University of Zurich[UZH]

Lecture "Forces & Molecular Dynamics"

Dr. Giacomo Melani

Department of Chemistry, University of Zürich

6th African School on Electronic Structure Methods and Applications

Virtual school, 8/06/2021

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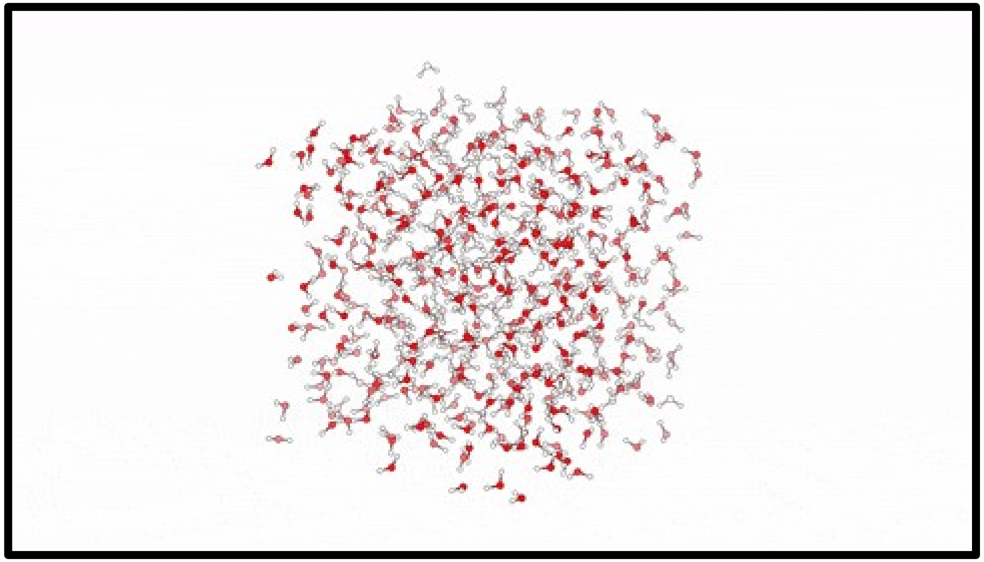
Outline of this lecture:

- Why doing molecular dynamics and simulations?
- Recap of classical and statistical mechanics
- Propagation schemes for MD
- Force fields vs Ab initio approaches
- Born-Oppenheimer Molecular Dynamics
- Moving across statistical ensembles

Why doing molecular dynamics and simulations?

- Condensed-phase systems often experience many different structures at a given temperature.
- Static approaches do not take into account fluctuations and finite-time effects.
- Dynamical (even reactive) processes can be seen in “real time”.



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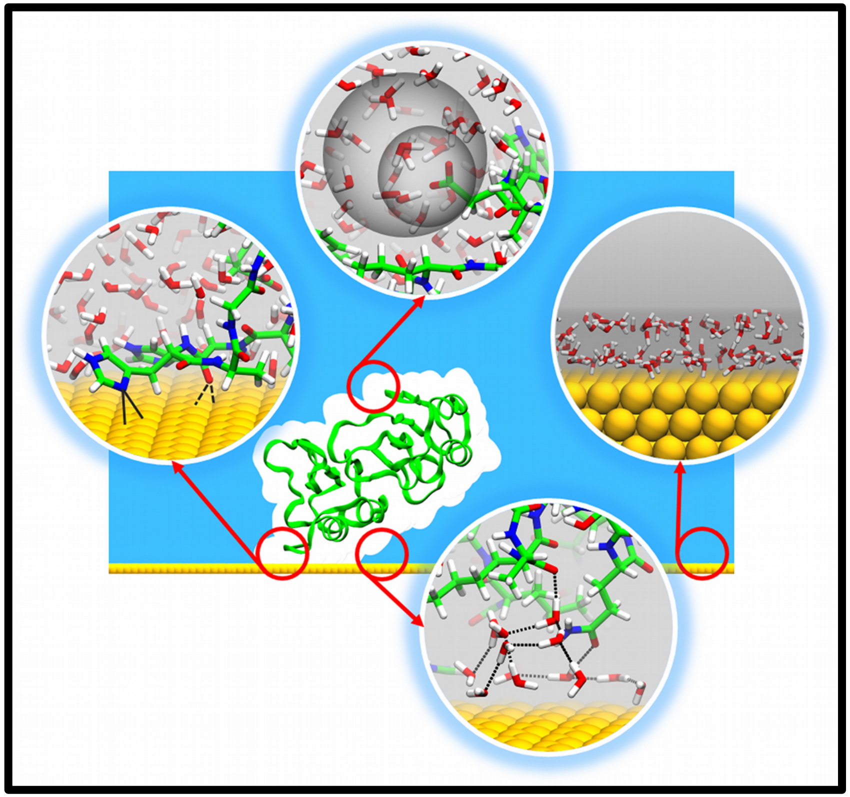

Picture taken from: M. Ozboyaci et al., Q. Rev. Biophys., 49, 1-45 (2016)

Recap of classical and statistical mechanics

- Let's consider a system of N particles (atoms) moving in absence of an external field. From the BOA we know atoms move much slower than electrons and, if we're interested only in the nuclear dynamics we can assume they move classically*:

**Be careful when treading light nuclei like H (NQEs become important)*

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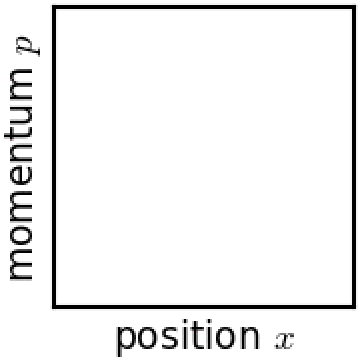
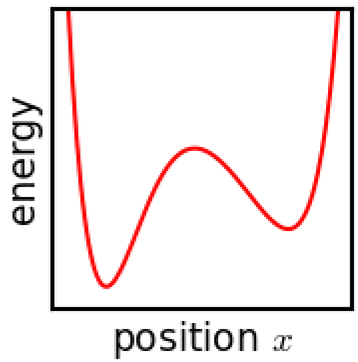


$$H(\underline{r},\underline{p})=\sum_{I}^{N}\frac{\underline{p}_I^2}{2m_I}+V(\underline{r}) \longrightarrow$$

