Introduction to Numerical Simulations and High Performance Computing: From Materials Science to Biochemistry

Ecole Doctorale de Physique et Chimie Physique

Université de Strasbourg

Mauro Boero

Institut de Physique et Chimie des Matériaux de Strasbourg

University of Strasbourg - CNRS, F-67034 Strasbourg, France

@ Dept. of Applied Physics, The University of Tokyo, 7-3-1 Hongo, Tokyo 113-8656, Japan

Post K computer
-ポスト京開発プロジェクト

Computational Materials Science Initiative
計算物質科学イニシアティブ

Outline of the lectures

- **Classical Molecular Dynamics (MD):** Newtonian and Lagrangean dynamics; basic algorithms; time/ensemble averages

- **First Principles MD:** Brief review of Hartree-Fock approaches and Density Functional Theory; First Principles Molecular Dynamics (FPMD); Mermin functional and Free Energy MD (FEMD)

- **Hybrid schemes:** Combined classical MD and DFT-based MD: Hybrid QM/MM methods

- **Advanced Methods - Reactive schemes:** Free Energy sampling techniques and reaction path sampling

- **Advanced Methods - Path Integral and non-Adiabatic Methods:** Quantum nuclei and surface hopping dynamics

- **Brief overview of HPC architectures and parallel programming**

Time and Length scales in simulations
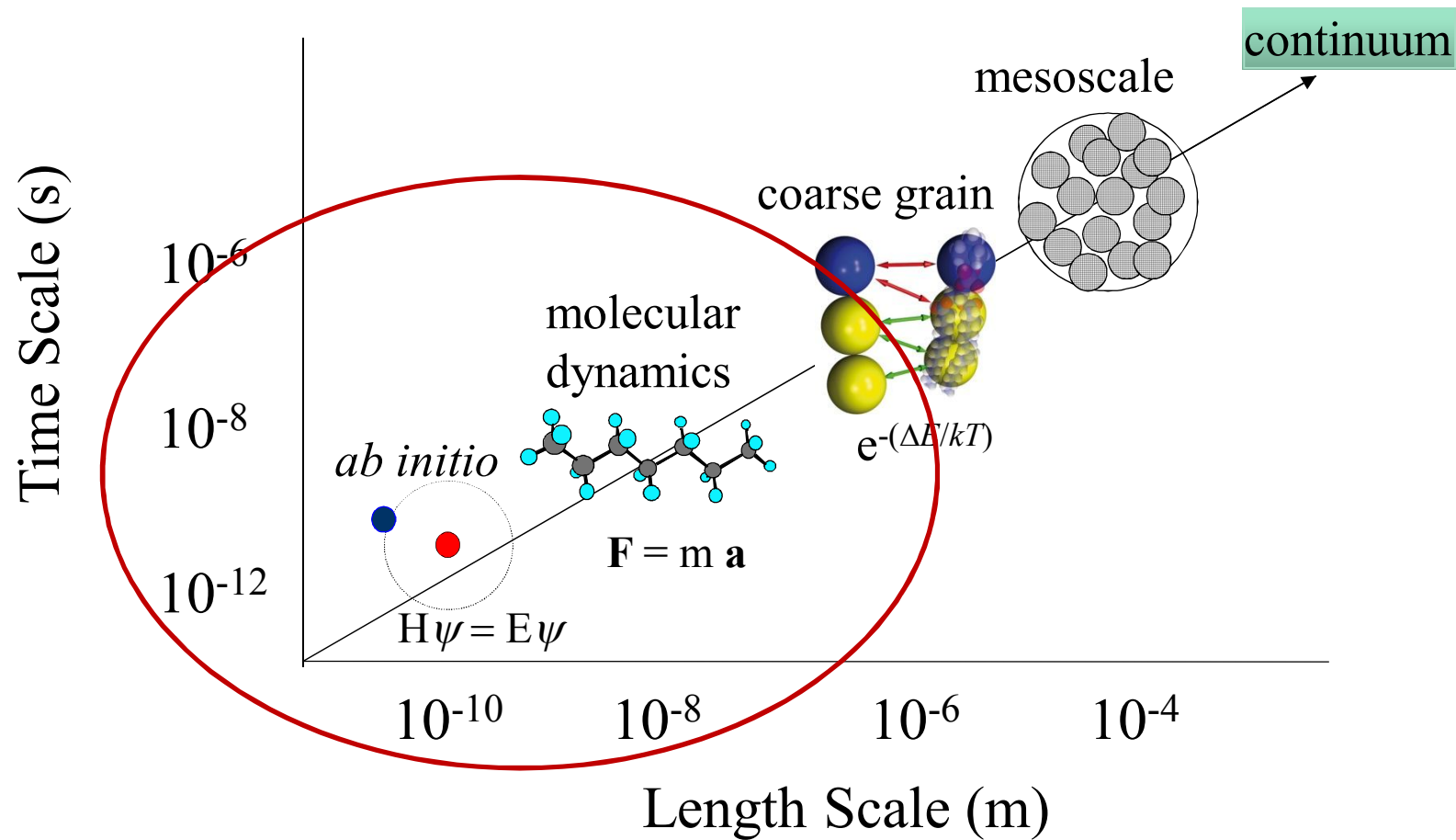
Molecular Dynamics & Monte Carlo
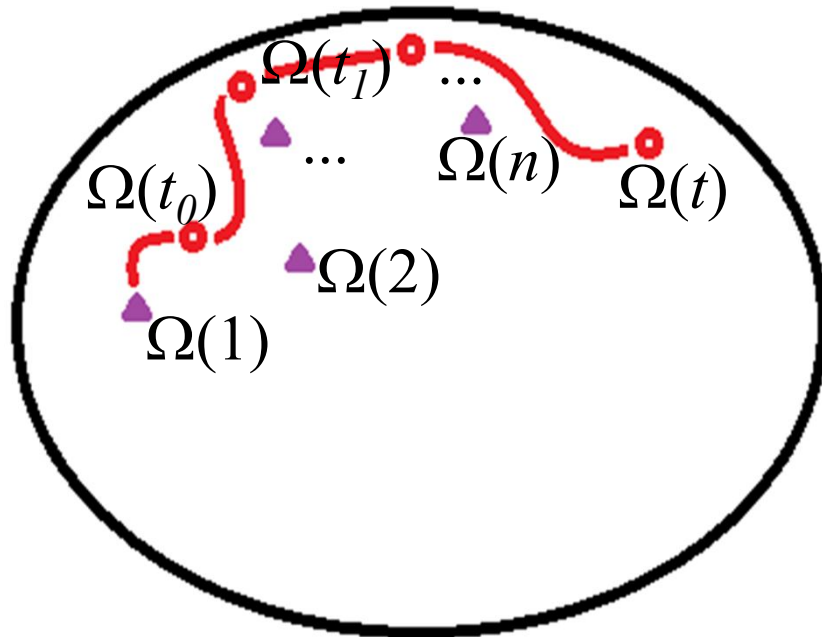
Ω = physical observable

▲ Monte Carlo

○—○ Molecular Dynamics
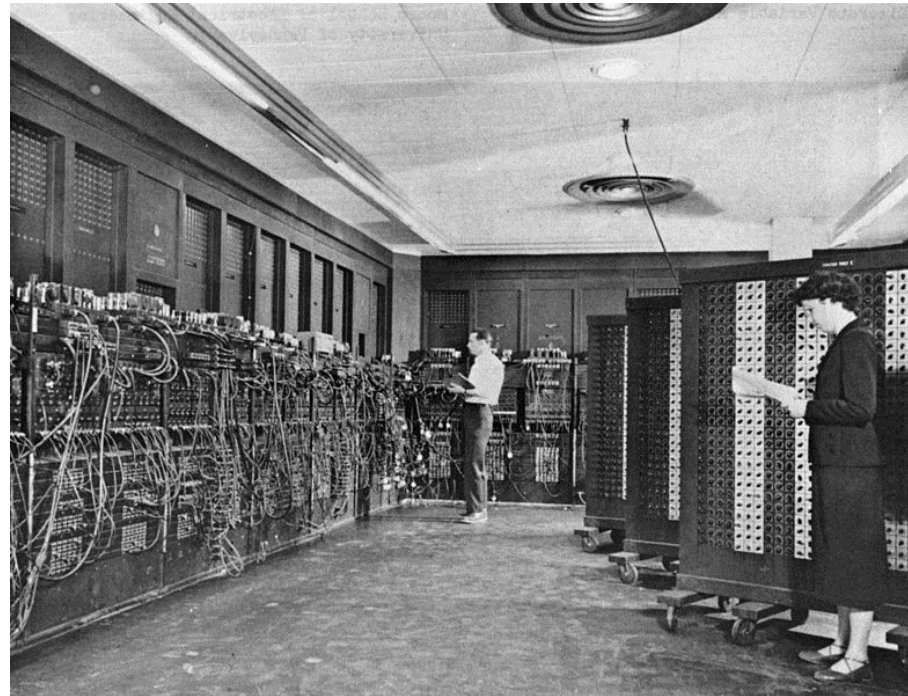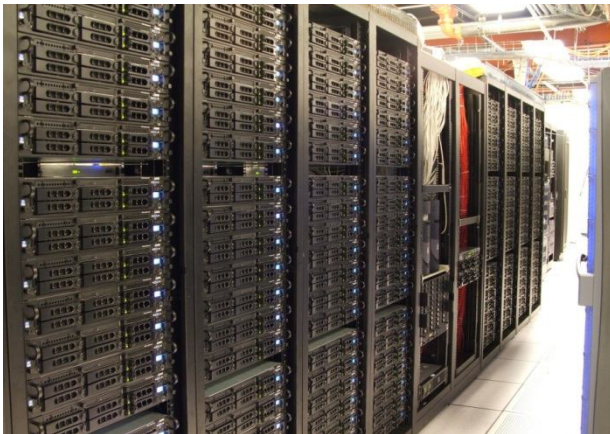
$$\langle \Omega \rangle = \lim_{n \to \infty} \langle \Omega(n) \rangle_{MC} = \lim_{t \to \infty} \langle \Omega(t) \rangle_{MD} \Longrightarrow \text{Ergodic principle}$$

In the limit of long simulation time (time average) and large sampling (ensemble average) the same result is reached
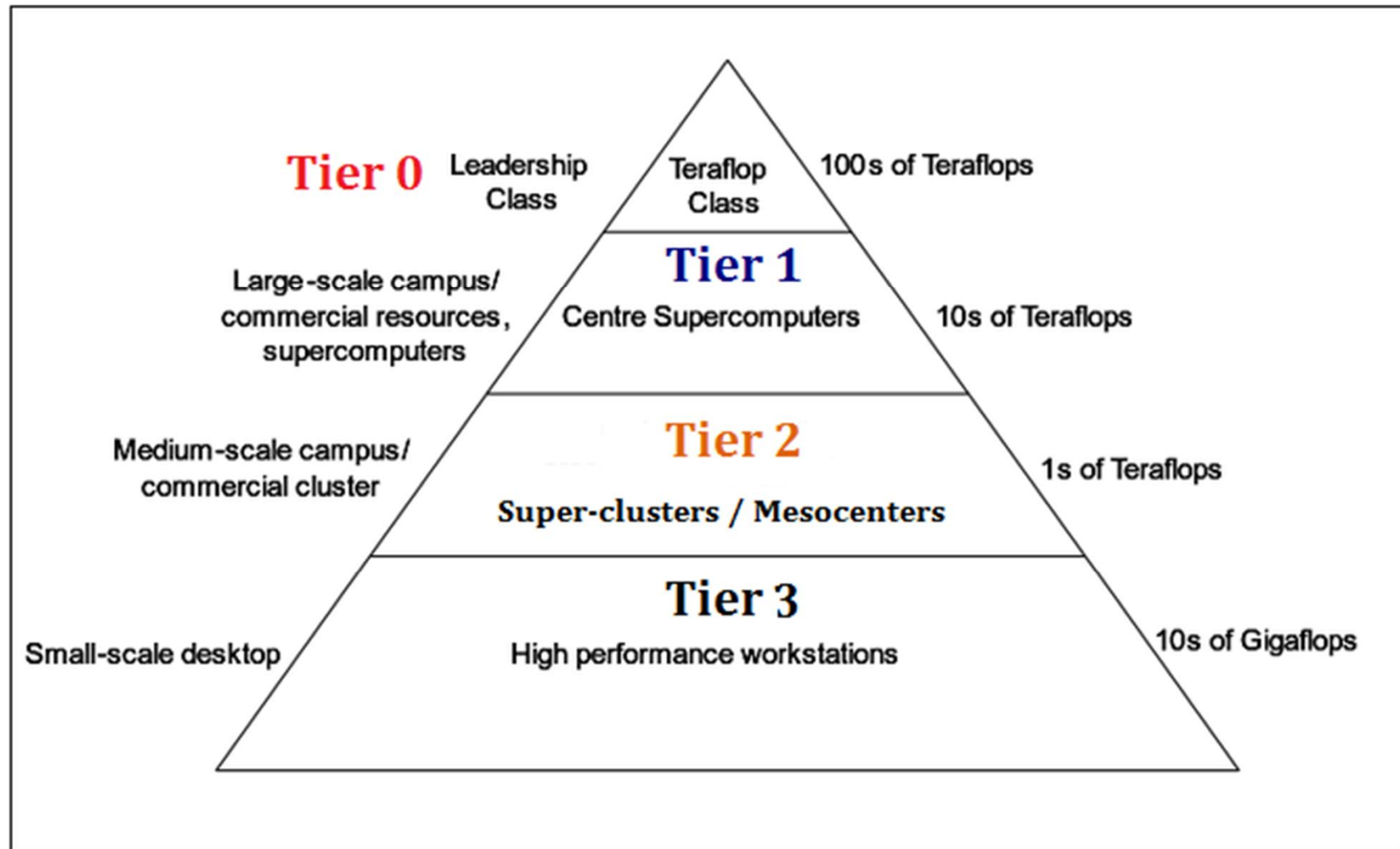
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High Performance Computing(HPC) in a nutshell

• John von Neumann (Manhattan Project) programmed the first algorithm on ENIAC (**Electronic Numerical Integrator And Computer)**
• ENIAC was designed to calculate artillery firing tables for US Army's ballistic reseach (1946)

Nowadays
ENIAC@ IPCMS

Massive computing hierarchy @ 21th century

Tier 0 Leadership Class — Teraflop Class — 100s of Teraflops

Large-scale campus/ commercial resources, supercomputers — **Tier 1** Centre Supercomputers — 10s of Teraflops

Medium-scale campus/ commercial cluster — **Tier 2** Super-clusters / Mesocenters — 1s of Teraflops

Small-scale desktop — **Tier 3** High performance workstations — 10s of Gigaflops

Science (Math.Phys.Chem.Bio…)

Modeling (methods & Co.)

