Info
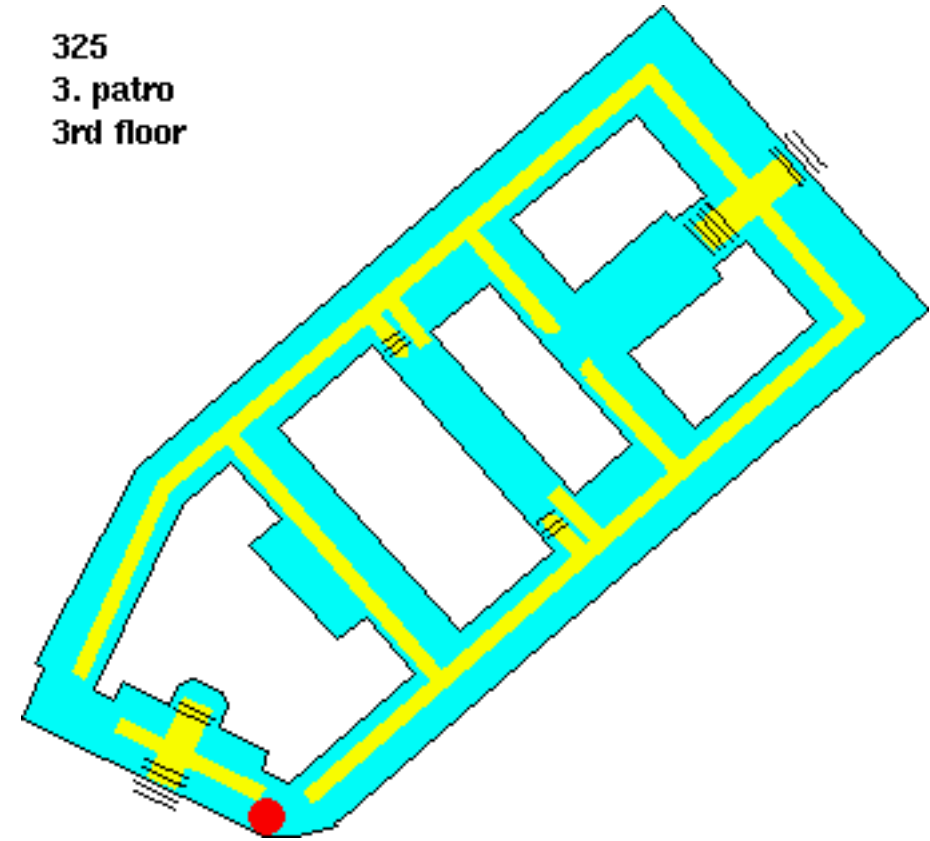
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220 444 257

325
3. patro
3rd floor

Sources:

🟣 for TUL: https://nanoed.tul.cz/course/view.php?id=56

🟣 more advanced: http://old.vscht.cz/fch/en/tools/kolafa/S403027.html

🟣 Google: Kolafa Molecular modeling and simulation
Kolafa Molekulární modelování a simulace

⚪ *? elementary particles + gravity*, GUT, dark energy, . . .

⚪ *known elementary particles*: Standard model, atomic nuclei,. . .

⚪ *Nuclei + electrons + photons*: QED, accurate spectroscopy

🟣 *Nuclei + electrons*: Schrödinger equation – small molecules, spectra, gas-phase equilibria, chemical kinetic, photochemistry . . .

🟣 *Atoms** – classical (or quantum) atomistic modeling

🟣 *Coarsed-grained models*: meso/nanoscopic scale
element = polyatomic group
(surfactant = head + tail, polymer = [bead]$_n$. . .)

🟣 *Microscopic scale* (dispersions, granular materials)

🟣 *Continuum*: partial differential equations

⚪ *gravity*: spacetime

---

multiscale modeling: QM/MM, . . .

*optionally: auxiliary interaction centers (sites), bigger groups (-CH$_3$)

Potential Energy Surface (PES)

Nuclei are much heavier than electrons $\Rightarrow$ electron motion is much faster (Born–Oppenheimer **approximation**)
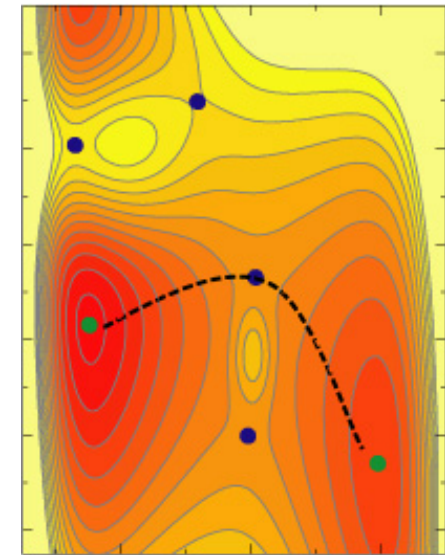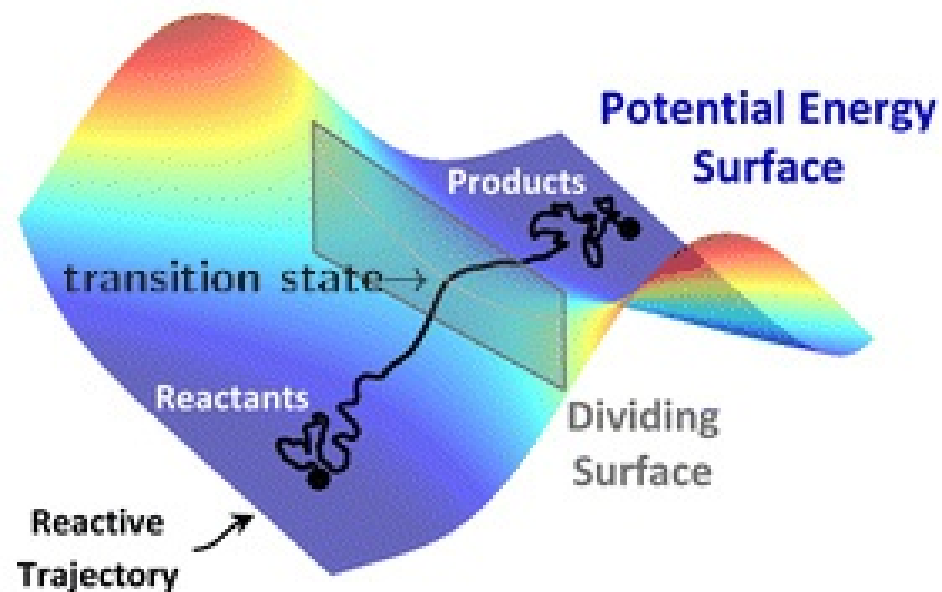
Potential energy surface (PES):

energy as a function of positions of all nuclei

$$E_{\text{pot}}(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N)$$

Chemical example:
reaction coordinate

A reaction proceeds over (near to) a saddle point (transition state)

Potential Energy Surface

Products

transition state →

Reactants

Dividing Surface

Reactive Trajectory

● Minima
● Saddle Points

credits: *http://www.ucl.ac.uk/~ucecmst/publications.html, http://theory.cm.utexas.edu/henkelman/research/ltd/*

How to obtain PES?

🟣 from quantum calculations (Schrödinger equation: *ab initio*, DFT)

🟣 approximated by a formula ("force field", "potential", "model", . . .)
  force field: E_{pot} = sum of many terms
  term = function form + parameters for atoms/groups

🟣 combination: QM/MM methods (**q**uantum **m**echanics/**m**olecular **m**echanics)

PES and modeling in chemistry

🟣 using classical mechanics:
  static calculations: minimum of energy, potential around a molecule
  time development of system (**m**olecular **d**ynamics, MD)
  thermodynamic variables by sampling (**M**onte **C**arlo, MC)

🟣 using quantum mechanics to nuclei:
  path integral methods (PI MC, PI MD)

🟣 classical mechanics + quantum corrections

combination force field + classical mechanics = "**m**olecular **m**echanics" (MM); strictly speaking does not include MC and MD

Molecular mechanics: static approach

We use PES, usually described by a force field

- ⬤ Energy minimization ($T = 0$)
  "molecular mechanics", "structure optimization"

- ⬤ Refinement – more accurate structure (from diffraction data)