($\underline{r}$,$\underline{p}$) are the phase-space (or canonical) coordinates



$$\frac{d\underline{q}}{dt}=\frac{\partial H}{\partial \underline{p}} \qquad \frac{d\underline{p}}{dt}=-\frac{\partial H}{\partial \underline{r}} \longrightarrow$$

Hamilton’s classical EOM

**Be careful when treading light nuclei like H (NQEs become important)*

Recap of classical and statistical mechanics

- Any (thermodynamic) property of the system is given by its expectation value <A>:

$$\langle A \rangle_E = \frac{1}{Z} \int d\underline{r} \int d\underline{p}\, e^{-\beta H} A(\underline{p}, \underline{r})$$

Ensemble average

$$\langle A \rangle_T = \frac{1}{T} \int_0^T dt' A(\underline{p}(t'), \underline{r}(t'))$$

Time average

Ensemble <A> = Time <A>
Ergodic Theorem

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Recap of classical and statistical mechanics

- We can also extend this equivalence to dynamical properties → time correlation functions:

$$\langle A(0)B(t)\rangle = \frac{1}{Z}\int d\underline{r}\int d\underline{p}\, e^{-\beta H} A(\underline{p}(0),\underline{r}(0))\,B(\underline{p}(t),\underline{r}(t))$$

$$\langle A(0)B(t)\rangle = \frac{1}{T}\int_0^T dt'\, A(t')\,B(t+t')$$

- Examples of TCFs:

$$I(\omega)\propto \tilde{C}_{\mu\mu}(\omega),\, C_{\mu\mu}(t)=\langle \underline{\mu}(0)\underline{\mu}(t)\rangle$$

$$VDOS(\omega)\propto \tilde{C}_{vv}(\omega),\, C_{vv}(t)=\langle \underline{v}(0)\underline{v}(t)\rangle$$

Propagation schemes in Molecular Dynamics

- For a small change in time Δ(t), we can Taylor expand the coordinates r:

$$r(t+\Delta t)=r(t)+\frac{p(t)}{m}\Delta t+\frac{\dot{p}(t)}{2m}\Delta t^2+\frac{\dddot{r}(t)}{3!}\Delta t^3+O(\Delta t^4)$$

$$r(t-\Delta t)=r(t)-\frac{p(t)}{m}\Delta t+\frac{\dot{p}(t)}{2m}\Delta t^2-\frac{\dddot{r}(t)}{3!}\Delta t^3+O(\Delta t^4)$$

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$$r(t+\Delta t)+r(t-\Delta t)=2r(t)+\frac{\dot{p}(t)}{2m}\Delta t^2+O(\Delta t^4)$$

$$r(t+\Delta t)\approx 2r(t)-r(t-\Delta t)+\frac{\dot{p}(t)}{2m}\Delta t^2$$

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Integration error

$$r(t+\Delta t)+r(t-\Delta t)=2r(t)+\frac{\dot{p}(t)}{2m}\Delta t^2+O(\Delta t^4)$$

$$r(t+\Delta t)\approx 2r(t)-r(t-\Delta t)+\frac{\dot{p}(t)}{2m}\Delta t^2$$

Verlet Algorithm

Propagation schemes in Molecular Dynamics

- In most of codes, the preferred algorithm is the **"Velocity Verlet"**:

1 $$p(t+\Delta t/2)=p(t)+F(t)\frac{\Delta t}{2}$$

First change of momenta from initial values and forces

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② $$r(t+\Delta t)=r(t)+\frac{p(t+\Delta t/2)}{m}\Delta t$$

New positions given initial coordinates and modified momenta

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3. $$p(t+\Delta t) = p(t+\Delta t/2) + F(t+\Delta t)\frac{\Delta t}{2}$$ New force evaluation

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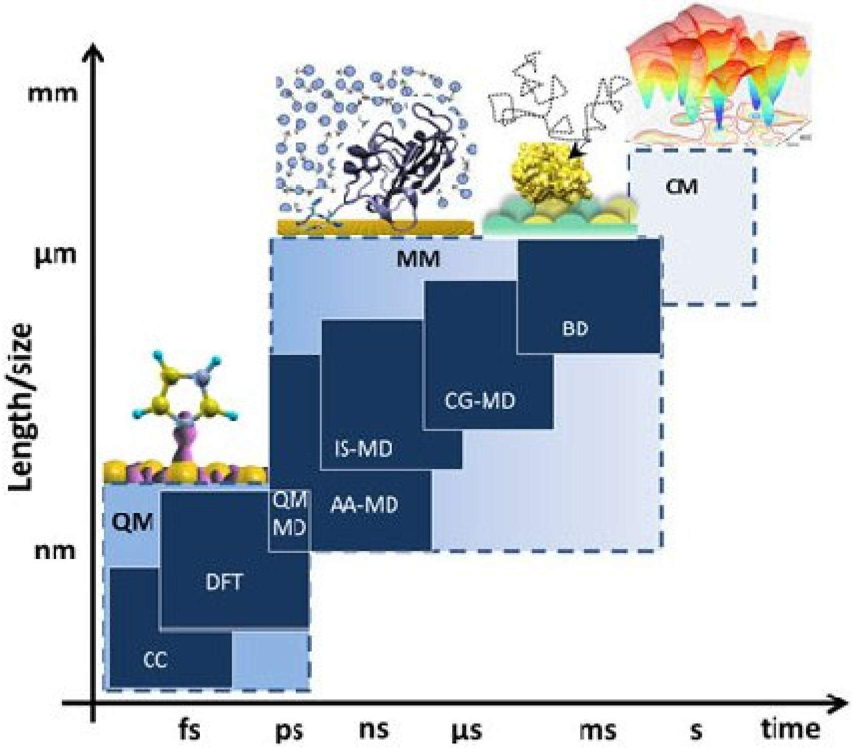
The choice of Δt determines the accuracy of integration:
$\Delta t \sim 1/10\omega_{max}$ (highest vibrational frequency of the system)

Force fields (MM) vs Ab initio (DFT) approaches

- Condensed phase systems (eg. liquids, biomolecules) often require long trajectories and can be therefore studied using empirical force fields.



