Computational Physics 2023

Sommersemester, 3th April, 2022 – 14th Juli, 2022

1) Introduction
2) Numbers and errors
3) Differentiation and integration
4) Ordinary differential equations
5) Molecular dynamics simulations
6) Partial differential equations
7) Iteration processes
8) Matrixdiagonalisation & Eigenvalue problems
9) Minimization
10) Random numbers
11) Monte Carlo (MC) Simulations
12) Perkolation
13) Stochastic Dynamics

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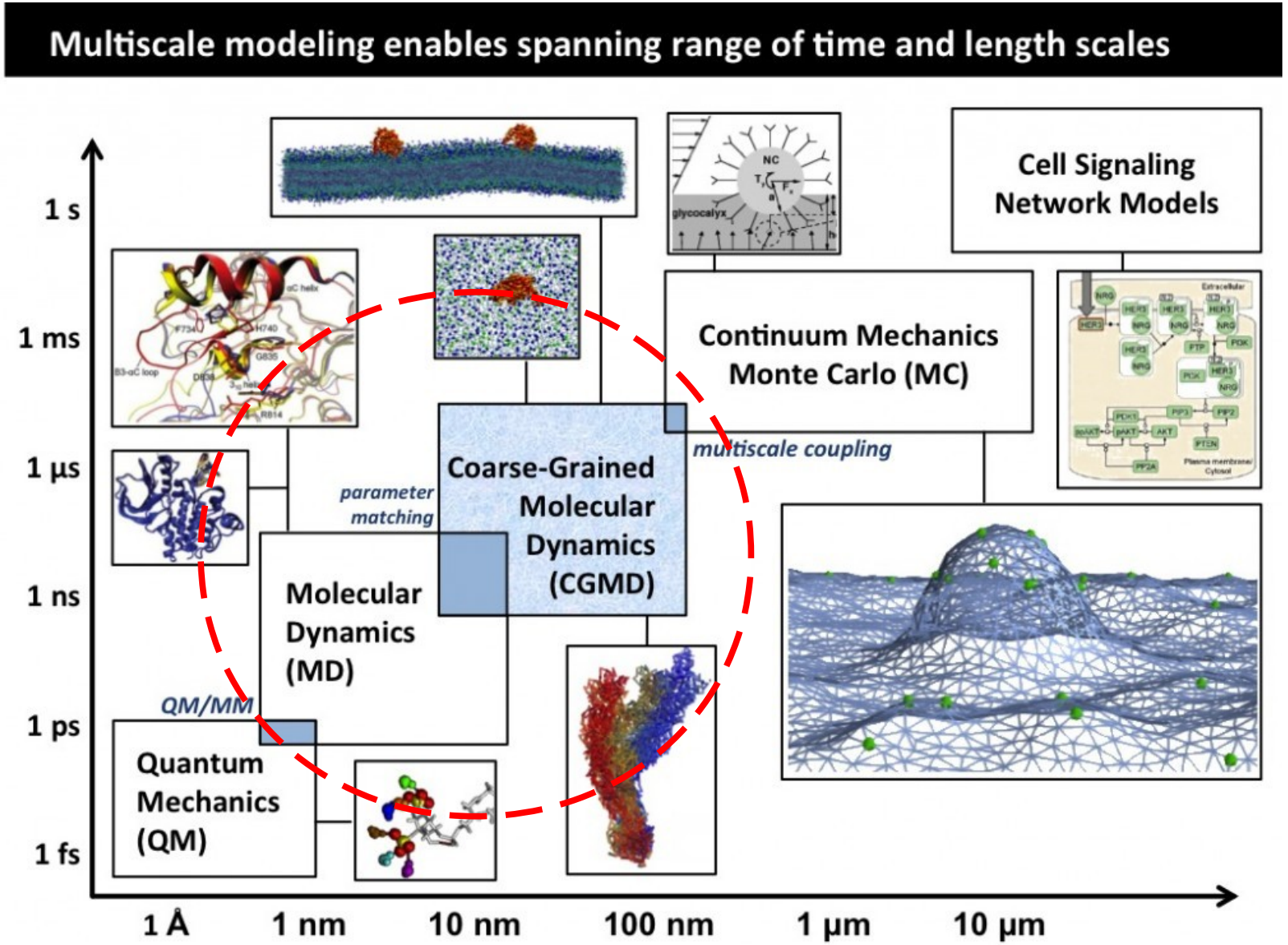
The field of molecular simulations

