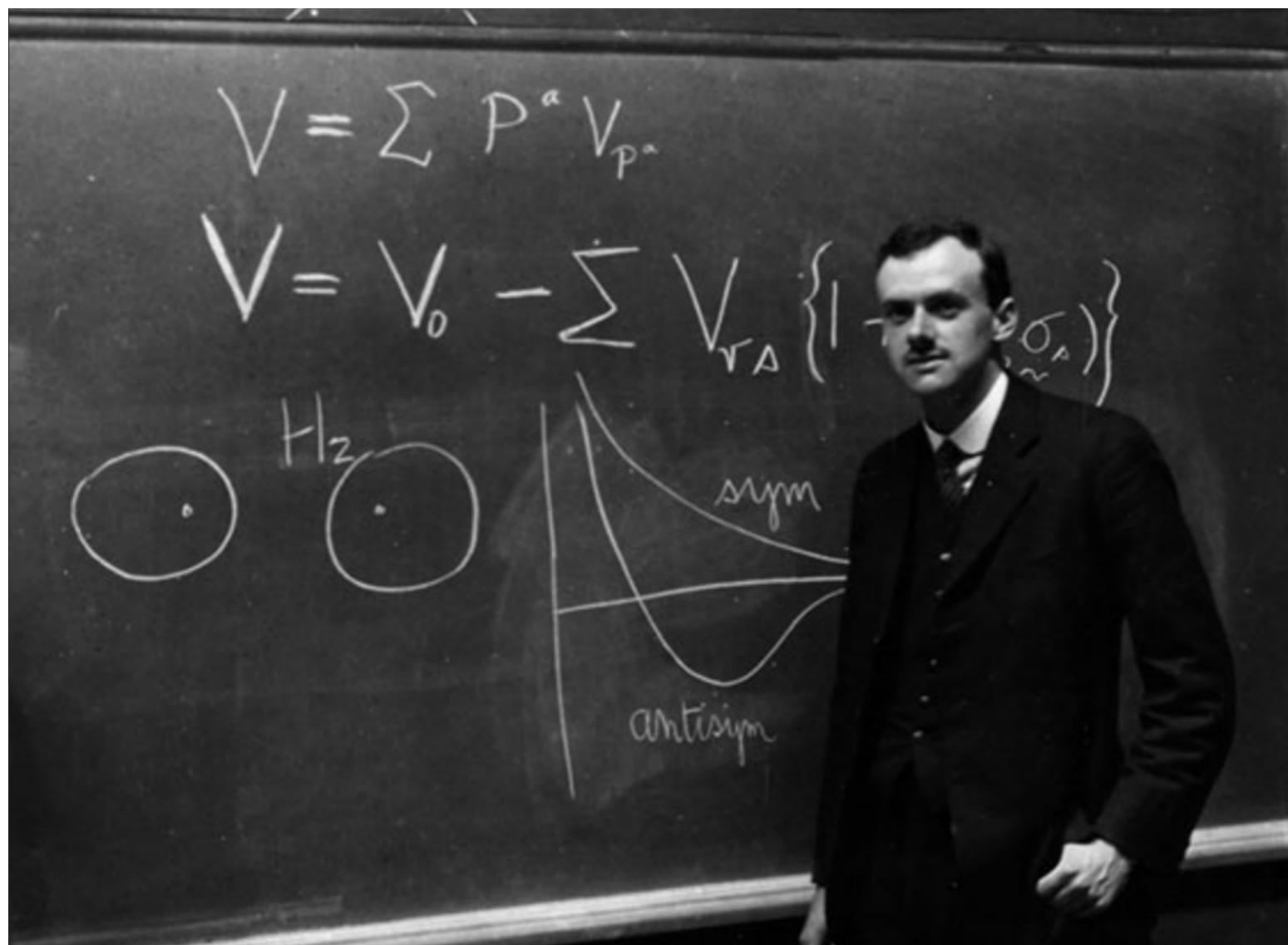


How is MD Used?

1. **Thermodynamic sampling** of all-atom models (classical, Born-Oppenheimer, QM/MM) for biology, chemistry, physics, materials science
2. **Nonequilibrium MD** modelling (tribology, complex liquids, applied fields, ...)
3. **Coarse-grained models** - mesoscale (polymers, colloidal systems...)
4. In conjunction **with continuum** (solid/fluid) models (nanomechanics)
....
5. and, increasingly, as a starting point in “non-molecular” **statistical modelling**, e.g. for “big data” applications.

Classical MD

Quantum Mechanics

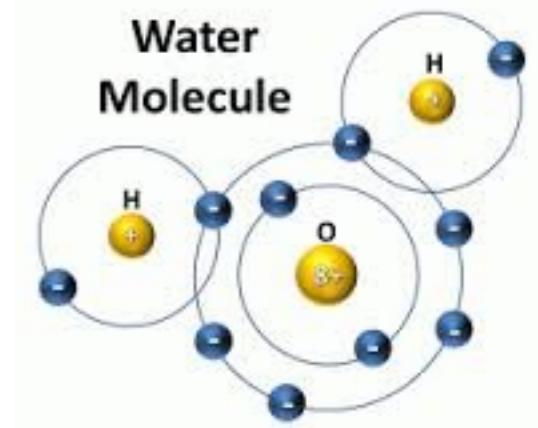
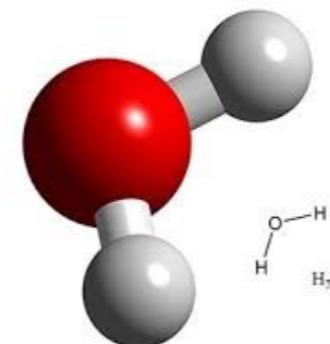


The underlying physical laws necessary for the mathematical theory of the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble

- Paul Dirac

Schrödinger Equation

For a water molecule (H_2O)



$$i\hbar \frac{\partial \Phi}{\partial t} = -\hbar^2 \sum_{j=1}^{13} \frac{1}{2\mu_j} \left(\frac{\partial^2 \Phi}{\partial q_{j,x}^2} + \frac{\partial^2 \Phi}{\partial q_{j,y}^2} + \frac{\partial^2 \Phi}{\partial q_{j,z}^2} \right) + U_{\text{P}}(q_{1,x}, q_{1,y}, \dots, q_{13,z}) \Phi.$$

- A PDE in 39 space dimensions + time
- Intractable by any direct dynamics methods

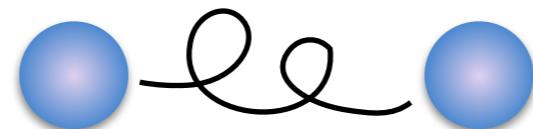
Born-Oppenheimer Approximation

$$m_e = \frac{1}{1840} m_{p,n}$$

Electronic degrees of freedom relax rapidly after movement of the nuclei.

Two nuclei feel an effective force which is defined by the relaxed electronic structure.

Allows to decouple nuclear and electronic degrees of freedom.



We can think of the nuclei as moving on the Born-Oppenheimer energy surface (as long as it is valid!)

no excited states, bond-breaking, etc...

Empirical Approximation

For our water molecule, even if we fix the nuclei, we still have a **huge QM system** (30 space dimensions) to solve for the electrons.

In the empirical approximation (the basis for perhaps 98% of molecular dynamics) the whole QM perspective is thrown away with the electrons...

Instead, just **design a classical potential** for the nuclear interaction of the form

$$U = U_1 + U_2 + \dots$$

The different terms are meant to represent various physical properties of realistic interactions.

Why?

By doing this, we can model the system using **Newton's equations**. For our water molecule:

$$m_O \ddot{q}_O = F_O(q_O, q_{H1}, q_{H2})$$

$$m_H \ddot{q}_{H1} = F_{H1}(q_O, q_{H1}, q_{H2})$$

$$m_H \ddot{q}_{H2} = F_{H2}(q_O, q_{H1}, q_{H2})$$

$$\mathbf{F} = -\nabla U$$

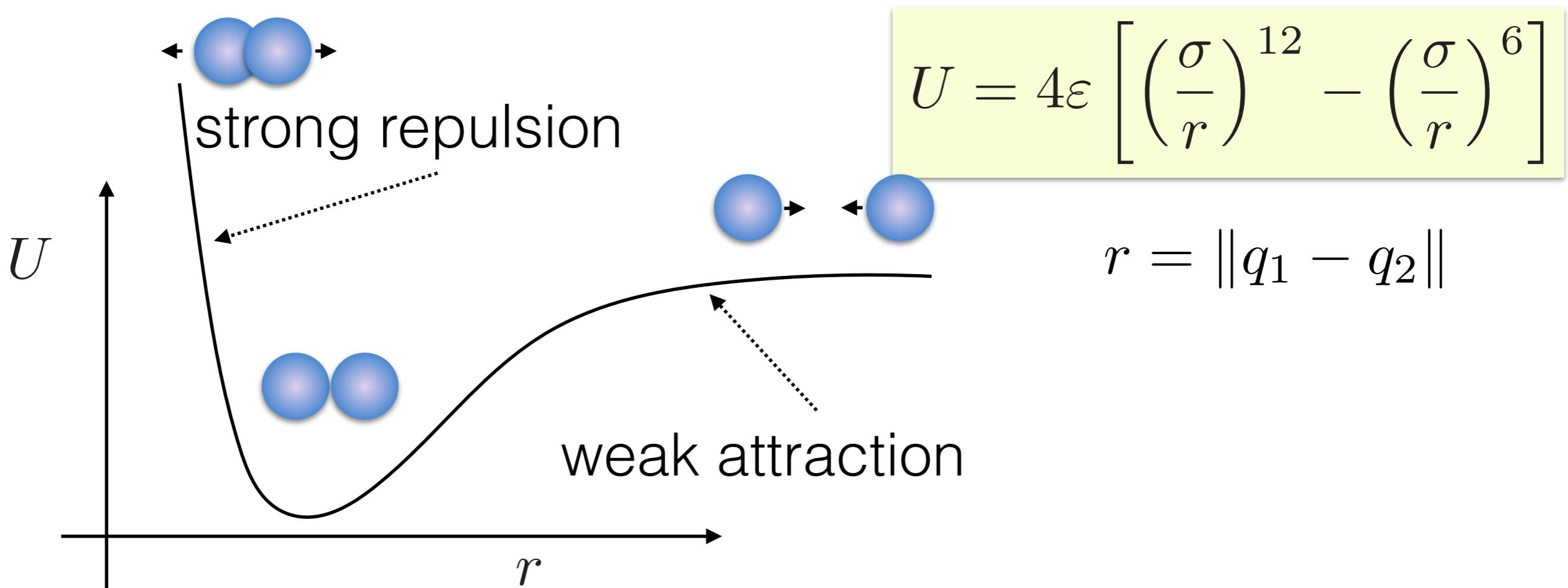
- ODEs *not* PDEs
- *Much easier to solve numerically*

Examples of MD Problems

What sorts of potentials U ?

There is a limitless variety of different potentials or potential terms. Some specific motifs are very common.

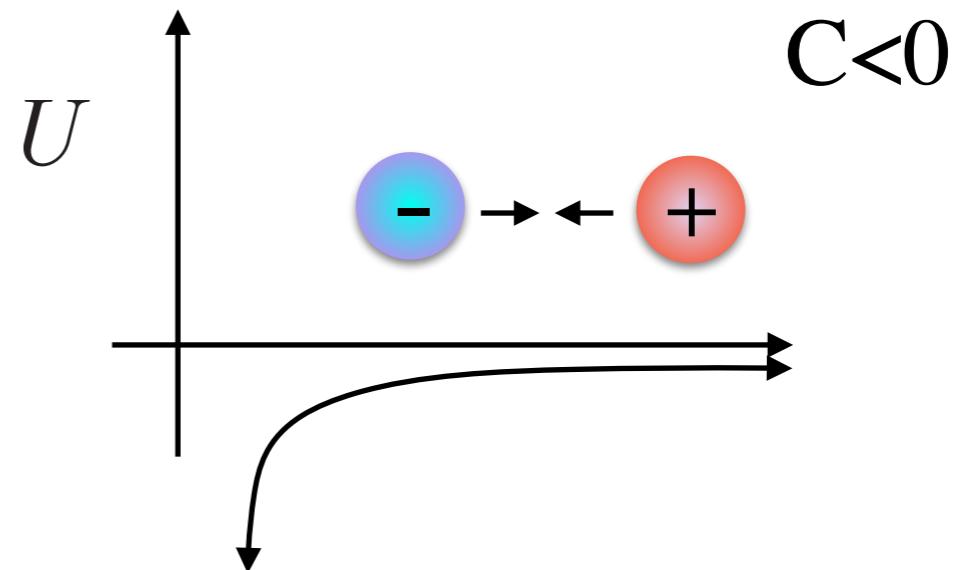
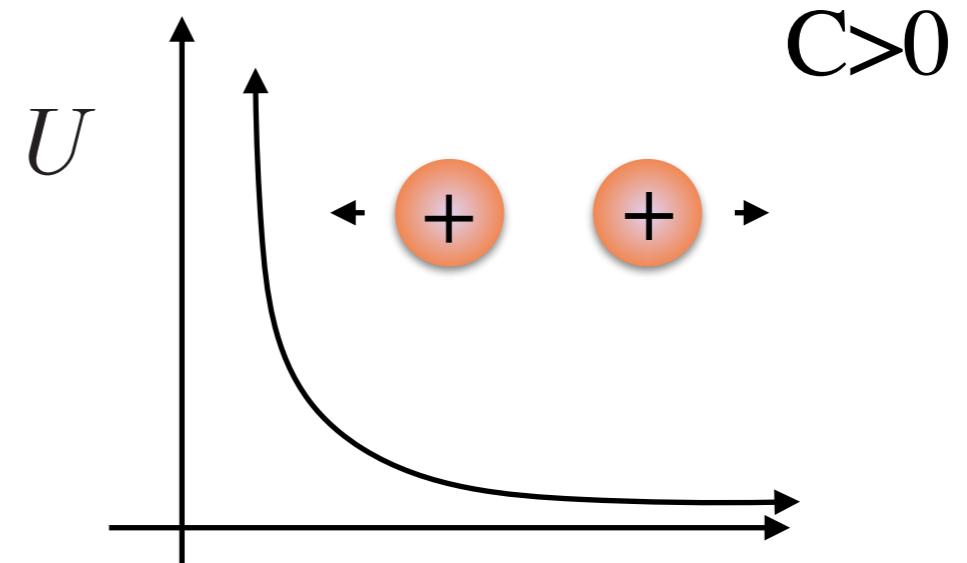
1. Morse or Buckingham or Lennard-Jones potentials to model short ranged interactions of charge clouds.