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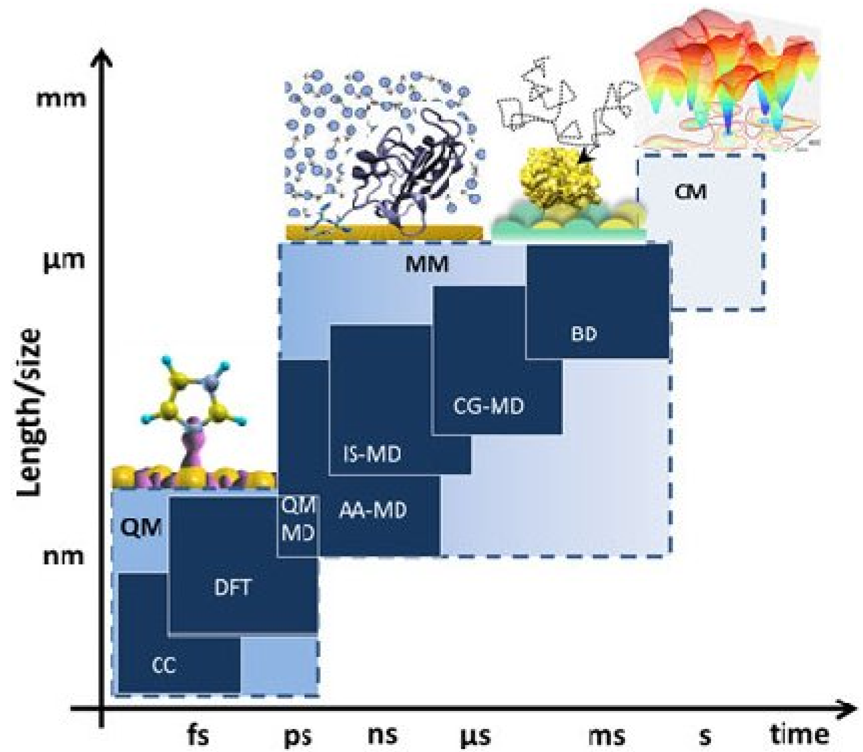

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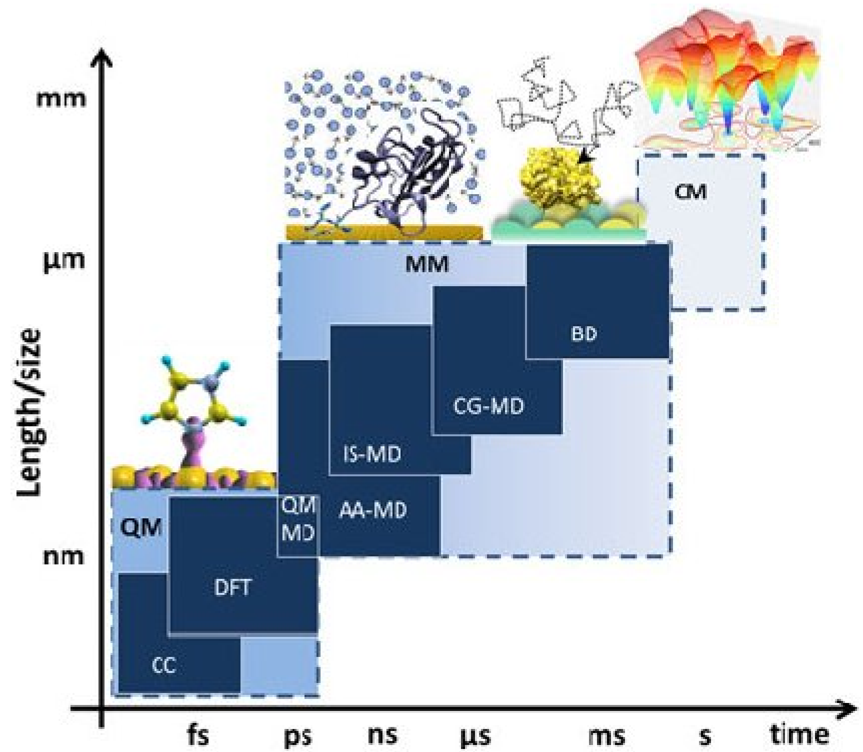
- There are many parametrized molecular mechanics FFs, based on empirical and QM-data:
  - AMBER, CHARMM, GROMOS (organic and biological molecules)
  - OPLS (liquids), SPC and TIPxP (water)



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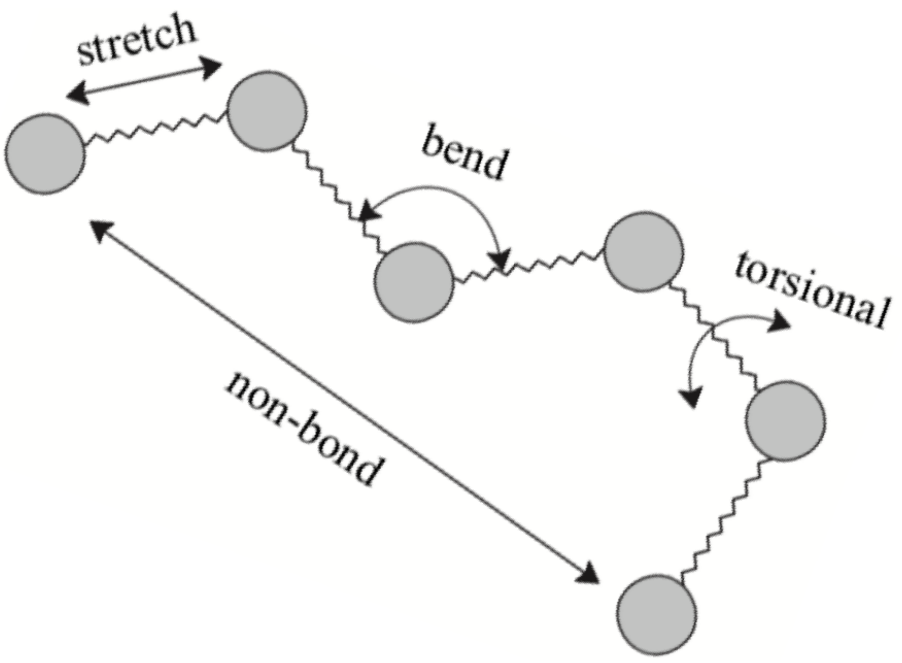

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Potential Energy

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Harmonic approximation

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$$+ \sum_{j>i}\left(4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right] + \frac{q_i q_j}{4\varepsilon_0 r_{ij}}\right)$$

Potential Energy

Electrostatic terms (sometimes including polarizable charges)

Force fields (MM) vs Ab initio (DFT) approaches

- Empirical FFs are often not easily transferable to other systems (especially when considering solid materials) and cannot describe reactive processes*.