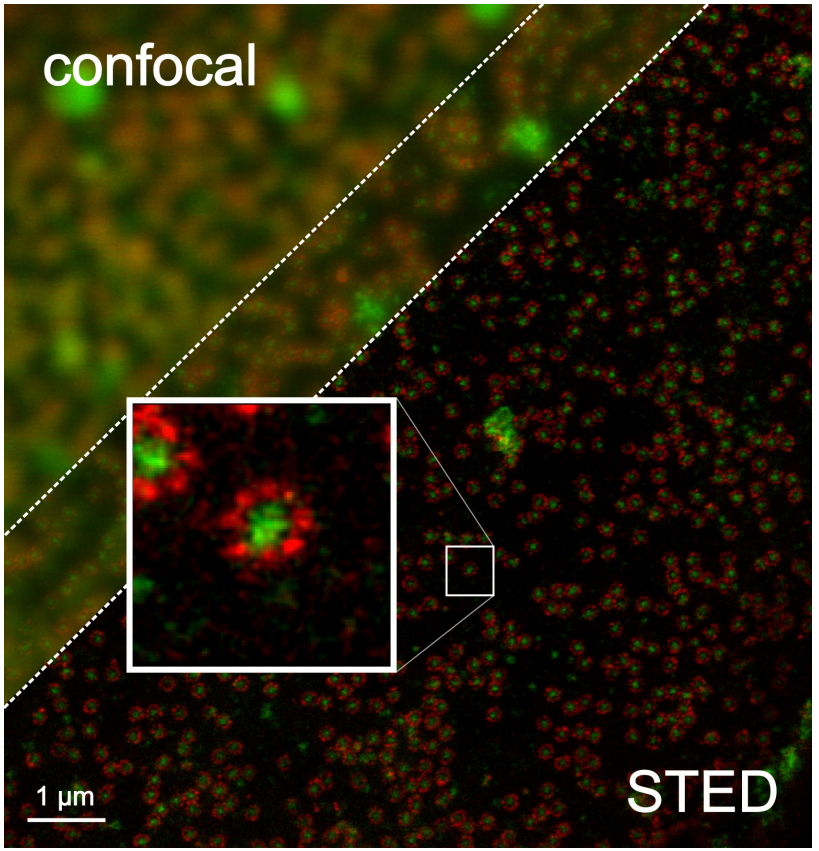


Different methods for different scales: This course will mainly focus on the molecular scale

The idea of an "computational microscope"

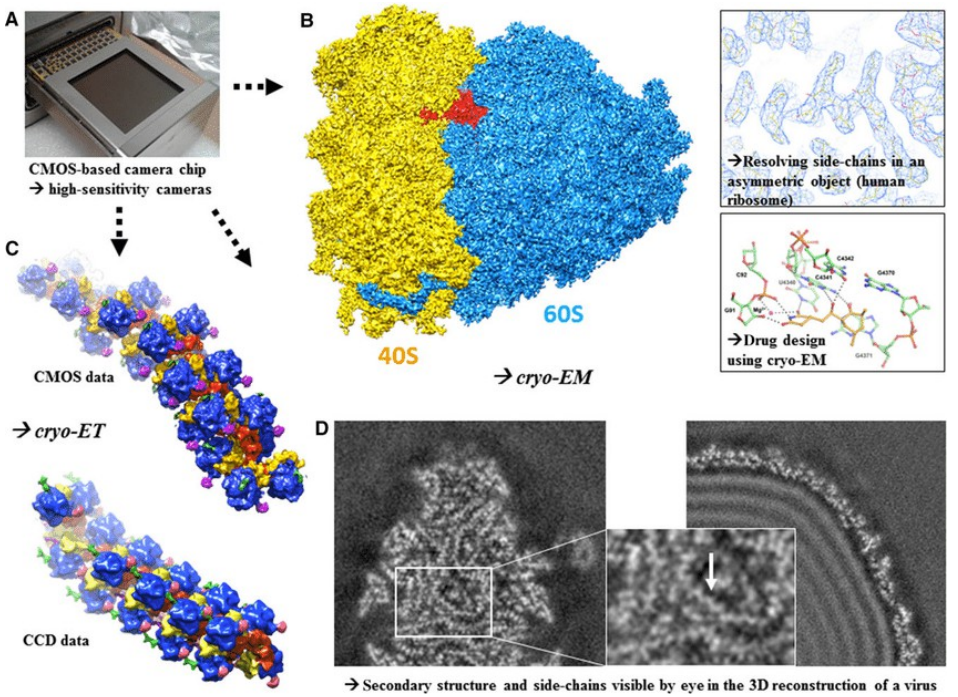
Recent "high" resolution microscopic techniques:

Stimulated emission depletion (STED) microscopy (dynamic)



Nobel Prize chemistry 2014

cryo-electron microscopy (static)