Algorithms (translate eq. into codes)

Software (codes & programming)

Hardware (computer arch.)

Average … Very Good

THE UNIVERSITY OF TOKYO

Experience and knowledge of parallel programming are key advantages for the development of code for complicated, large-scale problems on massively parallel computers. At the University of Tokyo, we started a special "Interdisciplinary HPC Education Program for CSE" from FY2008 with the collaboration of four graduate schools, two research institutes, and ITC. Flexible and comprehensive classes and courses are provided based on the **SMASH** (Science-Modeling-Algorithm-Software-Hardware) model.

Science
Modeling
Algorithm
Software
Hardware

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Part 1:
Classical
Molecular Dynamics

Molecular Dynamics (MD)

The aim of Molecular Dynamics (MD) is to study a system of *interacting* particles by recreating it on a computer in a way as close as possible to nature and by simulating its dynamics over a *physical length of time* relevant to the properties of interest.

Any MD method is an iterative numerical scheme for solving some equations of motion (EOM), coded in a computer program, that represent the physical evolution of the system under study
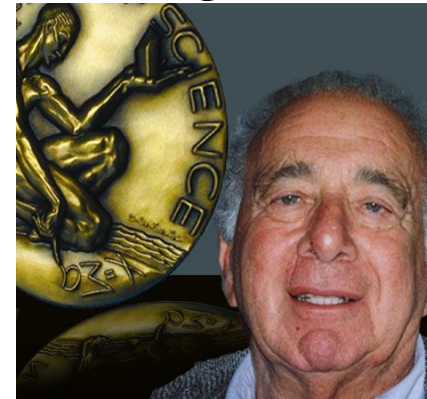
Molecular Dynamics (MD): Brief History

• MD was introduced by Alder and Wainwright in the late 1950's to study the interactions of hard spheres. Many important insights concerning the behavior of simple liquids emerged from their studies.

B. J. Alder and T. E. J. Wainwright,

Chem. Phys. **27**, 1208 (1957)

J. Chem. Phys. **31**, 459 (1959)

• The next major advance was in 1964 by A. Rahman: first simulation using a realistic potential for liquid Ar

A. Rahman, *Phys. Rev. A* **136**, 405 (1964)

• The first molecular dynamics simulation of a realistic system (liquid water) was done by Rahman and Stillinger in 1974.

F. H. Stillinger and A. Rahman, *J. Chem. Phys.* **60**, 1545 (1974)

Classical Molecular Dynamics (MD)

The objects described by Molecular Dynamics (MD) are particles (atoms, molecules, polymers) represented as deterministic variables having positions and velocities.

The Cartesian positions $(x_1, y_1, z_1), \ldots, (x_N, y_N, z_N)$ of a system of N particles can be denoted by $\mathbf{R}_I = (x_I, y_I, z_I)$ where $I = 1, \ldots, N$
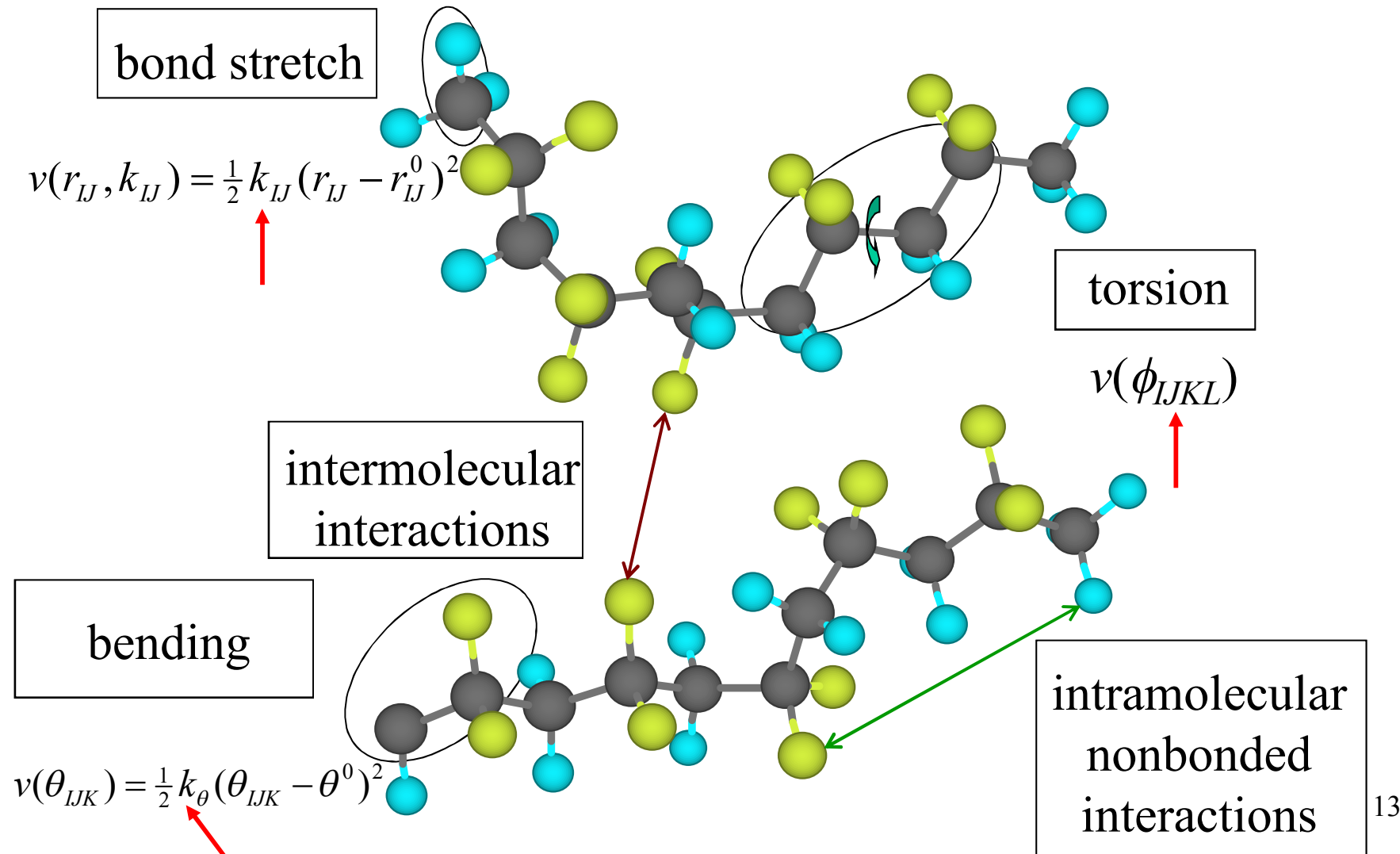
These particles interact via a given function of the positions $\mathbf{R}_I$, the potential $V(\mathbf{R}_I)$. The forces $\mathbf{f}_I$ on each particle are simply the gradients (derivative) of this potential,

$$\mathbf{f}_I = -\frac{\partial V(\mathbf{R}_I)}{\partial \mathbf{R}_I}$$

and the analytical 3xN dimensional function $\mathbf{f}_I$ is called **force field**

MD Simulations: how to construct a Force Field?
We need to consider all the relevant motions of the system
that we want to study

bond stretch

$$v(r_{IJ}, k_{IJ}) = \tfrac{1}{2} k_{IJ}(r_{IJ} - r_{IJ}^0)^2$$

torsion

$$v(\phi_{IJKL})$$

intermolecular interactions

bending

$$v(\theta_{IJK}) = \tfrac{1}{2} k_\theta (\theta_{IJK} - \theta^0)^2$$

intramolecular nonbonded interactions

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Typical form of a classical potential (not unique):

$$V^{\mathrm{MM}}(\mathbf{R}_I^{\mathbf{MM}}) = \sum_{I<J} k_{IJ}\left[(\mathbf{R}_I - \mathbf{R}_J) - d_{IJ}^0\right]^2 \qquad \text{Bond stretching}$$

$$+ \sum_{I<J} k_{\theta}\left[\theta(\mathbf{R}_I) - \theta^0\right]^2 \qquad \text{Bond bending}$$

$$+ \sum_{I<J} k_{\phi}\left[1 + \cos(n\phi(\mathbf{R}_I) + \delta)\right] \qquad \text{Torsion angles}$$

$$+ \frac{1}{4\pi\varepsilon_0} \sum_{non-bond\ IJ} \frac{q_I q_J}{|\mathbf{R}_I - \mathbf{R}_J|} \qquad \text{Coulomb interaction}$$

$$+ \sum_{non-bond\ IJ} \varepsilon_{IJ}\left[-\left(\frac{\sigma_{IJ}}{|\mathbf{R}_I - \mathbf{R}_J|}\right)^6 + \left(\frac{\sigma_{IJ}}{|\mathbf{R}_I - \mathbf{R}_J|}\right)^{12}\right] \qquad \text{Van der Waals}$$

MD Simulations: How do we get the parameters k_{IJ}, k_θ, etc… for the force field ?

From experiments

    molecular and bulk properties

    X-ray / neutron scattering structure factors

    isotopic substitutions, etc…

From *ab initio* calculations

    molecular and cluster properties

   static geometry optimization (minima, saddle points)

    first principles methods

Motion of Particles as Point-like Objects

Atoms are generally not fixed at a given position $\mathbf{R}_I$, but they move due to e.g finite temperature $T > 0$ K, collisions, external fields, etc…so they are rather described by *dynamical* variables $\mathbf{R}_I(t)$. The evolution of $\mathbf{R}_I(t)$ for each atom $I=1,…,N$ is described in analytical mechanics by a Lagrangean(*)

$$L\left(\mathbf{R}_I,\dot{\mathbf{R}}_I\right) = K - V = \sum_{I=1}^{K} \frac{1}{2} M_I \dot{\mathbf{R}}_I^2 - V\left(\mathbf{R}_I\right)$$

(*) after Joseph Louis Lagrange, Torino (Italy), 1736-1813. See *Mechanique analytique* and *Miscellanea Taurinensia,* 1766-1773 (5 volumes).
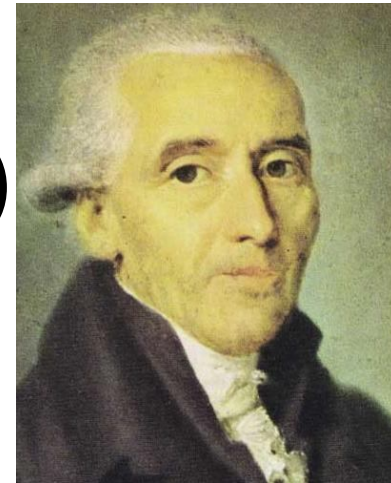
The Euler-Lagrange equations give us the equations of motion (EOM) of Classical MD

The atoms move from a position $\mathbf{R}_I(t)$ to a new position $\mathbf{R}_I(t+dt)$ via standard dynamics:

$$\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{\mathbf{R}}_I}\right) - \frac{\partial L}{\partial \mathbf{R}_I} = 0$$

or, more explicitly, the *old good* Newton equation

$$M_I \ddot{\mathbf{R}}_I = -\nabla V(\mathbf{R}_I) = \mathbf{f}_I$$

where M_I is the mass of the Ith particle of our system moving in the force field $\mathbf{f}_I$

A quantity often useful in MD formalism and statistical mechanics is the momentum $\mathbf{p}_I(t)$, that in Cartesian coordinates is simply

$$M_I \dot{\mathbf{R}}_I = \mathbf{p}_I \equiv \frac{\partial L}{\partial \dot{\mathbf{R}}_I}$$

Forces acting among particles are relatively weak compared to forces related to chemical bonds keeping molecules together.
These are the forces that MD can model.
A good *first approximation* for particle-particle (atom-atom or molecule-molecule) interactions is that they are pair-wise additive, e.g. particle 1 interacts with particle 2 with a potential (analytic Function $v(r_{12})$ ($r_{12}=|\mathbf{R}_1-\mathbf{R}_2|$), then with particle 3 with $v(r_{13})$ ($r_{13}=|\mathbf{R}_1-\mathbf{R}_3|$), etc. in an isotropic way, so that only the relative distance comes into play

$$V(\mathbf{R}_I) = \sum_{I=1}^{N} \sum_{J>I}^{N} v(r_{IJ}) = \frac{1}{2} \sum_{I,J=1}^{N} v(r_{IJ})$$

The force on particle I is now a superposition of pair forces

$$\mathbf{f}_I = -\frac{\partial V}{\partial \mathbf{R}_I} = -\sum_{J \neq I}^{N} \frac{\partial v(r_{IJ})}{\partial \mathbf{R}_I} = \sum_{J \neq I}^{N} \mathbf{f}_{IJ}$$

A crucial property of a typical MD system is that the total energy is conserved during the motion. Of course, in our case, the total energy E is just the sum of the kinetic, K, and potential, V, parts

$$E = K + V = \sum_{I=1}^{N} \frac{1}{2} M_I \dot{\mathbf{R}}_I^2 + V(\mathbf{R}_I) \equiv H$$

H is the Hamiltonian[#] of the system.