**Exception of the ReaxFF*

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$$\Phi(\boldsymbol{R}) = E_{\mathrm{KS}}^{\mathrm{DFT}}\left[\{\psi_i\};\boldsymbol{R}\right] + E_{II}(\boldsymbol{R}) = E\left[\{\psi_i\};\boldsymbol{R}\right]$$

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Lagrangian

Ground state PES

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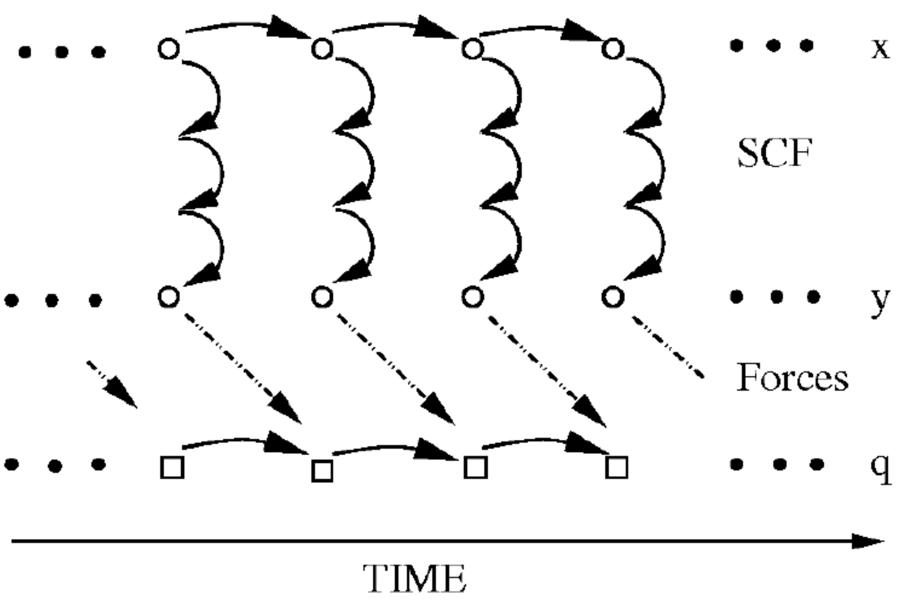
Born-Oppenheimer Molecular Dynamics

- There are two crucial steps in a BOMD: the SCF cycle and the time integration.
- Both can strongly affect the calculation of **forces**, which also determines the accuracy of the dynamics.



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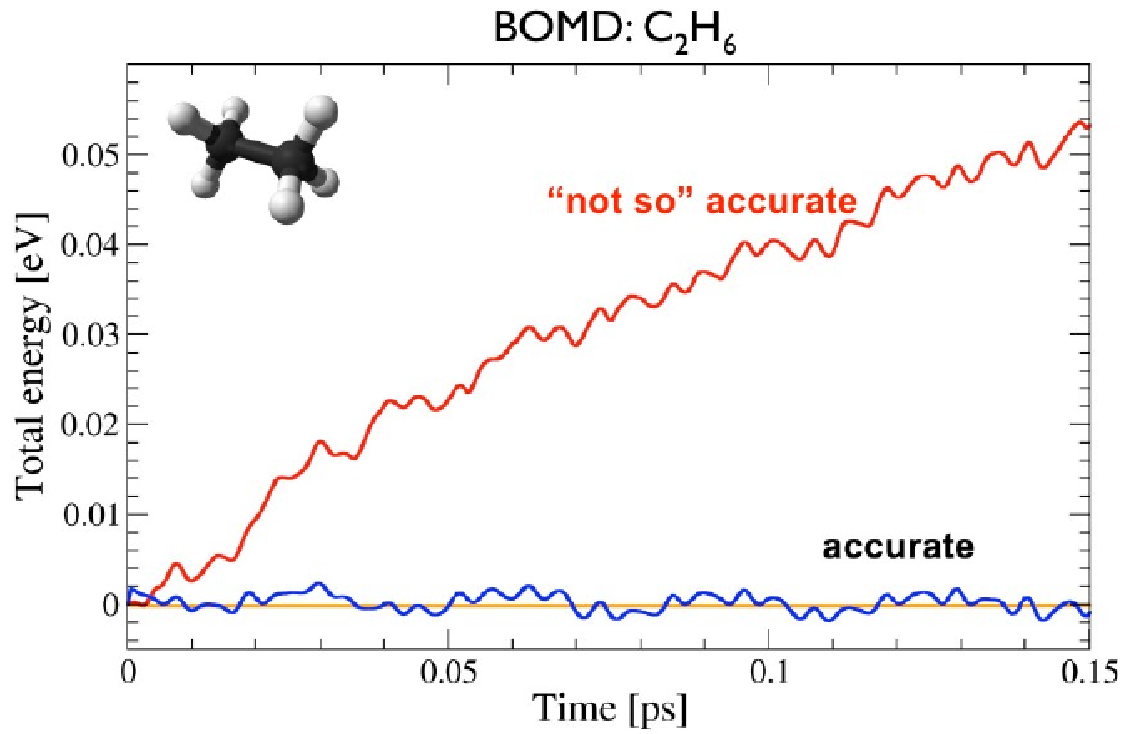