Nobel Prize chemistry 2017

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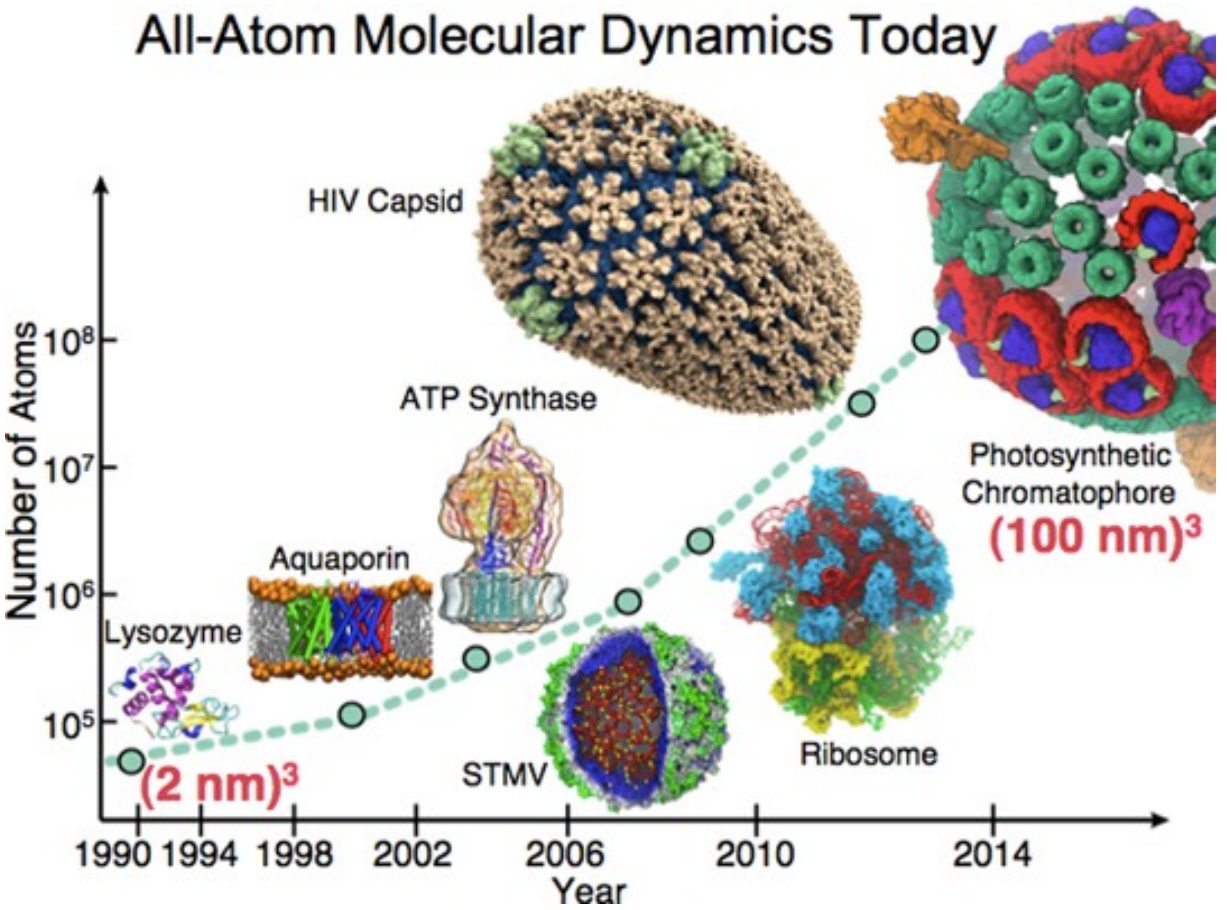
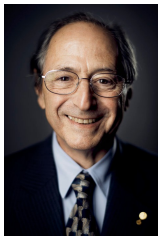
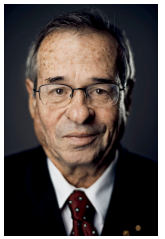
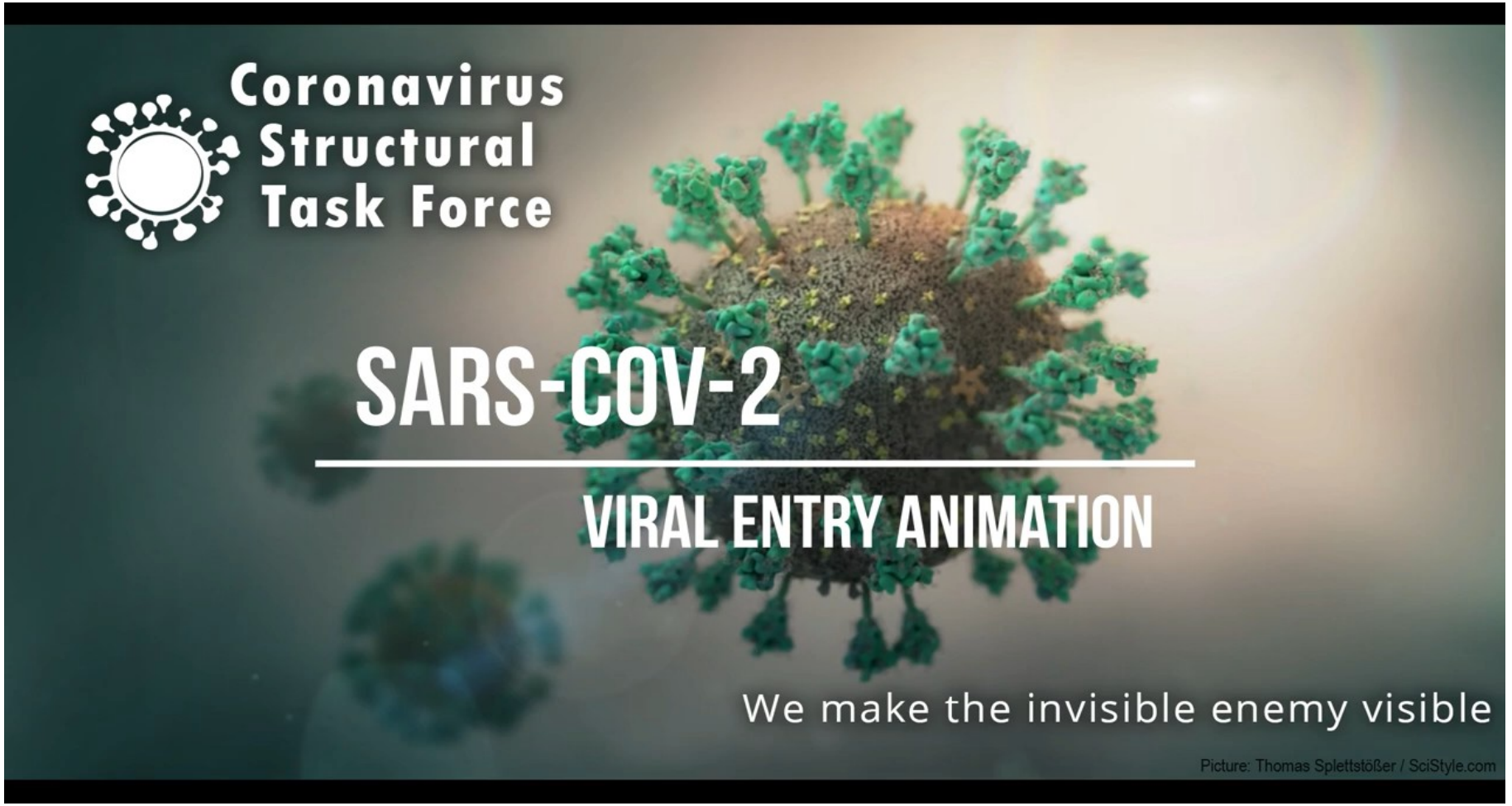
The idea of an “computational microscope”