- ⬤ Biochemistry: molecular shape (lock and key), hydrophillic/hydrophobic

- ⬤ QSAR (**Q**uantitative **S**tructure–**A**ctivity **R**elationship) descriptors
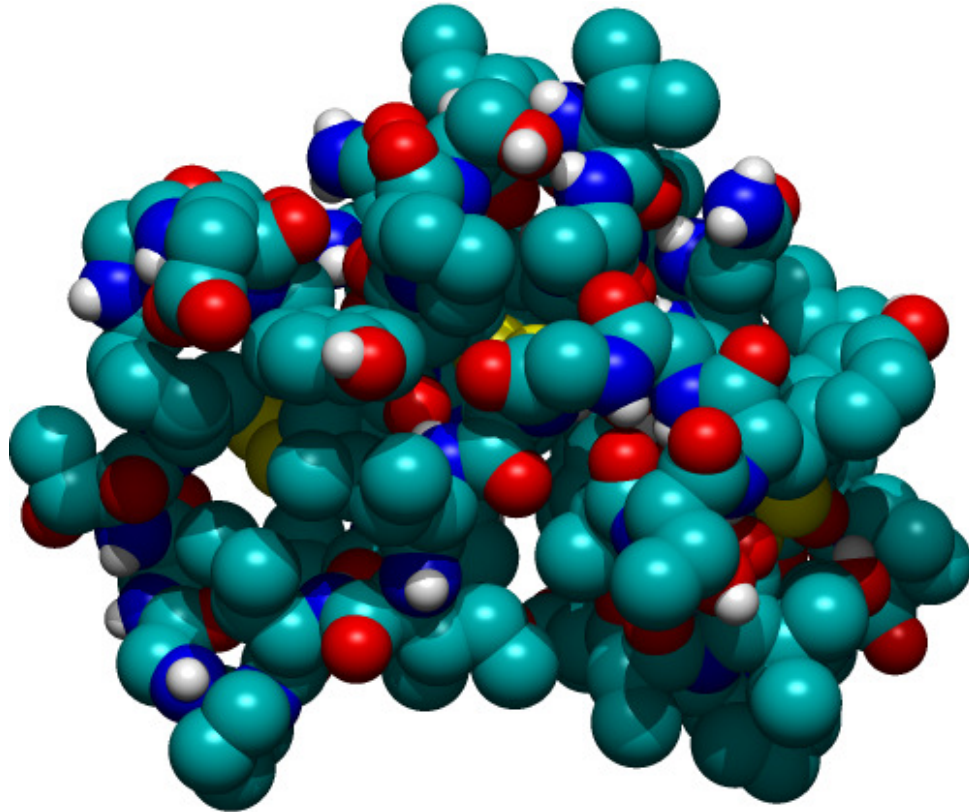
. . . but what about **motion**?

🟣 "Real" motion of molecules in time

🟣 All possible configurations averaged in time:

 →
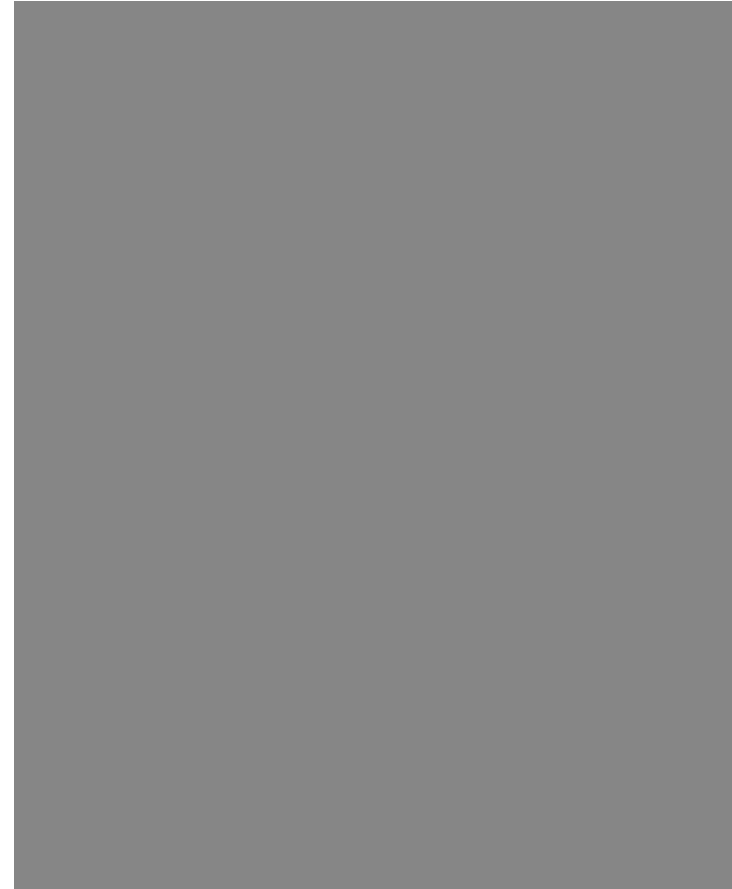
Statistical thermodynamics calculates quantities (boiling point, ligand–receptor affinity, . . .) based on the idea of a (macro)state of a system as an "average" of all possible configurations

🔴 molecular dynamics (MD)

- 🔵 time development of a system composed of many molecules

- 🔵 instantaneous forces acting on atoms cause their motion

🔴 Monte Carlo (MC); more precisely: Metropolis method and its variants

- 🔵 a sequence of configurations of the system is generated using random numbers

- 🔵 an attempt is made to move a molecule (randomly with a certain distribution)

- 🔵 this trial move is accepted or rejected so that its probability is the same as in real system

🔴 kinetic Monte Carlo

- 🔵 the simulated process is divided into elementary events (e.g., adsorption of an atom on a growing crystal, catalytical reaction)

- 🔵 the event to happen is chosen according to a known probability

⚪ quantum simulations – MD, MC

⚪ Las Vegas algorithms – deterministic result (random pivot, search for minimum)

What can be studied

🔴 Liquids:

   🔵 how structure affects properties (anomalies of water), solutions

   🔵 phase equilibria, solubility

   🔵 surfaces, interfaces, surfactants

🔴 Solids:

   🔵 crystal structure, materials (defects)

   🔵 adsorption (zeolites)

🔴 Biochemistry:

   🔵 proteins, nucleic acids, ion channels, lipid membranes

🔴 Nanoobjects:

   🔵 micelles, polymers, self-assembly (coarse-grained models, lattices)
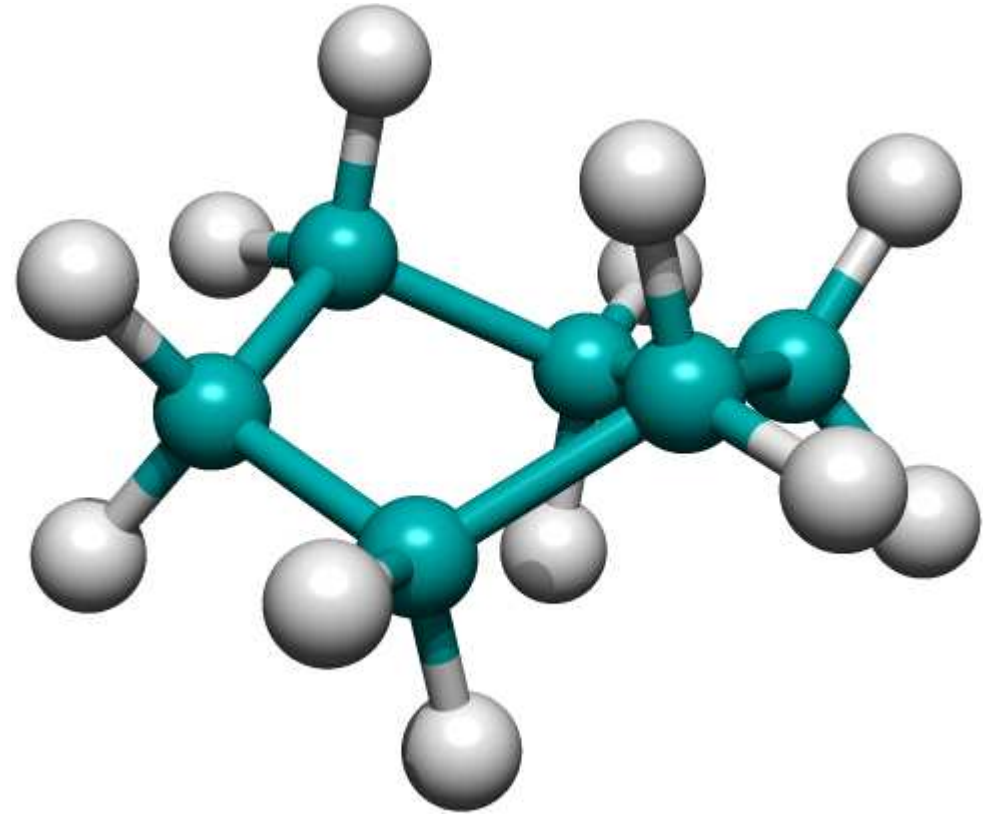
🔴 Similar methods can be used for:

   🔵 granular materials, optimization, spreading of epidemies, evo-devo . . .