2.Coulombic potentials (repulsive or attractive)

$$U = \frac{C}{r}$$

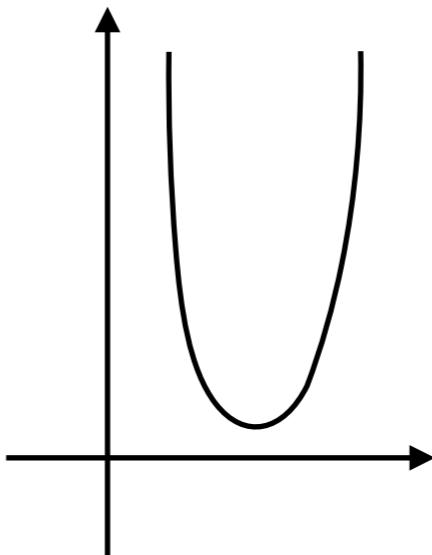
$$r = \|q_1 - q_2\|$$



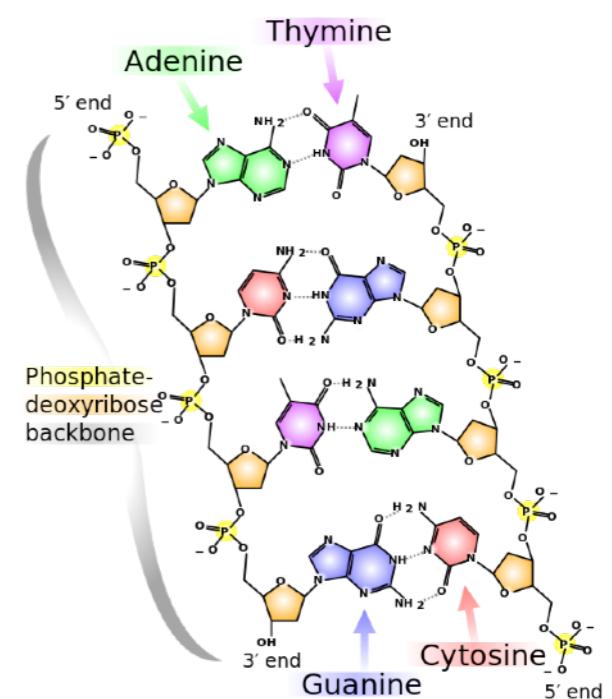
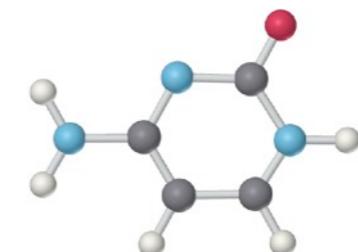
3. Harmonic Bonds

$$U = \frac{k_b}{2} (r - r_0)^2$$

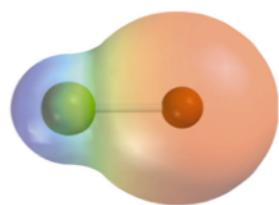
$$r = \|q_1 - q_2\|$$



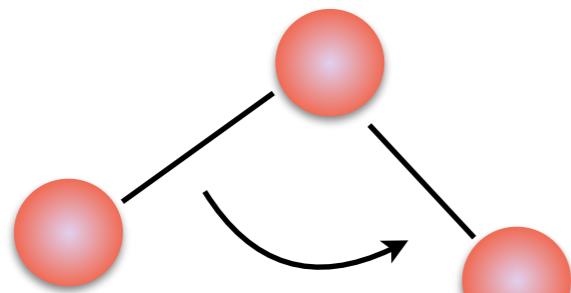
covalent bonds
in cytosine



ionic bond
 Na^+Cl^-

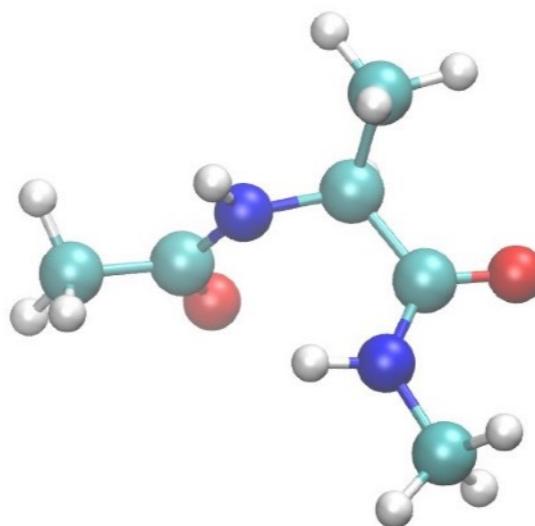
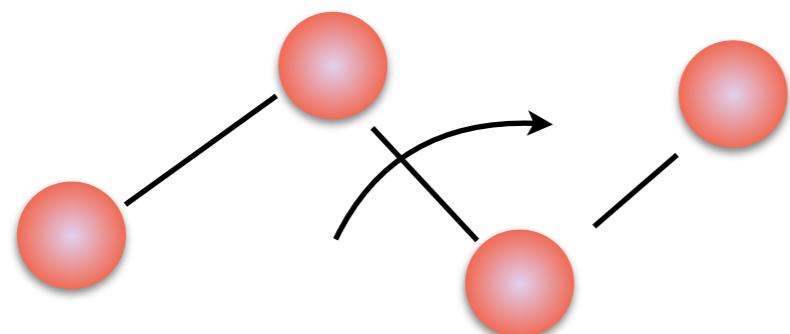


4.Angle and dihedral bonds

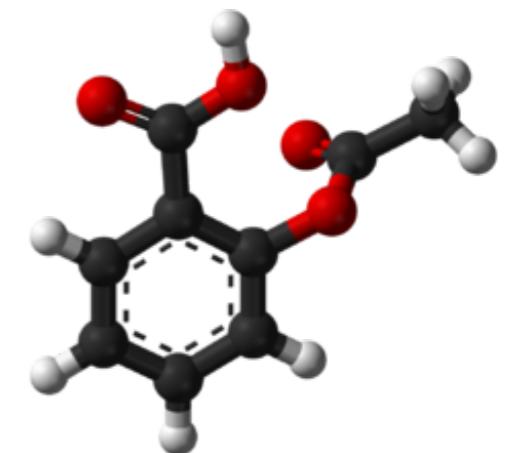


$$\frac{k_\theta}{2} (\theta(q_1, q_2, q_3) - \theta_0)^2$$

$$\theta = \arcsin \left(\frac{(q_1 - q_2) \cdot (q_3 - q_2)}{|q_1 - q_2| |q_3 - q_2|} \right)$$

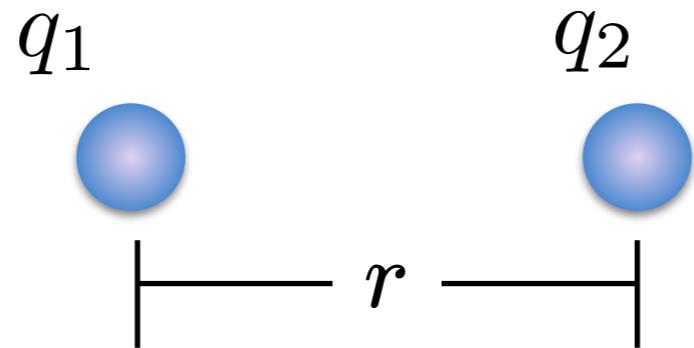


alanine dipeptide



aspirin

Computing Forces



$$U = U(r)$$

$$r = \|q_1 - q_2\|$$

$$q = \begin{bmatrix} q_1 \\ q_2 \end{bmatrix}$$

$$F = -\nabla_q U$$

$$F = -\frac{U'(\|q_1 - q_2\|)}{\|q_1 - q_2\|} \begin{bmatrix} q_1 - q_2 \\ q_2 - q_1 \end{bmatrix}$$

$$U = U_{\text{SR}} + U_{\text{Coulomb}} + U_{\text{lbonds}} + U_{\text{abonds}} + U_{\text{dbonds}}$$

SR: Short-ranged, often **steep potentials** (wall-like) between all pairs

Coulomb: Long-ranged, soft potentials active between all charged pairs of atoms. The **most costly part** of typical MD simulations.

Bonds: responsible for much of the **structure** of organic molecules and materials. Decomposed into **length**, **angle** and **dihedral** bonds.

More complicated potentials for specific applications, coarse-graining, quantum effects (e.g. polarization)

Equations of Motion

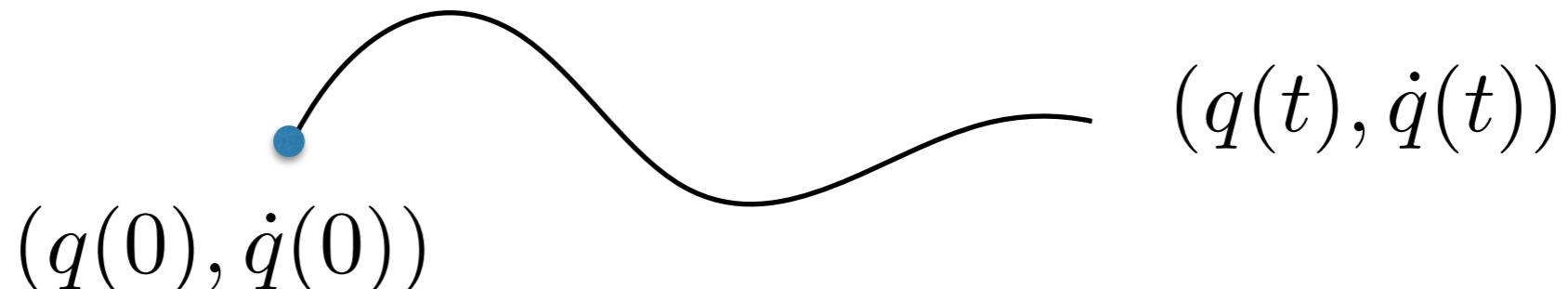
Newton's equations (2nd order ODE system)

$$M\ddot{q} = -\nabla U(q)$$

MASS x ACCELERATION

FORCE

Supplement by Initial Conditions to define trajectory



'1st Order' Forms

position-velocity

$$\dot{q} = v$$

$$M\dot{v} = -\nabla U(q)$$

position-momentum

$$\dot{q} = M^{-1}p$$

$$\dot{p} = -\nabla U(q)$$

HAMILTONIAN

Compactly:

$$\dot{z} = J \nabla H(z) \quad z = \begin{bmatrix} q \\ p \end{bmatrix}$$

$$H(z) = H([q, p]^T) = p^T M^{-1} p / 2 + U(q) \quad J = \begin{bmatrix} 0 & I \\ -I & 0 \end{bmatrix}$$

Conservation Laws

$$\dot{q} = M^{-1}p \quad \dot{p} = -\nabla U(q)$$

Energy conservation $H(q, p) = \frac{1}{2}p^T M^{-1}p + U(q)$

$$H(q, p) \equiv \text{constant}$$

Central forces: $V(q_1, q_2) = \phi(|q_1 - q_2|)$

Momentum $P = \sum_i p_i$

Angular Momentum $L = \sum_i q_i \times p_i$

Link Between Symmetries and Invariants

Under central forces, the total linear and angular momentum are conserved, i.e.

$$\dot{P} = 0 \quad \dot{L} = 0$$

It is possible to show that linear and angular momentum are also conserved for angle bonds

- a. directly, by time differentiation
- b. via **Noether's theorem**
symmetries (**translation, rotation**)

Conservation Laws

$$\dot{q} = M^{-1}p \quad \dot{p} = -\nabla U(q)$$

Momentum

$$P = \sum_i p_i$$

Central forces:

$$V(q_1, q_2) = \phi(|q_1 - q_2|)$$

$$\nabla_{q_1} V(q_1, q_2) = \frac{\phi'(|q_1 - q_2|)}{|q_1 - q_2|} (q_1 - q_2)$$

$$\nabla_{q_1} V(q_1, q_2) + \nabla_{q_2} V(q_1, q_2) = 0$$

$$\dot{P} = 0 \Rightarrow P \equiv \text{constant}$$

Angular Momentum

$$L = \sum_i q_i \times p_i$$

General Hamiltonian Systems

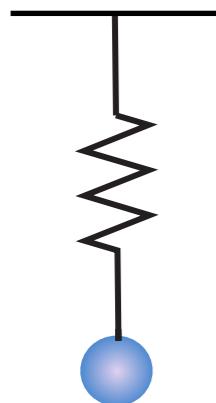
$$H(q_1, q_2, \dots, q_d, p_1, p_2, \dots, p_d)$$

$$\begin{aligned}\dot{q}_i &= +\frac{\partial H}{\partial p_i} & i = 1, 2, \dots, d \\ \dot{p}_i &= -\frac{\partial H}{\partial q_i}\end{aligned}$$

alternative: $\dot{z} = J \nabla H(z)$

$$z = \begin{bmatrix} q \\ p \end{bmatrix} \quad J = \begin{bmatrix} 0 & I \\ -I & 0 \end{bmatrix}$$

Examples: **Harmonic Oscillator**



$$\dot{q} = p$$

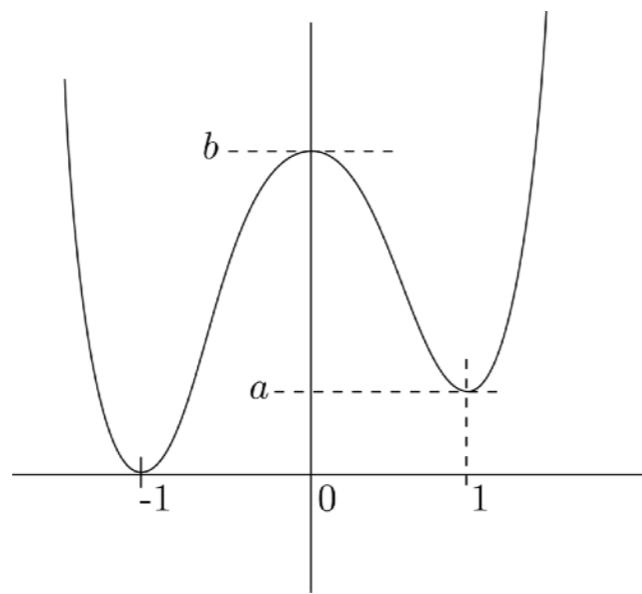
$$\dot{p} = -\omega^2 q$$

$$q(t) = A \cos(\omega t) + B \sin(\omega t)$$

$$= q(0) \cos(\omega t) + \omega^{-1} p(0) \sin(\omega t)$$

Double Well

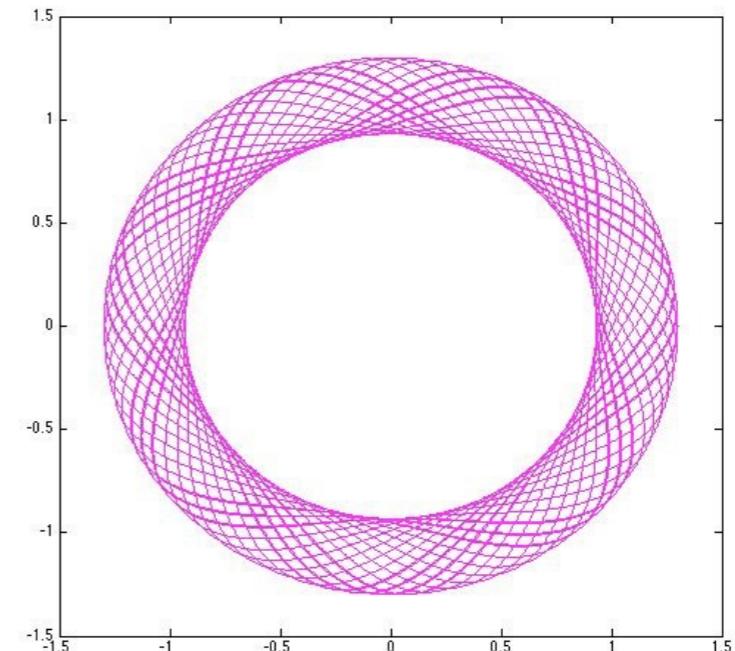
$$U(q) = (b - a/2)(q^2 - 1)^2 + (a/2)(q + 1)$$