The Nobel Prize in Chemistry 2013 was awarded jointly to Martin Karplus (left), Michael Levitt (middle) and Arieh Warshel (rright) *"for the development of multiscale models for complex chemical systems."*

SARS-COV2 (art+MD simulation)



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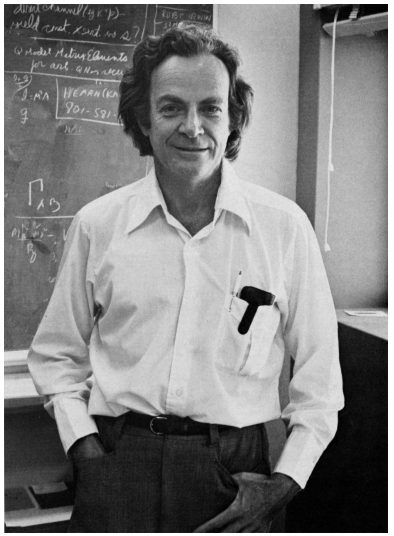
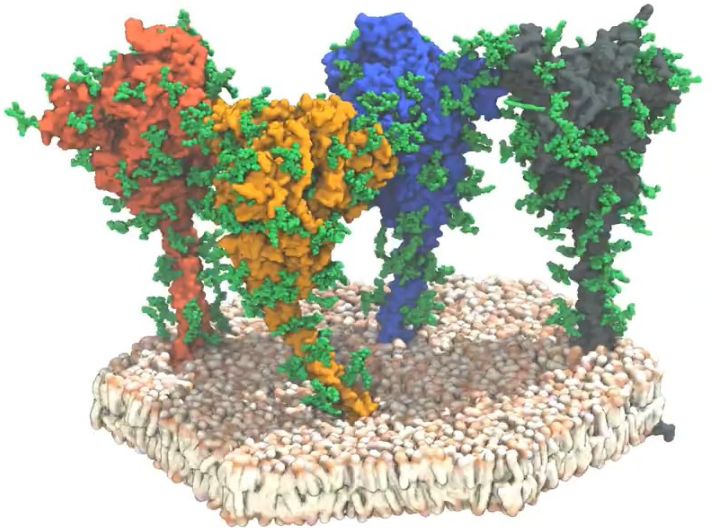
MD simulation



Richard Feynman



“everything that living things do can be understood in terms of the jigglings and wigglings of atoms.”

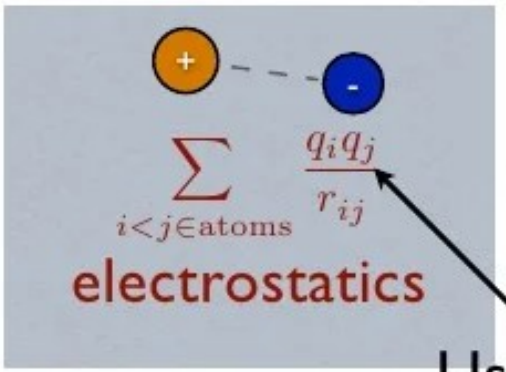
https://www.youtube.com/watch?v=v3pYRn5j7oI

Molecular models/force fields

Typical energy function

$$E = \sum_{b \in \text{bonds}} k_b (r_b - r_b^0)^2 + \sum_{a \in \text{angles}} \kappa_a (\theta_a - \theta_a^0)^2 + \sum_{d \in \text{dihedrals}} \sum_n l_{dn} \cos(n\pi)$$

bond stretch angle torsion dihedrals



$$+ \sum_{i<j \in \text{atoms}} \frac{q_i q_j}{r_{ij}}$$

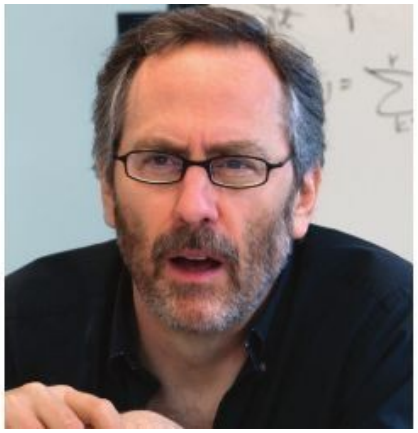
electrostatics

$$+ \sum_{i<j \in \text{atoms}} 4\epsilon_{ij} \left(\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^{6} \right)$$

dispersion

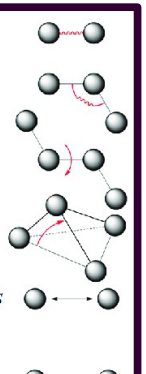
Usually fixed charges

MD simulation & $$$$$$$$$



David E. $haw
(PhD student: Jeff Bezo$)