Structure optimization (molecular mechanics)
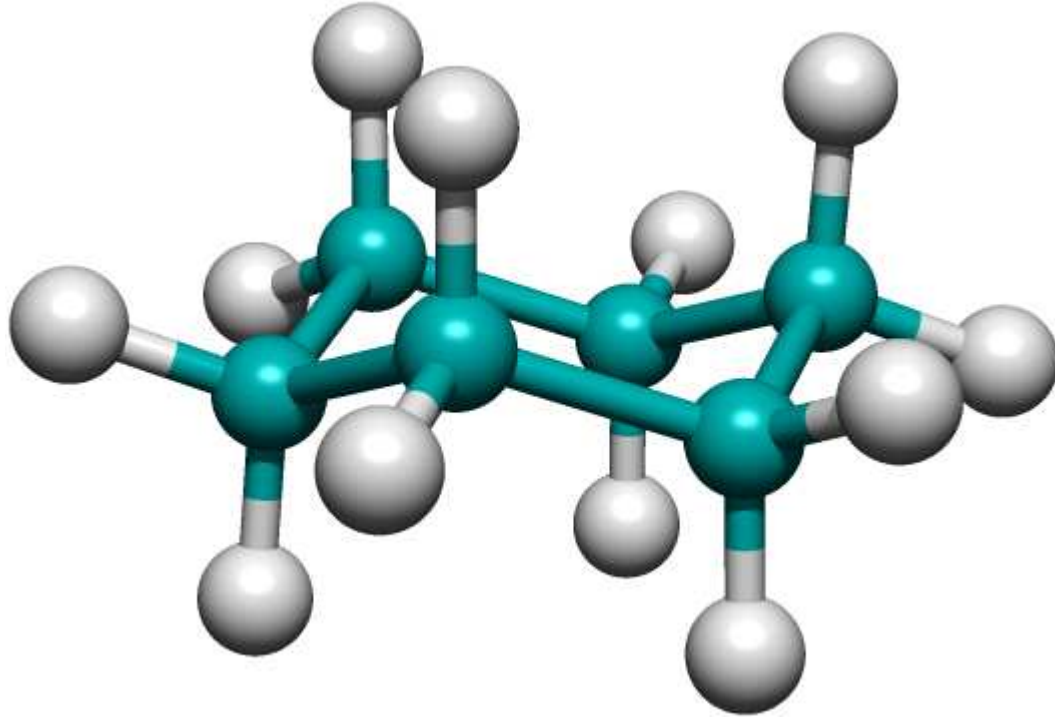
chair
experiment: 28 kJ/mol
model: 26 kJ/mol

twist (skew) boat
experiment: 45 kJ/mol
model: 53 kJ/mol

Liquid water

- 10000 molecules
- 300 K
- periodic in x, y
- adhesive pad
- nonadhesive lid

More movies: https://vesmir.cz/cz/on-line-clanky/2014/07/struktura-anomalie-vody.html
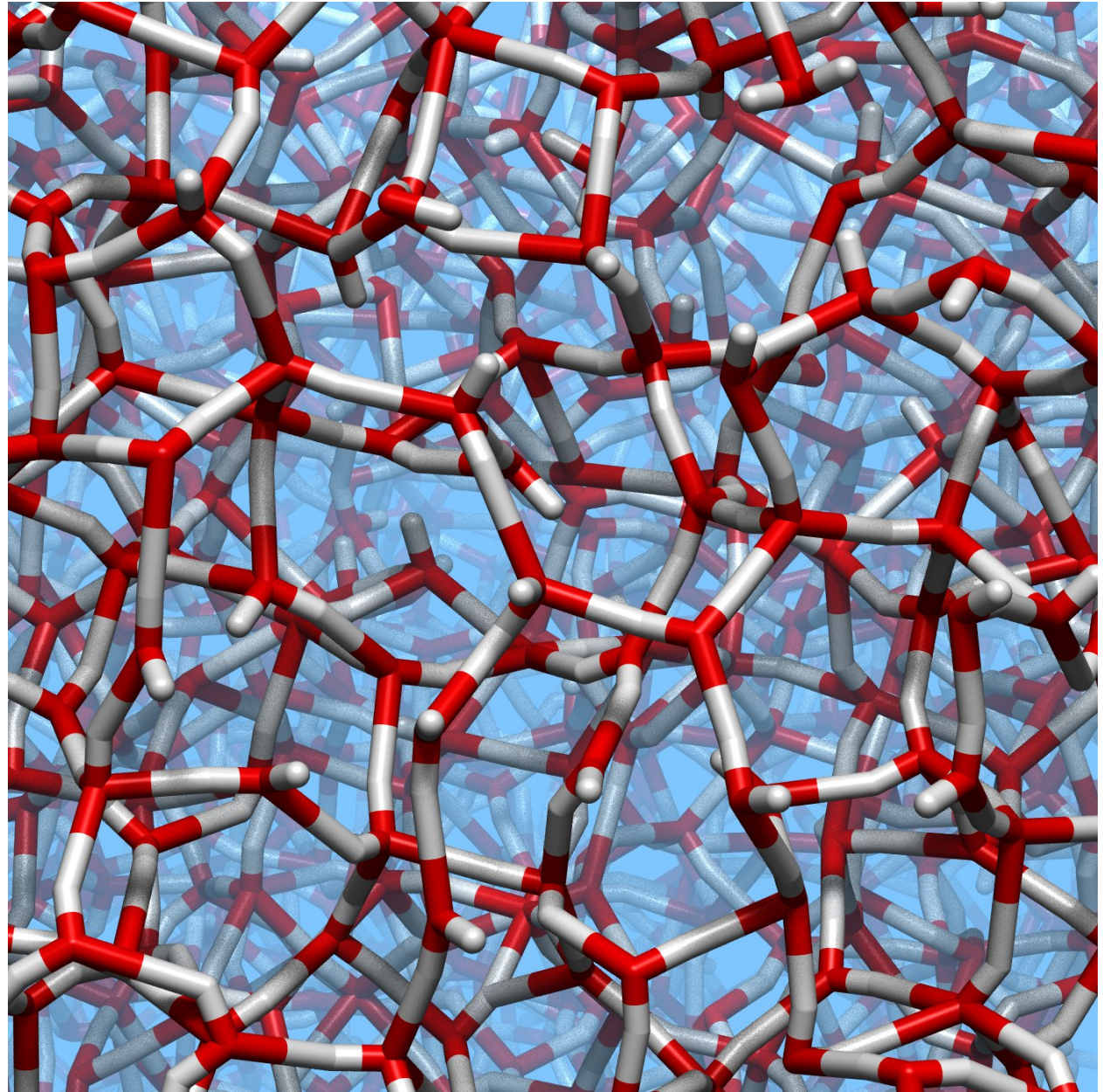
Electrospray of Cytochrome C

