Ab initio molecular dynamics

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Density-functional theory and beyond: Computational materials science for real materials
09.08.2013, Trieste, Italy

What are we interested in?

- Thermodynamic ensemble properties:

Static equilibrium properties:

$$\langle A \rangle = \frac{1}{Z} \int d^{3N}R \int d^{3N}p \; \mathrm{e}^{-\mathcal{H}/k_B T} A(p, R)$$

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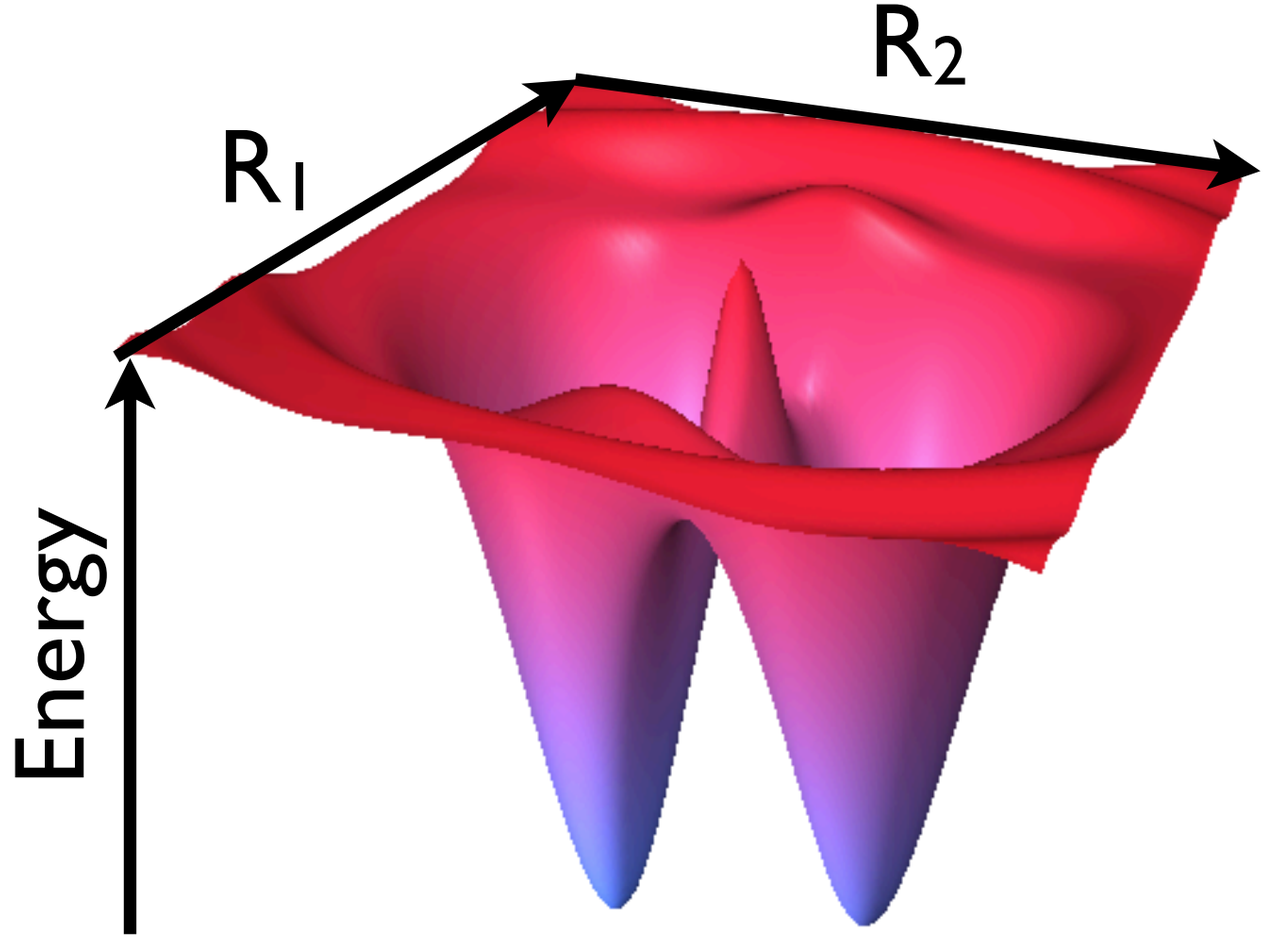