2 dof Models

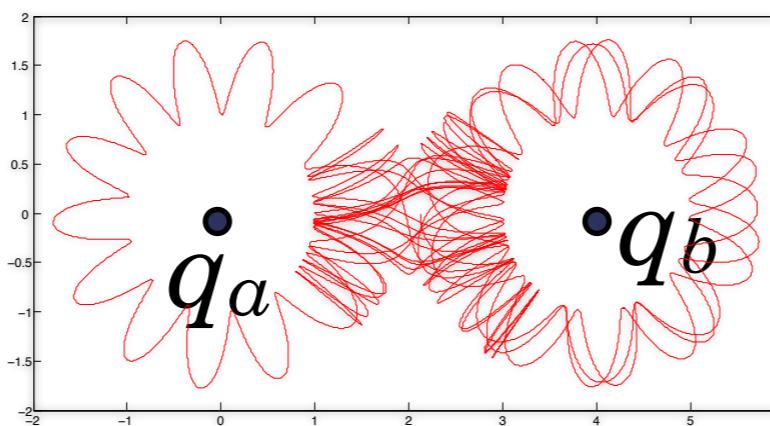
‘Soft’ Pendulum

$$H(q, p) = \frac{|p|^2}{2m} + \frac{k}{2}(|q| - L_0)^2$$



Two fixed centers

$$H = \frac{|p|^2}{2} + \phi_{\text{LJ}}(|q - q_a|) + \phi_{\text{LJ}}(|q - q_b|)$$

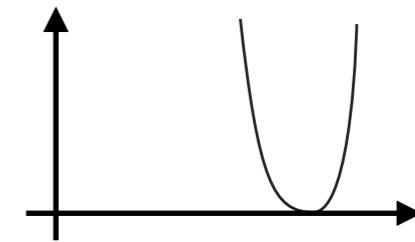
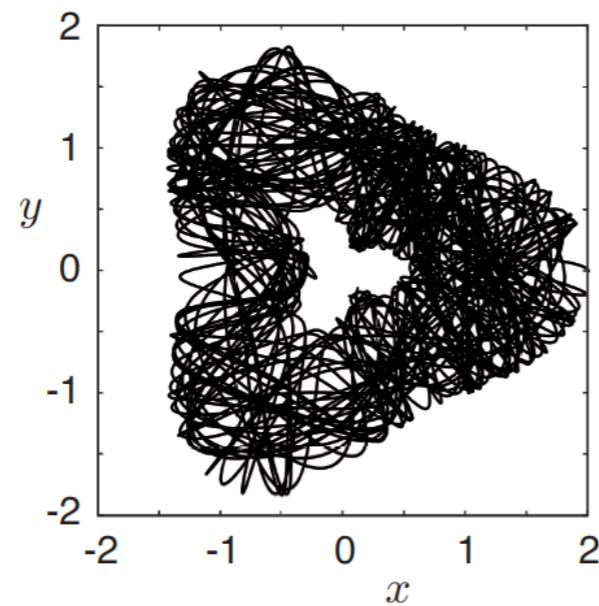
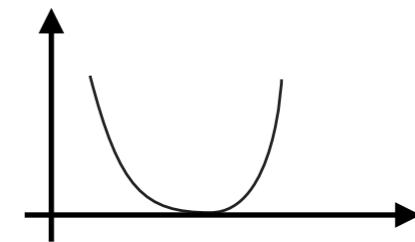


2D Anisotropic Oscillator

$$E(x, y, \dot{x}, \dot{y}) = \frac{1}{2}(\dot{x}^2 + \dot{y}^2) + \frac{\kappa(c_3)}{2}(r - l(c_3))^2$$

$$r = \sqrt{x^2 + y^2}, \quad c_3 = 4c^3 - 3c, \quad \cos \theta = c = \frac{x}{r}$$

$$\kappa(c_3) = \kappa_0(1 - \frac{1}{2}\varepsilon c_3), \quad l(c_3) = l_0(1 + \frac{1}{2}\varepsilon c_3)$$

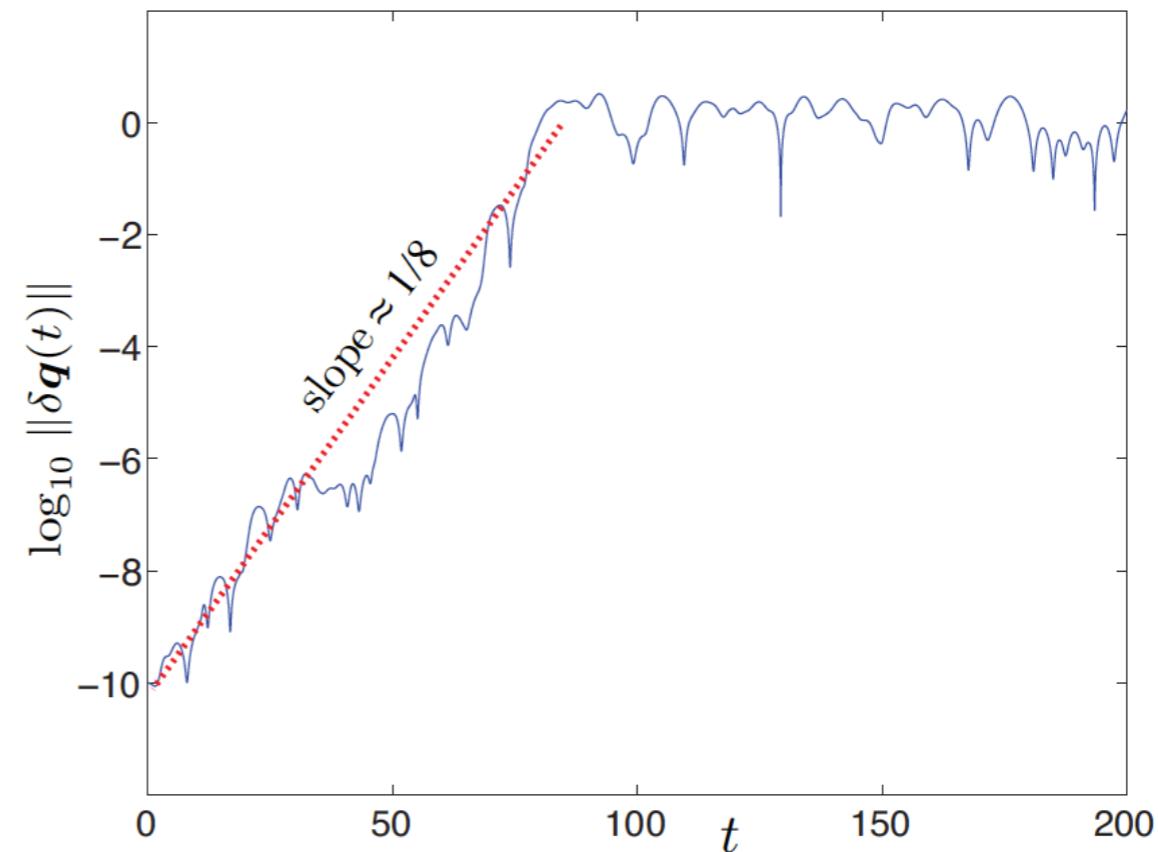
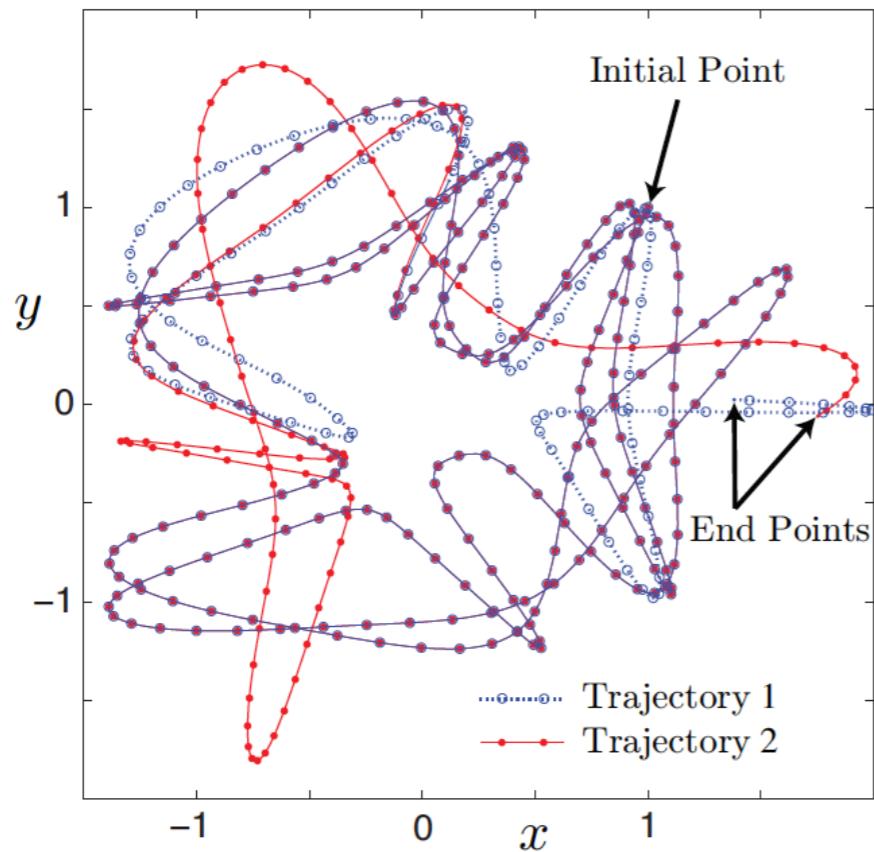


Chaotic Dynamics

1. sensitive dependence on initial conditions
2. topological transitivity (on an invariant set)

$$E(x, y, \dot{x}, \dot{y}) = \frac{1}{2}(\dot{x}^2 + \dot{y}^2) + \frac{\kappa(c_3)}{2}(r - l(c_3))^2 \quad r = \sqrt{x^2 + y^2}, \quad c_3 = 4c^3 - 3c, \quad \cos \theta = c = \frac{x}{r}$$

$$\kappa(c_3) = \kappa_0(1 - \frac{1}{2}\varepsilon c_3), \quad l(c_3) = l_0(1 + \frac{1}{2}\varepsilon c_3)$$



$$\frac{d}{dt} \mathbf{W}(t) = f'(\mathbf{z}(t, \zeta)) \mathbf{W}(t)$$

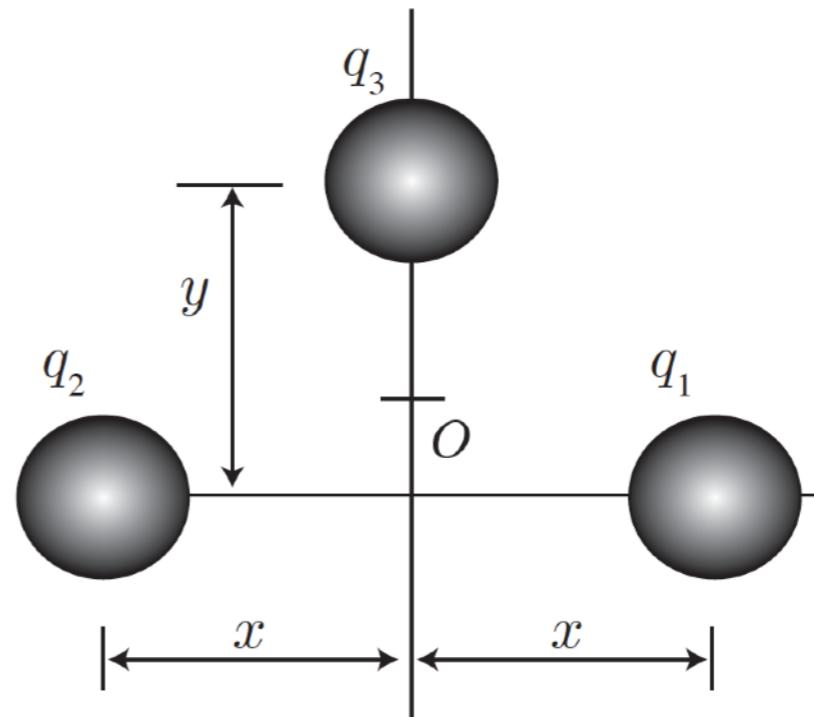
Lyapunov exponents

$$\lambda_i = \limsup_{t \rightarrow \infty} \frac{1}{t} \log \sigma_i(\mathbf{W})$$

Trimer

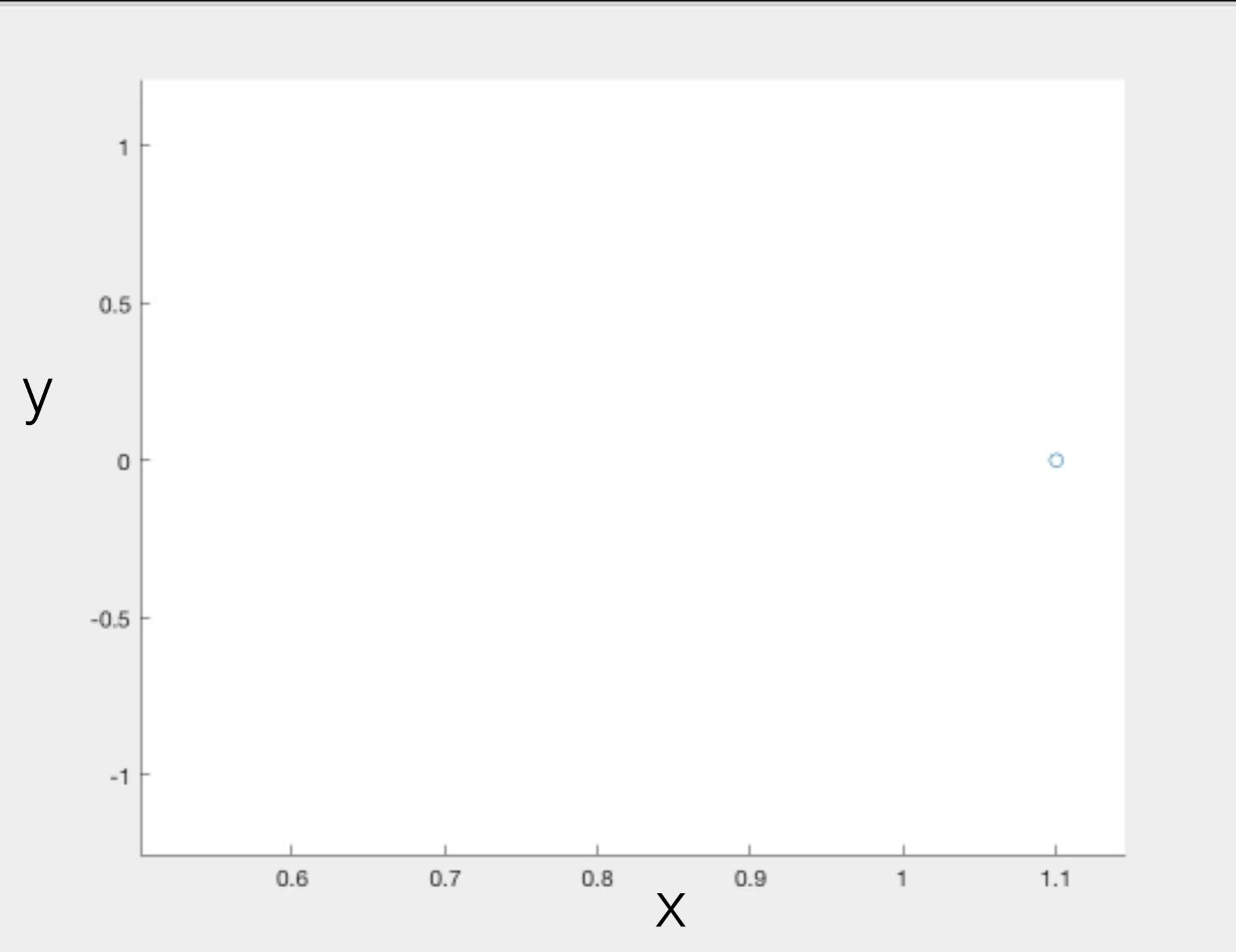
3 atoms moving in the plane
interactions governed
by Lennard-Jones
potentials

isosceles configuration



$$E = \dot{x}^2 + \frac{\dot{y}^2}{3} + 2\hat{\varphi}_{\text{LJ}}(\sqrt{x^2 + y^2}) + \hat{\varphi}_{\text{LJ}}(2x)$$