🟣 Electrospray: spray of charged aerosol

🟣 Cross section is determined
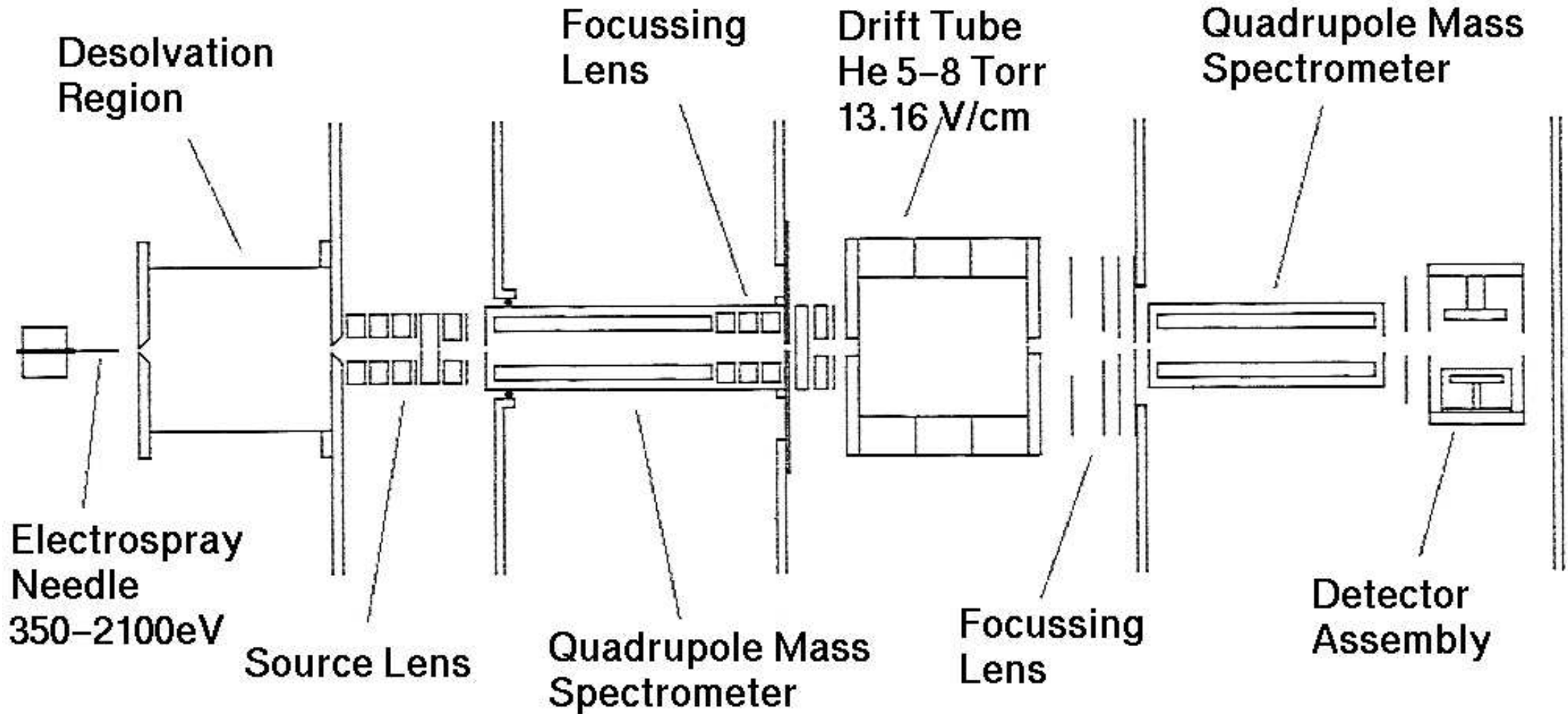
Yi Mao, J. Woenckhaus, J. Kolafa, M. A. Ratner, M. F. Jarrold: *J. Am. Chem. Soc.* **121**, 2712–2721 (1999)

SIMOLANT

Features:

- 2D "atoms" with a Lennard-Jones type potential (8–4)

- repulsive/attractive walls, gravity

- MC and MD

- constant energy and thermostat

Phenomena:

- condensation of vapor

- freezing of a droplet

- crystal defects

- capilary action

- gas in a gravitational field

- vapor-liquid equilibrium

- nucleation

Install SIMOLANT: http://old.vscht.cz/fch/software/simolant/index-en.html

Self-assembly
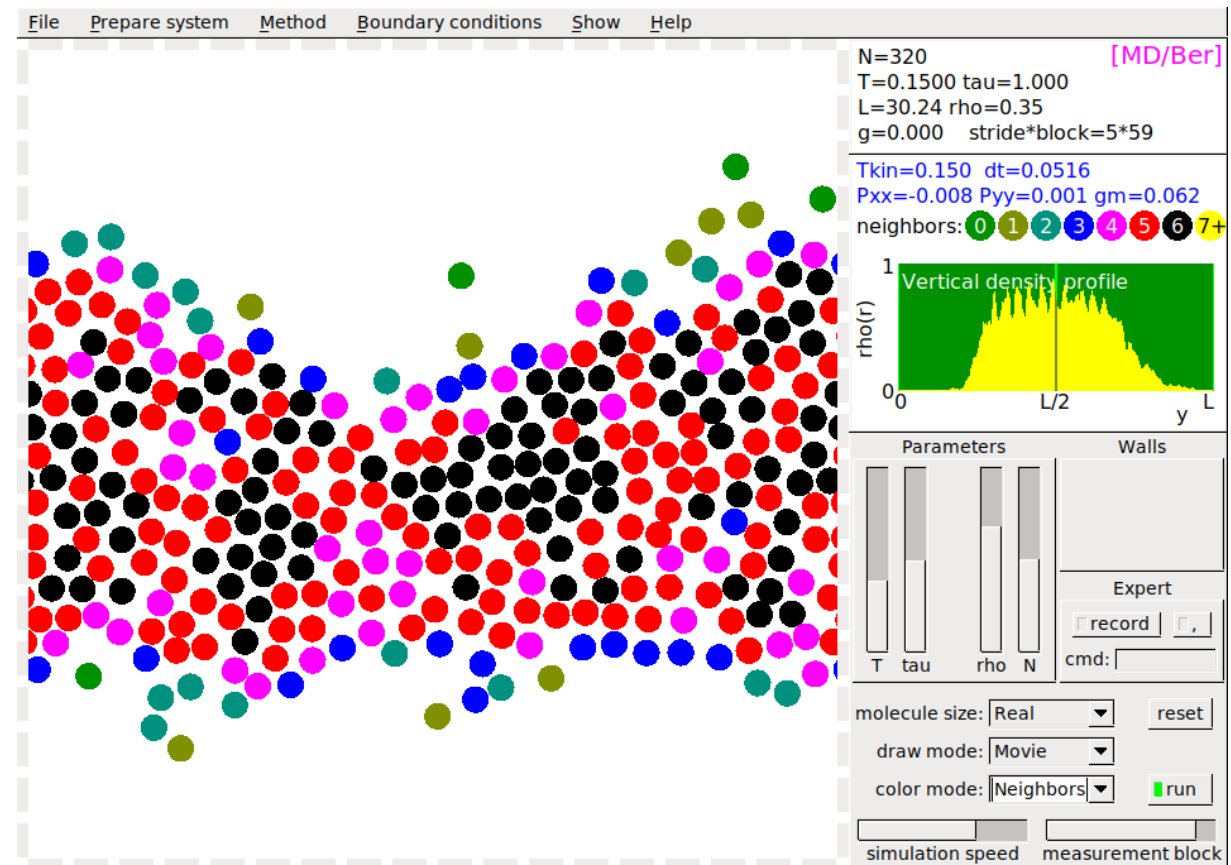
Supramolecular chemistry: assembling molecules using noncovalent forces (van der Waals, hydrogen bonds) to higher structural elements

🟣 Show: bivalent particles in a solution ≈ "Janus particles"