[#] after William Rowan Hamilton, Dublin (Ireland), 1805-1865

The Hamiltonian of the system is *constant of motion*, which means

$$\frac{dH}{dt} = 0$$

if the force field $\mathbf{f}_I(\mathbf{x})$ can be expressed as (minus) the gradient of a potential function $V(\mathbf{R}_I)$

$$\mathbf{f}_I = -\nabla V(\mathbf{R}_I)$$

as always happens in classical and quantum dynamical simulations.

The proof is indeed rather trivial, because we know the EOM

$$M_I \ddot{\mathbf{R}}_I = -\nabla V(\mathbf{R}_I) = \mathbf{f}_I$$

so, we have simply to compute the time derivative of the hamiltonian

$$\frac{dH}{dt} = \frac{dK}{dt} + \frac{dV}{dt} = \sum_{I=1}^{N} M_I \dot{\mathbf{R}}_I \cdot \ddot{\mathbf{R}}_I - \sum_{I=1}^{N} \mathbf{f}_I \cdot \dot{\mathbf{R}}_I =$$

$$= \sum_{I=1}^{N} (M_I \ddot{\mathbf{R}}_I - \mathbf{f}_I) \cdot \dot{\mathbf{R}}_I = 0$$

thus, the Hamiltonian H is indeed a true ***constant of motion*** and represents one of the parameters to be monitored and controlled during a MD simulation.

Numerical integration of the EOM: Verlet algorithm

To solve numerically the EOM, the first step is a *discretization* of the time t in terms of small increments called time steps of (arbitrary) length δt. The system then passes across a set of time ordered configurations

$$\ldots \mathbf{R}_I(t_{m-1}) \longrightarrow \mathbf{R}_I(t_m) \longrightarrow \mathbf{R}_I(t_{m+1}) \ldots$$

separated in time by $\delta t = t_m - t_{m-1} = t_{m+1} - t_m = \ldots$

An easy but successful integrator in MD is the Verlet algorithm; if we make a Taylor expansion of $\mathbf{R}_I(t+\delta t)$ and $\mathbf{R}_I(t-\delta t)$ we get

$$\mathbf{R}_I(t+\delta t) = \mathbf{R}_I(t) + \delta t \cdot \mathbf{v}_I(t) + \frac{\delta t^2}{2M_I} \mathbf{f}_I(t) + \frac{\delta t^3}{6} \mathbf{b}_I(t) + O\left(\delta t^4\right)$$

$$\mathbf{R}_I(t-\delta t) = \mathbf{R}_I(t) - \delta t \cdot \mathbf{v}_I(t) + \frac{\delta t^2}{2M_I} \mathbf{f}_I(t) - \frac{\delta t^3}{6} \mathbf{b}_I(t) + O\left(\delta t^4\right)$$

We use the standard notation $\mathbf{v}_I = \dot{\mathbf{R}}_I$, $\mathbf{a}_I = \ddot{\mathbf{R}}_I$, $\mathbf{b}_I = \dddot{\mathbf{R}}_I$

and the EOM $\quad \mathbf{f}_I = M_I \mathbf{a}_I$

By simply summing up the two Taylor expansions, we get

$$\mathbf{R}_I(t+\delta t) = 2\mathbf{R}_I(t) - \mathbf{R}_I(t-\delta t) + \frac{\delta t^2}{M_I}\mathbf{f}_I(t) + O\!\left(\delta t^4\right)$$

and this has an accuracy which is third order in time.
The velocity results, in a similar way, as

$$\mathbf{v}_I(t) = \frac{1}{2\delta t}\left[\mathbf{R}_I(t+\delta t) - \mathbf{R}_I(t-\delta t)\right] + O\!\left(\delta t^4\right)$$

This expression may be a bit inconvenient, because we need the position at $t+\delta t$ to compute the velocity at t. We can then rewrite the Taylor expansion keeping up to the second order (force) term

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$$\mathbf{R}_I(t+\delta t) = \mathbf{R}_I(t) + \delta t \cdot \mathbf{v}_I(t) + \frac{\delta t^2}{2M_I}\mathbf{f}_I(t)$$

From the advanced position we compute the force at time $t+\delta t$

$$\mathbf{f}_I(t+\delta t) = \mathbf{f}_I\big[\mathbf{R}_I(t+\delta t)\big] = \mathbf{f}_I\left[\mathbf{R}_I(t) + \delta t \cdot \mathbf{v}_I(t) + \frac{\delta t^2}{2M_I}\mathbf{f}_I(t)\right]$$

Then we substitute in the Taylor expansion $t \leftarrow t+\delta t$ (backward)

$$\mathbf{R}_I(t) = \mathbf{R}_I(t+\delta t) - \delta t \cdot \mathbf{v}_I(t+\delta t) + \frac{\delta t^2}{2M_I}\mathbf{f}_I(t+\delta t)$$

and we finally obtain the forward prediction for the velocity

$$\mathbf{v}_I(t+\delta t) = \mathbf{v}_I(t) + \frac{\delta t}{2M_I}\big[\mathbf{f}_I(t) + \mathbf{f}_I(t+\delta t)\big] \qquad \text{(velocity Verlet algorithm)}$$

Note that we are solving second order EOM, thus we need two initial conditions:

$$\{\mathbf{R}_I(0), \mathbf{R}_I(\delta t)\}$$

positions of the particles at $t = 0$ and the subsequent time step $t = \delta t$
or

$$\{\mathbf{R}_I(0), \dot{\mathbf{R}}_I(0)\} \equiv \{\mathbf{R}_I(0), \mathbf{v}_I(0)\}$$

positions and velocities at $t = 0$.

Exercise 1: Demonstrate the equivalence of Verlet and velocity Verlet algorithms (hint: eliminate the velocity from the above)

Exercise 2: Write a Verlet or velocity Verlet (the one you prefer) formula for the 1-dim harmonic oscillator $V(r) = k\, r^2\, /2$

Special features of the Verlet algorithm(s):

• Algorithm is time reversible. Propagate the system forward

$$\{\mathbf{R}_I(t), \mathbf{v}_I(t)\} \rightarrow \{\mathbf{R}_I(t+\delta t), \mathbf{v}_I(t+\delta t)\}$$

then change the sign of the velocity and propagate over another time interval δt

$$\{\mathbf{R}_I(t+\delta t), -\mathbf{v}_I(t+\delta t)\} \rightarrow \{\mathbf{R}_I(t), -\mathbf{v}_I(t)\}$$
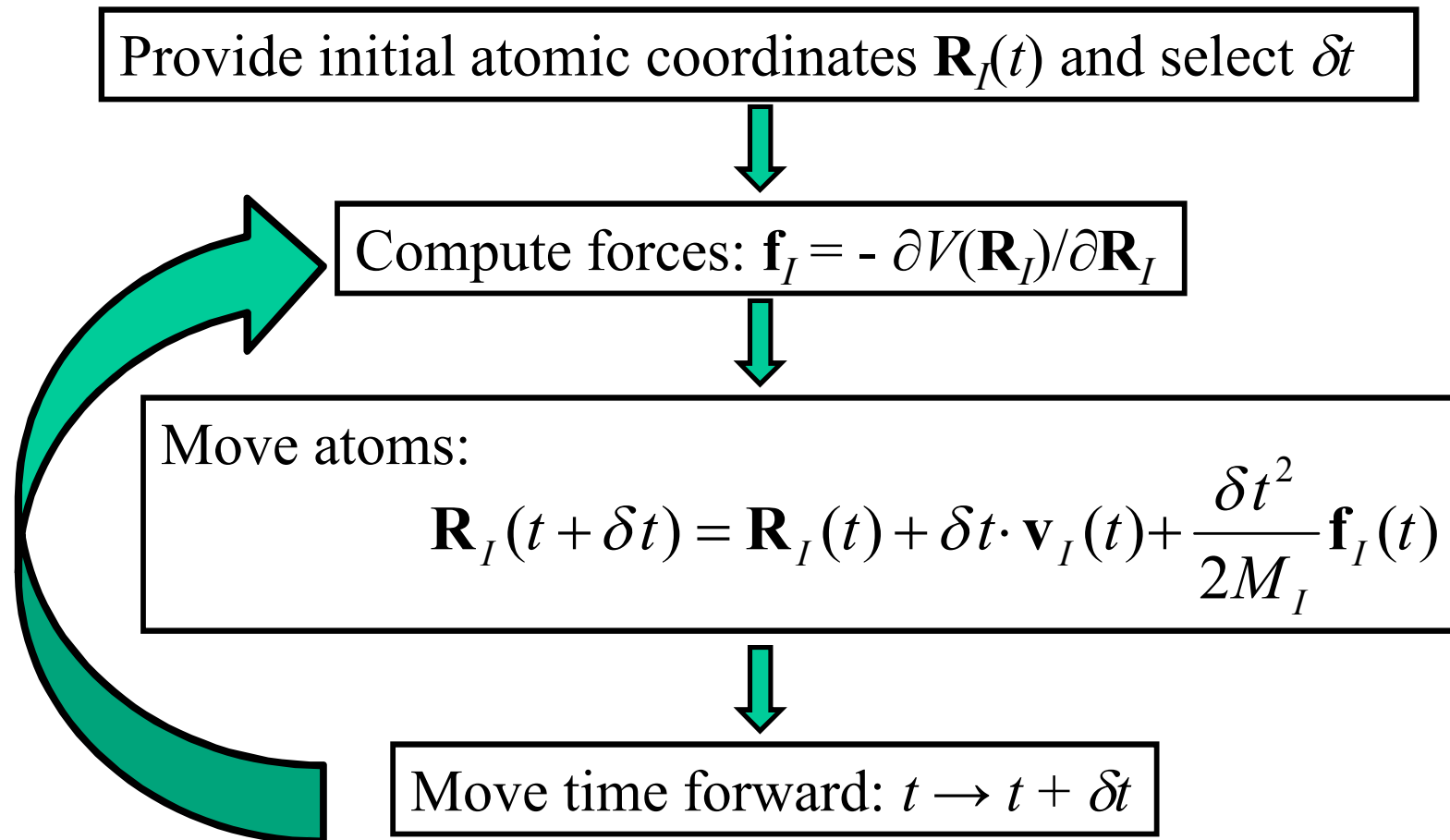
and we are back at the starting position.
• Algorithm shows a very good total energy conservation
• Updating of velocity is always one step behind updating of position

Computational cost in MD:

The calculation of forces is by far the most demanding in terms of CPU time (memory is in general not a problem)

General scheme of a computer code for MD:

Provide initial atomic coordinates $\mathbf{R}_I(t)$ and select δt

⬇

Compute forces: $\mathbf{f}_I = -\partial V(\mathbf{R}_I)/\partial \mathbf{R}_I$

⬇

Move atoms:

$$\mathbf{R}_I(t+\delta t) = \mathbf{R}_I(t) + \delta t \cdot \mathbf{v}_I(t) + \frac{\delta t^2}{2M_I}\mathbf{f}_I(t)$$

⬇

Move time forward: $t \rightarrow t + \delta t$

Thermodynamic control methods:
Constant temperature (I)

From a statistical mechanics point of view, the temperature T of a system of particles having masses M_I and moving with velocities $\mathbf{v}_I$ is simply given by the average

$$\left\langle \sum_{I=1}^{N} \frac{M_I \mathbf{v}_I^2}{2} \right\rangle = \frac{3}{2} N \cdot k_B T$$

It seems than that if we can control in some way the velocities $\mathbf{v}_I$ then we can keep under control the related parameter T.
From statistical mechanics textbooks, we know that this control is operated by a thermostat, ideally a system with ***infinite degrees of freedom*** in contact with our system of particles and acting as a heat reservoir.

Thermodynamic control methods:
Constant temperature (II)

An original idea of S. Nosé, extended by W.G. Hoover, was that we do not really need infinite degrees of freedom, but only **one**.

This additional degree of freedom takes care of the proper scaling of the velocities, reproduces the canonical ensemble (N,V,T) and reduces the problem of the thermostat to deterministic dynamical equations.