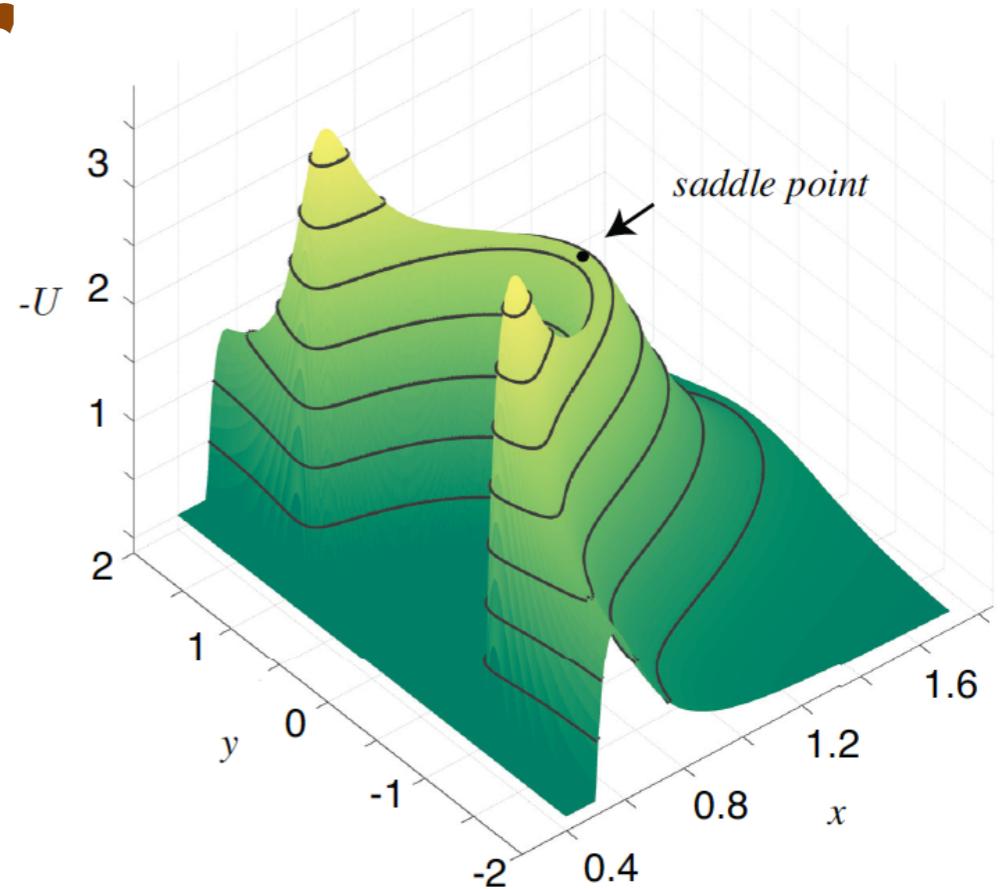
$$\hat{\varphi}_{\text{LJ}}(r) = r^{-12} - r^{-6}$$



Trimer

Negative Potential:

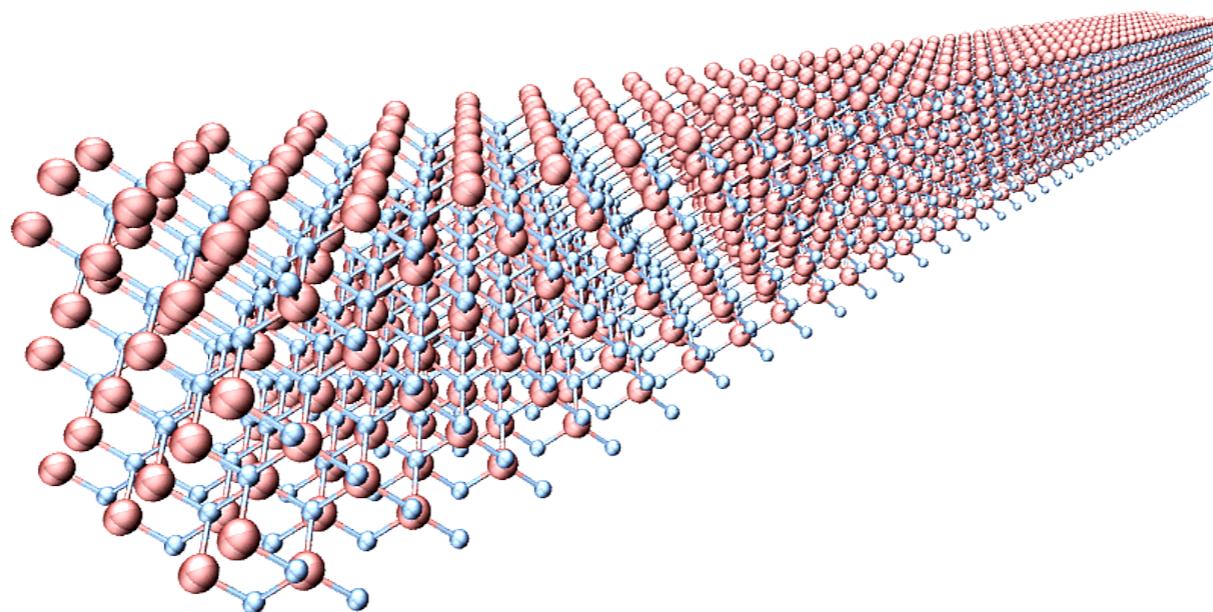
1. No closed form solution
2. Motion is **chaotic**, confined by energy
3. Most of the time is spent in one or the other basin, with relatively **rare transitions** between the two
4. two stable equilibrium points (basin bottoms) and a saddle point



Boundary Conditions

Boundary Conditions

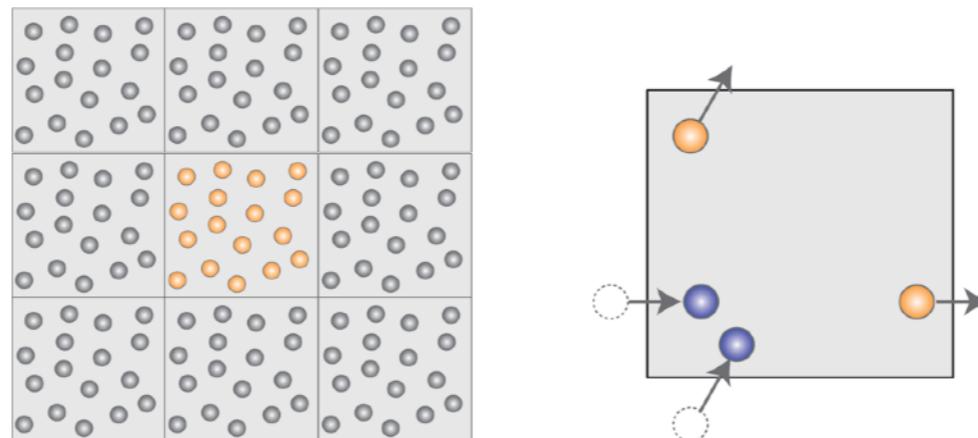
A small molecular system, treated in isolation, will typically have different properties than would be observed at large scales. Boundary conditions make simulations more relevant



The most common type of boundary conditions used in molecular dynamics are **periodic boundary conditions**

alternatives: **droplet, spherical, stochastic boundaries**

Periodic Boundary Conditions



$$U^{\text{pbc}}(\mathbf{q}) = \sum_{klm} \sum_{i=1}^{N-1} \sum_{j=i+1}^N \varphi_{ij}(\mathbf{q}_i, \mathbf{q}_j + k\boldsymbol{\nu}_1 + l\boldsymbol{\nu}_2 + m\boldsymbol{\nu}_3)$$

possibly continued to infinity...

for short ranged potentials, truncated to neighbors of the simulation domain.

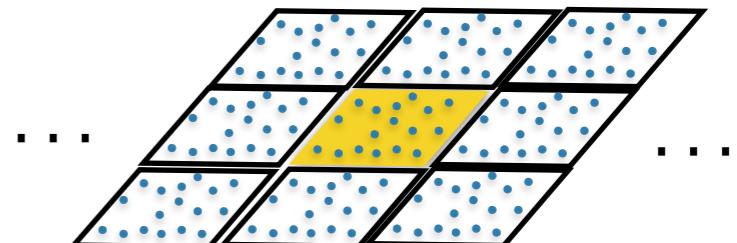
Ewald (Poisson) summation: fast method for computing electrostatic potential due to an infinite periodic lattice.

Ewald Summation

Assume a pair potential

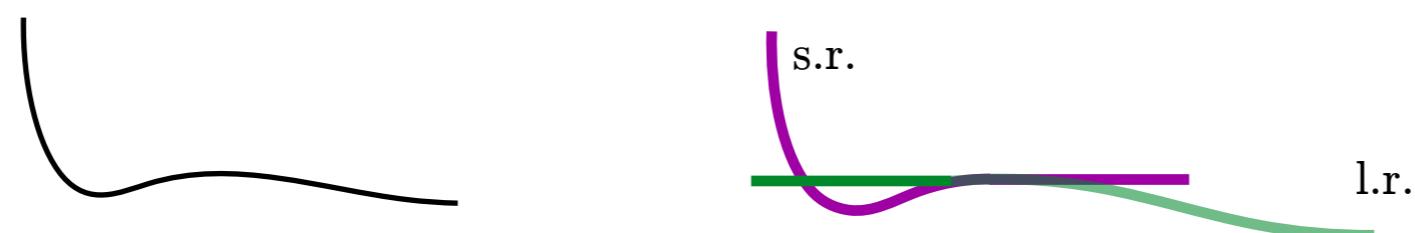
$$U = \sum_{i < j} \varphi(q_i - q_j)$$

assume ‘charge neutral’
unit cell (zero net charge)



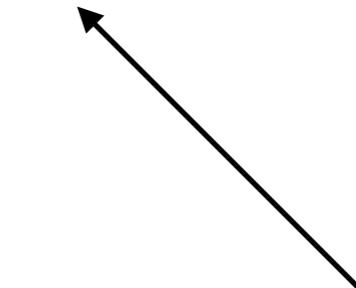
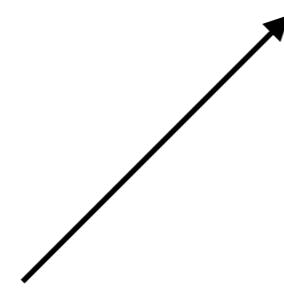
Split the potential into short-ranged and long-ranged parts

$$\varphi(q_i - q_j) = \varphi_{\text{sr}}(q_i - q_j) + \varphi_{\text{lr}}(q_i - q_j)$$



Ewald Summation

$$U = U_{\text{sr}} + U_{\text{lr}}$$



cheap to compute **directly**
as only have a modest
number of particles
in a local region

cheap to compute
in **Fourier space**
using Parceval
relation

Ewald Summation

long ranged part of interaction energy:

$$\varphi_{\text{l.r.}}(q_1 - q_2)$$

lr energy

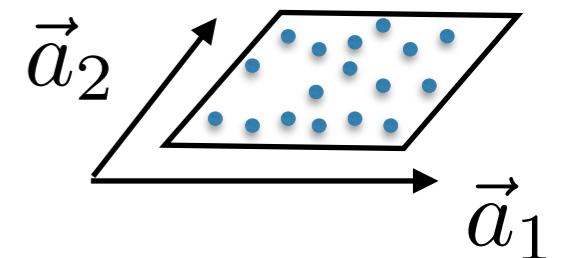
$$U_{\text{l.r.}} = \int \int dq_1 dq_2 \varrho_{\text{uc}}(q_2) \varrho_{\text{tot}}(q_1) \varphi_{\text{l.r.}}(q_1 - q_2)$$

$$\varrho_{\text{uc}}(q) = \sum_i Q_i \delta(q - q_i)$$

$$\varrho_{\text{tot}}(q) = \sum_{n_1, n_2} \sum_i Q_i \delta(q - q_i - n_1 \vec{a}_1 - n_2 \vec{a}_2)$$

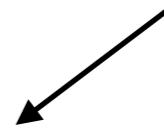
ϱ_{tot} is the convolution of ϱ_{uc} with a ***lattice function***

$$L(q) = \sum_{n_1, n_2} \delta(q - n_1 \vec{a}_1 - n_2 \vec{a}_2)$$



$$\varrho_{\text{tot}} = L * \varrho_{\text{uc}}$$

also write as a lattice function



Fourier Transform

$$\hat{\varrho}_{\text{tot}}(\vec{k}) = \hat{L}(\vec{k})\hat{\varrho}_{\text{uc}}(\vec{k})$$

$$\Psi(q_1) = \int dq_2 \varrho_{\text{uc}}(q_2) \varphi_{\text{l.r.}}(q_1 - q_2)$$

$$\hat{\Psi} = \hat{\varrho}_{\text{uc}} \hat{\varphi}_{\text{l.r.}}$$

$$U_{\text{l.r.}} = \int \int dq_1 dq_2 \varrho_{\text{uc}}(q_2) \varrho_{\text{tot}}(q_1) \varphi_{\text{l.r.}}(q_1 - q_2)$$

$$= \int dq_1 \Psi(q_1) \rho_{\text{tot}}(q_1)$$

$$\hat{\varrho}_{\text{tot}}(\vec{k}) = \hat{L}(\vec{k})\hat{\varrho}_{\text{uc}}(\vec{k}) \quad \hat{\Psi} = \hat{\varrho}_{\text{uc}}\hat{\varphi}_{\text{l.r.}}$$

Parseval's Relation yields:

$$\begin{aligned} U_{\text{l.r.}} &= (2\pi)^{-2} \int \hat{\varrho}_{\text{tot}}^*(\vec{k}) \hat{\Psi}(\vec{k}) d\vec{k} \\ &= (2\pi)^{-2} \int \hat{L}^*(\vec{k}) |\hat{\varrho}_{\text{uc}}(\vec{k})|^2 \hat{\varphi}_{\text{l.r.}}(\vec{k}) \\ &= \text{const} \times \sum_{m_1, m_2} |\hat{\varrho}_{\text{uc}}(\vec{K})|^2 \hat{\varphi}_{\text{l.r.}}(\vec{K}) \end{aligned}$$

falls off rapidly

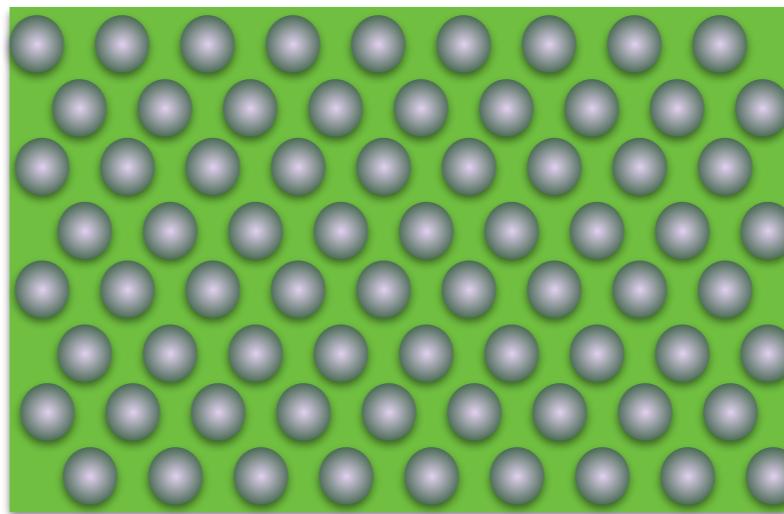
$$\vec{K} = m_1 \vec{b}_1 + m_2 \vec{b}_2$$