Janus

Janus

Iapetus
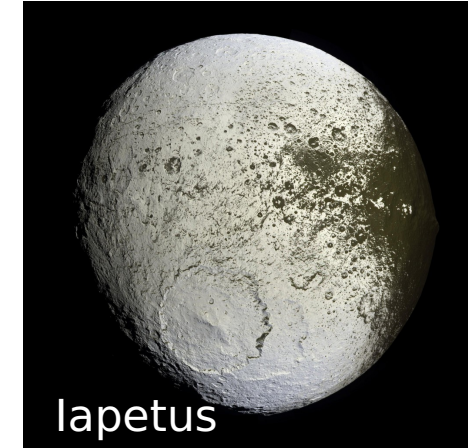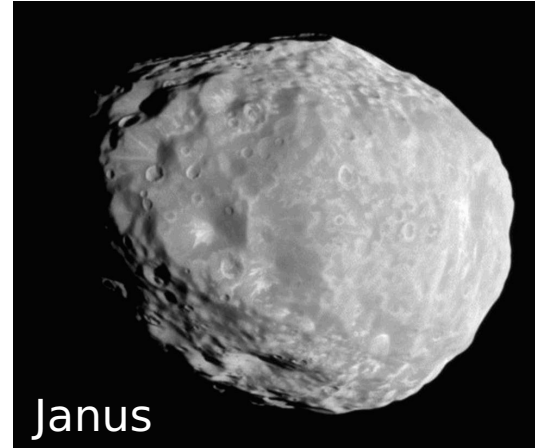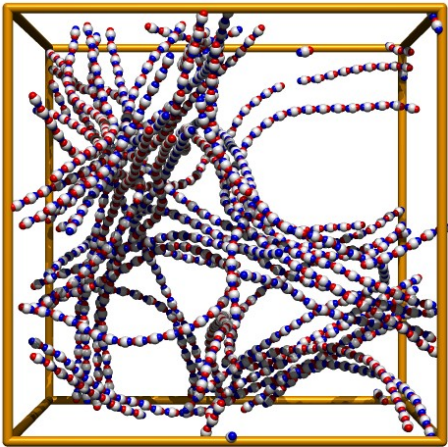
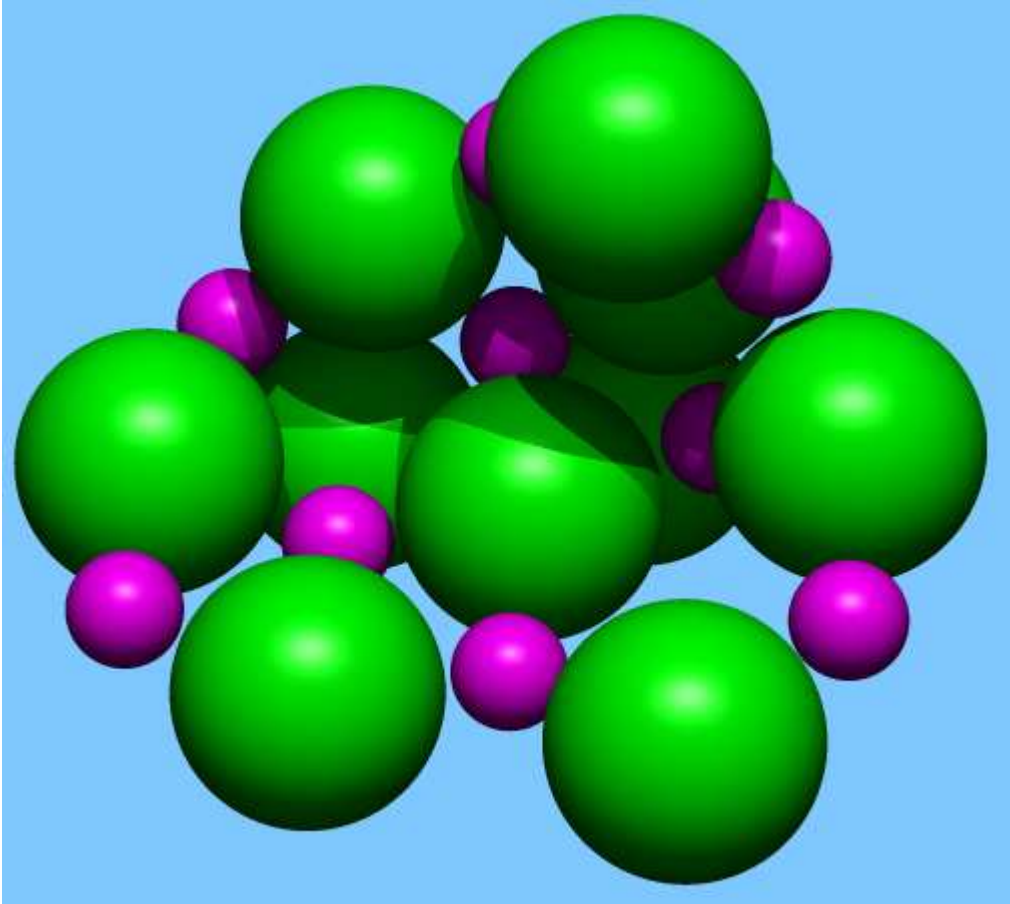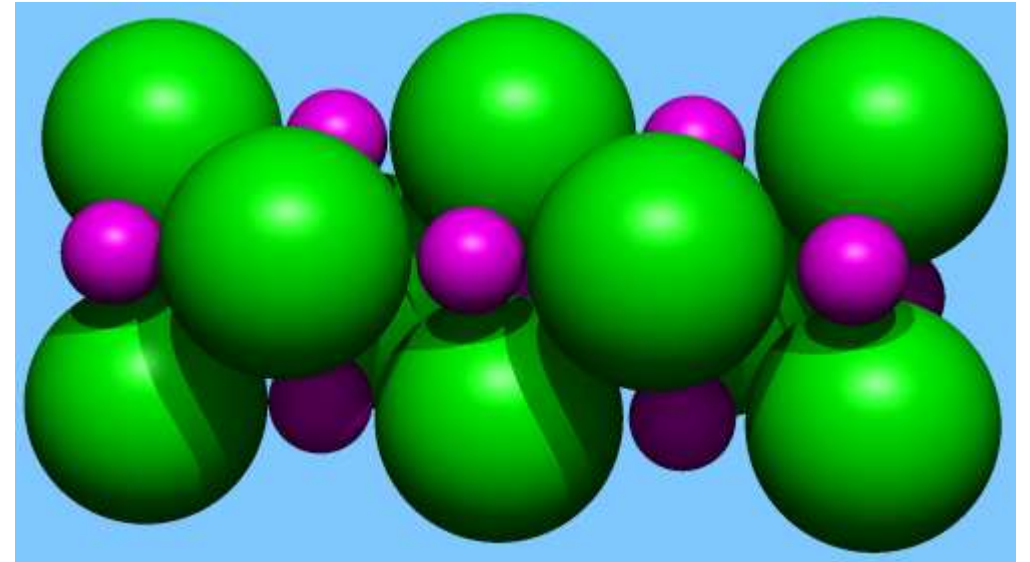*credit: wikipedie, www.nasa.gov/mission_pages/cassini*

🟣 Show: + tetratetravalent particles
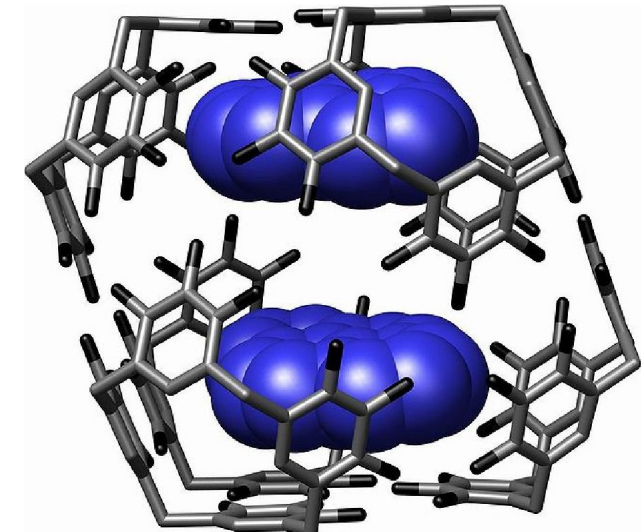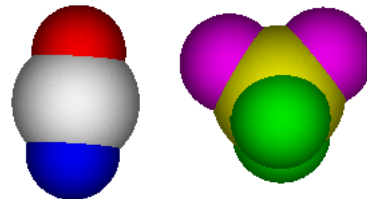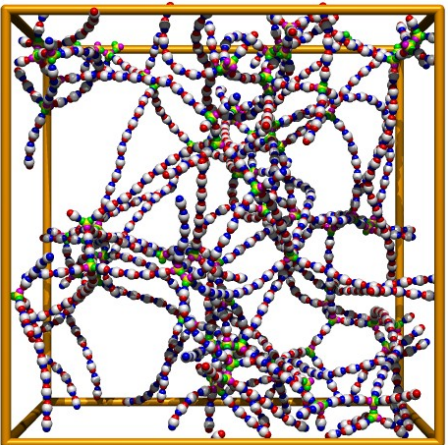
credit: Atwood et al., Science 309, 2037 (2005)

How to get energy minimum

Minimum energy of (a model of) $Na_{10}Cl_{10}$ cluster

fast cooling (quenching)

slow cooling (annealing)

Optimization by simulated annealing

We are looking for the **global minimum** of function $U(A_i)$ (with many local minima)

- Configuration changes $A_i \rightarrow A_j$

- Metropolis MC simulation while decreasing "temperature" T

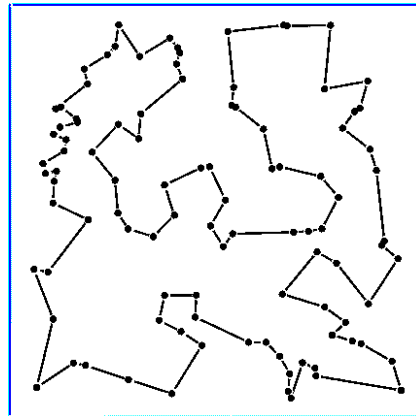**Example:** Traveling salesman problem

- 100 cities randomly in square 1×1

- Configuration = sequence of cities

- U = path length

- Configuration change = interchange of 2 randomly chosen cities

for me (uvodsim/salesman.sh):
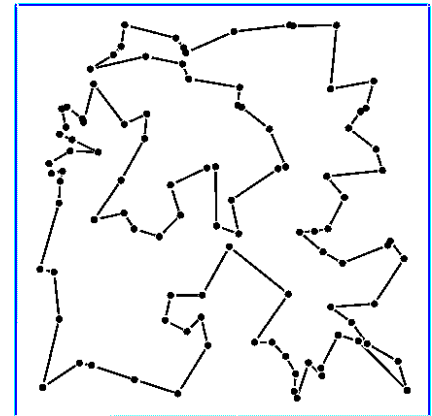- random start
- numerical results in the console

"greedy"
(Metropo-
lis $T = 0$)
$l = 8.5778$
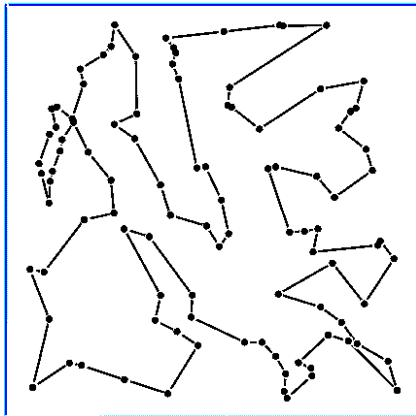
simulated
annealing
$l = 7.6663$

genetic
algorithm
$l = 8.1817$

The function to maximize is called here "fitness"