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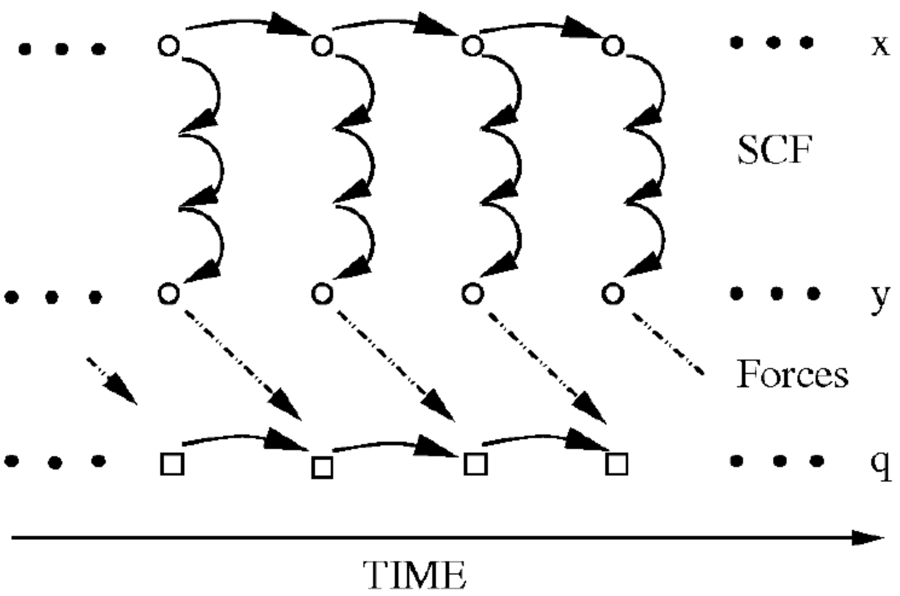

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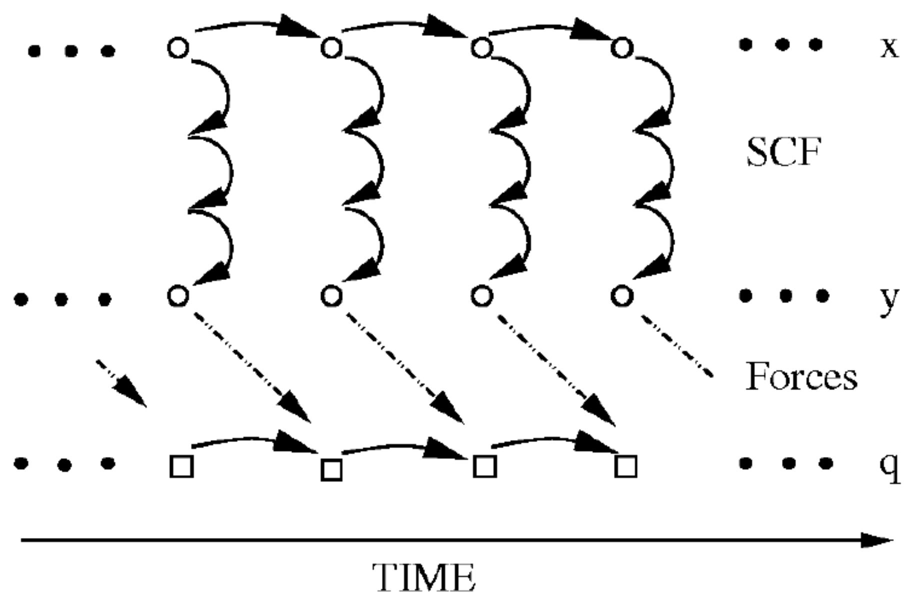

$$\frac{\mathrm{d}E}{\mathrm{d}\mathbf{R}} = \frac{\mathrm{d}}{\mathrm{d}\mathbf{R}}\langle\psi|\hat{H}|\psi\rangle$$
$$= \left\langle\frac{\mathrm{d}\psi}{\mathrm{d}\mathbf{R}}\middle|\hat{H}\middle|\psi\right\rangle + \left\langle\psi\middle|\hat{H}\middle|\frac{\mathrm{d}\psi}{\mathrm{d}\mathbf{R}}\right\rangle + \left\langle\psi\middle|\frac{\mathrm{d}\hat{H}}{\mathrm{d}\mathbf{R}}\middle|\psi\right\rangle$$
$$= E\left\langle\frac{\mathrm{d}\psi}{\mathrm{d}\mathbf{R}}\middle|\psi\right\rangle + E\left\langle\psi\middle|\frac{\mathrm{d}\psi}{\mathrm{d}\mathbf{R}}\right\rangle + \left\langle\psi\middle|\frac{\mathrm{d}\hat{H}}{\mathrm{d}\mathbf{R}}\middle|\psi\right\rangle.$$

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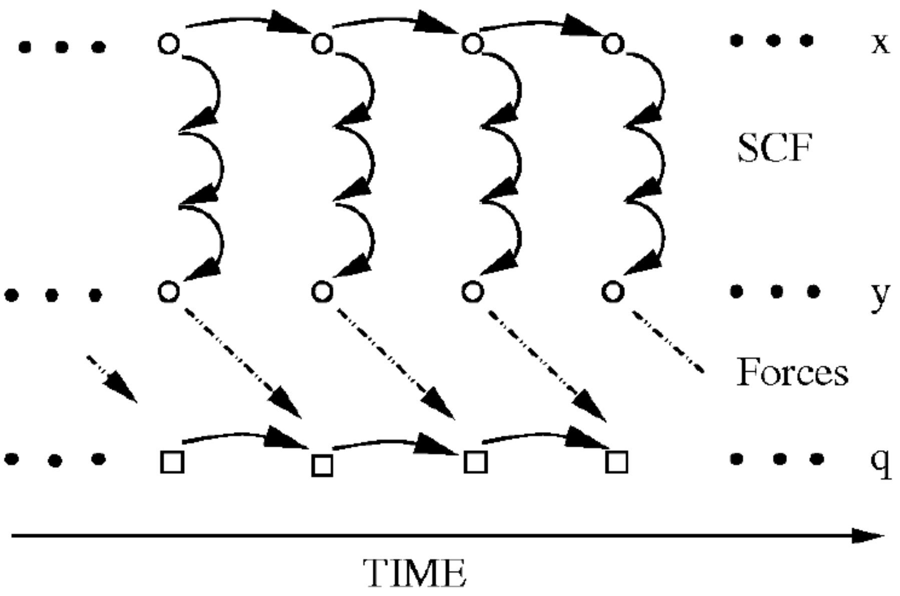