$$U(R) = \sum_{bonds} k_r (r - r_{eq})^2 \quad \text{bond}$$
$$+ \sum_{angles} k_\theta (\theta - \theta_{eq})^2 \quad \text{angle}$$
$$+ \sum_{dihedrals} k_\phi (1 + \cos[n\phi - \gamma]) \quad \text{dihedral}$$
$$+ \sum_{impropers} k_\omega (\omega - \omega_{eq})^2 \quad \text{improper}$$
$$+ \sum_{i<j}^{atoms} \varepsilon_{ij} \left[\left(\frac{r_m}{r_{ij}} \right)^{12} - 2 \left(\frac{r_m}{r_{ij}} \right)^{6} \right] \quad \text{van der Waals}$$
$$+ \sum_{i<j}^{atoms} \frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}} \quad \text{electrostatic}$$



- Anton2 is a dedicated GPU being a factor 1000x faster than consumer GPUs. Motivation?: Plausibly demonstration and $$ (big pharma)

The Euler scheme (otherwise "known" as "the high school method"):

$$\mathbf{r}_i(t+\Delta t) = \mathbf{r}_i(t) + \Delta t\ \mathbf{v}_i(t) + \frac{\Delta t^2}{2m_i}\mathbf{f}_i(t) + \mathcal{O}(\Delta t^3)$$

$$\mathbf{v}_i(t+\Delta t) = \mathbf{v}_i(t) + \frac{\Delta t}{m_i}\ \mathbf{f}_i(t) + \mathcal{O}(\Delta t^2)$$

What is the problem?

Time integration: Operators

Lets derive a proper scheme……

$$i\hbar\frac{\partial}{\partial t}\Psi = H\Psi \longrightarrow |\Psi(t)\rangle = e^{-iHt}|\Psi(0)\rangle$$

$$e^{-iH}e^{iH} = I$$

Erwin Schrödinger

$$\dot{A} = \{A, H\} \rightarrow A(t) = A(0)e^{\{A,H\}t}$$

Joseph Liouville

$$\{.., H\} := i\mathcal{L}$$ **(Liouville operator)**

$$A(t) = A(0)e^{i\mathcal{L}t}$$

Time integration: Operators

Lets split the Liouville operator in a position and momentum dependent part:

$$i\mathcal{L} = i\mathcal{L}_{\mathbf{r}} + i\mathcal{L}_{\mathbf{p}},$$

$$i\mathcal{L}_{\mathbf{r}} = \sum_i \dot{\mathbf{r}}_i \frac{\partial}{\partial \mathbf{r}_i} \qquad\qquad i\mathcal{L}_{\mathbf{p}} = \sum_i \dot{\mathbf{p}}_i \frac{\partial}{\partial \mathbf{p}_i}.$$

Lets now construct a symmetric version of this operator (Trotter decomposition):

$$e^{i(\mathcal{L}_{\mathbf{r}}+\mathcal{L}_{\mathbf{p}})\Delta t} = e^{i\frac{\Delta t}{2}\mathcal{L}_{\mathbf{p}}}\ e^{i\Delta t\mathcal{L}_{\mathbf{r}}}\ e^{i\frac{\Delta t}{2}\mathcal{L}_{\mathbf{p}}} + \mathcal{O}(\Delta t^3).$$

This sequence of opperators commutes due to symmetry!

Time integration: Operators

$$e^{a\frac{\partial}{\partial x}}x \rightarrow (1 + a\frac{\partial}{\partial x})x = x + a \quad (a \ll 1)$$

$$e^x = \sum_{n=0}^{\infty} \frac{x^n}{n!} = 1 + x + \frac{x^2}{2!} + \frac{x^3}{3!} + \cdots$$

$$i\mathcal{L} = i\mathcal{L}_{\mathbf{r}} + i\mathcal{L}_{\mathbf{p}},$$

$$i\mathcal{L}_{\mathbf{r}} = \sum_i \dot{\mathbf{r}}_i \frac{\partial}{\partial \mathbf{r}_i} \qquad i\mathcal{L}_{\mathbf{p}} = \sum_i \dot{\mathbf{p}}_i \frac{\partial}{\partial \mathbf{p}_i}.$$

These are the rules!

$$e^{i\frac{\Delta t}{2}\mathcal{L}_{\mathbf{p}}}\ \mathbf{r}_i = \mathbf{r}_i \qquad e^{i\frac{\Delta t}{2}\mathcal{L}_{\mathbf{p}}}\ \mathbf{p}_i = \mathbf{p}_i + \frac{\Delta t}{2}\dot{\mathbf{p}}_i$$

$$e^{i\Delta t\mathcal{L}_{\mathbf{r}}}\ \mathbf{r}_i = \mathbf{r}_i + \Delta t\ \dot{\mathbf{r}}_i \qquad e^{i\Delta t\mathcal{L}_{\mathbf{r}}}\ \mathbf{p}_i = \mathbf{p}_i.$$

Time integration: Operators

These are the rules!