🟣 configuration → individual → genom = chromosome = list of alleles
("column of numbers")

🟣 initial (e.g., random) population

🟣 next generation:
  – kill the least fit individuals
  – copying (parthenogenesis) with a mutation
  – breeding from two parents with crossover

Numbers are coded by a Gray code
(consecutive integers differ by one bit)

Application:
– logistics, economy, control of processes
– biochemistry – protein folding
– electronics – circuit design, antena shape
– algorithm design

|	
0	0000
1	0001
2	0011
3	0010
4	0110
5	0111
6	0101
7	0100
8	1100
9	1101
10	1111
11	1110
12	1010
13	1011
14	1001
15	1000

- 🟣 several layers

- 🟣 discrete or continuous signal

- 🟣 usually →, rarely with feedback

- 🟣 nonlinear activation function (sigmoid)

- 🟣 weights for input mixing are adjustable

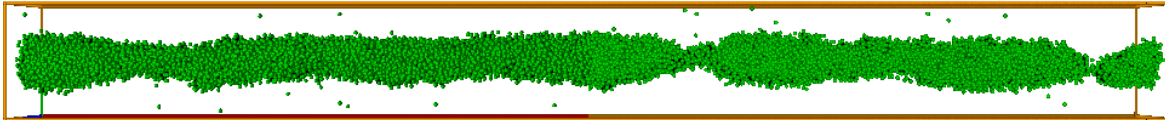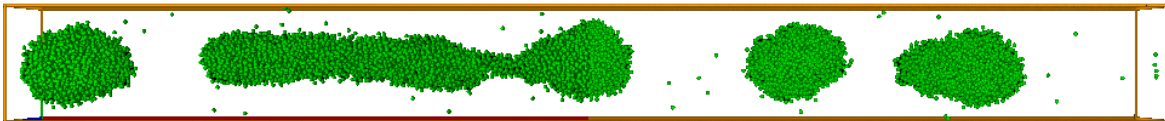**learning** = determining the weights using a training set
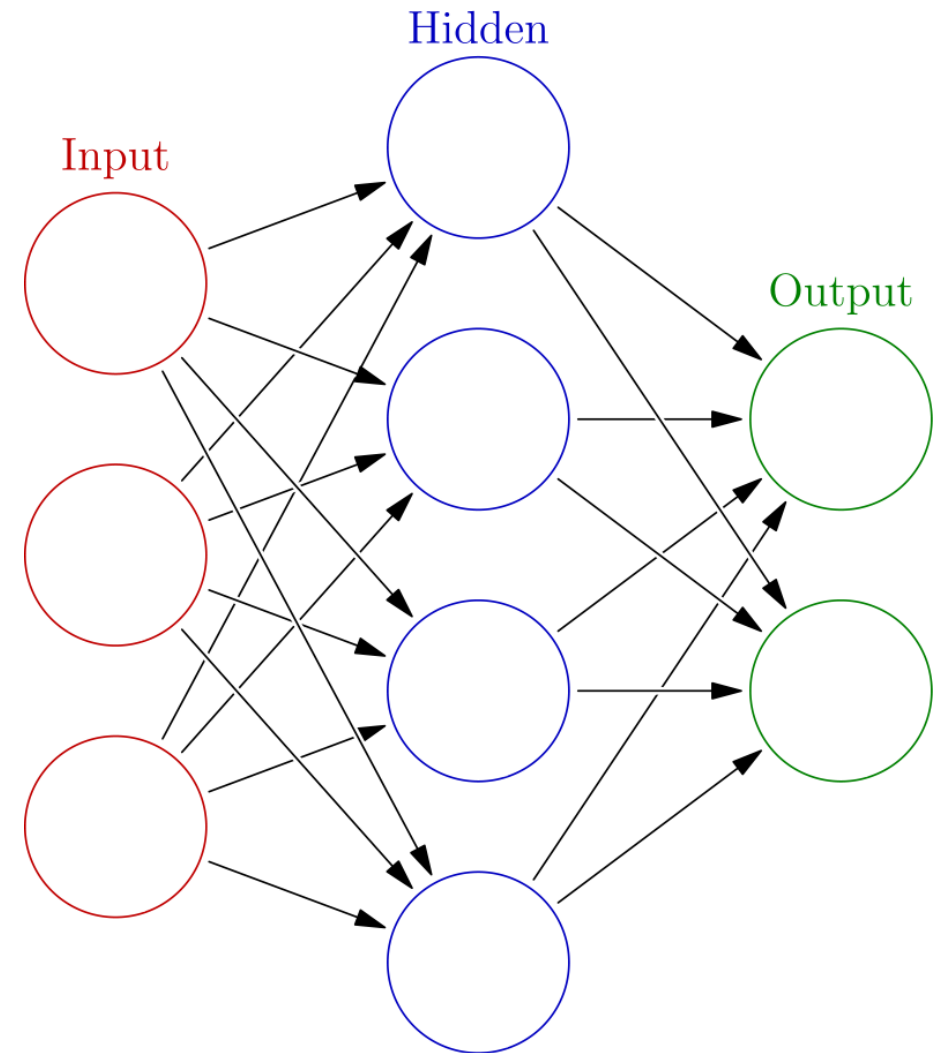
(Plateau-)Rayleigh instability

A stream of water splits into droplets. Instability for $kr < 1$ (for perturbation $\propto \sin(kz)$), max. instability for $kr = \ln 2$.
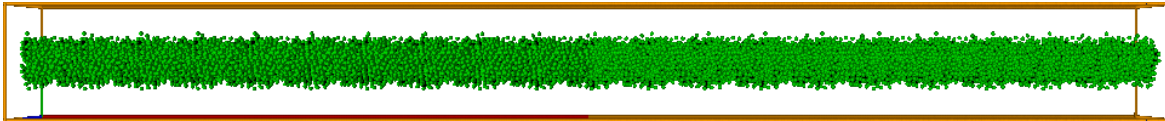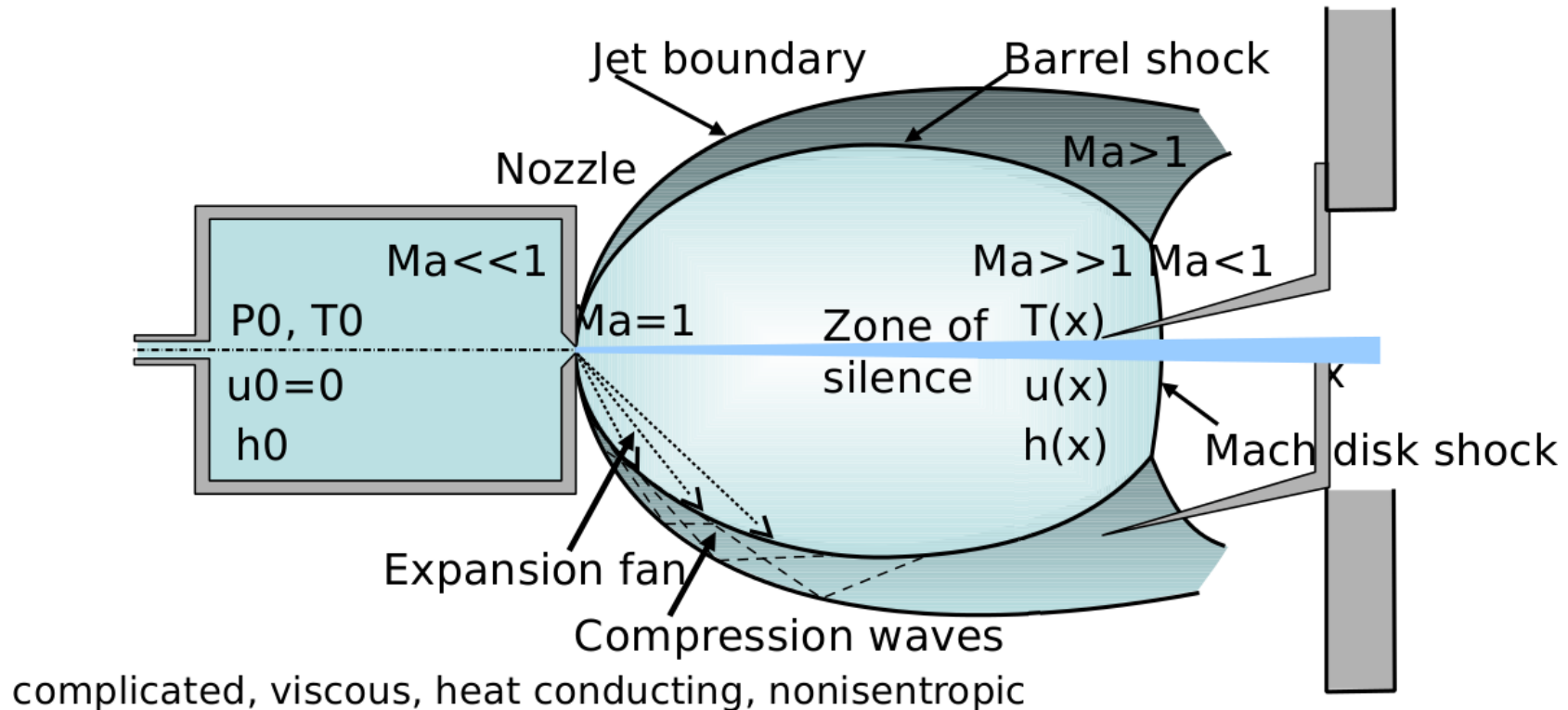