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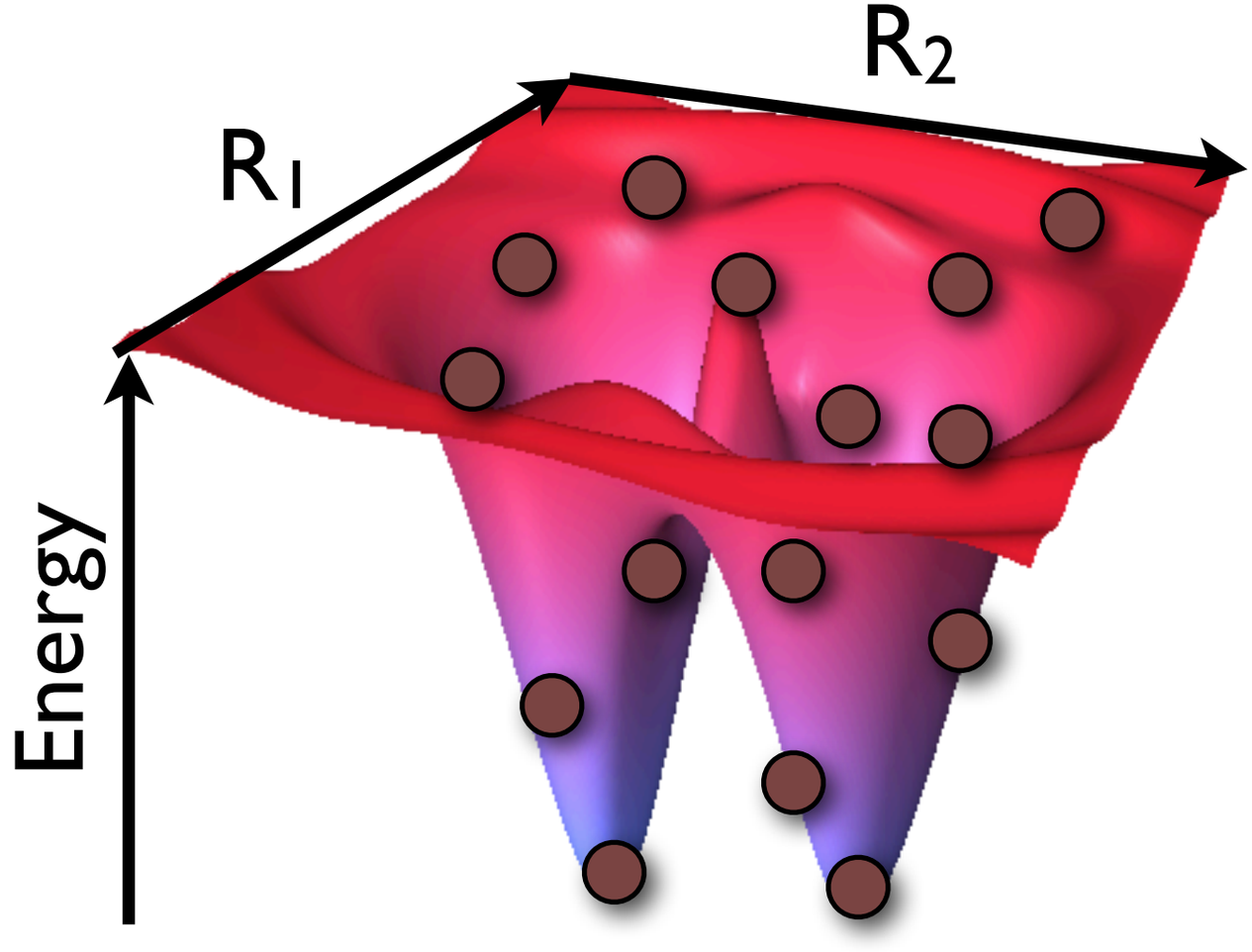

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- Ergodic hypothesis: ensemble average equal to time average