This single degree of freedom, s, does a rescaling of the velocities $\mathbf{v}_I$ during the simulation,

$$\dot{\mathbf{R}}_I = \mathbf{v}_I \rightarrow s \cdot \mathbf{v}_I$$

and is similar to a friction force $\mathbf{f}^c_I = -s\mathbf{p}_I$ if $s > 0$ or to a heating-up process if $s < 0$.

Thermodynamic control methods: Constant temperature (III)

The simplest realization is the velocity rescaling: Multiply all the velocities of any particle by a factor, s

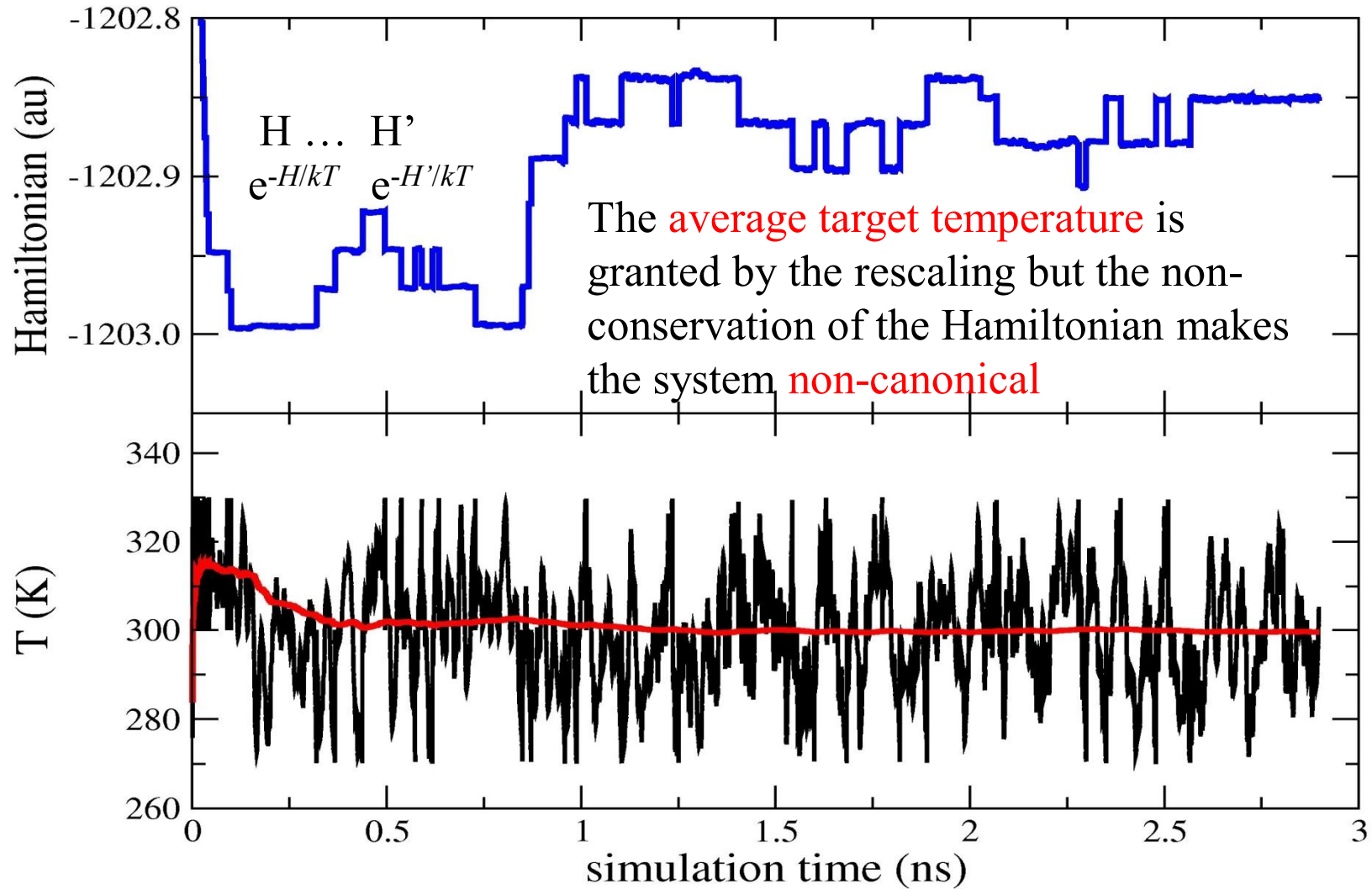$$\mathbf{v}_I \rightarrow s \cdot \mathbf{v}_I$$

calculated by enforcing the total kinetic energy K to be equal to the kinetic energy K_0 at the target temperature T

$$K_0 = \frac{N_f}{2} k_B T \qquad N_f = \text{number of degrees of freedom.}$$

Problem: All velocities / momenta are rescaled by $s = \sqrt{\dfrac{K_0}{K}}$

thus **affecting the momenta** and hence not conserving the Hamiltonian …

Thermodynamic control methods:
Constant temperature (IV)

H … H'

$e^{-H/kT}$ $e^{-H'/kT}$

The average target temperature is granted by the rescaling but the non-conservation of the Hamiltonian makes the system non-canonical
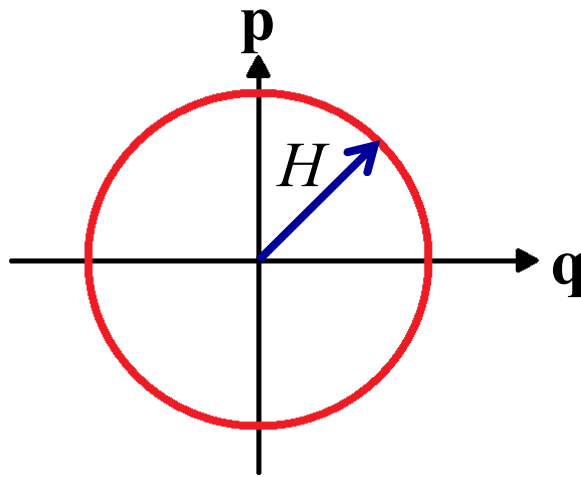
Thermodynamic control methods: Constant temperature (V)

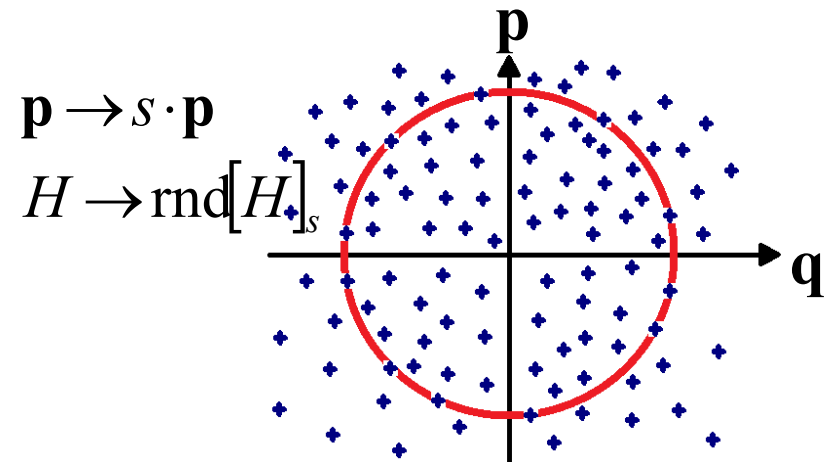…and the system becomes **non-ergodic** ! Simple example: harmonic oscillator

$$H = \frac{1}{2}m\mathbf{v}^2 + \frac{1}{2}k\mathbf{x}^2 = \frac{\mathbf{p}^2}{2m} + \frac{m\omega^2}{2}\mathbf{q}^2 = \text{const}$$

Without rescaling

$$H = \frac{\mathbf{p}^2}{2m} + \frac{m\omega^2}{2}\mathbf{q}^2 \equiv \text{const}$$

With rescaling

$$\mathbf{p} \rightarrow s \cdot \mathbf{p}$$

$$H \rightarrow \text{rnd}[H]_s$$

$$H = \frac{s \cdot \mathbf{p}^2}{2m} + \frac{m\omega^2}{2}\mathbf{q}^2 \neq \text{const}$$

Thermodynamic control methods: Constant temperature (VI)

A possible modification to the scaling algorithm is to enforce the canonical distribution by selecting a target kinetic energy K_t with a stochastic procedure, i.e. randomly sampled from

$$P(K_t)dK_t = K_t^{(N_f/2-1)} \cdot e^{-K_t/k_B T} dK_t$$

The velocity rescaling factor becomes then

$$s = \sqrt{\frac{K_t}{K}}$$

although velocities undergo again abrupt changes at each rescaling

see *J. Chem. Phys.* **126**, 014101 (2007)

…But: The new degree of freedom s can be added to the Lagrangean of the MD as a new variational (dynamical) variable $s(t)$. The extended Lagrangean then reads

$$L = \frac{1}{2} \sum_{I=1}^{N} M_I s^2 \dot{\mathbf{R}}_I^2 - V(\mathbf{R}_I) + \frac{1}{2} Q \dot{s}^2 - (3N+1) k_B T \ln s$$

The new variable $s(t)$ has a kinetic term in which Q represents the fictitious mass, basically the time scaling of the motion of $s(t)$ with respect to the motion of $\mathbf{R}_I(t)$. The velocities are rescaled as $s\mathbf{v}_I$ and the virtual potential for $s(t)$ is given by the Boltzmann-like canonical term $(3N+1) k_B T \ln s$, where $3N+1$ are all the degrees of freedom: $3N$ for the atomic coordinates plus one for the new variable s.

Thermodynamic control methods:
Constant temperature (VIII)

Upon Legendre tranformation, $\quad \mathbf{p}_I = \nabla_{\dot{\mathbf{R}}_I} L = M_I \dot{\mathbf{R}}_I$

$$p_s = \partial L / \partial \dot{s}$$

the extended Hamiltonian then reads

$$H = \sum_{I=1}^{N} \frac{\mathbf{p}_I^2}{s^2 M_I} + V(\mathbf{R}_I) + \frac{p_s^2}{2Q} + (3N+1)k_B T \ln s$$

$$= H_0 + \frac{p_s^2}{2Q} + (3N+1)k_B T \ln s$$

and this is our new constant of motion

$$\frac{dH}{dt} = \sum_I \left(\frac{\partial H}{\partial \mathbf{p}_I} \dot{\mathbf{p}}_I + \frac{\partial H}{\partial \mathbf{R}_I} \dot{\mathbf{R}}_I \right) + \frac{\partial H}{\partial p_s} \dot{p}_s + \frac{\partial H}{\partial s} \dot{s} = 0$$

Thermodynamic control methods:
Constant temperature (IX)

The (*coupled*) Euler-Lagrange equations of motion, under the rescaling of the Nosé-Hoover thermostat become then

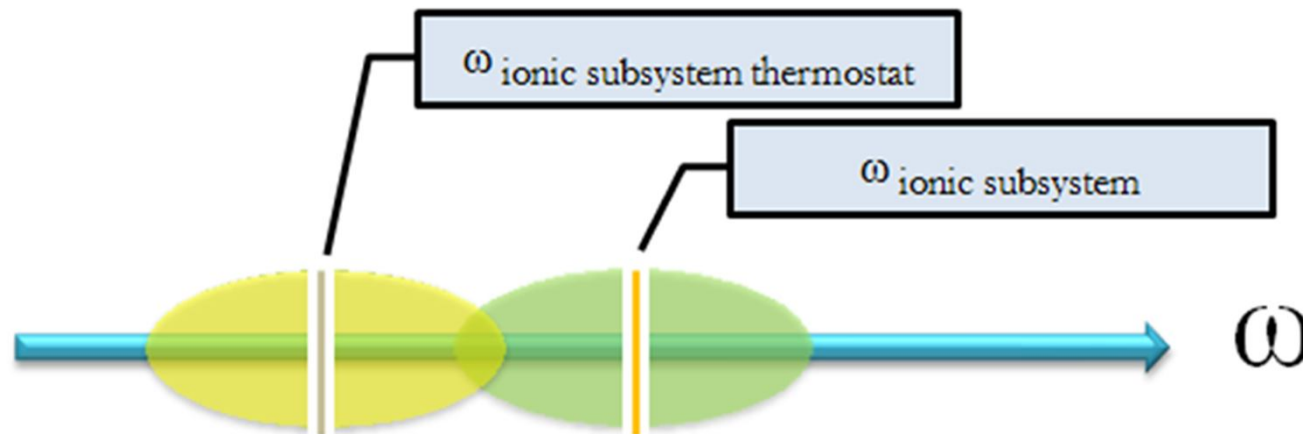$$M_I \ddot{\mathbf{R}}_I = \frac{\mathbf{f}_I}{s^2} - 2\frac{\dot{s}}{s} M_I \dot{\mathbf{R}}_I$$

$$Q\ddot{s} = \frac{1}{s} \cdot \left[s^2 \sum_{I=1}^{N} M_I \dot{\mathbf{R}}_I^2 - (3N+1)k_B T \right]$$

and these can be solved numerically with the Verlet algorithm. Note that now we have two more input parameters: the target temperature *T* and the Nosé-Hoover thermostat mass *Q*.