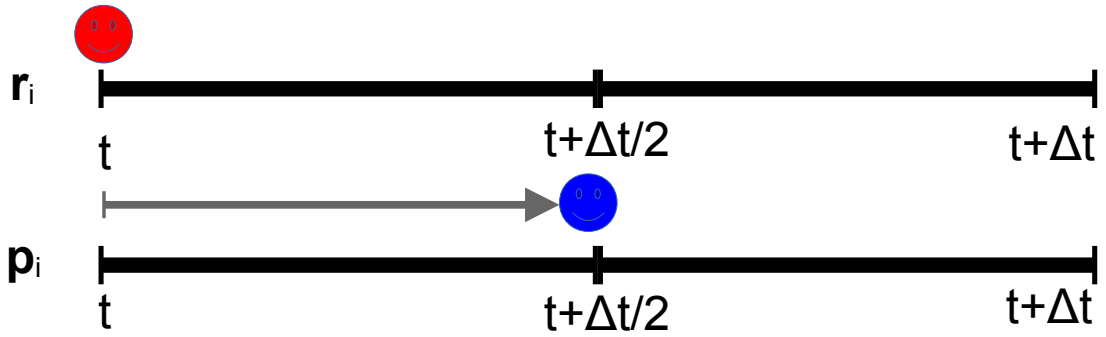
$$e^{i\frac{\Delta t}{2}\mathcal{L}_{\mathbf{P}}}\ \mathbf{r}_i = \mathbf{r}_i \qquad e^{i\frac{\Delta t}{2}\mathcal{L}_{\mathbf{P}}}\ \mathbf{p}_i = \mathbf{p}_i + \frac{\Delta t}{2}\dot{\mathbf{p}}_i$$

$$e^{i\Delta t\mathcal{L}_{\mathbf{r}}}\ \mathbf{r}_i = \mathbf{r}_i + \Delta t\ \dot{\mathbf{r}}_i \qquad e^{i\Delta t\mathcal{L}_{\mathbf{r}}}\ \mathbf{p}_i = \mathbf{p}_i.$$

The first operator:

$$e^{i\frac{\Delta t}{2}\mathcal{L}_{\mathbf{P}}} e^{i\Delta t\mathcal{L}_{\mathbf{r}}} e^{i\frac{\Delta t}{2}\mathcal{L}_{\mathbf{P}}}\ \mathbf{r}_i(t) \rightarrow \mathbf{r}_i(t)$$

$$e^{i\frac{\Delta t}{2}\mathcal{L}_{\mathbf{P}}} e^{i\Delta t\mathcal{L}_{\mathbf{r}}} e^{i\frac{\Delta t}{2}\mathcal{L}_{\mathbf{P}}}\ \mathbf{p}_i(t) \rightarrow \mathbf{p}_i(t+\tfrac{\Delta t}{2}) = \mathbf{p}_i(t) + \tfrac{\Delta t}{2}\dot{\mathbf{p}}_i(t)$$



Time integration: Operators

These are the rules!

$$e^{i\frac{\Delta t}{2}\mathcal{L}_{\mathbf{P}}}\ \mathbf{r}_i = \mathbf{r}_i \qquad e^{i\frac{\Delta t}{2}\mathcal{L}_{\mathbf{P}}}\ \mathbf{p}_i = \mathbf{p}_i + \frac{\Delta t}{2}\dot{\mathbf{p}}_i$$

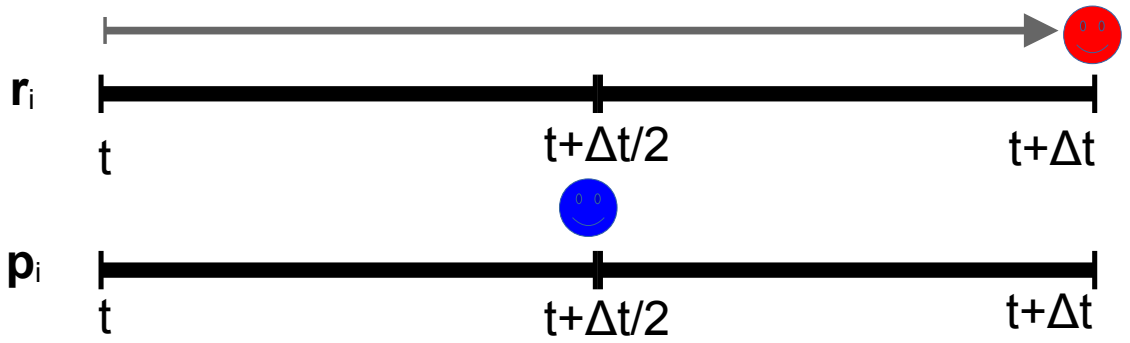
$$e^{i\Delta t\mathcal{L}_{\mathbf{r}}}\ \mathbf{r}_i = \mathbf{r}_i + \Delta t\ \dot{\mathbf{r}}_i \qquad e^{i\Delta t\mathcal{L}_{\mathbf{r}}}\ \mathbf{p}_i = \mathbf{p}_i.$$

The second operator:

$$e^{i\frac{\Delta t}{2}\mathcal{L}_{\mathbf{P}}}e^{i\Delta t\mathcal{L}_{\mathbf{r}}}\ \mathbf{r}_i(t) \rightarrow \mathbf{r}_i(t+\Delta t) = \mathbf{r}_i(t) + \Delta t\dot{\mathbf{r}}_i(t+\frac{\Delta t}{2})$$

velocities already 'live' at Δt/2!

$$e^{i\frac{\Delta t}{2}\mathcal{L}_{\mathbf{P}}}e^{i\Delta t\mathcal{L}_{\mathbf{r}}}\ \mathbf{p}_i(t+\frac{\Delta t}{2}) \rightarrow \mathbf{p}_i(t+\frac{\Delta t}{2})$$