$$\begin{aligned}\frac{\mathrm{d}E}{\mathrm{d}\mathbf{R}} &= \frac{\mathrm{d}}{\mathrm{d}\mathbf{R}}\langle\psi|\hat{H}|\psi\rangle \\ &= \left\langle\frac{\mathrm{d}\psi}{\mathrm{d}\mathbf{R}}\middle|\hat{H}\middle|\psi\right\rangle + \left\langle\psi\middle|\hat{H}\middle|\frac{\mathrm{d}\psi}{\mathrm{d}\mathbf{R}}\right\rangle + \left\langle\psi\middle|\frac{\mathrm{d}\hat{H}}{\mathrm{d}\mathbf{R}}\middle|\psi\right\rangle \\ &= \boxed{E\left\langle\frac{\mathrm{d}\psi}{\mathrm{d}\mathbf{R}}\middle|\psi\right\rangle + E\left\langle\psi\middle|\frac{\mathrm{d}\psi}{\mathrm{d}\mathbf{R}}\right\rangle} + \left\langle\psi\middle|\frac{\mathrm{d}\hat{H}}{\mathrm{d}\mathbf{R}}\middle|\psi\right\rangle.\end{aligned}$$

This terms vanish if we have a complete basis

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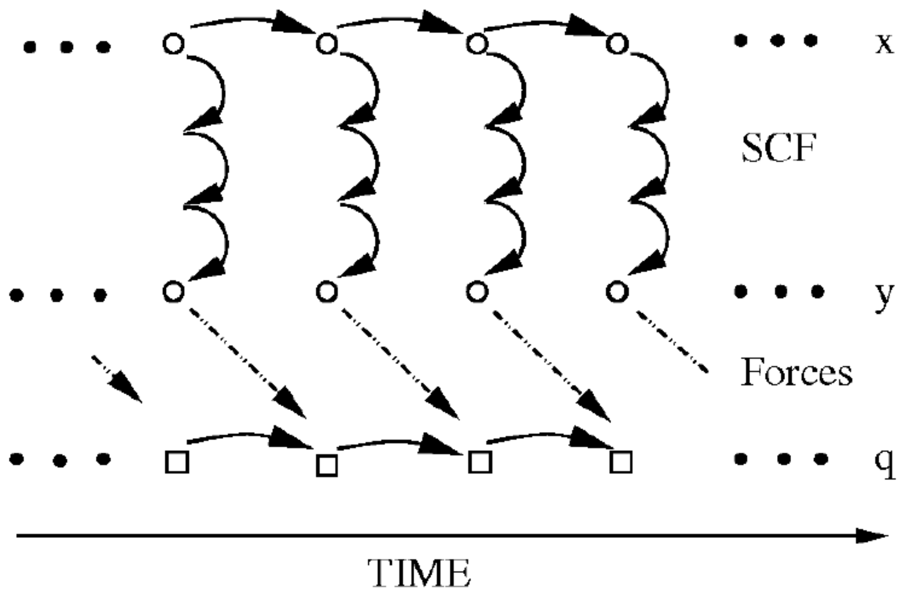


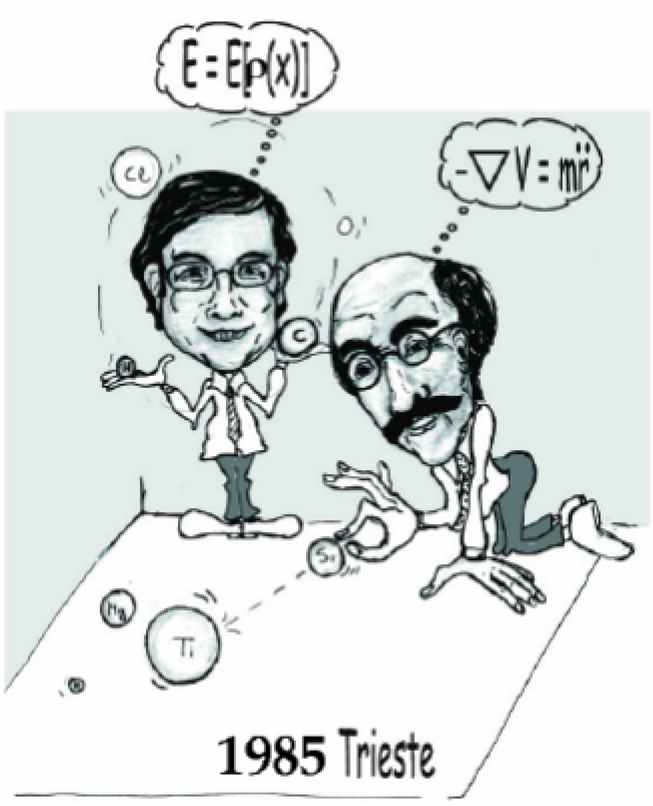
- When using an incomplete basis or if the basis is position-dependent, an additional term will appear
  → *Pulay forces (or stresses)*
- Pulay forces vanish in the CBS limit and also for position-independent basis functions, like PWs

Car-Parrinello Molecular Dynamics

- In the early days of BOMD this technique was impractical to use. Therefore, R. Car and M. Parrinello designed a way to combine DFT with MD at a reasonable computational cost.
- They introduced an "extended Lagrangian" formulation, assigning a mass the electrons.

$$\mathcal{L}_{\mathrm{CP}}(\{\psi_i\};\boldsymbol{R},\dot{\boldsymbol{R}}) = \frac{1}{2}\mu\sum_i\langle\dot{\psi}_i|\dot{\psi}_i\rangle + \frac{1}{2}\sum_{I=1}^{N} M_I\dot{\boldsymbol{R}}_I^2 - E[\{\psi_i\};\boldsymbol{R}] + \sum_{i,j}\Lambda_{ij}(\langle\psi_i|\psi_j\rangle - \delta_{ij})$$