Thermodynamic control methods: Constant temperature (X)

The choice of the Nosé-Hoover thermostat mass **Q** and of the target temperature **T** is equivalent to the choice of a characteristic frequency at which the thermostat oscillates because of the 2nd order EOM:

$$Q\ddot{s} = \frac{1}{s} \cdot \left[s^2 \sum_{I=1}^{N} M_I \dot{\mathbf{R}}_I^2 - (3N+1)k_B T \right] \quad \Longrightarrow \quad \omega = \sqrt{\frac{2(3N+1)k_B T}{Q\langle s \rangle^2}}$$

ω ionic subsystem thermostat

ω ionic subsystem

ω

weak coupling with the ionic normal modes $\Longrightarrow$ good control of T

Thermodynamic control methods: Constant temperature (XI)

- Why does such an approach give a canonical ensemble ?
  The partition function of the system becomes:

$$Z = \int dp_s \int ds \int d\mathbf{p} \int d\mathbf{R}\, \delta\left[H_0\left(\frac{\mathbf{p}}{s}, \mathbf{R}\right) + \frac{p_s^2}{2Q} + (3N+1)k_B T \ln s - E \right]$$

Then, rewriting the scaled momenta

$$\mathbf{p}'_I = p_I / s \quad d\mathbf{p}\, d\mathbf{R} = s^{3N} d\mathbf{p}'\, d\mathbf{R}$$

we get

$$Z = \int dp_s \int d\mathbf{p}' \int d\mathbf{R} \int ds\, s^{3N} \delta\left[H_0(\mathbf{p}', \mathbf{R}) + \frac{p_s^2}{2Q} + (3N+1)k_B T \ln s - E \right]$$

Thermodynamic control methods: Constant temperature (XII)

Using the relationship $\delta[f(s)] = \delta(s - s_0)/f'(s_0)$, s_0 being the zero of $f(s_0)$, we arrive at

$$Z = \frac{1}{(3N+1)k_B T} \int dp_s \int d\mathbf{p}' \int d\mathbf{R} \int ds \, s^{3N} \delta\left[s - \exp\left\{ -\left[H_0(\mathbf{p}', \mathbf{R}) + \frac{p_s^2}{2Q} - E \right] \right\} \right]$$

$$= \frac{1}{(3N+1)k_B T} \exp(E/k_B T) \int dp_s \exp\left\{ -\left[\frac{p_s^2}{2Q k_B T} \right] \right\} \int d\mathbf{p}' \int d\mathbf{R} \exp\left\{ -\left[\frac{H_0(\mathbf{p}', \mathbf{R})}{k_B T} \right] \right\}$$

which means that, apart from a constant C the partition function is the one of a canonical (Boltzmann-like) ensemble:

$$Z = C \cdot \int d\mathbf{p}' \int d\mathbf{R} \exp\left\{ -\left[\frac{H_0(\mathbf{p}', \mathbf{R})}{k_B T} \right] \right\}$$

Thermodynamic control methods:
Constant temperature (XIII)

Warning: For particularly pathological systems the Nosé-Hoover thermostat suffers from non-ergodicity problems.
A possible way of overcoming the problem is to use a chain of thermostats: s_1, then s_2 controlling s_1, ..., s_k controlling s_{k-1} ($k=2,...,K$)

$$M_I \ddot{\mathbf{R}}_I = \mathbf{f}_I - M_I \dot{s}_1 \mathbf{R}_I$$

$$Q_1 \ddot{s}_1 = \frac{1}{s} \cdot \left[\sum_{I=1}^{N} M_I \dot{\mathbf{R}}_I^2 - (3N+1)k_B T \right] - Q_1 \dot{s}_1 \dot{s}_2$$

$$Q_k \ddot{s}_k = \left[Q_{k-1} \dot{s}_{k-1}^2 - k_B T \right] - Q_k \dot{s}_k \dot{s}_{k+1} \left(1 - \delta_{kK} \right)$$

Martyna, Klein and Tuckerman *J. Chem. Phys.* **97**, 2635 (1992)

Thermodynamic control methods:
Constant pressure (I)

The extended Lagrangean method was originally introduced by H.C. Andersen to control the pressure of a system in a box $\ell \times \ell \times \ell$. In this case, the new Lagrangean variable is represented by the volume Ω and we have

$$L = \frac{1}{2}\sum_{I=1}^{N} M_I \ell^2 \dot{\mathbf{r}}_I^2 - V(\ell\mathbf{r}_I) + \frac{1}{2}Q\dot{\Omega}^2 - P_0\Omega$$

For convenience, the atomic coordinates $\mathbf{R}_I$ are rewritten as

$$\mathbf{r}_I = \mathbf{R}_I / \ell$$

so that the $\mathbf{r}_I$ variable are not directly related to the volume. Ω is then a completely independent dynamical variable.

Thermodynamic control methods:
Constant pressure (II)

The Euler-Lagrange equations of motion for the particles $\mathbf{r}_I$ and the volume Ω read

$$M_I \ddot{\mathbf{r}}_I = \frac{1}{\ell} \mathbf{f}_I - \frac{2}{3} \frac{\dot{\Omega}}{\Omega} M_I \dot{\mathbf{r}}_I$$

$$Q\ddot{\Omega} = P - P_0$$

where the fictitious mass parameter Q and the external pressure P_0 are now the two new input parameters. The quantity P, instead, is the dynamically computed pressure given by

$$P = \frac{1}{3\Omega} \left[\sum_I M_I \ell^2 \dot{\mathbf{r}}_I^2 + \sum_{I>J} \left(\mathbf{R}_I - \mathbf{R}_J \right) \cdot \mathbf{f}_{IJ} \right]$$

Thermodynamic control methods:
Constant pressure (III)

The constant pressure method was generalized by M. Parrinello and
A. Rahman to the non isotropic case.* The position $\mathbf{R}_I$ of a particle is
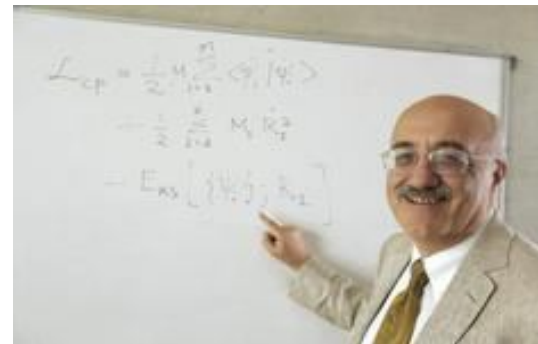given in terms of lattice vectors $\mathbf{a}$, $\mathbf{b}$, $\mathbf{c}$ as

$$\mathbf{R}_I = x_I\mathbf{a} + y_I\mathbf{b} + z_I\mathbf{c} = \mathbf{h}\cdot\mathbf{x}_I$$

where $\mathbf{h}$ is the matrix representation of the lattice vectors, i.e.
$\mathbf{h} = (\mathbf{a}, \mathbf{b}, \mathbf{c})$ and its transpose

$$\mathbf{h}^T = \begin{pmatrix} \mathbf{a} \\ \mathbf{b} \\ \mathbf{c} \end{pmatrix}$$

so that $\mathbf{R}_I^2 = \mathbf{x}_I \mathbf{h}^T \mathbf{h} \mathbf{x}_I$ and $\dot{\mathbf{R}}_I = \mathbf{h}\cdot\dot{\mathbf{x}}_I$

*Phys. Rev. Lett. **45**, 1196 (1980)

Thermodynamic control methods: Constant pressure (IV)

The Parrinello-Rahman Lagrangean reads then

$$L = \frac{1}{2}\sum_{I=1}^{N} M_I \dot{\mathbf{x}}_I \cdot \mathbf{h}^T \cdot \mathbf{h} \cdot \dot{\mathbf{x}}_I - V(\mathbf{R}_I) + \frac{1}{2} Q \operatorname{Tr}\left(\dot{\mathbf{h}}^T \cdot \dot{\mathbf{h}}\right) - P_0 \Omega$$

where the volume. Ω is now given by $\Omega = \mathbf{a} \cdot (\mathbf{b} \times \mathbf{c})$

In the special case in which $\mathbf{h}$ is diagonal, we have the Andersen barostat:

$$\mathbf{h} = \begin{pmatrix} \Omega^{1/3} & 0 & 0 \\ 0 & \Omega^{1/3} & 0 \\ 0 & 0 & \Omega^{1/3} \end{pmatrix}$$

although the Andersen's equation of motion for $d^2\Omega/dt^2$ cannot be obtained in a straightforward way.

Thermodynamic control methods:
Constant pressure (V)

For convenience, the matrix product $\mathbf{G} = \mathbf{h}^T\mathbf{h}$ is introduced

$$\mathbf{G} \equiv \mathbf{h}^T \cdot \mathbf{h} = \begin{pmatrix} \mathbf{a} \cdot \mathbf{a} & \mathbf{a} \cdot \mathbf{b} & \mathbf{a} \cdot \mathbf{c} \\ \mathbf{b} \cdot \mathbf{a} & \mathbf{b} \cdot \mathbf{b} & \mathbf{b} \cdot \mathbf{c} \\ \mathbf{c} \cdot \mathbf{a} & \mathbf{c} \cdot \mathbf{b} & \mathbf{c} \cdot \mathbf{c} \end{pmatrix}$$

so that the square of the distance between two atoms, I and J reads

$$R_{IJ}^2 = \left(\mathbf{x}_I - \mathbf{x}_J\right)^T \cdot \mathbf{G} \cdot \left(\mathbf{x}_I - \mathbf{x}_J\right)$$

and the reciprocal space vectors become

$$\frac{2\pi}{\Omega}\left(\mathbf{b} \times \mathbf{c}, \mathbf{c} \times \mathbf{a}, \mathbf{a} \times \mathbf{b}\right) = \frac{2\pi}{\Omega}\boldsymbol{\sigma} \qquad \boldsymbol{\sigma} = \Omega\left(\mathbf{h}^T\right)^{-1}$$

Thermodynamic control methods: Constant pressure (VI)

The Parrinello-Rahman equations of motion then read

$$\ddot{\mathbf{x}}_I = -\sum_{\substack{J=1 \\ J \neq I}}^{N} \frac{1}{M_I} \frac{\partial V}{\partial R_{IJ}} \frac{\mathbf{x}_I - \mathbf{x}_J}{R_{IJ}} - \mathbf{G^{-1}} \cdot \mathbf{G} \cdot \mathbf{x}_I$$

$$Q\ddot{\mathbf{h}} = (P - P_0)\boldsymbol{\sigma}$$

where the pressure P is given by

$$P = \frac{1}{\Omega}\left(\sum_{I=1}^{N} M_I \dot{\mathbf{R}}_I \dot{\mathbf{R}}_I - \sum_{I=1}^{N}\sum_{J>I}^{N} \frac{\partial V}{\partial R_{IJ}} \frac{\mathbf{R}_{IJ}\mathbf{R}_{IJ}}{R_{IJ}} \right)$$

Thermodynamic control methods: Constant pressure (VII)

The Parrinello-Rahman method for the control of pressure can be further generalized by including an external stress tensor, i.e. the case in which an anisotropic pressure is applied or anisotropic structural modifications occur

$$\mathbf{S} = \left(s_{\alpha\beta} \right) \quad \alpha, \beta = 1,2,3$$

In this case, the former Lagrangean is modified as

$$L \rightarrow L - \frac{1}{2} \mathrm{Tr}\left[\mathbf{h}^{-1} \cdot \left(\mathbf{S} - P_0 \mathbf{1} \right) \cdot \left(\mathbf{h}^T \right)^{-1} \Omega \cdot \mathbf{G} \right]$$

Some nomenclature of the thermodynamic ensembles that can be simulated

- (N, V, E) constant → microcanonical ensemble
- (N, V, T) constant → canonical ensemble

  in this case, the distribution of each state i characterized by an energy E_i is a Boltzmann $p_i = (1/Z) \exp(- E_i / k_B T)$ and the system can exchange energy (but **<u>not</u>** particles) with a reservoir

- (μ, V, T) constant → grand canonical ensemble: much more difficult to simulate since it is an infinite collection of canonical ensembles

$$\widetilde{Z}(\mu, V, T) = \sum_{N=0}^{\infty} z^N Z(N, V, T) = \sum_{N=0}^{\infty} z^N \exp(- E_i / k_B T)$$

$$\mu = k_B T \ln z$$

What can we get out of a MD simulation ?

- Dynamical averages = statistical averages of several physical quantities: total and free energy, molecular velocity distributions, etc.

- Radial distribution function / pair correlation functions $g_{ij}(r)$ and angular distribution functions

- Temperature, pressure (stress tensor), crystal and non-crystal phases, local atomic structure, etc…

- Diffusion coefficients

- Vibrational spectra and normal modes

- etc…

Let's see each point one by one and how we can extract these data from a MD trajectory.

Connection to Statistical Mechanics:
time averages and ensemble averages

A successful MD run gives you, in output, a time-ordered sequence of positions $\mathbf{R}_I(t_m)$ and velocities $\mathbf{v}_I(t_m)$ at the discrete time points $t_m = m\delta t$, $m=1,\ldots,M$ for a total simulation time $\Delta t = M\,\delta t$.

We call this sequence ***trajectory*** and the trajectory represents the set of configurations "visited" by our system during the dynamics, i.e. during its motion under the action of the force field that you selected.

So, what do we do with such a sequences of numbers ?