Lennard-Jones System

MD Example: “Lennard-Jonesium”

N atoms governed by
LJ potential

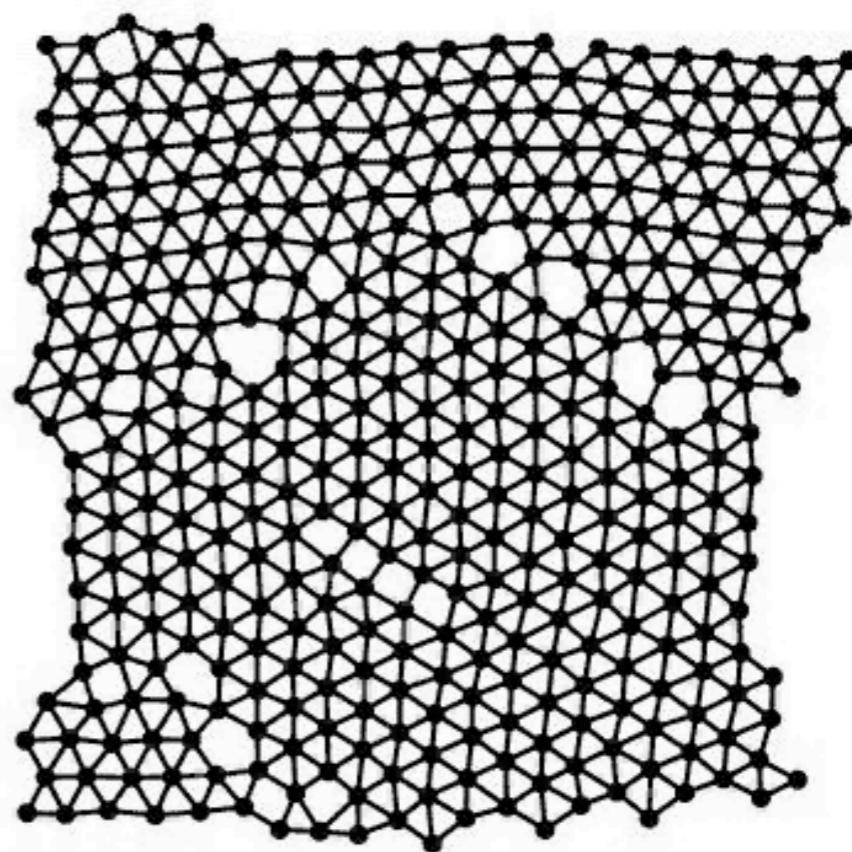
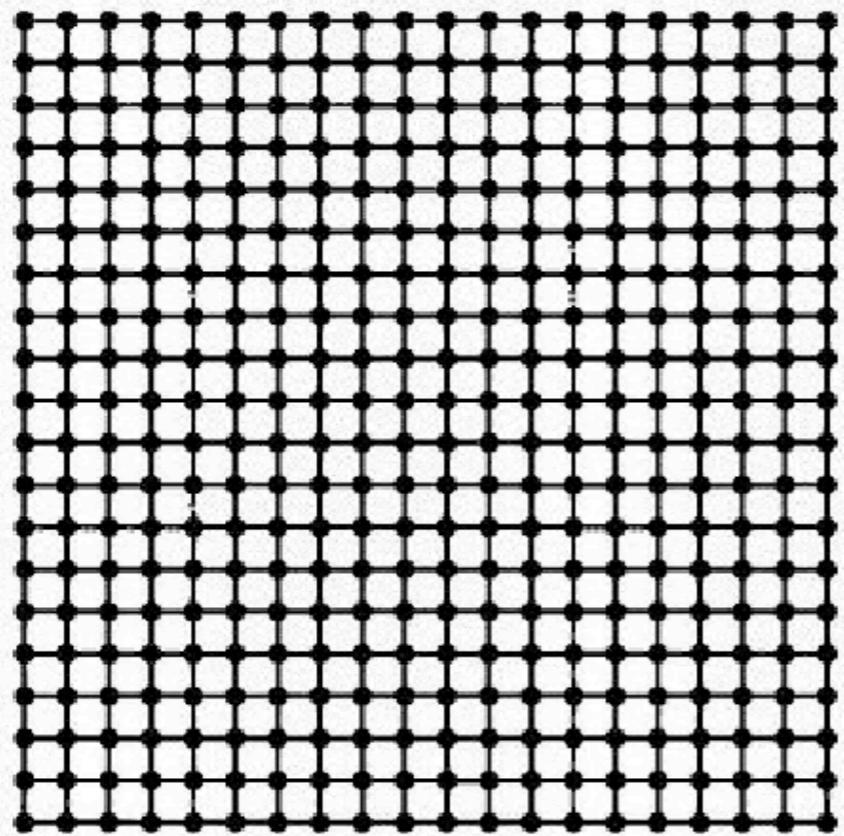
free boundary conditions
(droplet)



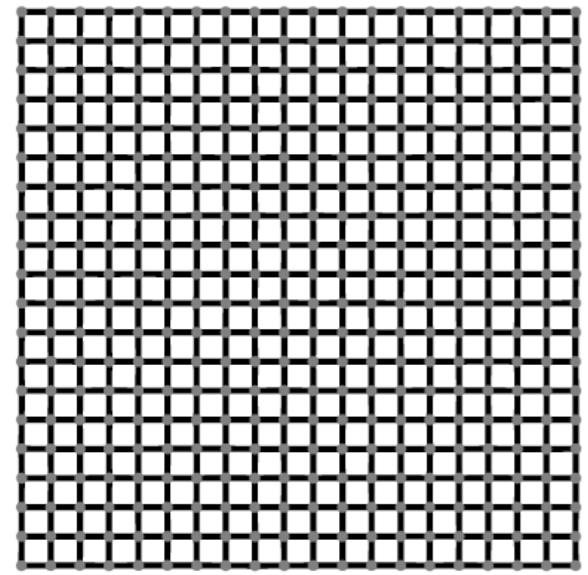
$$\hat{\varphi}_{\text{LJ}}(r) = r^{-12} - r^{-6}$$

Lennard-Jonesium

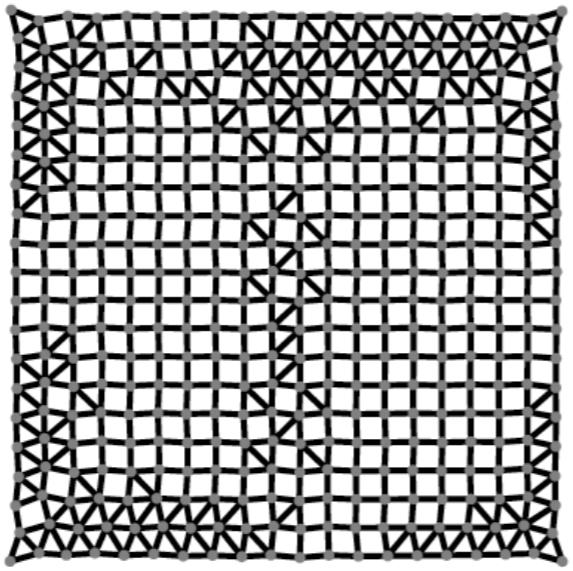
Forms defective hexagonal lattice



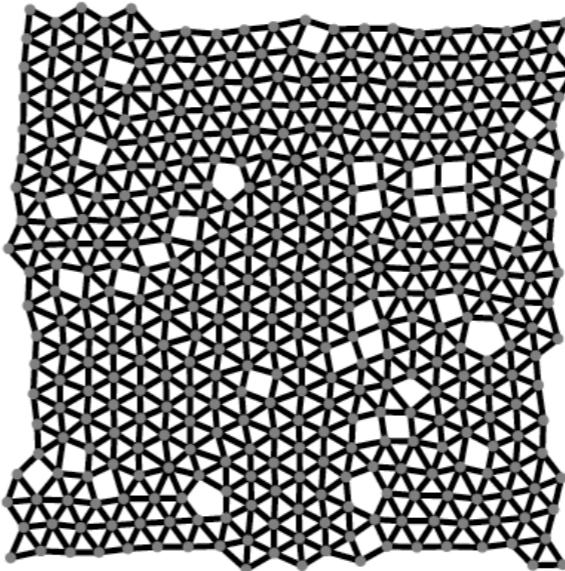
$t = 0$



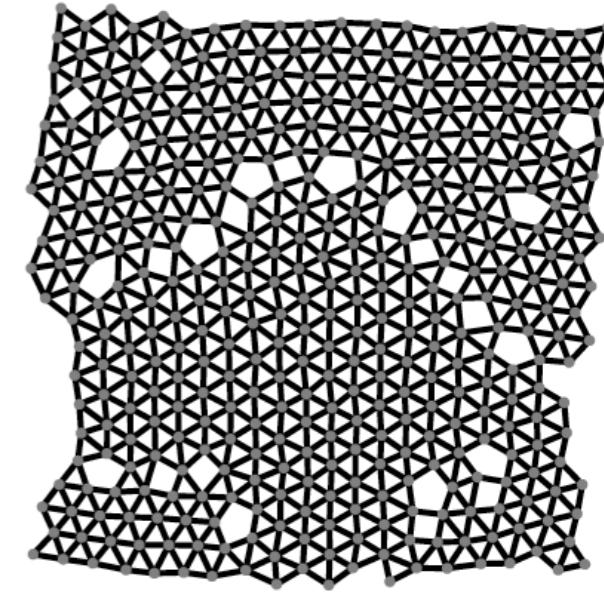
$t = 2$ (200 steps)



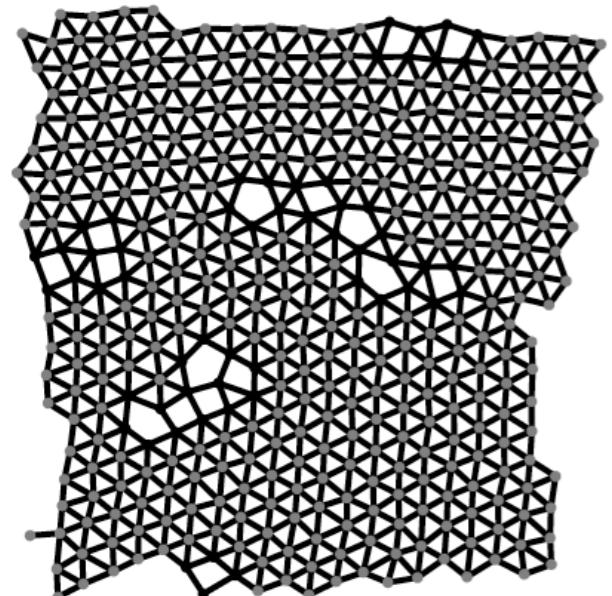
$t = 4$ (400 steps)



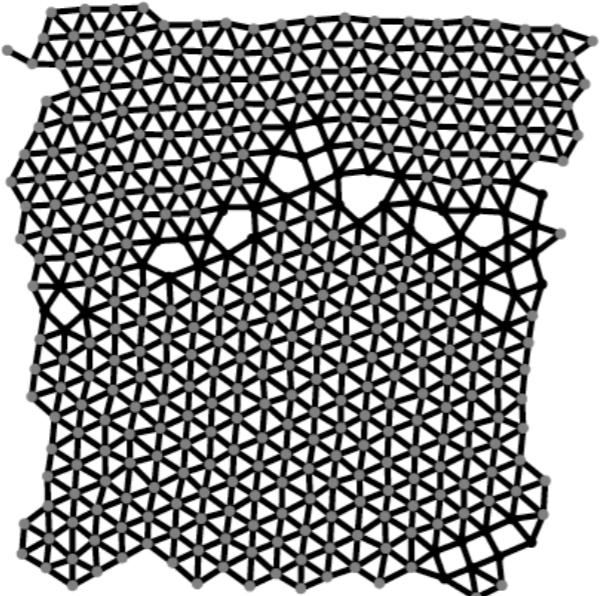
$t = 6$ (600 steps)



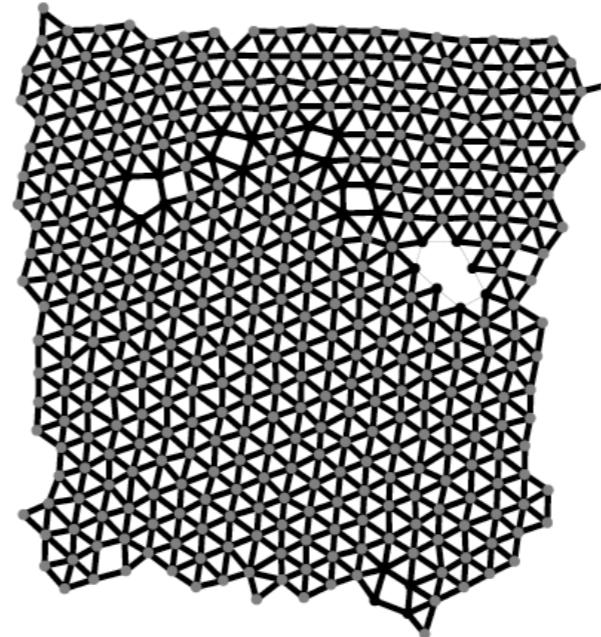
$t = 20$ (2000 steps)



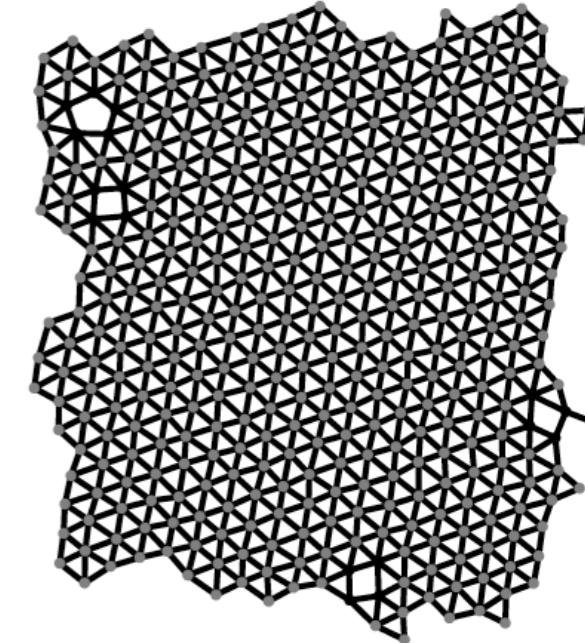
$t = 40$ (4000 steps)



$t = 80$ (8000 steps)



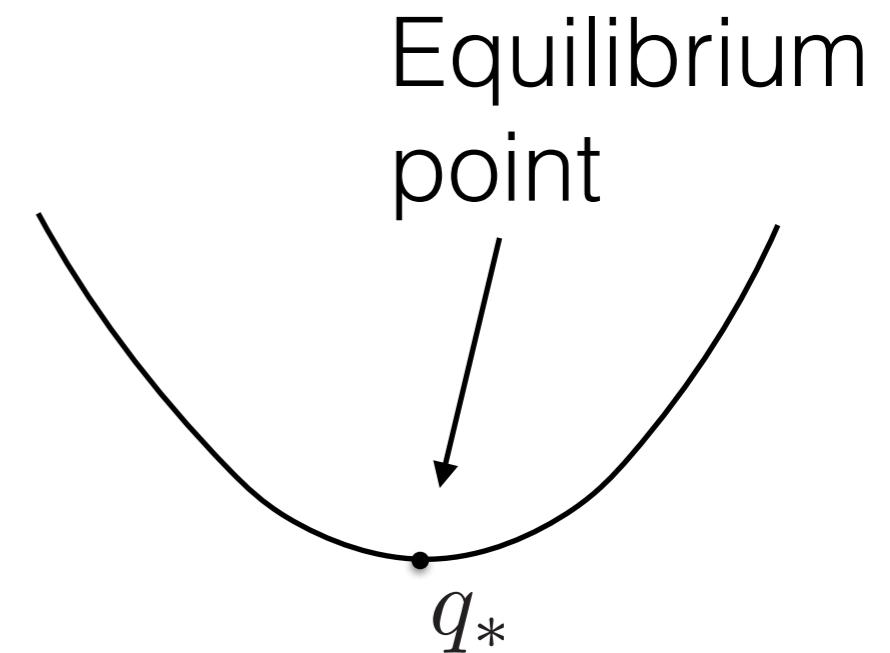
$t = 160$ (16000 steps)



Near-Equilibrium Vibrations

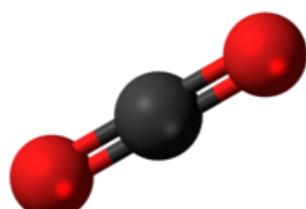
$$\frac{d\delta q}{dt} = M^{-1} \delta p$$

$$\frac{d\delta p}{dt} = -U''(q_*) \delta q$$

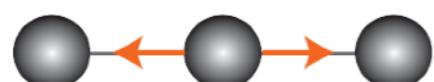


Eigenvectors of Hessian U'' define the “**normal modes**” of oscillation near a stable equilibrium point.