μ = *fictitious electron mass*



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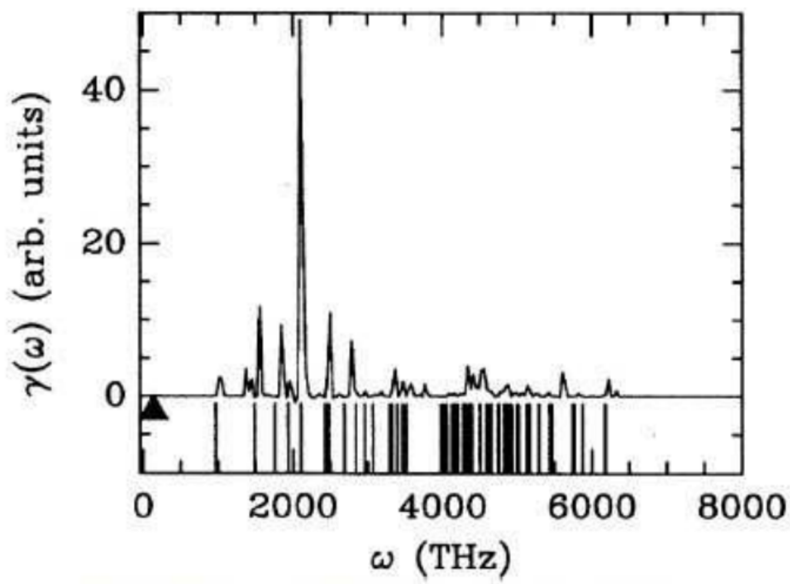

Triangle = highest ionic frequency

Car-Parrinello Molecular Dynamics

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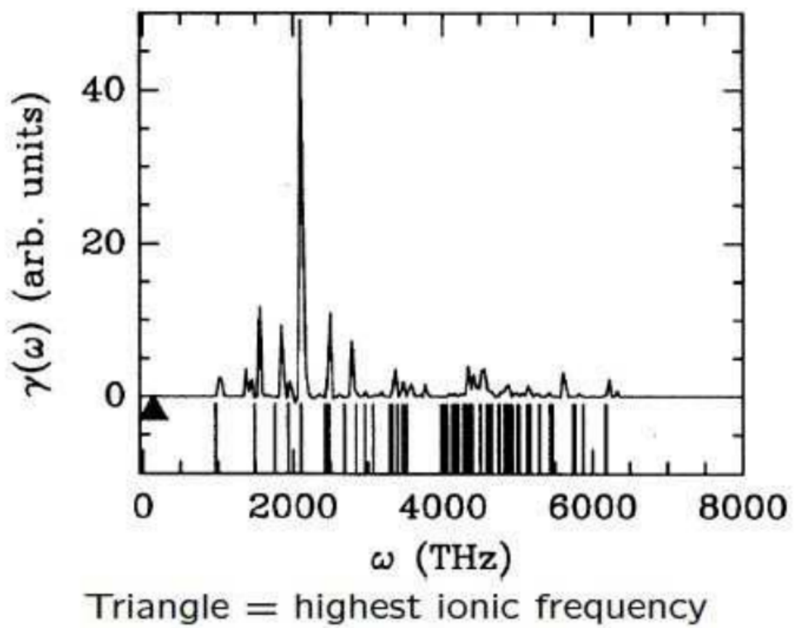
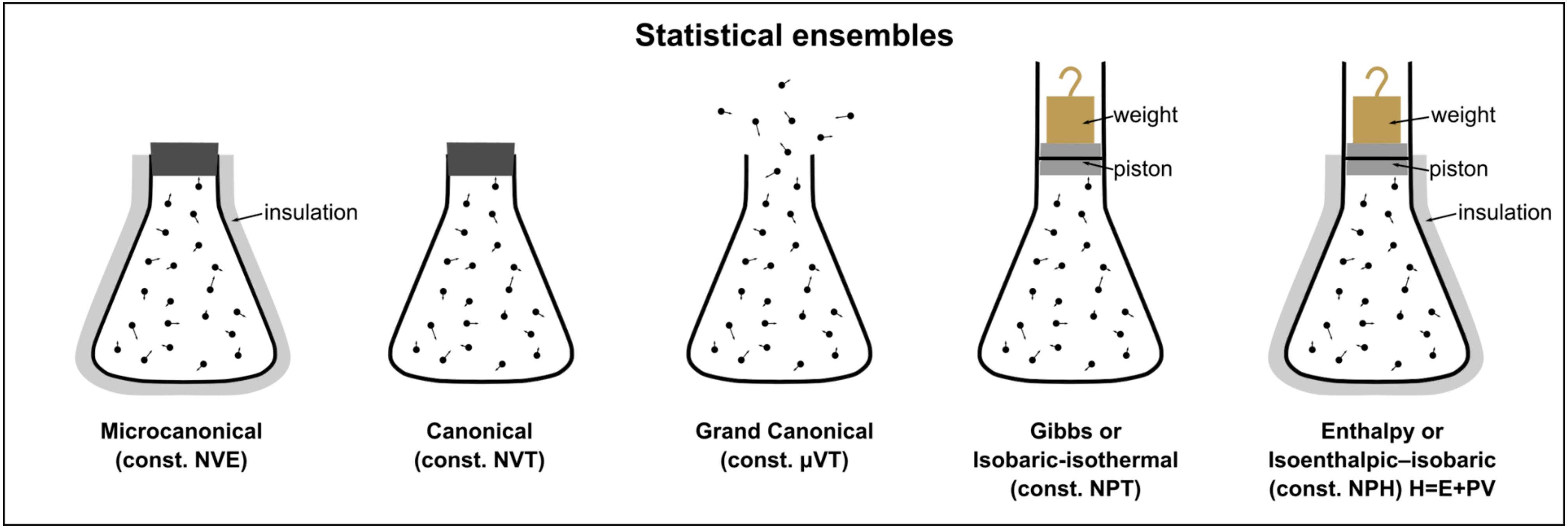
- They introduced an "extended Lagrangian" formulation, assigning a mass the electrons.
- Electronic and nuclear modes are artificially separated (like adiabatic) but have coupled EOMs.