We can use this discrete trajectory to visualize the motion of the particles on most of the graphical PCs, workstations…

…so, what do we see on our computer ?
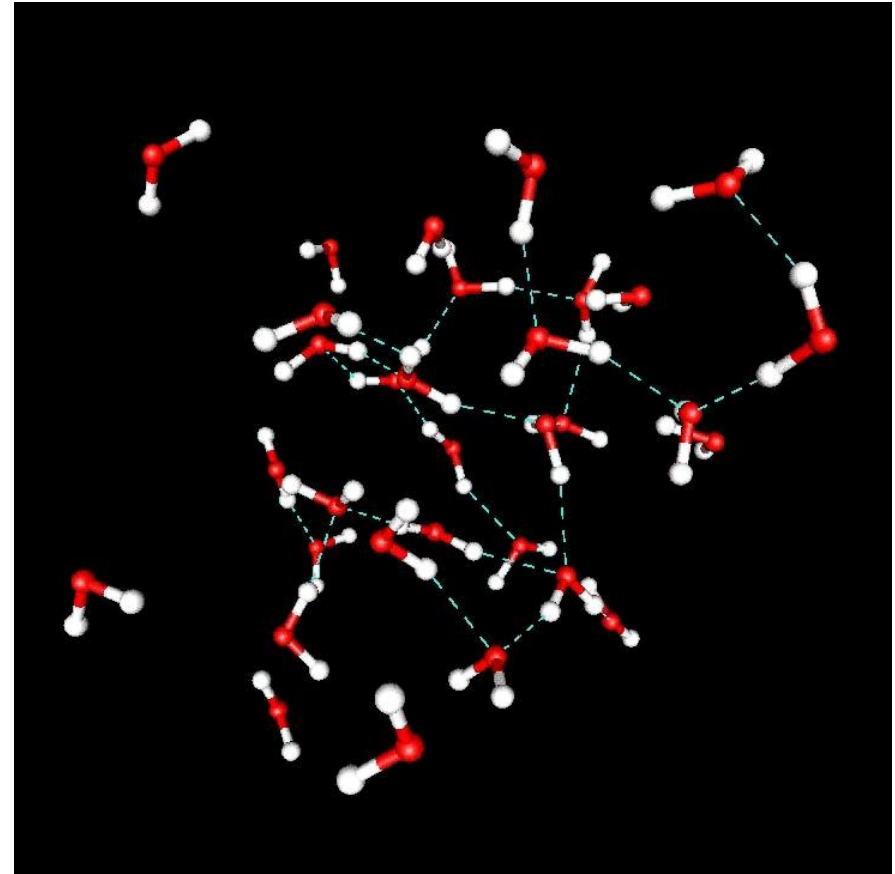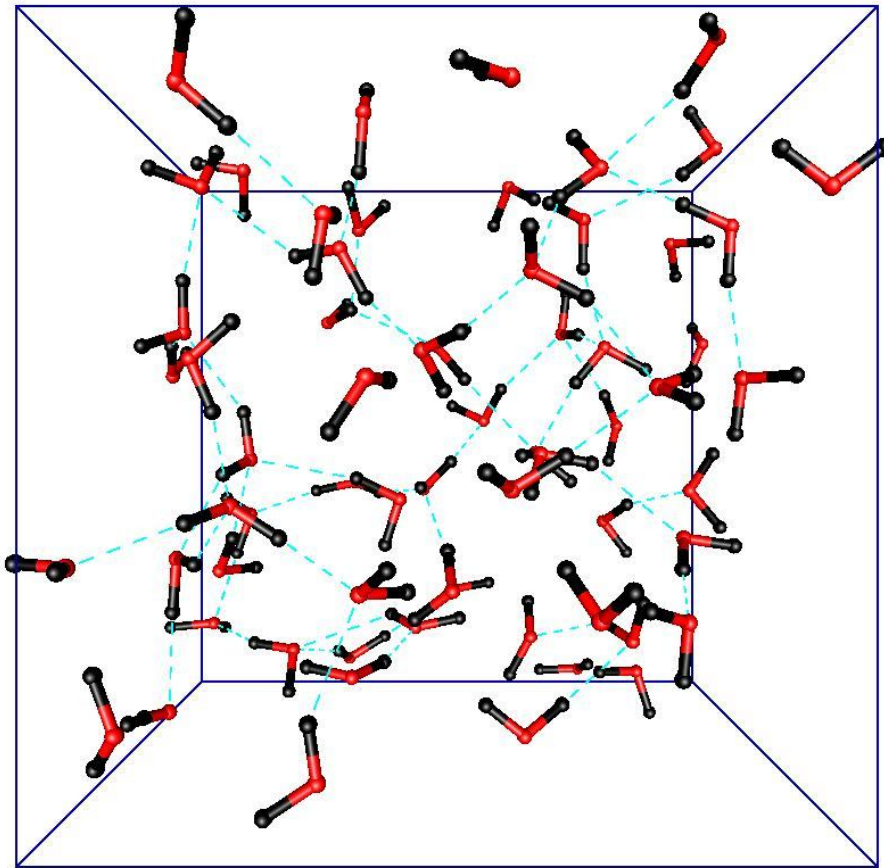
Example: the case of water at $T = 300$ K (temperature control)

Connection to Statistical Mechanics:
time averages and ensemble averages

…but this is just a visual inspection (= *no or very little science*).
In the end we want always to compute ensemble averages or, within
the *ergodic principle*, time averages of some function $A(\mathbf{R}_I(t),\mathbf{v}_I(t))$
of the positions and velocities, or, equivalently $A(\mathbf{R}_I(t),\mathbf{p}_I(t))$ of the
positions and momenta whose average value is a quantity that can be
measured experimentally.

Ergodic principle: if the dynamics is *long enough* so that our system
can explore its whole phase space $\{\mathbf{R}_I,\mathbf{p}_I\}$, then time averages are
identical to ensemble averages, which means, if $\Delta t \rightarrow \infty$

$$\left\langle A \right\rangle_{Ensemble} \equiv \left\langle A \right\rangle_{\Delta t} = \frac{1}{\Delta t}\int_0^{\Delta t} A\big(\mathbf{R}(t),\mathbf{p}(t)\big)dt \cong \frac{1}{M}\sum_{m=1}^{M} A\big(\mathbf{R}(t_m),\mathbf{p}(t_m)\big)$$

Connection to Statistical Mechanics:
a trivial example – Temperature

Suppose that we have run a MD simulation for a time long enough to have a good sampling of the phase space., which means a long series of positions and velocities $\{\mathbf{R}_I(t), \mathbf{v}_I(t)\}$, then we have

$$\left\langle \sum_{I=1}^{N} \frac{M_I \mathbf{v}_I^2}{2} \right\rangle_{Ensemble} \equiv \left\langle \sum_{I=1}^{N} \frac{M_I \mathbf{v}_I^2}{2} \right\rangle_{\Delta t} = \frac{3}{2} N \cdot k_B T$$

and, in our MD language,

$$\left\langle \sum_{I=1}^{N} \frac{M_I \mathbf{v}_I^2}{2} \right\rangle_{\Delta t} = \frac{1}{M} \sum_{m=1}^{M} \sum_{I=1}^{N} \frac{M_I [\mathbf{v}_I(t_m)]^2}{2} = \frac{3}{2} N \cdot k_B T$$

$$T = \frac{1}{3MNk_B} \sum_{m=1}^{M} \sum_{I=1}^{N} M_I [\mathbf{v}_I(t_m)]^2$$

Connection to Statistical Mechanics:
another trivial example – Total Energy

From our MD simulation we can compute also the (classical) total energy in a similar way:

$$\left\langle E^{Tot} \right\rangle_{Ensemble} \equiv \left\langle E^{Tot} \right\rangle_{\Delta t} = \left\langle \sum_{I=1}^{N} \frac{1}{2} M_I [\mathbf{v}_I(t)]^2 + V(\mathbf{R}_I(t)) \right\rangle = \frac{3}{2} N k_B T + \left\langle V \right\rangle$$

$$\frac{dE^{Tot}}{dt} = 0$$
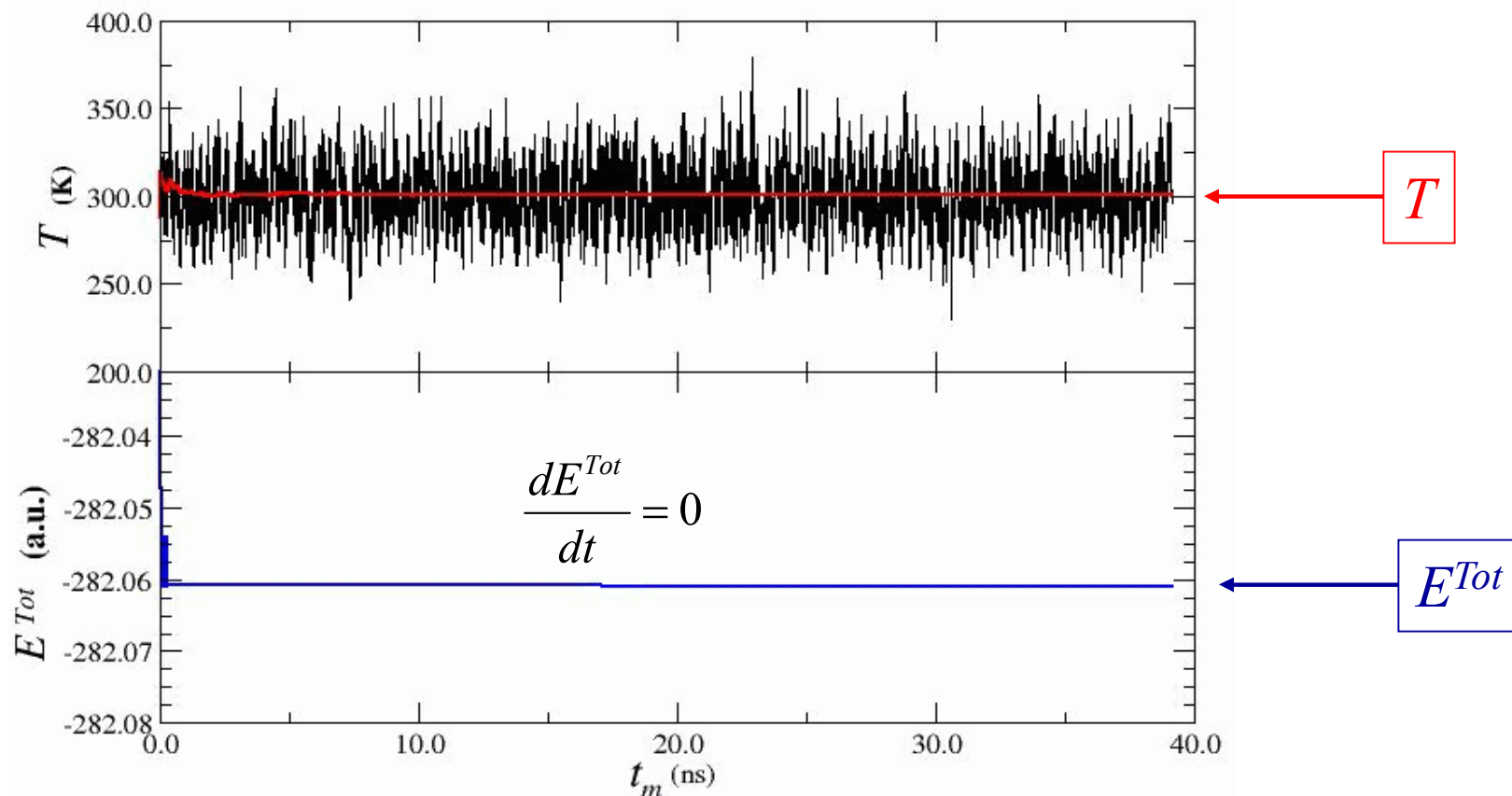
Connection to Statistical Mechanics: A WARNING

Why even in an (e.g.) NVT canonical system does the temperature oscillates ?
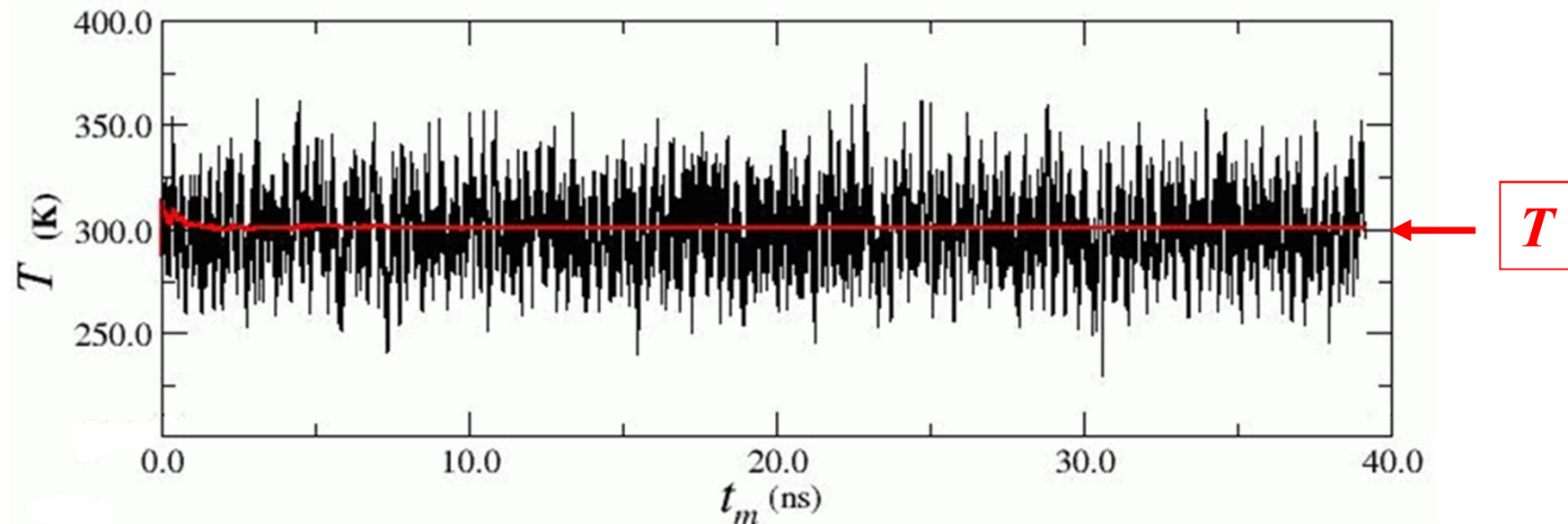
…it should be $\dfrac{2}{3k_B}\left\langle \sum_{I=1}^{N} \dfrac{M_I \mathbf{v}_I^2}{2} \right\rangle_N = \dfrac{2}{3k_B}\left\langle \sum_{I=1}^{N} \dfrac{\mathbf{p}_I^2}{2M_I} \right\rangle_N = T = \text{constant}$