NB: "$\propto$" = "is proportional to"

Nucleation at supersonic expansion

Water vapor (about 150 °C and 5 bar) expands through a small (100 μm) nozzle to a vacuum. It cools adiabatically below freezing point.

Motivation: stratospheric physical chemistry.
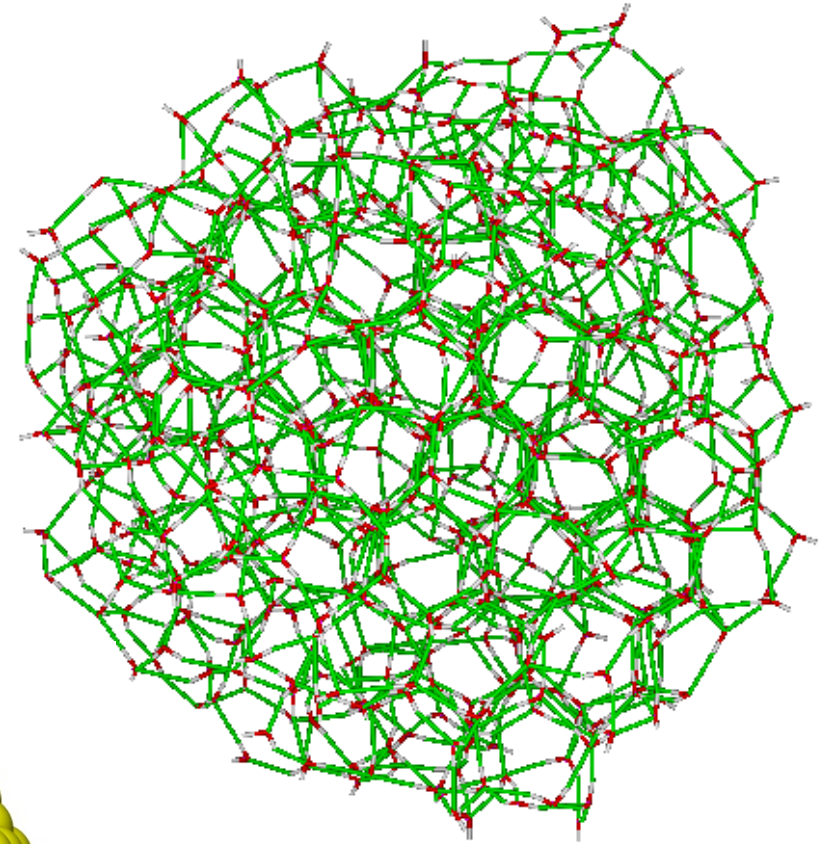

Free Jet Expansion

credit: M. Fárník

Question: what is the shape and structure of ice clusters?

J. Klíma, J. Kolafa: *J. Chem. Theory Comput.* **14**, 2332–2340 (2018)
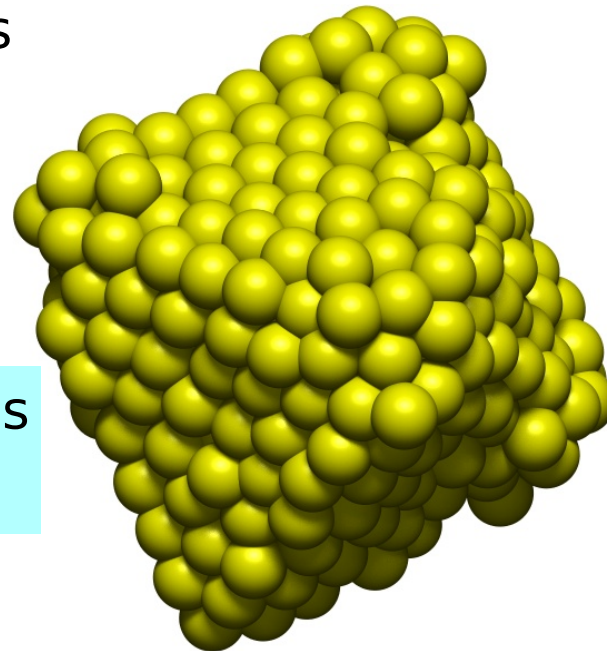
Melting of nanoparticles

Ice

- ⬤ hail of 600 water molecules (ice Ih)

- ⬤ gradual heating

- ⬤ simulation time = 5 ns
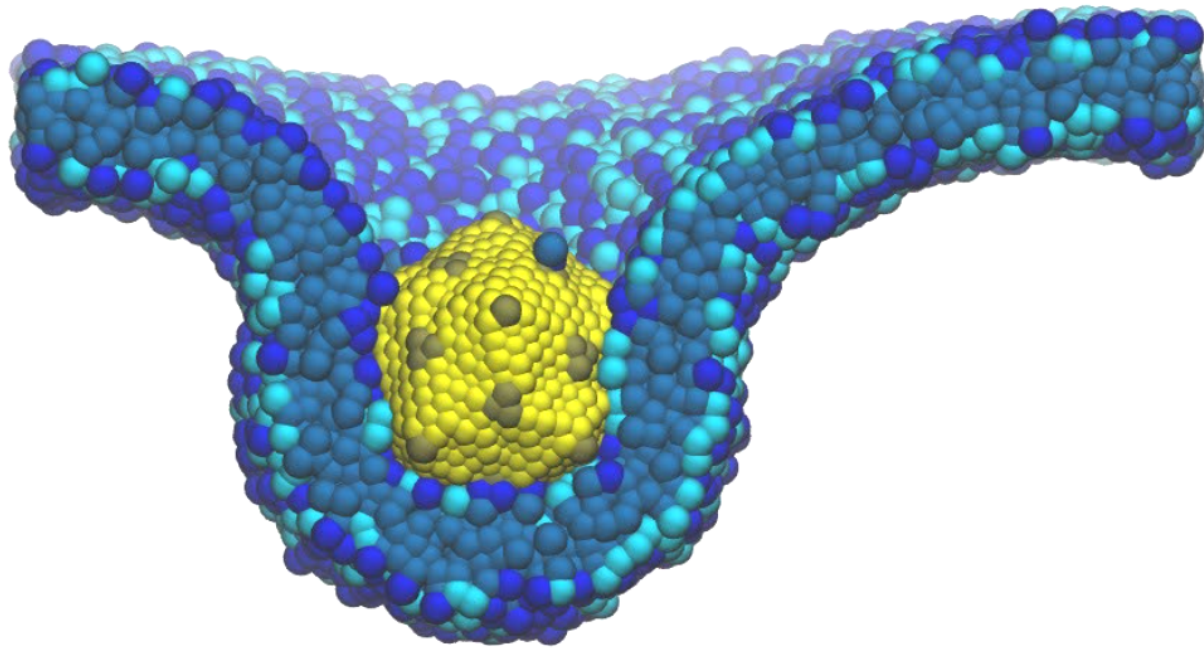
- ⬤ this model of water melts at 250 K