Time integration: Operators

These are the rules!

$$e^{i\frac{\Delta t}{2}\mathcal{L}_{\mathbf{P}}}\ \mathbf{r}_i = \mathbf{r}_i \qquad e^{i\frac{\Delta t}{2}\mathcal{L}_{\mathbf{P}}}\ \mathbf{p}_i = \mathbf{p}_i + \frac{\Delta t}{2}\dot{\mathbf{p}}_i$$

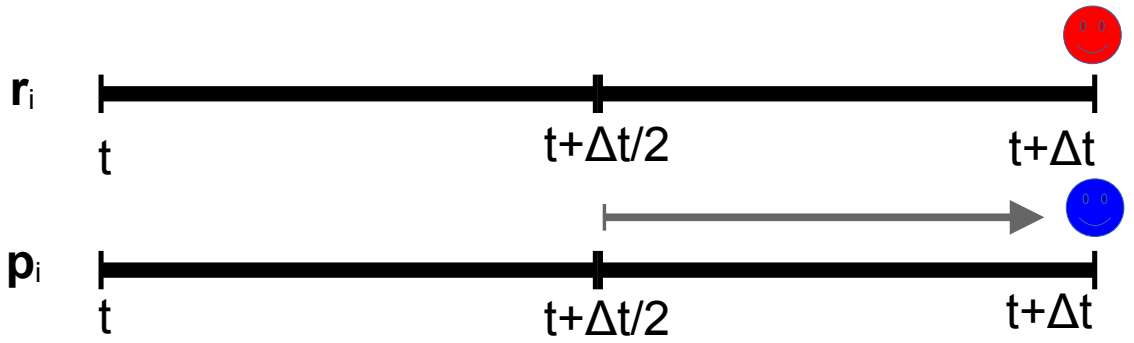
$$e^{i\Delta t\mathcal{L}_{\mathbf{r}}}\ \mathbf{r}_i = \mathbf{r}_i + \Delta t\ \dot{\mathbf{r}}_i \qquad e^{i\Delta t\mathcal{L}_{\mathbf{r}}}\ \mathbf{p}_i = \mathbf{p}_i.$$

The last operator:

$$e^{i\frac{\Delta t}{2}\mathcal{L}_{\mathbf{P}}}\ \mathbf{r}_i(t+\Delta t) \rightarrow \mathbf{r}_i(t+\Delta t) = \mathbf{r}_i(t) + \Delta t\dot{\mathbf{r}}(t+\frac{\Delta t}{2})$$

$$e^{i\frac{\Delta t}{2}\mathcal{L}_{\mathbf{P}}}\ \mathbf{p}_i(t+\frac{\Delta t}{2}) \rightarrow \mathbf{p}_i(t+\Delta t) = \mathbf{p}_i(t+\frac{\Delta t}{2}) + \frac{\Delta t}{2}\dot{\mathbf{p}}_i(t+\Delta t)$$

Position dependent forces already 'live' at t+Δt!



Time integration: Operators

These are the rules!

$$e^{i\frac{\Delta t}{2}\mathcal{L}_{\mathbf{p}}}\ \mathbf{r}_i = \mathbf{r}_i \qquad e^{i\frac{\Delta t}{2}\mathcal{L}_{\mathbf{p}}}\ \mathbf{p}_i = \mathbf{p}_i + \frac{\Delta t}{2}\dot{\mathbf{p}}_i$$

$$e^{i\Delta t\mathcal{L}_{\mathbf{r}}}\ \mathbf{r}_i = \mathbf{r}_i + \Delta t\ \dot{\mathbf{r}}_i \qquad e^{i\Delta t\mathcal{L}_{\mathbf{r}}}\ \mathbf{p}_i = \mathbf{p}_i.$$

$$\begin{aligned}
e^{i\frac{\Delta t}{2}\mathcal{L}_{\mathbf{p}}}\ e^{i\Delta t\mathcal{L}_{\mathbf{r}}}\ e^{i\frac{\Delta t}{2}\mathcal{L}_{\mathbf{p}}}\ \mathbf{r}_i(t) &= \mathbf{r}_i(t) + \Delta t\ \dot{\mathbf{r}}(\frac{\Delta t}{2}) \\
&= \mathbf{r}_i(t) + \Delta t\ \mathbf{v}_i(t) + \frac{\Delta t^2}{2m_i}\mathbf{f}_i(t) \\
e^{i\frac{\Delta t}{2}\mathcal{L}_{\mathbf{p}}}\ e^{i\Delta t\mathcal{L}_{\mathbf{r}}}\ e^{i\frac{\Delta t}{2}\mathcal{L}_{\mathbf{p}}}\ \mathbf{p}_i(t) &= \mathbf{p}_i(t) + \frac{\Delta t}{2}\left(\dot{\mathbf{p}}_i(t) + \dot{\mathbf{p}}_i(t+\Delta t)\right) \\
&= \mathbf{p}_i(t) + \frac{\Delta t}{2}\left(\mathbf{f}_i(t) + \mathbf{f}_i(t+\Delta t)\right).
\end{aligned}$$

This is called the Velocity-Verlet algorithm. It is time reversible and phase-space conserving by construction (Hamiltonian flow conserves phase-space = Liouville theorem).