Connection to Statistical Mechanics: A WARNING

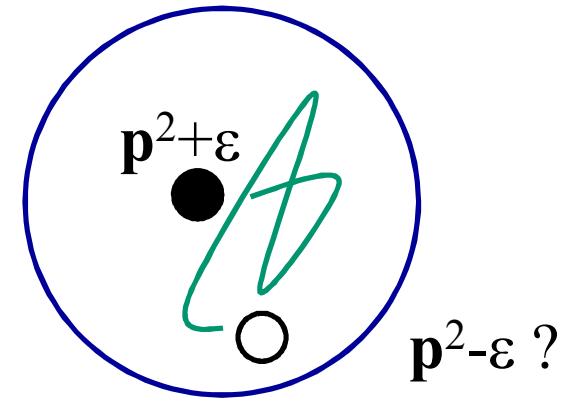…not really: A many-body system is not an "infinite-body" system !

$$N = \infty \qquad\qquad N < \infty$$
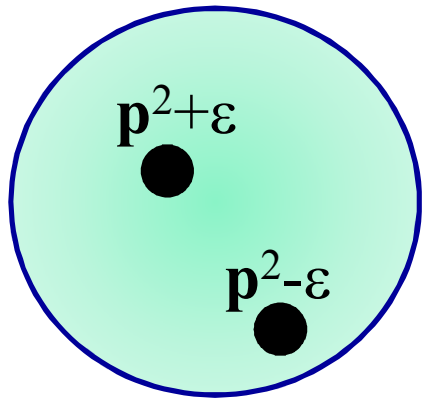
$$\forall \mathbf{p}^2 + \varepsilon \in \Omega \;\; \exists \mathbf{p}^2 - \varepsilon \in \Omega \qquad\qquad \forall \mathbf{p}^2 + \varepsilon \in \Omega \;\; \mathbf{p}^2 - \varepsilon \exists ???$$

$$\frac{2}{3k_B} \left\langle \sum_{I=1}^{N} \frac{\mathbf{p}_I^2}{2M_I} \right\rangle_N = T = \text{constant} \qquad\qquad \lim_{t \to \infty} \left[\frac{1}{t - t_0} \int_{t_o}^{t} T(t') \, dt' \right] = \text{constant}$$

…running average: we have to wait (*ergodicity*)

Connection to Statistical Mechanics:
static properties

If our system has an average density ρ ($\rho = 1$ g/cm^3 for H_2O), this density fluctuates as a function of the distance from a given point…

$$\rho(r) = \rho\, g(r)$$
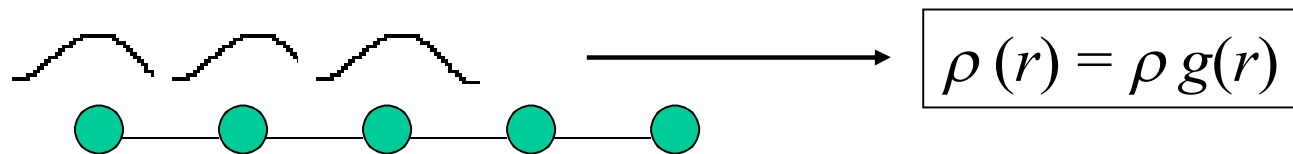
The density at a given radial distance r depends on whether or not another particle is present at r and is a measure of the structure of the system (crystal, liquid, etc…). The adimensional function $g(r)$ is called ***radial distribution function*** and must be zero at $r = 0$ because two particles cannot occupy the same place, and it is also clear that

$$\lim_{r \to \infty} g(r) = 1$$

because if we consider all the volume of the system, $\rho(r) = \rho$.

Connection to Statistical Mechanics:
static properties

From a MD trajectory :
$$g(r) = \frac{1}{\rho N} \left\langle \sum_{I \neq J}^{N} \delta(r - r_{IJ}) \right\rangle$$

where, $r_{IJ} = |\mathbf{R}_I(t) - \mathbf{R}_J(t)|$ and the ensemble average is of course the time average. The radial distribution function is related to the static structure factor $S(k)$ by a simple Fourier transform

$$S(k) = 4\pi\rho \int_0^\infty \frac{\sin(kr)}{kr} [g(r) - 1] r^2 dr$$

and $S(k)$ is the quantity measured in X-ray or neutron scattering experiments ($k = 4\pi \sin(\theta/2)/\lambda_{in}$). And the bulk pressure is

$$P = \rho k_B T - \frac{2\pi\rho^2}{3} \int_0^\infty \frac{\partial V(r)}{\partial r} g(r) r^3 dr$$

from the virial theorem, where $V(r)$ = MD potential.

Connection to Statistical Mechanics: extracting properties from simulations

Summarizing:

static properties such as structure, pressure etc.. are obtained from $g(r)$ pair (radial) distribution functions
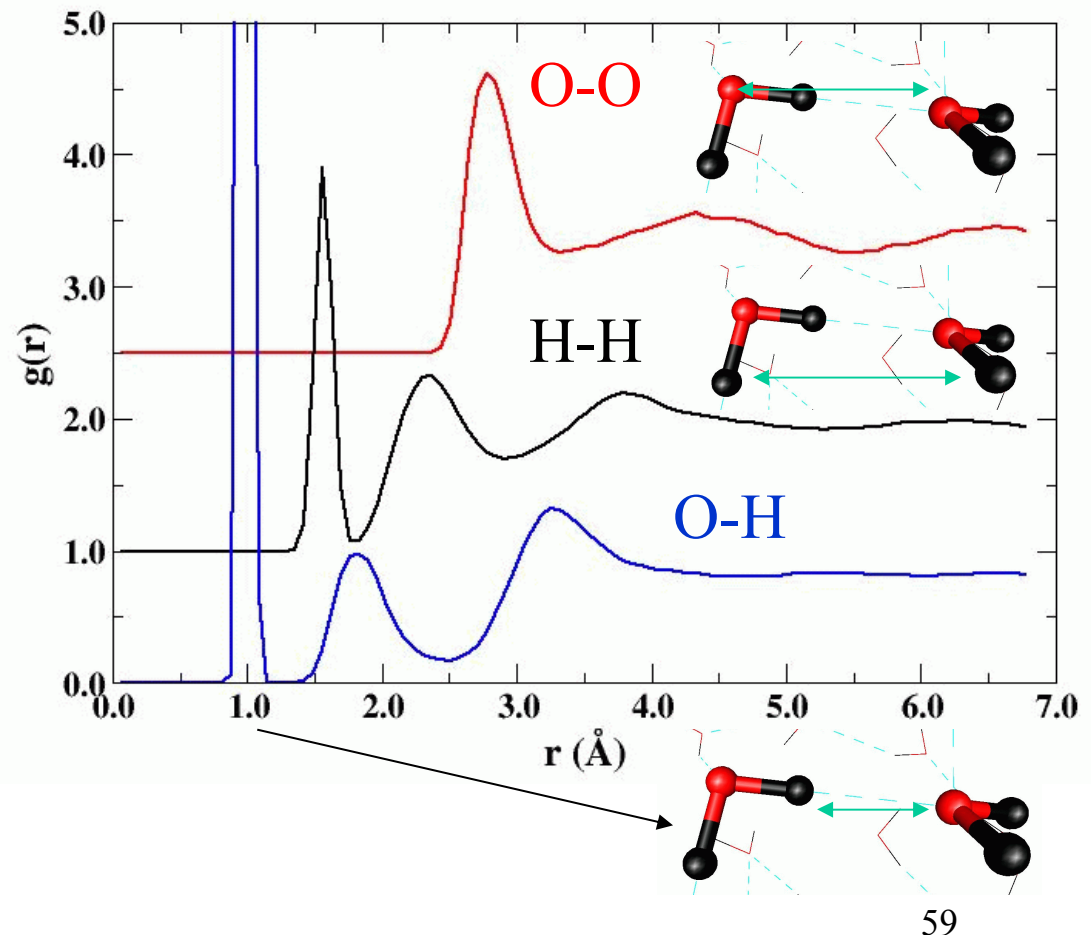
Connection to Statistical Mechanics:
dynamic properties

The dynamics of the system can be measured from the displacement
of its particles in time or, equivalently, from the velocities. An easy
quantity to compute is the mean square displacement (MSD)

$$\Delta R^2(t) = \frac{1}{N} \sum_{I=1}^{N} \left[\mathbf{R}_I(t) - \mathbf{R}_I(0) \right]^2$$

In general, for a solid $\Delta R^2(t)$ is small and almost constant in time
(non-diffusive regime). For a liquid or a gas, instead, it grows almost
linearly (diffusive regime)

$$\Delta R^2(t) = 6Dt + \Delta R^2(0) \longrightarrow \frac{1}{6} \frac{d}{dt} \Delta R^2(t) = D$$

D is the (self)*diffusion coefficient* to be compared with experiments

Connection to Statistical Mechanics:
dynamic properties

The velocities provided by the MD can be used in a mathematically equivalent way since

$$\mathbf{R}_I(t) - \mathbf{R}_I(0) = \int_0^t \mathbf{v}_I(t')dt'$$

and if we evaluate the time derivative of the MSD,

$$\frac{d}{dt}\Delta R^2(t) = \frac{d}{dt}\int_0^t dt'\int_o^t dt''\langle\mathbf{v}(t')\cdot\mathbf{v}(t'')\rangle = 2\int_o^t dt'\langle\mathbf{v}(t)\cdot\mathbf{v}(t')\rangle$$

$$= 2\int_o^t dt'\langle\mathbf{v}(t-t')\cdot\mathbf{v}(0)\rangle = 2\int_o^t dt'\langle\mathbf{v}(t')\cdot\mathbf{v}(0)\rangle$$