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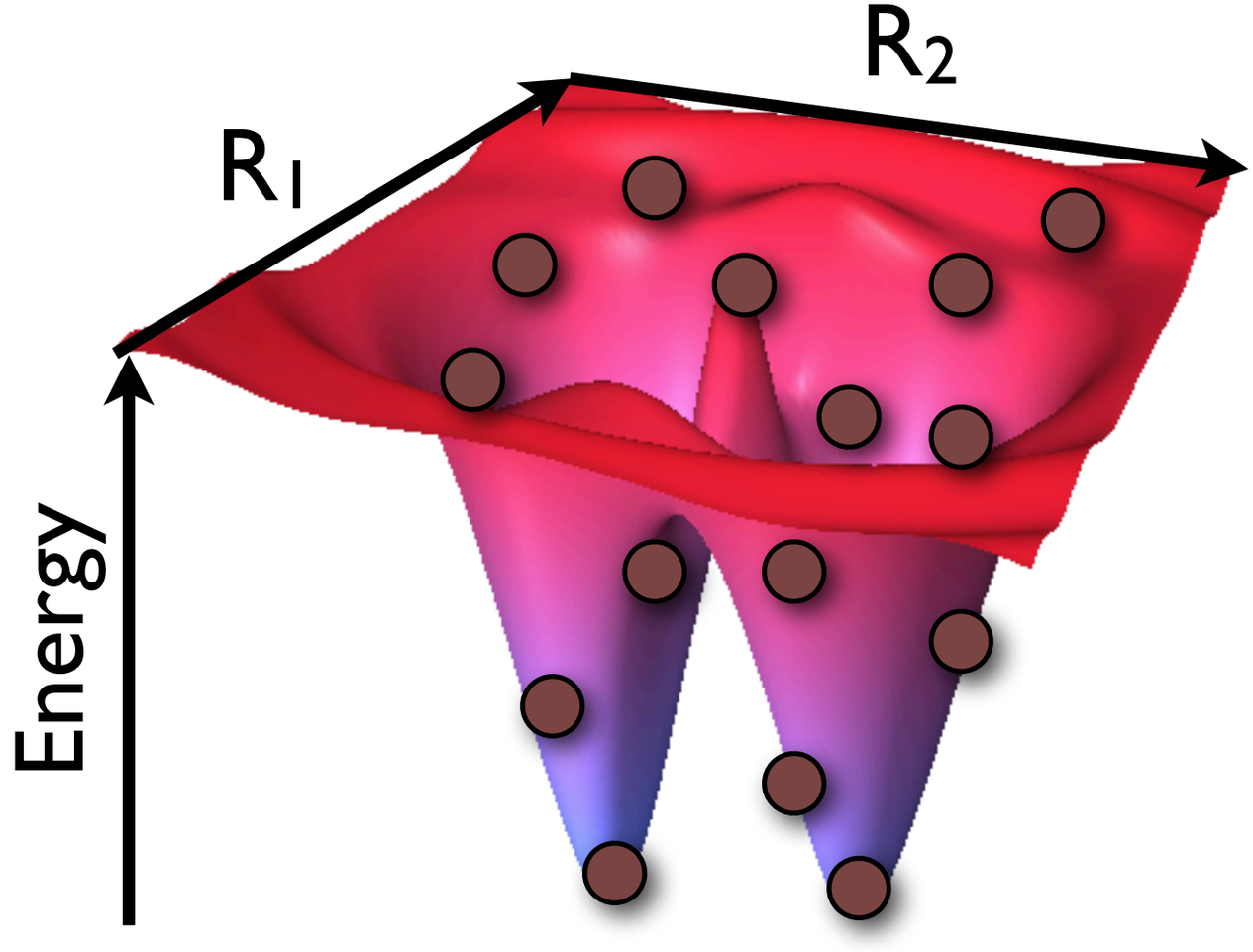