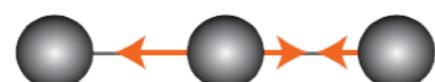
Normal modes of CO₂



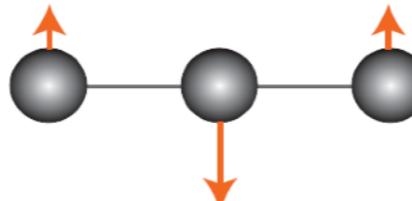
Symmetric Stretch



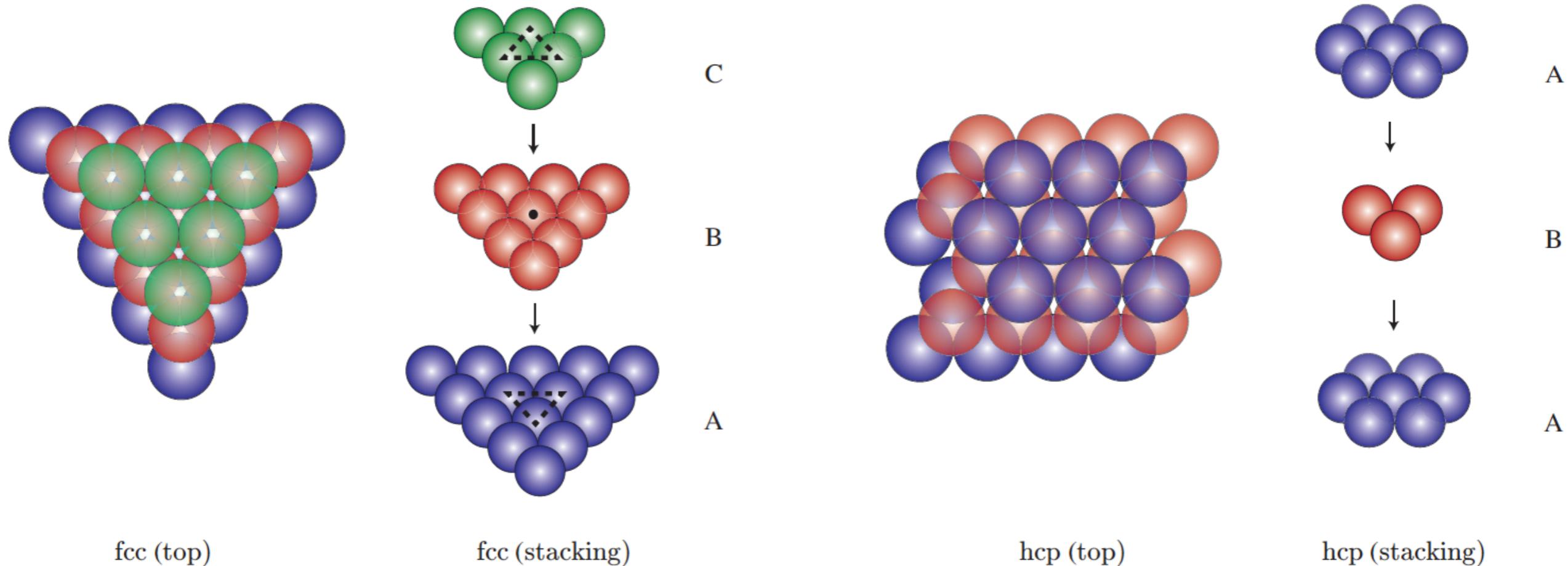
Asymmetric Stretch



Bend



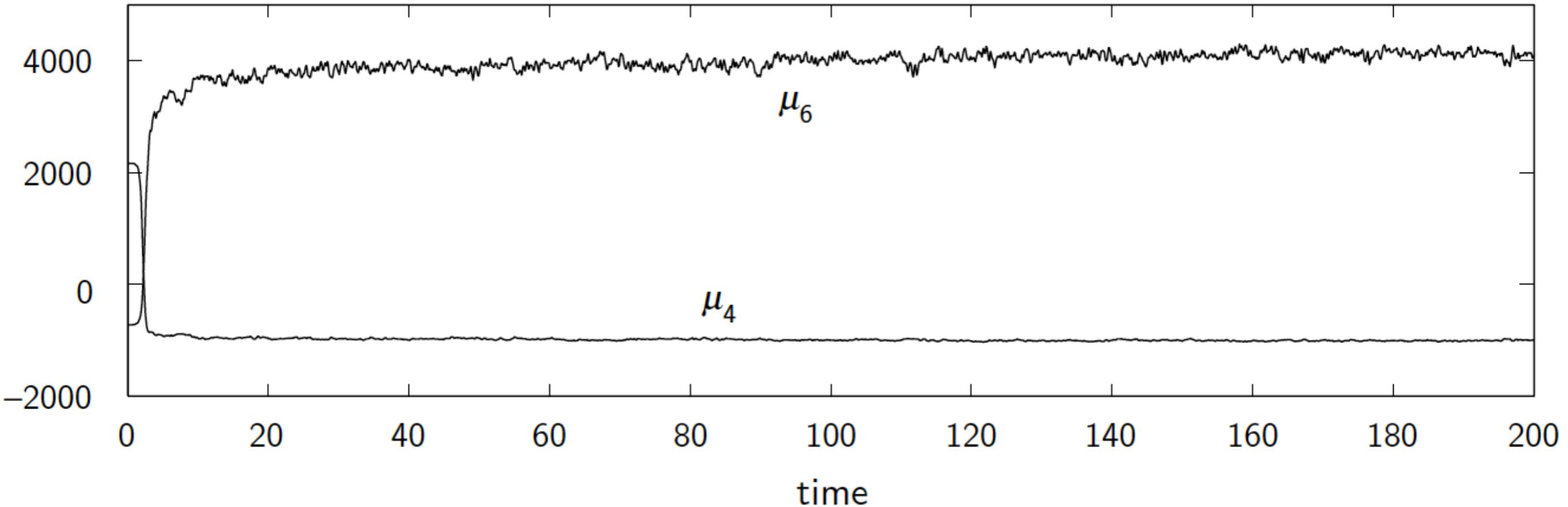
Lattice structures



- minimum of potential energy
- “relaxation” to the equilibrium structure may be slow
- possibility of disordered or glassy states
- metastable landscapes

Order Parameter in LJ system

$$\mu_m = \sum_{i=1}^N \sum_{j,k \in \mathcal{I}_i} \cos(m \theta_{jik})$$



- slow relaxation to ordered state
- simulation in “**pre-equilibrium**” conditions

Computational Methods

Numerical Methods

Timestepping method:

a computable approximation to the flow map

$$\frac{dx}{dt} = f(x)$$

flow map:

$$x(t + t_0) = \Phi_t(x(t_0))$$

Numerical Method

$$\hat{\Phi}_h$$

Euler's Method

$$x_{n+1} = x_n + h f(x_n)$$

$$\hat{\Phi}_h(x) = x + h f(x)$$

Numerical Trajectory

$$\{x_n\}$$

$$x_{n+1} = \hat{\Phi}_h(x_n)$$

Local Consistency $\|\hat{\Phi}_h(x) - \Phi_h(x)\| \rightarrow 0$ as $h \rightarrow 0$

Growth of Error

$$x_{n+1} = \hat{\Phi}_h(x_n)$$

Suppose

$$\|\hat{\Phi}_h(u) - \hat{\Phi}_h(v)\| \leq (1 + hL)\|u - v\|$$

and

$$\|\hat{\Phi}_h(x) - \Phi_h(x)\| \leq Ch^{s+1}$$

then

$$\|\hat{\Phi}_h^N(x) - \Phi_h^N(x)\| \leq Ke^{LT}h^s$$

$$hN = T$$

Numerical Methods

On a fixed finite time interval, typically, we have
(s the order of the method)

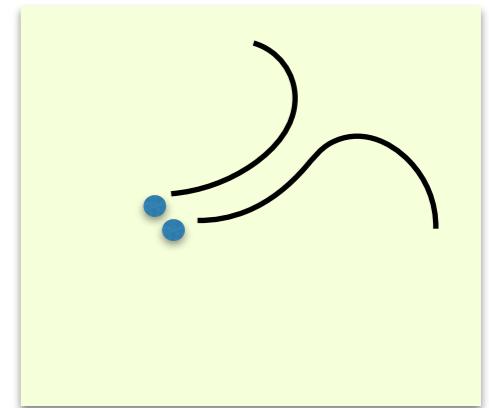
$$\text{error} \leq C(T)h^s$$

Generically, $C(T) \geq K \exp(\beta T)$,
where β is the maximal Lyapunov exponent.

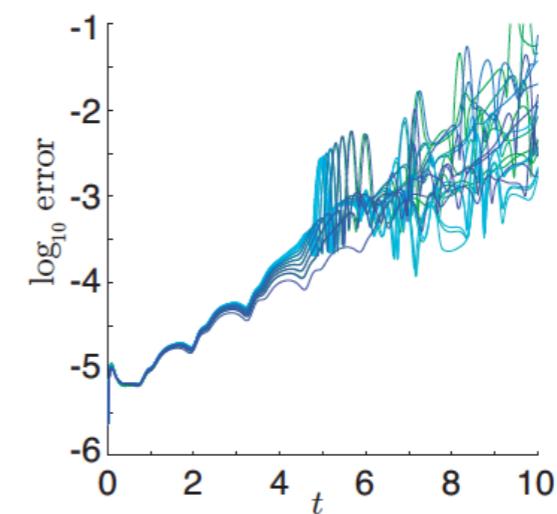
Chaotic Nature of Molecular Dynamics

positive Lyapunov exponents (chaotic)

Separation time: (for two trajectories started ϵ_M apart) ~**10ps**
but **simulation times** ~ **1-1000 ns**



Exponential growth of error

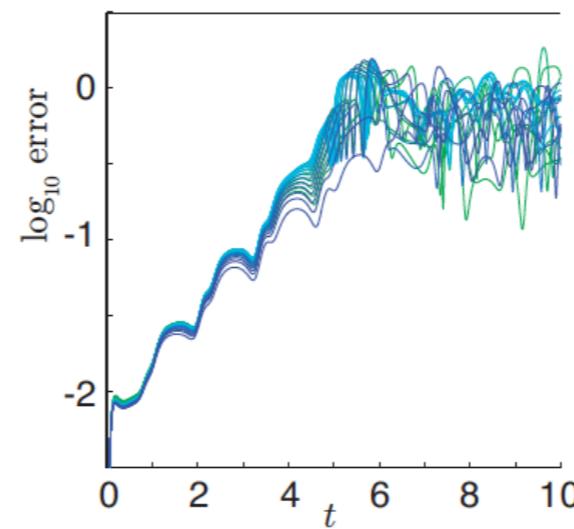


Meaninglessness of the discrete trajectory in practice

Numerical Methods

The global error typically grows exponentially, meaning that on long time intervals, the Euclidean distance between the exact solution and the numerical method is large.

Global error
for **Euler's** method
applied to the **trimer**

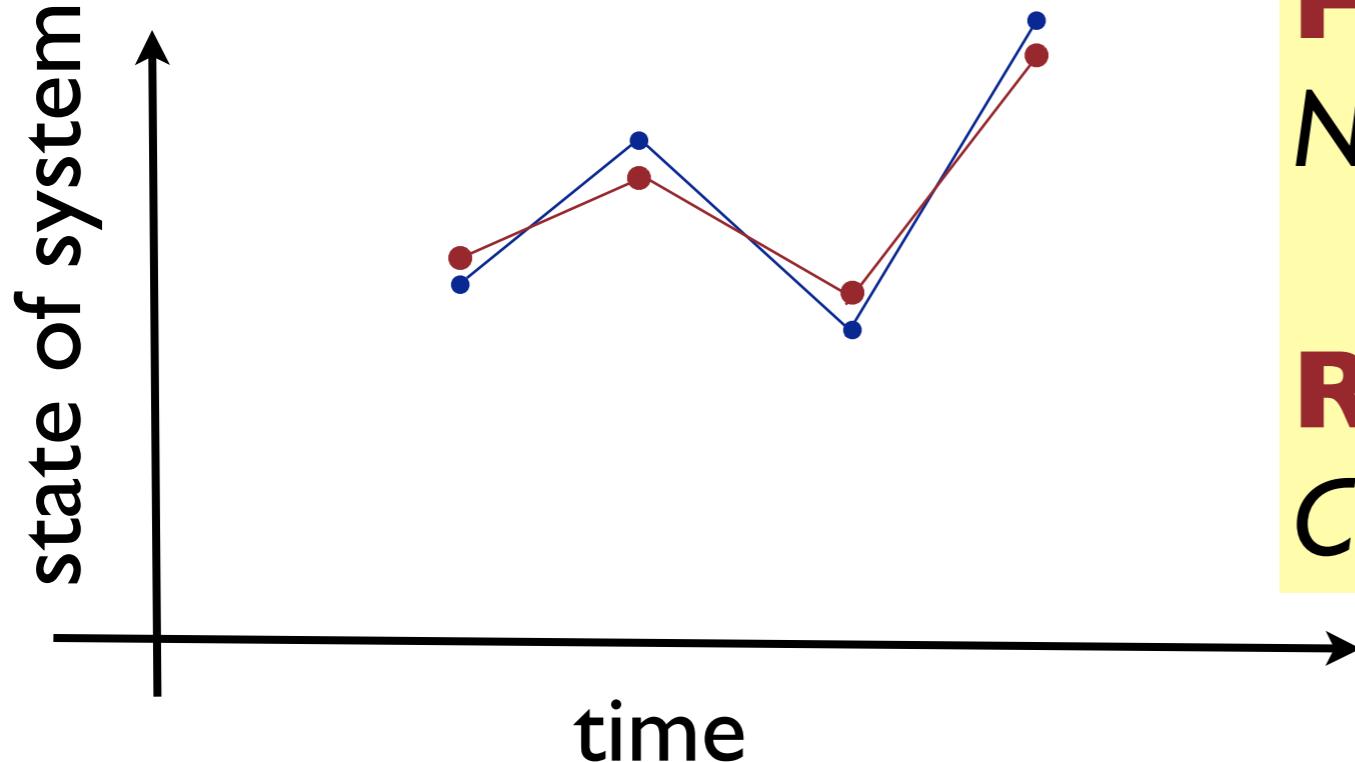


***Exponential
growth!***

How to make sense of numerical solutions?