Gold

- ⬤ nanocrystal of 489 gold atoms

- ⬤ gradual heating
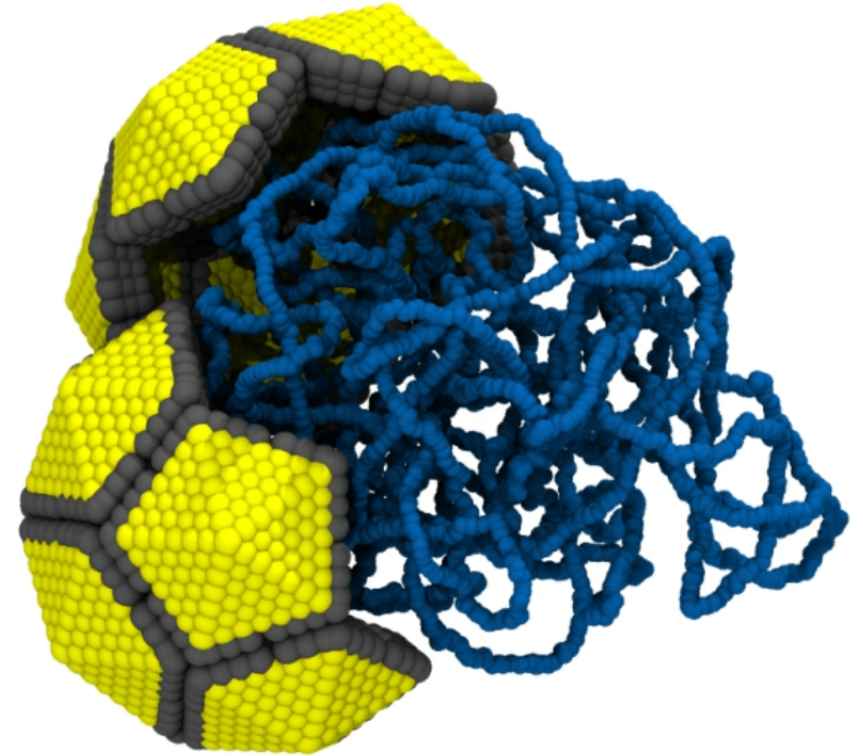
- ⬤ simulation time = 77 ps

the melting point of nanoparticles
is lower than in the bulk

Coarse-grained simulations

🟣 Coarse-grained model, Langevin thermostat (random forces)
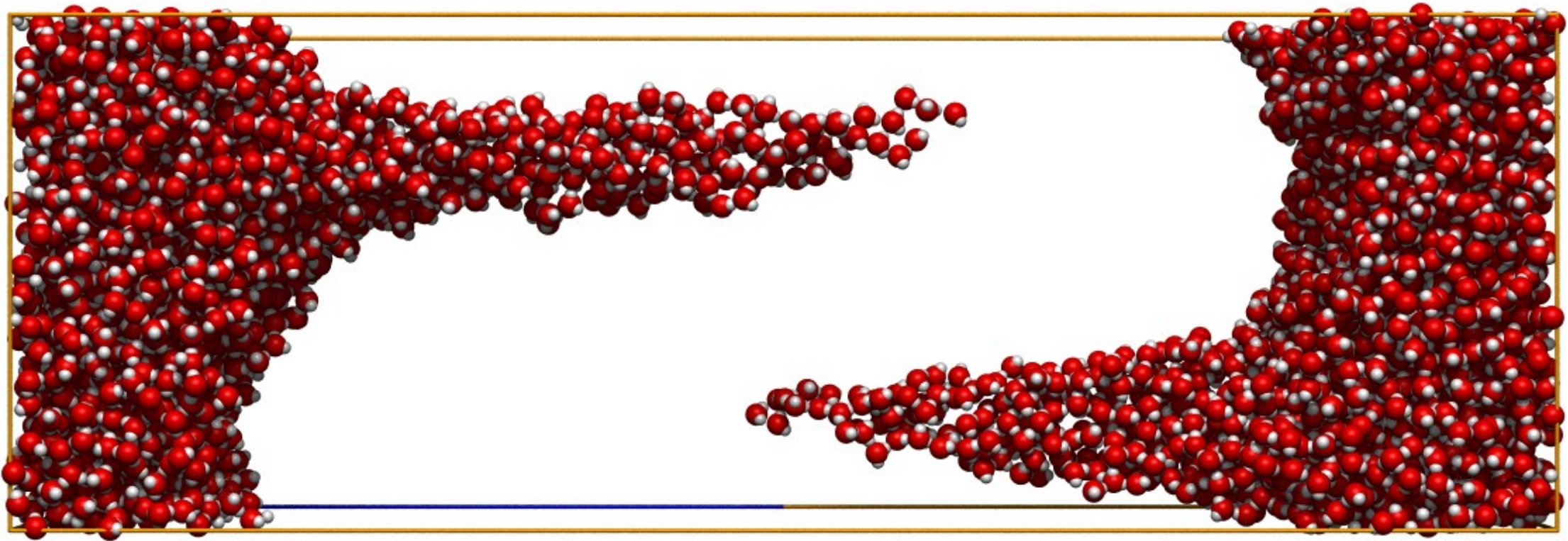
🟣 Water not shown

endocytosis
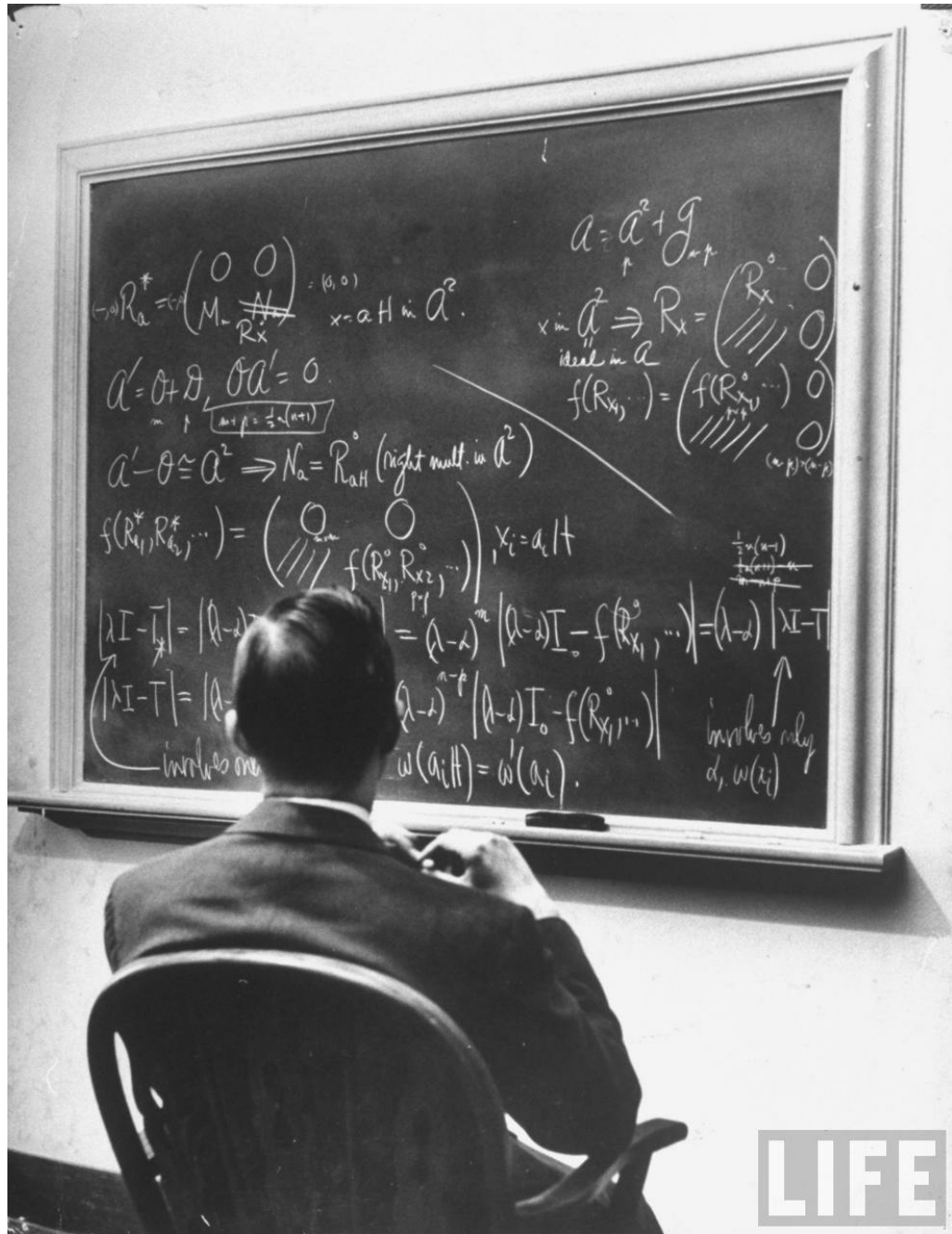
release of RNA from the capsid

Courtesy: © Robert Vácha (CEITEC)

Electrospinning

- 5000 SPC/E water molecules, field 1.5 V/nm, simulation time 135 ps

- electrospinning starts by the "Taylor cone"

- the tip elongates and produces a jet stabilized by electric field

Jan Jirsák, Filip Moučka, Ivo Nezbeda: *Ind. Eng. Chem. Res.* **53**, 8257–8264 (2014)

End of introduction – real lecture ahead. . .