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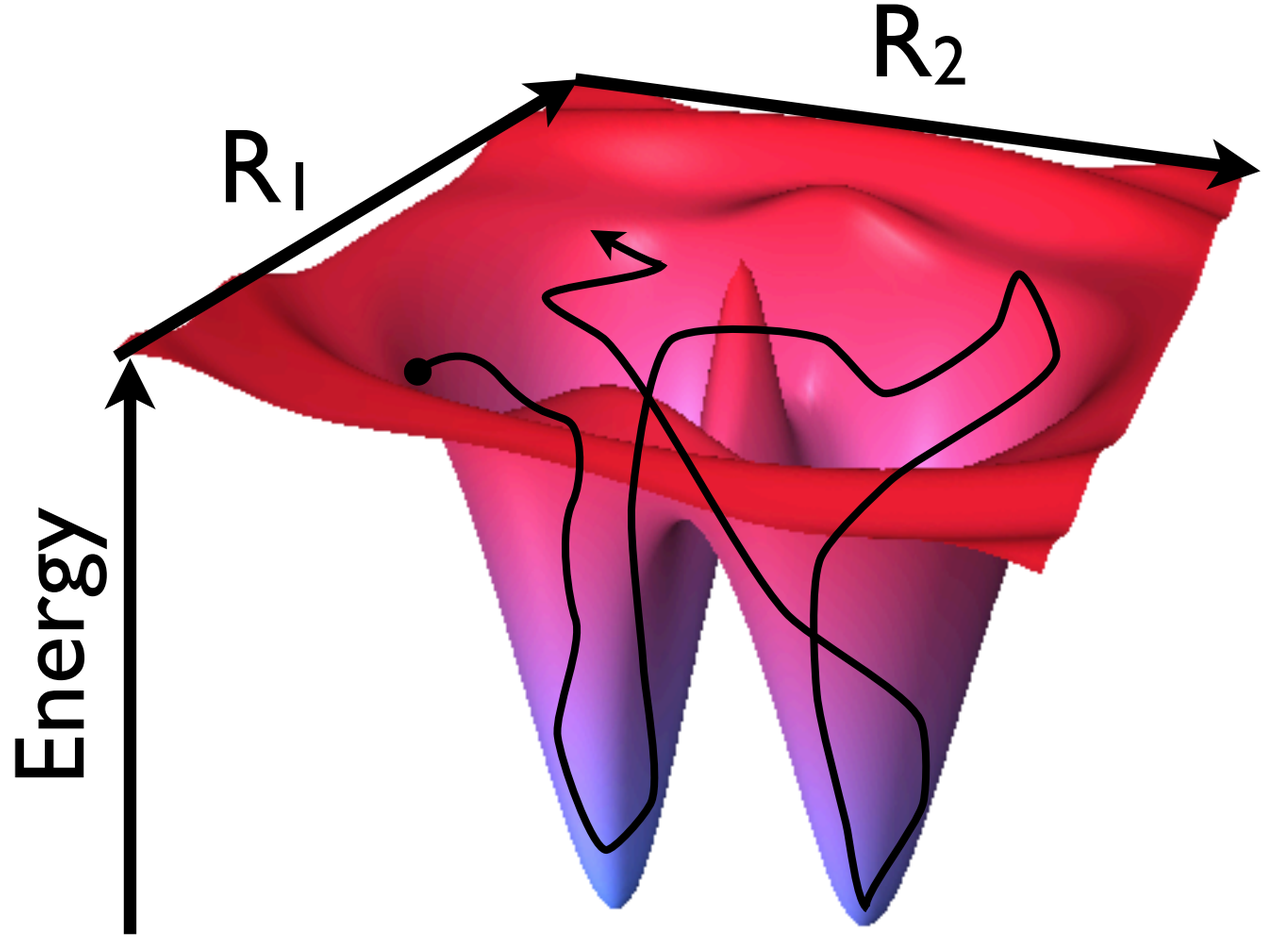
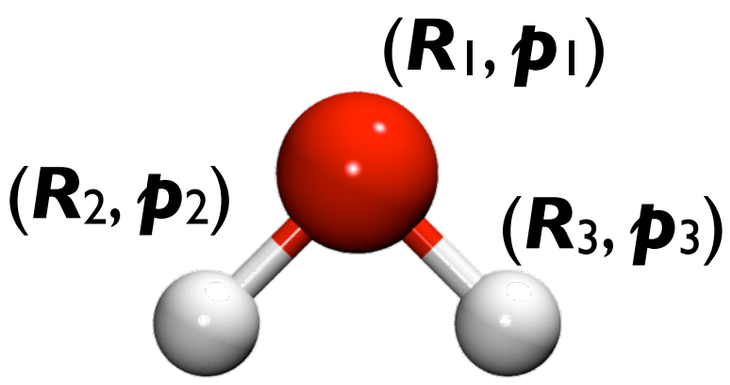


How to get (classical) trajectories?