MD Timestepping

The Goal: Timestep-by-timestep approximation of a **representative trajectory**



High Local Accuracy:
Not Important!

Representativeness:
Crucial!

Constraints: **stability** (fast oscillations), **cost** of Force

Verlet Method

Leapfrog/Verlet Method

$$M(\mathbf{q}_{n+1} - 2\mathbf{q}_n + \mathbf{q}_{n-1}) = -h^2 \nabla U(\mathbf{q}_n)$$

or, in first order form (position-velocity),

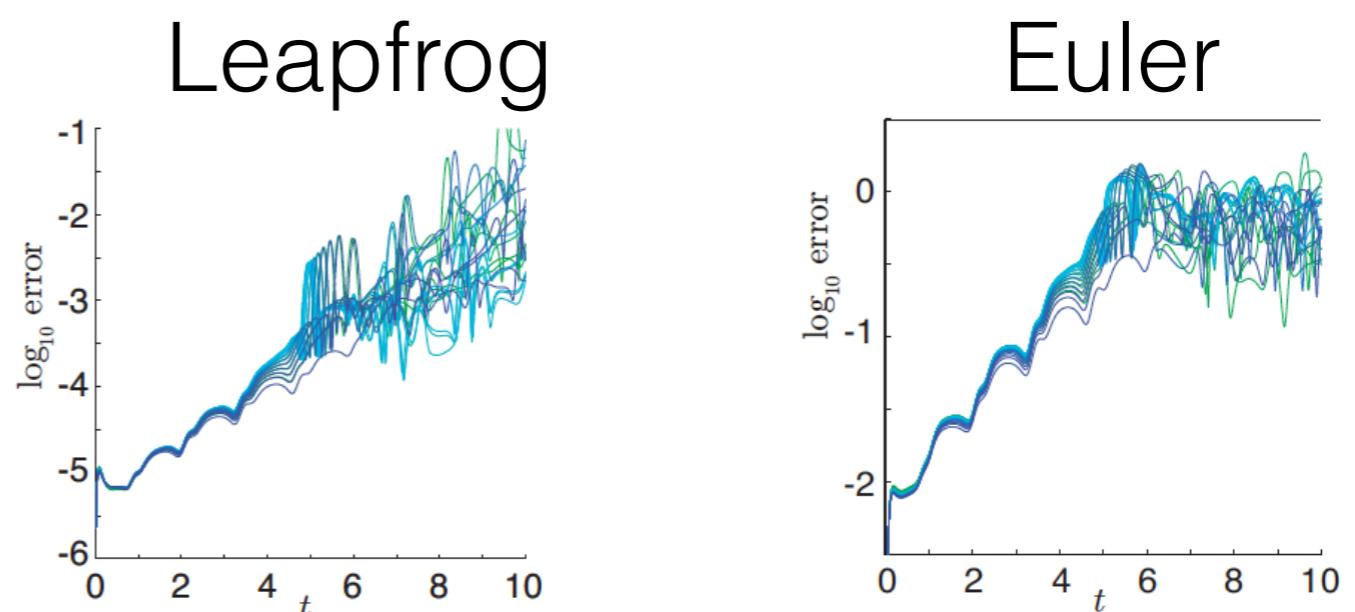
$$\mathbf{v}_{n+1/2} = \mathbf{v}_n + (h/2)M^{-1}\mathbf{F}_n,$$

$$\mathbf{q}_{n+1} = \mathbf{q}_n + h\mathbf{v}_{n+1/2},$$

$$\mathbf{v}_{n+1} = \mathbf{v}_{n+1/2} + (h/2)M^{-1}\mathbf{F}_{n+1}$$

- **one force evaluation/timestep**
- “2nd order” method

exponential
growth of error



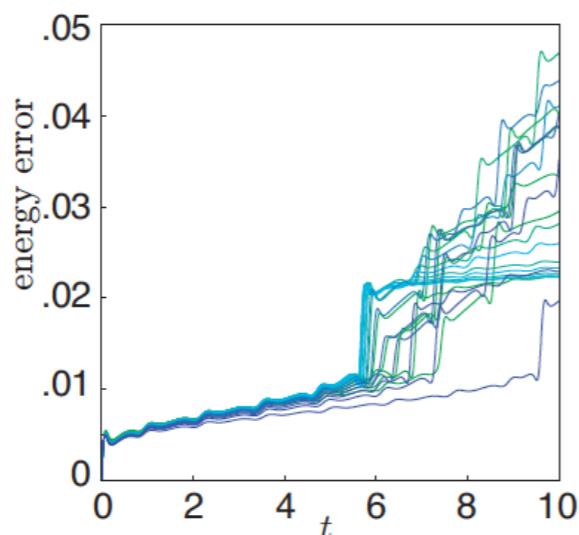
Energy Errors

Recall that the energy is a “conserved quantity” in molecular dynamics. We expect it to be constant along solutions.

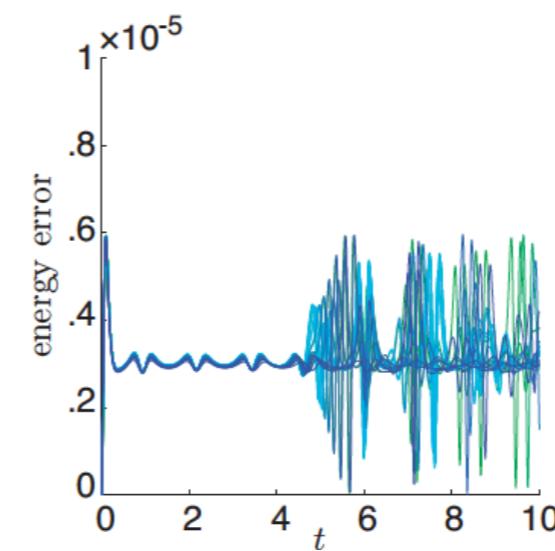
However, in discretization, it is not conserved.

Interestingly the growth of energy error is very different for different schemes.

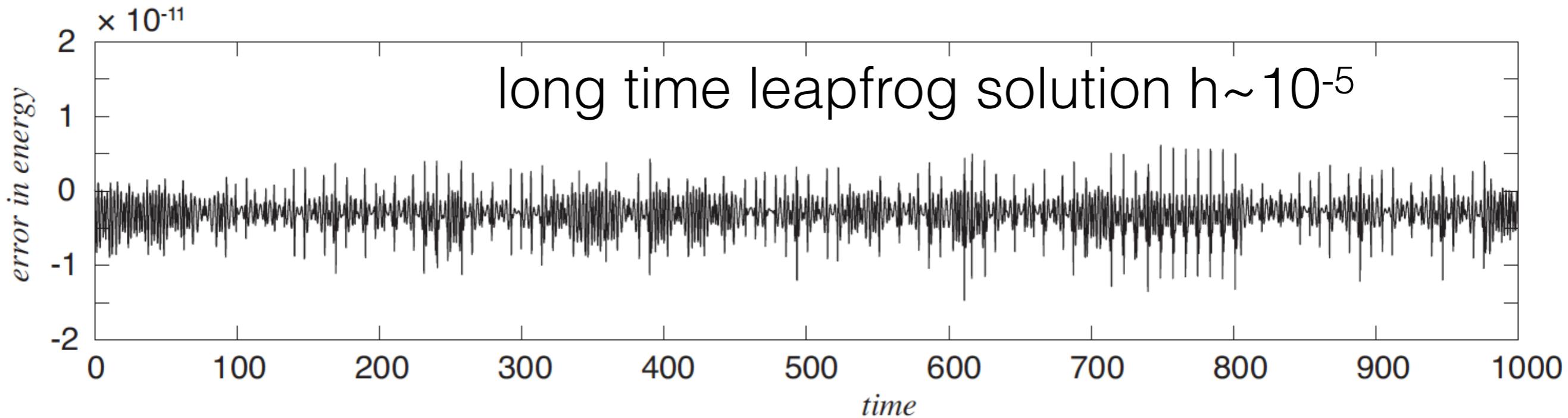
Euler



Leapfrog



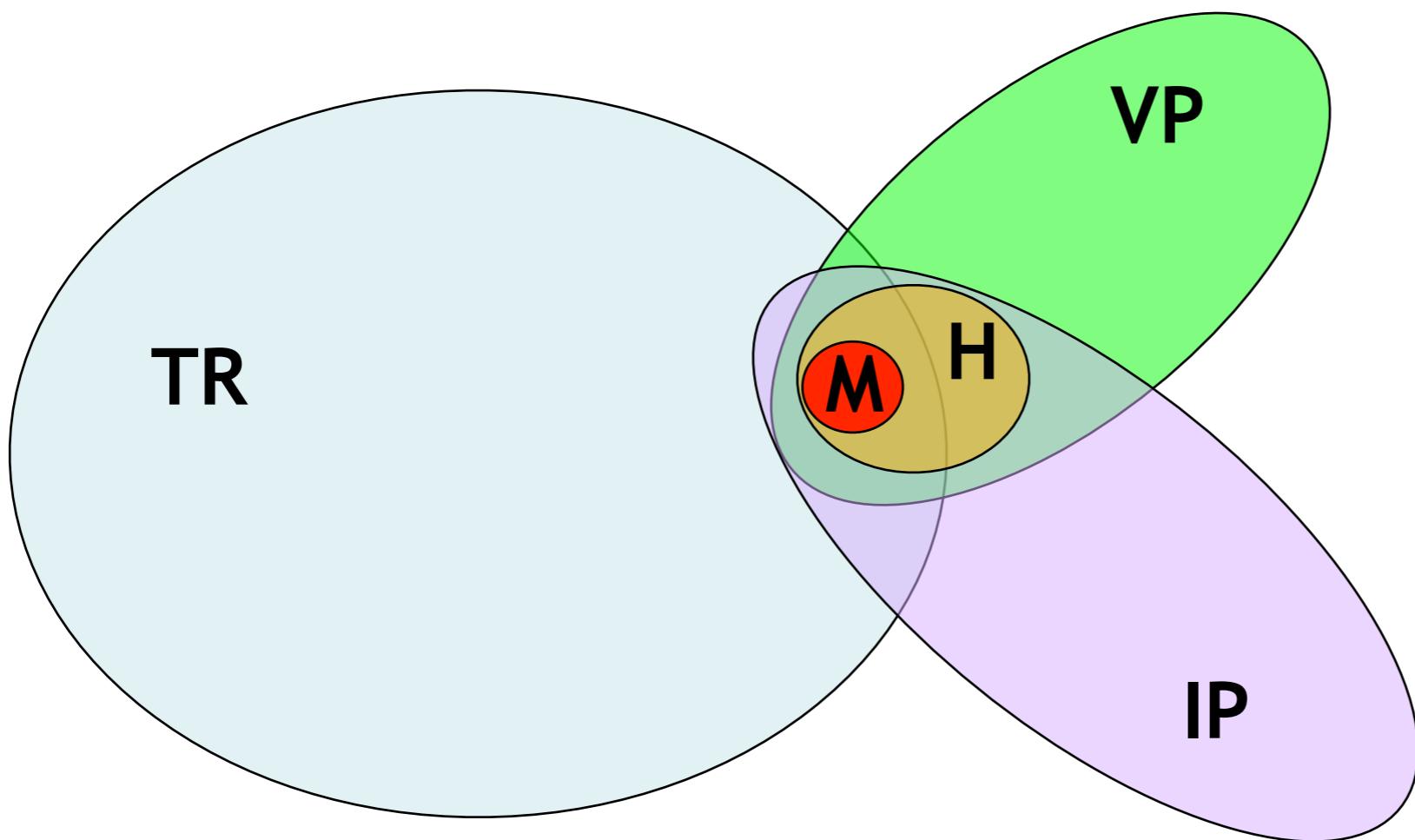
Approximate Energy Conservation



Hints at existence of a '**perturbed**' energy invariant.