- Advantage: no SCF iteration procedure
- Disadvantage: very small time step

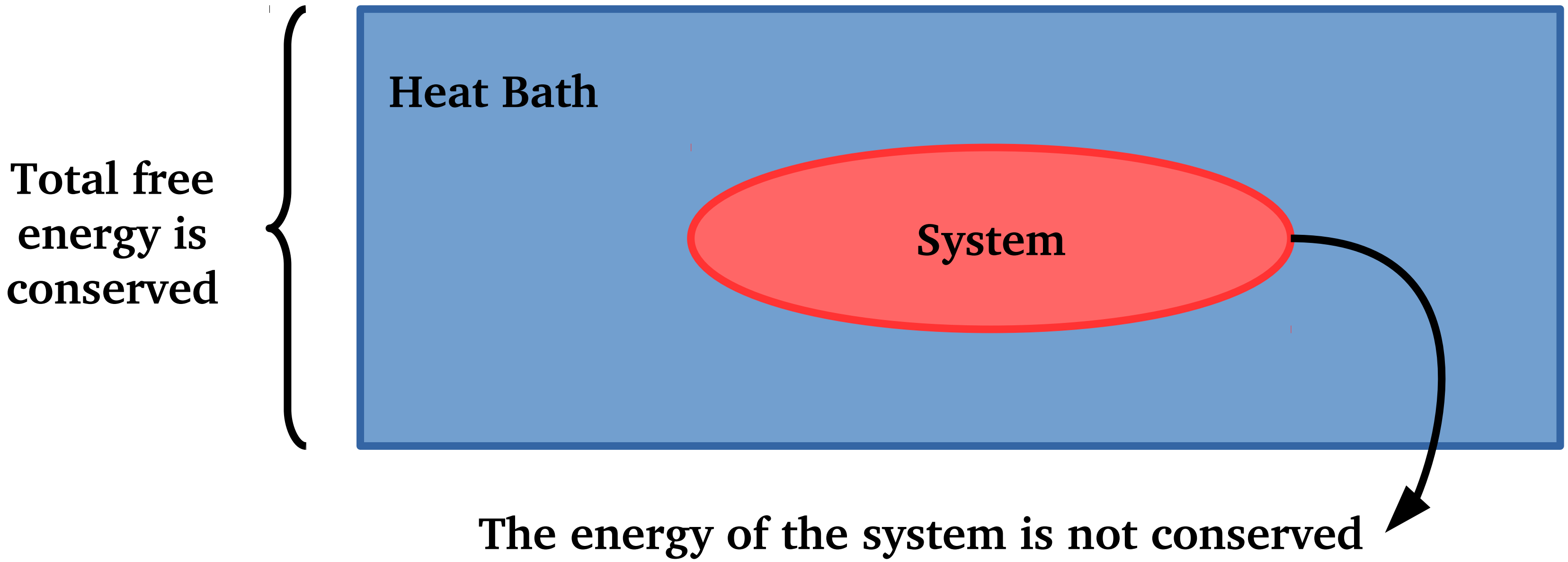


Moving across statistical ensembles



Moving across statistical ensembles: the NVT case

- Simulating at a given temperature (like "real life" conditions) is important, but how to implement it in a MD scheme?



Moving across statistical ensembles: the NVT case

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- One needs to apply a thermostat: A few examples

→ Langevin dynamics, add a frictional force

$$m\ddot{r}_i(t) = F_i(t) - m\Gamma p_i(t) + \gamma_i(t) \qquad \langle \gamma_i(t)\gamma_i(t')\rangle = \delta_{ij}\delta(t-t')6m\Gamma k_B T$$

→ Velocities rescaling ("Andersen" method)

$$\Delta T = (\lambda^2 - 1) T(t)$$

Moving across statistical ensembles

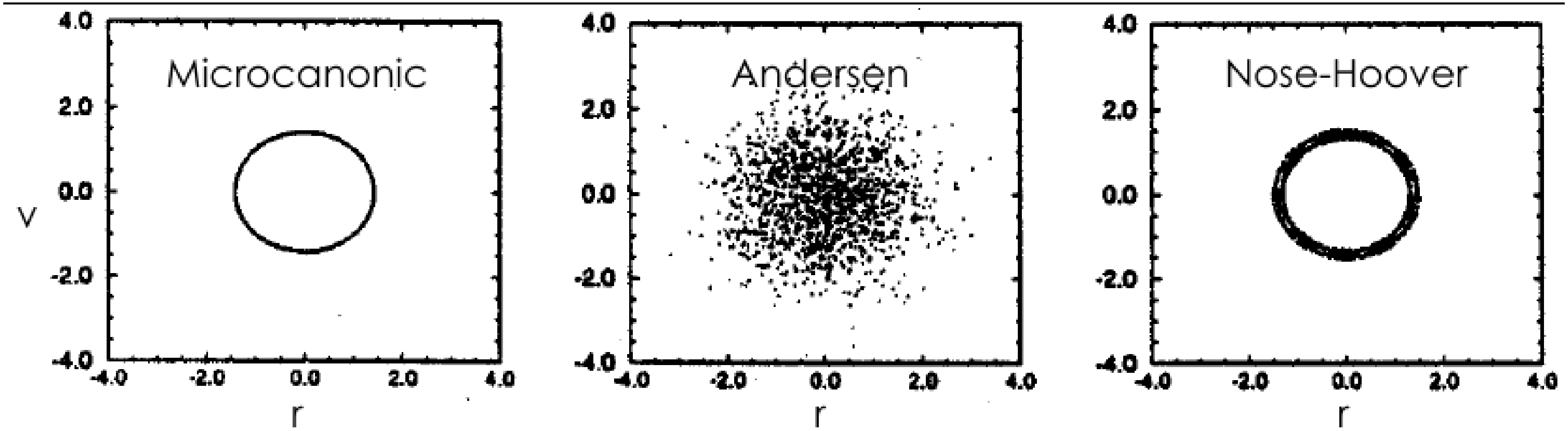
- Coupling of each coordinate with a fictitious oscillator (“Nosé-Hoover” method)

$$\dot{p}_i = F_i - \frac{p_\eta}{Q} p_i$$

Q determines the coupling to the heath bath

$$H_{NH} = \sum_I^N \frac{p_I^2}{2m_I} + \frac{p_\eta^2}{2Q} + 3Nk_B T$$

Moving across statistical ensembles



Further readings:

"Computer Simulation of Liquids"
Michael P. Allen, Dominic J. Tildesley, OUP (2017)

"Ab Initio Molecular Dynamics: Basic Theory and Advanced Methods"
Dominik Marx, Jürg Hutter, CUP (2012)

Thank you very much for your attention!