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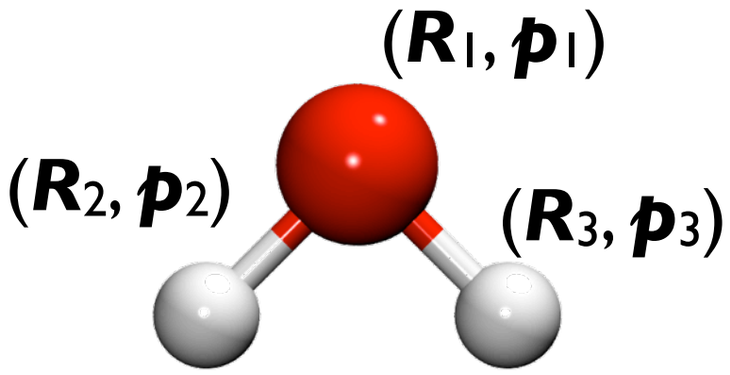

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$$\mathcal{H}(\mathbf{R}, \mathbf{p}) = \sum_I \frac{\mathbf{p}_I^2}{2M_I} + V(\mathbf{R})$$

$$\dot{\mathbf{p}}_I = -\frac{\partial \mathcal{H}}{\partial \mathbf{R}_I} = -\nabla_I V(\mathbf{R}) \rightarrow M_I \ddot{\mathbf{R}}_I = \mathbf{F}_I \qquad \dot{\mathbf{R}}_I = \mathbf{p}_I / M_I$$

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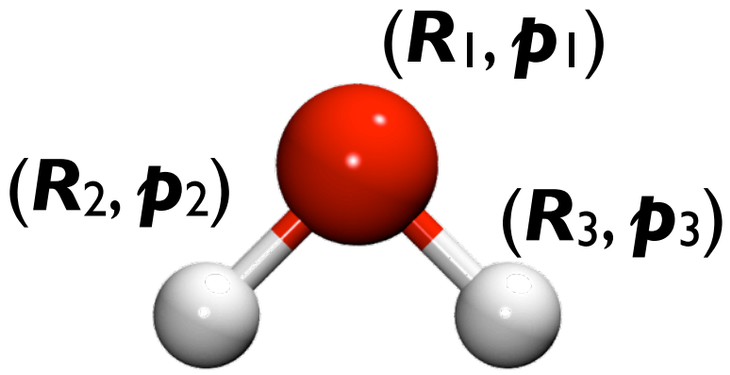

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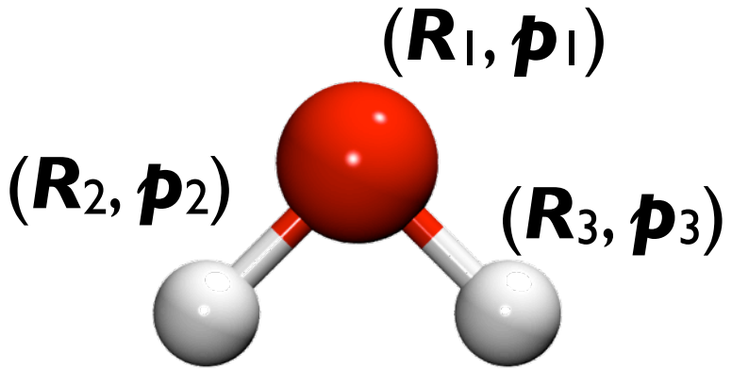