Symplectic integrators

Venn Diagram



TR - time-reversal symmetry, **VP** - volume preserving system,

IP - integral preserving system, **H** - Hamiltonian system,

M - classical MD: $H=p^T M^{-1} p/2 + U(q)$

Hamiltonian Systems

$$\dot{q}_i = + \frac{\partial H}{\partial p_i}$$

equality of mixed partials

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

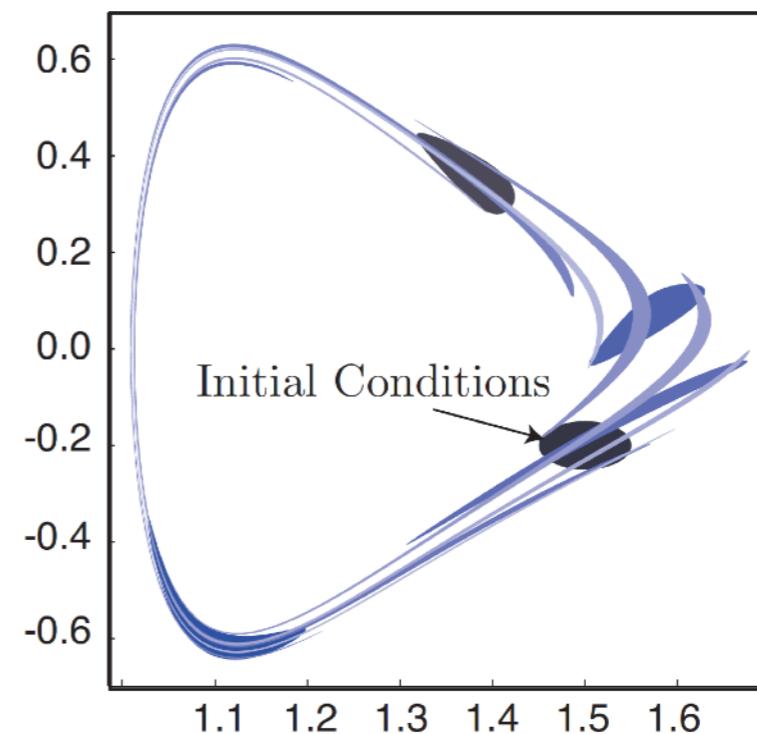
$$\operatorname{div} f = 0$$

**Volume
Preserving
Flow**

$$\dot{q} = p$$

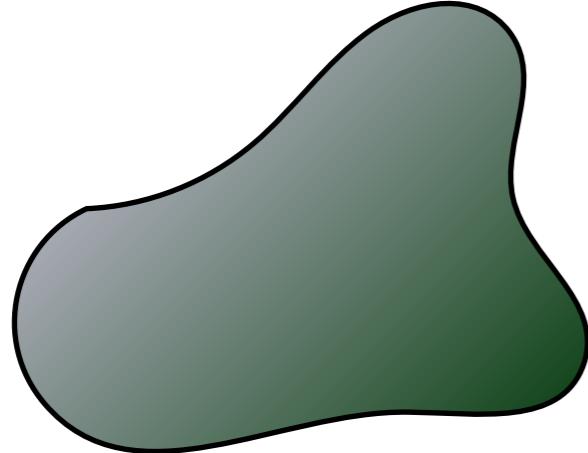
$$\dot{p} = -\varphi'_{\text{LJ}}(q)$$

$$\varphi_{\text{LJ}}(q) = q^{-12} - q^{-6}$$

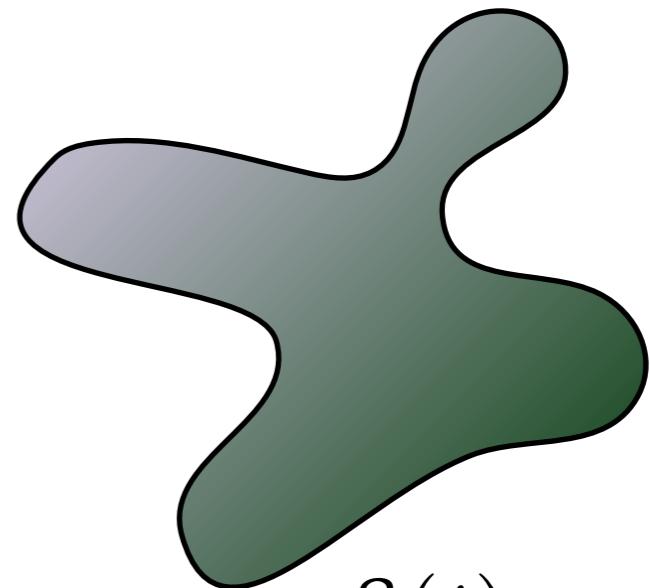


Geometric Integrators

$$\dot{z} = f(z) \quad z(t + \tau) = \Phi_\tau(z(t))$$



$$\mathcal{S}(0)$$



$$\mathcal{S}(t) = \Phi_\tau(\mathcal{S}(0))$$

Liouville's Theorem: $\text{div}(f) = 0 \Rightarrow \text{vol}(\mathcal{S}(t)) \equiv \text{vol}(\mathcal{S}(0))$

*When do **numerical methods** mimic this property?*

Volume Preserving Integrators

How to build a scheme which preserves volume?

$$Z = \Psi_h(z) \quad \Psi_h \approx \Phi_h$$

$$\det(\Psi'_h) = 1$$



Jacobian matrix

Non-obvious how to construct in general.

Instead: preserve a **deeper property** of Hamiltonian systems... ***symplecticness!***

Symplectic Map

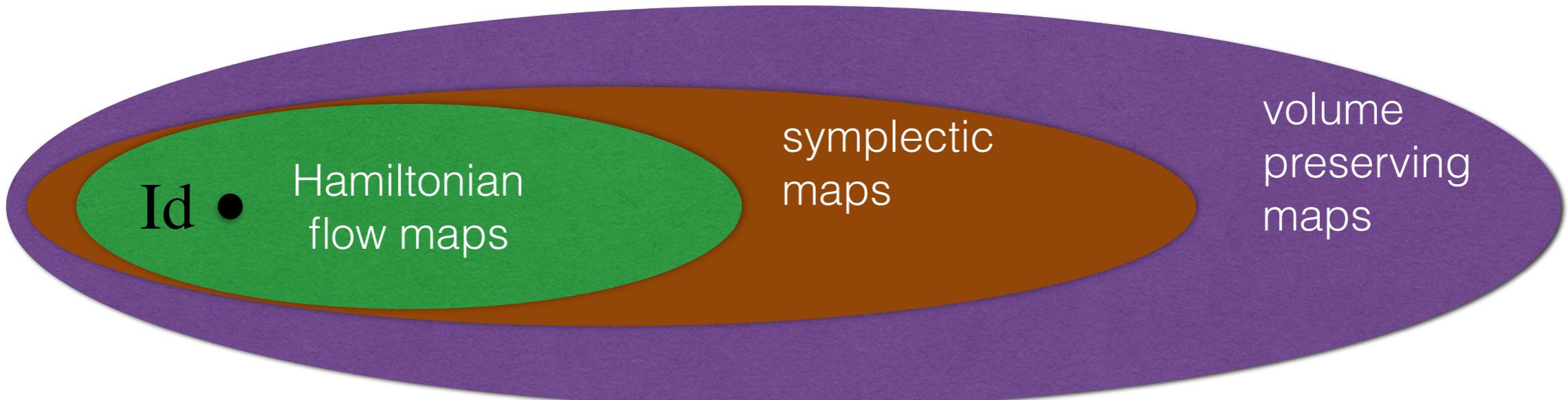
$$\Phi' J \Phi' = J \quad J^T = -J$$

“canonical” choice of J :

$$J = \begin{bmatrix} 0 & I \\ -I & 0 \end{bmatrix}$$

canonical
two-form:

$$\Omega = \sum_{i=1}^d dq_i \wedge dp_i \quad \Omega(\xi, \eta) = \xi^T J \eta$$



In coordinates

$$\begin{bmatrix} Q_1 \\ Q_2 \\ \vdots \\ Q_d \\ P_1 \\ P_2 \\ \vdots \\ P_d \end{bmatrix} = \Phi \begin{pmatrix} q_1 \\ q_2 \\ \vdots \\ q_d \\ p_1 \\ p_2 \\ \vdots \\ p_d \end{pmatrix}$$

$$\sum_{i=1}^d dQ_i \wedge dP_i = \sum_{i=1}^d dq_i \wedge dp_i$$

A canonical (symplectic) map preserves the canonical two-form

Geometrically

Given an oriented 2-surface Σ in R^{2d}

The sum of the oriented areas of projections of Σ onto the $p_i q_i$ coordinate planes is invariant under the action of the map

“Symplectic Euler”

$$H(q, p) = \frac{|p|^2}{2} + U(q) \quad \dot{q} = p, \quad \dot{p} = -\nabla U(q)$$

$$\begin{aligned} q_{n+1} &= q_n + hp_{n+1} \\ p_{n+1} &= q_n - h\nabla U(q_n) \end{aligned}$$

$$\begin{aligned} dq_{n+1} \wedge dp_{n+1} &= d(q_n + hp_{n+1}) \wedge dp_{n+1} \\ &= dq_n \wedge dp_{n+1} \\ &= dq_n \wedge d(p_n - h\nabla U(q_n)) \\ &= dq_n \wedge dp_n - h dq_n \wedge U''(q_n) dq_n \\ &= dq_n \wedge dp_n \end{aligned}$$

Splitting Methods

Splitting Methods

$$y' = f(y) \quad f = f_1 + f_2$$

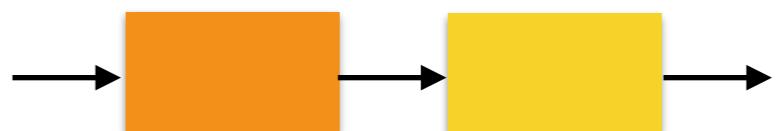
Suppose $y' = f_1(y)$ $y' = f_2(y)$ “integrable”
(analytically solvable)

flow maps:

$$\Phi_{1,h}(y)$$

$$\Phi_{2,h}(y)$$

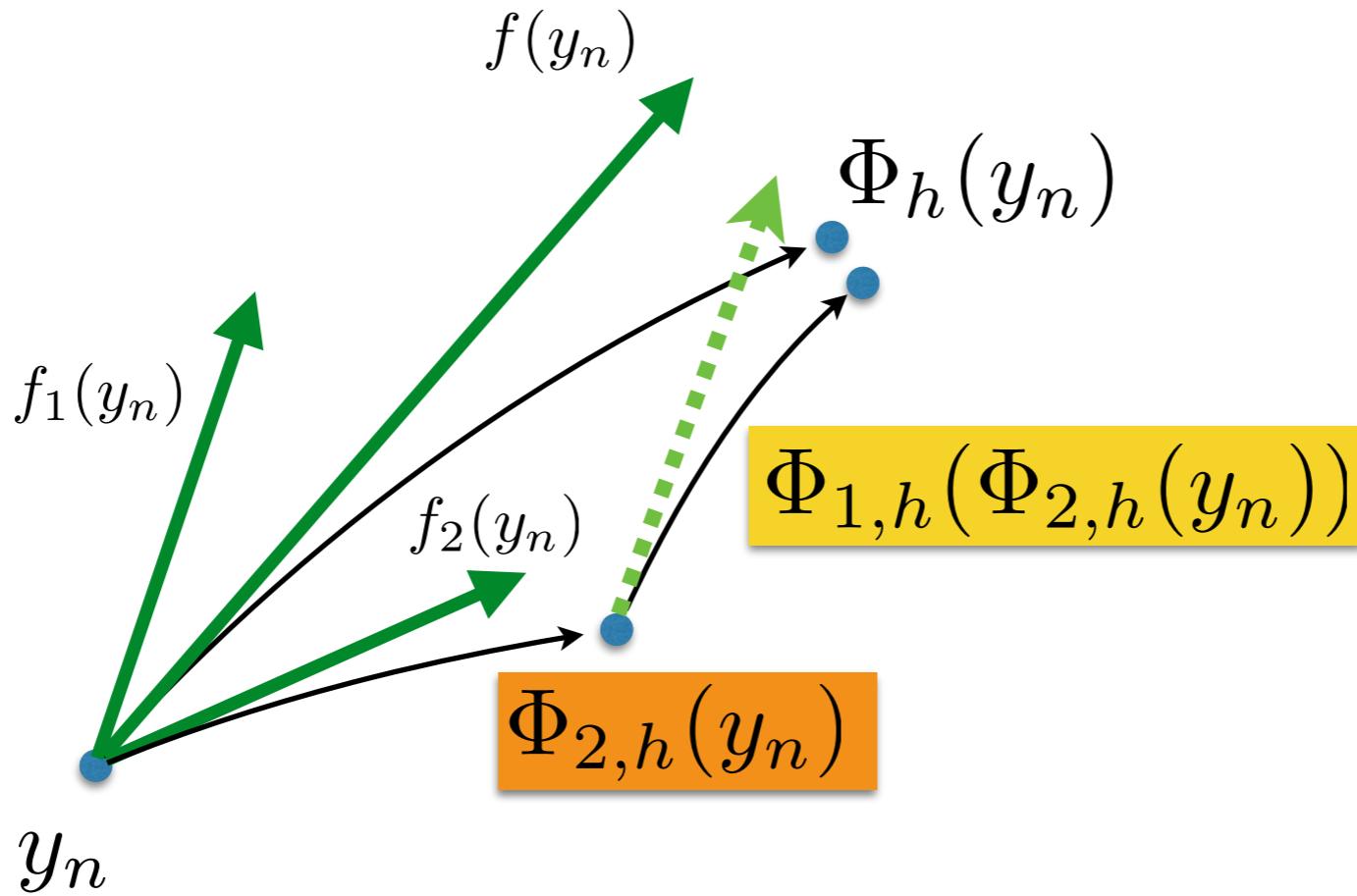
Splitting (composition) methods:



$$\hat{\Phi}_h(y) = \Phi_{1,h}(\Phi_{2,h}(y)) = \Phi_{1,h} \circ \Phi_{2,h}(y)$$

$$\tilde{\Phi}_h(y) = \Phi_{2,h}(\Phi_{1,h}(y)) = \Phi_{2,h} \circ \Phi_{1,h}(y)$$

Splitting Methods



Under *suitable smoothness assumptions*,

the composition method $\hat{\Phi}_h(y) = \Phi_{1,h}(\Phi_{2,h}(y))$
satisfies:

$$\|\hat{\Phi}_h(y) - \Phi_h(y)\| = O(h^2)$$

$$\|\hat{\Phi}_h(u) - \hat{\Phi}_h(v)\| \leq (1 + hR)\|u - v\|$$

So it is **first order** convergent.

Ex. 1: Linear Systems

$$y' = By \quad y(t) = e^{Bt}y(0)$$

$$B = C + D$$

$$\Phi_{1,h}(y) = e^{Ch}y$$

$$\Phi_{2,h}(y) = e^{Dh}y$$

$$\Phi_{1,h}(\Phi_{2,h}(y)) = e^{Ch}e^{Dh}y$$

$$\Phi_{1,h}(\Phi_{2,h}(y)) = e^{Ch}e^{Dh}y$$

$$e^{Ch} = I + Ch + \frac{1}{2}C^2h^2 + \dots$$

$$e^{Dh} = I + Dh + \frac{1}{2}D^2h^2 + \dots$$

$$e^{Ch}e^{Dh} = (I + Ch + \frac{1}{2}C^2h^2 + O(h^3))(I + Dh + \frac{1}{2}D^2h^2 + O(h^3))$$

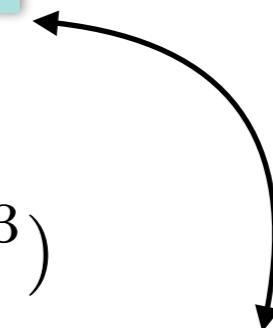
$$= I + Ch + Dh + \frac{1}{2}C^2h^2 + CDh^2 + \frac{1}{2}D^2h^2 + O(h^3)$$

$$= I + (C + D)h + \frac{h^2}{2}(C^2 + 2CD + D^2) + O(h^3)$$

$$e^B h = e^{(C+D)h}$$

$$= I + (C + D)h + \frac{h^2}{2}(C + D)^2 + O(h^3)$$

$$= I + (C + D)h + \frac{h^2}{2}(C^2 + CD + DC + D^2) + O(h^3)$$



$$e^{Ch} e^{Dh} = e^{Bh} + \frac{h^2}{2}(CD - DC) + O(h^3)$$

$$= e^{Bh} + \frac{h^2}{2}[C, D] + O(h^3)$$

↑

commutator

$$[C, D] = CD - DC$$

Even for linear systems, splittings are never “exact” unless the matrices commute.

Symplectic Euler as a “splitting method”

$$H(q, p) = \frac{|p|^2}{2} + U(q)$$

$$H = \frac{|p|^2}{2}$$

$$\dot{q} = p$$

$$\dot{p} = 0$$

$$q(t) = q(0) + tp(0)$$

$$p(t) = p(0)$$

$$H = U(q)$$

$$\dot{q} = 0$$

$$\dot{p} = -\nabla U(q)$$

$$q(t) = q(0)$$

$$p(t) = p(0) - t\nabla U(q(0))$$

Compose $t=h$ flows of the two parts to get
the symplectic Euler method

Each map is symplectic, so the method is too!

Next Up

Monday PM - examples led by Matthias Sachs [***Hands On - computer***]

python • miniMD • deterministic methods - Euler's method vs Verlet

Tuesday - Improving Accuracy and Stability in MD

stability threshold • multiple timestepping • constraints • SHAKE and RATTLE

Wednesday - Stochastic differential equations -

Brownian dynamics • Euler-Maruyama • SDE accuracy •

Leimkuhler-Matthews • Langevin dynamics • splitting • BAOAB and ABOBA

Thursday - push up stepsize in SDE numerics • multiple

timestepping for SDEs • Constraints • g-BAOAB • isokinetic

multiple timestepping

Friday - thermostats (deterministic and stochastic) • ergodic properties

• applications - nonequilibrium and in data science