Time integration: Operators

These are the rules!

$$e^{i\frac{\Delta t}{2}\mathcal{L}_{\mathbf{p}}}\ \mathbf{r}_i = \mathbf{r}_i \qquad e^{i\frac{\Delta t}{2}\mathcal{L}_{\mathbf{p}}}\ \mathbf{p}_i = \mathbf{p}_i + \frac{\Delta t}{2}\dot{\mathbf{p}}_i$$

$$e^{i\Delta t\mathcal{L}_{\mathbf{r}}}\ \mathbf{r}_i = \mathbf{r}_i + \Delta t\ \dot{\mathbf{r}}_i \qquad e^{i\Delta t\mathcal{L}_{\mathbf{r}}}\ \mathbf{p}_i = \mathbf{p}_i.$$

$$e^{i\frac{\Delta t}{2}\mathcal{L}_{\mathbf{p}}}\ e^{i\Delta t\mathcal{L}_{\mathbf{r}}}\ e^{i\frac{\Delta t}{2}\mathcal{L}_{\mathbf{p}}}\ \mathbf{r}_i(t) = \mathbf{r}_i(t) + \Delta t\ \dot{\mathbf{r}}(\frac{\Delta t}{2})$$

$$= \mathbf{r}_i(t) + \Delta t\ \mathbf{v}_i(t) + \frac{\Delta t^2}{2m_i}\mathbf{f}_i(t)$$

$$e^{i\frac{\Delta t}{2}\mathcal{L}_{\mathbf{p}}}\ e^{i\Delta t\mathcal{L}_{\mathbf{r}}}\ e^{i\frac{\Delta t}{2}\mathcal{L}_{\mathbf{p}}}\ \mathbf{p}_i(t) = \mathbf{p}_i(t) + \frac{\Delta t}{2}\left(\dot{\mathbf{p}}_i(t) + \dot{\mathbf{p}}_i(t+\Delta t)\right)$$

$$= \mathbf{p}_i(t) + \frac{\Delta t}{2}\left(\mathbf{f}_i(t) + \mathbf{f}_i(t+\Delta t)\right).$$

Velocity-Verlet looks like the Euler scheme except for the force averaging!

Time integration: Atomic magnitudes

typical atomic magnitudes:

x (10^{-9} m)
v (+/- 600 m/s !!)
F (10^{-11} N)
a (10^{13} g !!!!!)
Δt (10^{-15}s)

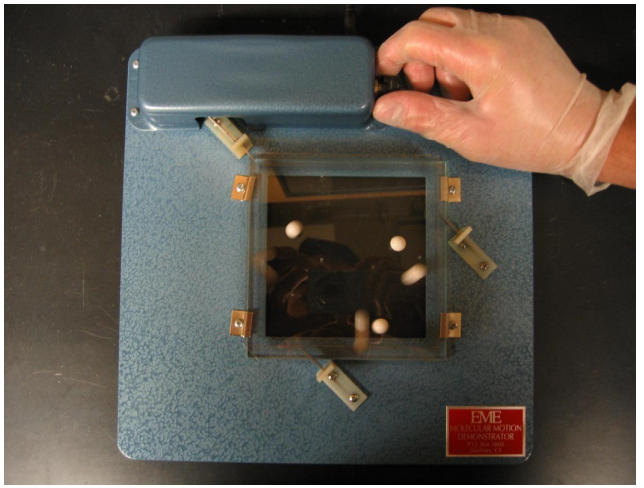
Velocity-Verlet scheme:

$$x_{i+1} = x_i + v_i \Delta t + \frac{1}{2} a_i \Delta t^2$$

$$v_{i+1} = v_i + \frac{1}{2}(a_i + a_{i+1}) \Delta t$$

$$t + \Delta t$$

- Note that gravity (1 vs 10^{13}g) does not play a significant role on the motion of individual atom.
- Speed of sound relates to the atomic velocities.



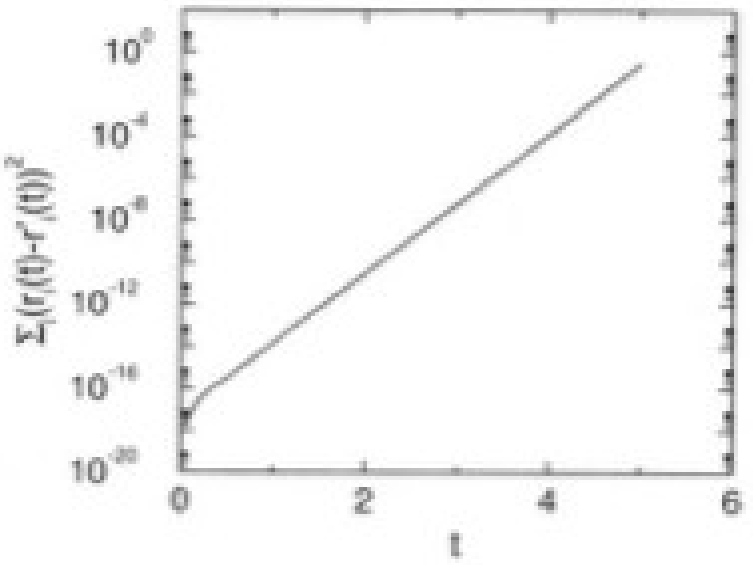


Figure 4.1: Illustration of the Lyapunov instability in a simulation of a Lennard-Jones system. The figure shows the time dependence of the sum of squared distances between two trajectories that were initially very close (see text). The total length of the run in reduced units was 5, which corresponds to 1000 time steps. Note that, within this relatively short time, the two trajectories become essentially uncorrelated.