using the invariance of the origin of time. So, finally,

$$D = \frac{1}{3}\int_0^t dt'\langle\mathbf{v}(t')\cdot\mathbf{v}(0)\rangle$$

Connection to Statistical Mechanics:
dynamic properties

The quantity

$$\langle \mathbf{v}(t') \cdot \mathbf{v}(0) \rangle = \frac{1}{N} \sum_{I=1}^{N} \langle \mathbf{v}_I(t') \cdot \mathbf{v}_I(0) \rangle$$
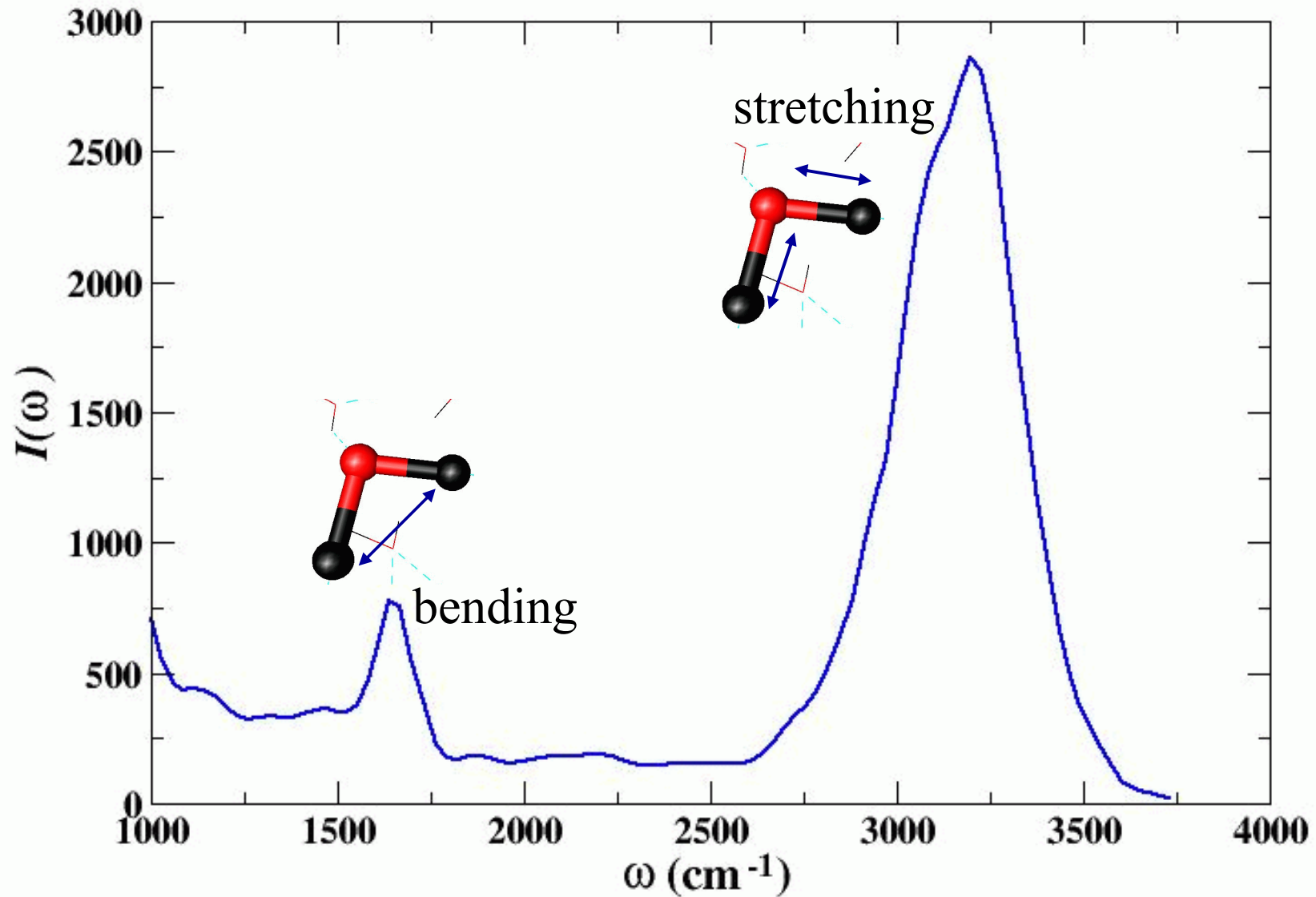
is called velocity autocorrelation function and is useful also to compute the vibrational spectrum of the system

$$I(\omega) = \int_{o}^{\infty} dt \langle \mathbf{v}(t) \cdot \mathbf{v}(0) \rangle e^{i\omega t}$$

as a simple Fourier transform from the time domain to the frequency domain.

Connection to Statistical Mechanics:
dynamic properties - Vibrational spectrum of water

Connection to Statistical Mechanics: extracting properties from simulations

Summarizing:

dynamic and transport properties are obtained from time correlation functions
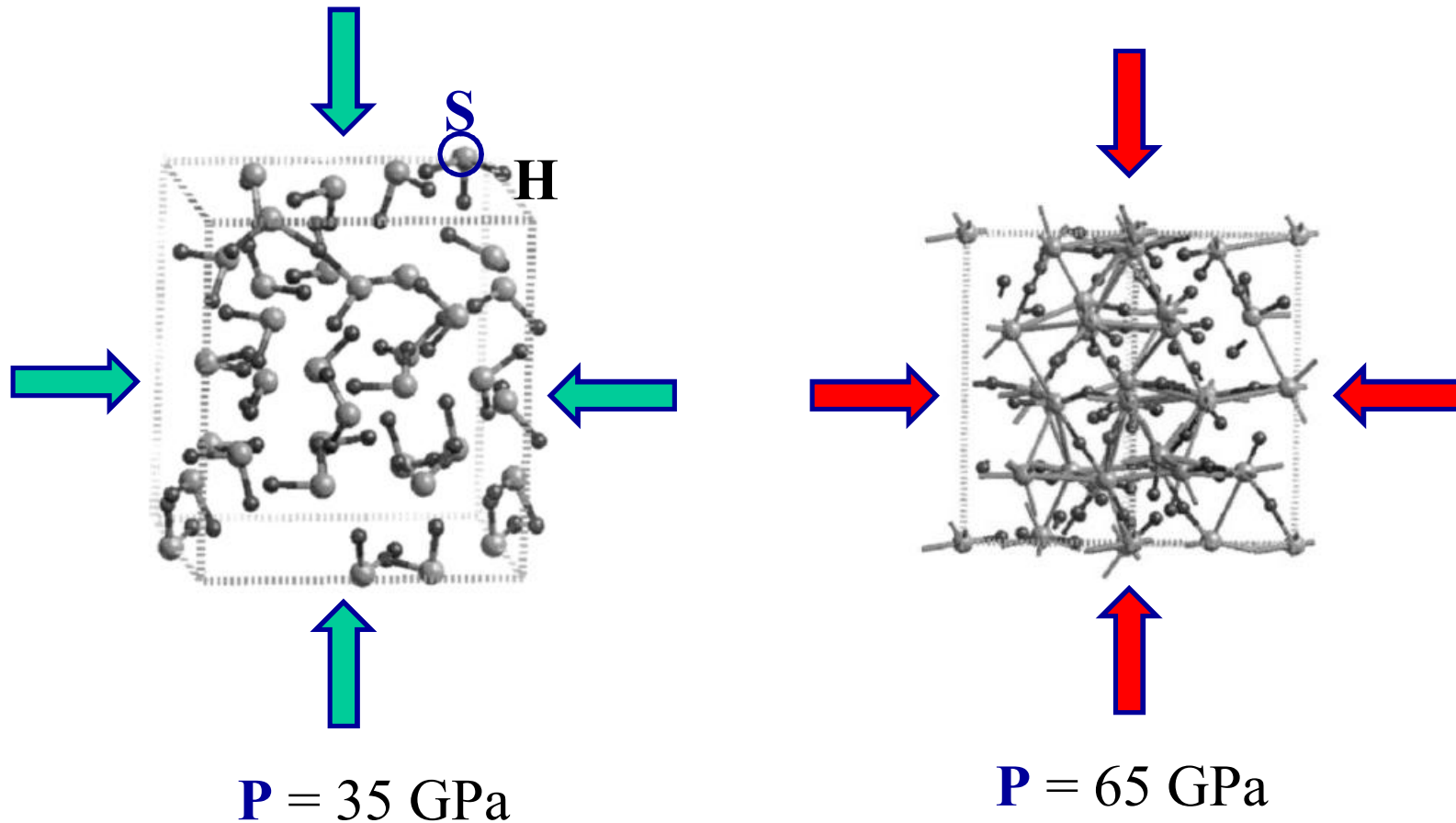
Example: self diffusion coefficient of water

D ($\times 10^{-5}$ cm^2/s)

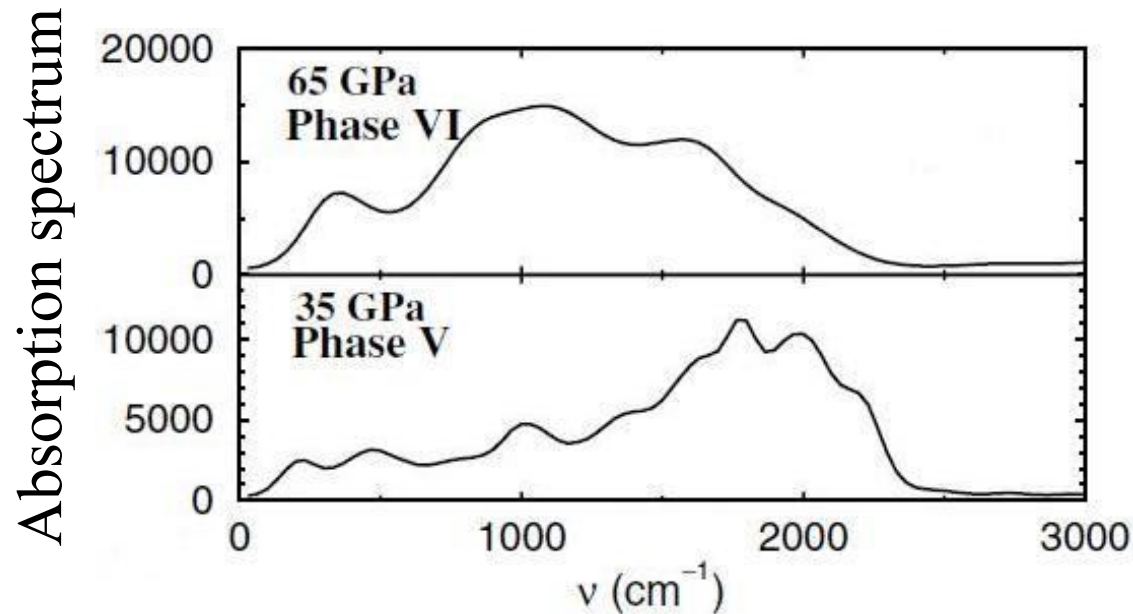| MD (good) simulation	Experiment
2.8 ± 0.5	2.4

Example of pressure control:
Parrinello-Rahman simulation of H$_2$S phases

R. Rousseau, M. B., M. Bernasconi, M. Parrinello and K. Terakura, *Phys. Rev. Lett*. **85**, 1254 (2000)
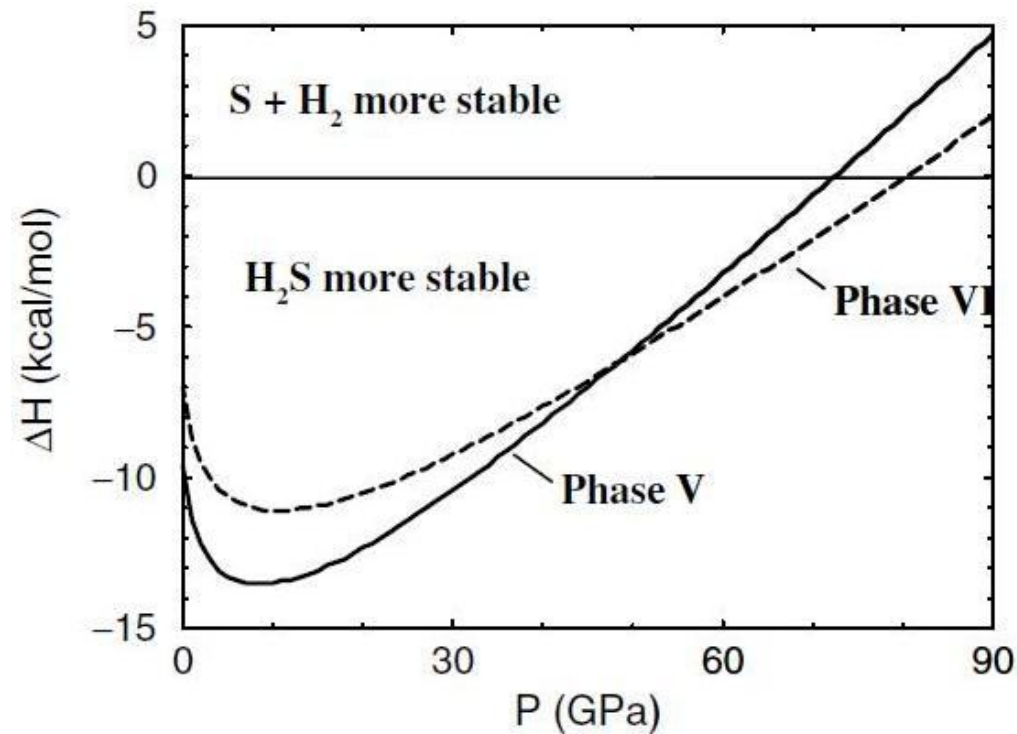

P = 35 GPa

P = 65 GPa

Parrinello-Rahman simulation of H_2S phases:
What can we say (compute) ?

The absorption spectrum computed from the trajectories of
the two phases at different pressures can be directly compared
to experiments.

Parrinello-Rahman simulation of H$_2$S phases: What can we say (compute) ?

The phase diagram of the energetics vs. applied pressure gives the relative stability of each structure at different thermodynamic conditions.

Parrinello-Rahman simulation of H_2S phases: What can we say (compute) ?

• Simulations provide an atomic-level model of H_2S structures at different pressures.

• The absorption spectrum, in agreement with experiments, provides an indirect validation of the atomic-level picture **not accessible to experimental probes**.

• Phase V is characterized by SH_3^+ and SH^- species dynamically formed and destroyed

• Phase VI is no longer a molecular phase but sheets of S with H intercalated between S layers

• The relative stability of the two phases depends on the thermodynamic conditions

Suggestions for further readings:

- *Understanding Molecular Simulations, From Algorithms to Applications*, D. Frenkel and B. Smit, Academic Press, San Diego, 1996
- *Computer Simulation of Liquids*, M. P. Allen and D. J. Tildesley, Clarendon Press, Oxford, 1987
- *An Introduction to Computational Physics*, T. Pang, Cambridge University Press, Cambridge, 1997
- http://www.fz-juelich.de/nic-series/volume23/volume23.html
  (freely downloadable)
- S. Nosé, *Mol. Phys.* **52**, 255 (1984)
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- W. G. Hoover, *Phys. Rev. A* **31**, 1695 (1985)
- H. C. Andersen, *J. Chem. Phys*. **72**, 2384 (1980)
- M. Parrinello and A. Rahman, *Phys. Rev. Lett*. **45**, 1196 (1980)
- M. Parrinello and A. Rahman, *J. Appl. Phys*. **52**, 7182 (1981)