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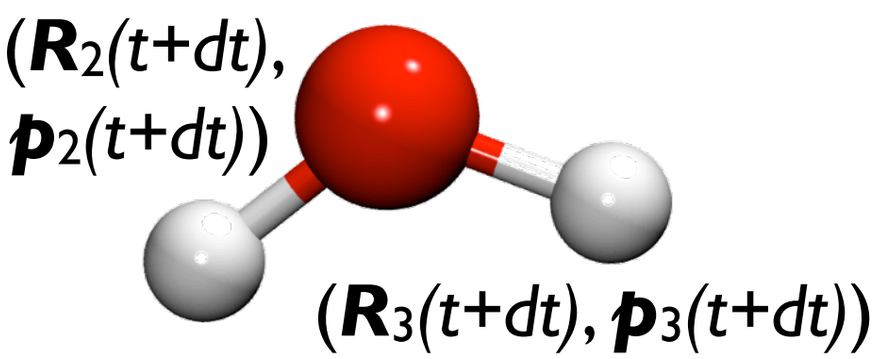

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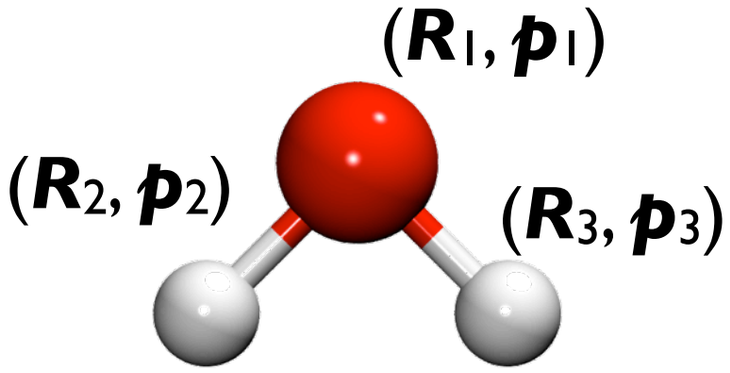

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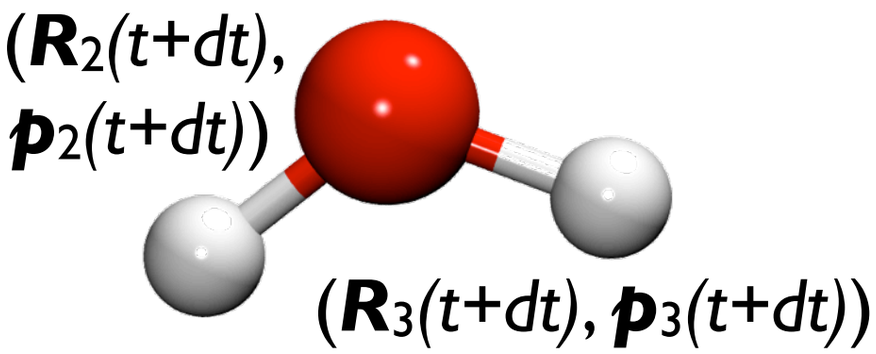

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"Computer experiment": equilibrate system and measure

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- Time scales you can reach: hundreds of picoseconds to nanosecond

Born Oppenheimer MD

1. Read initial $\boldsymbol{p}(t_0)$ and $\boldsymbol{R}(t_0)$
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Integrating the equations of motion

- First shot: Taylor expansion of *R*

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

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

Error

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

Verlet Algorithm

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Verlet Algorithm

"Verlet" is also symplectic: conserves dp∧dR and the form of Hamilton's equations

Velocity Verlet algorithm

- Implemented: velocity Verlet

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

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

New force evaluation

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

Time step and the accuracy of integration

$\Delta t = 3fs$

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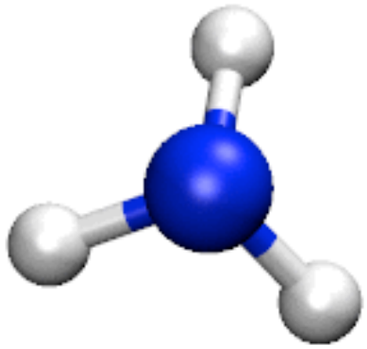

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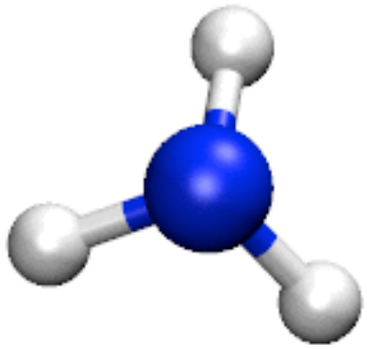

- What is a good time step?
  - Depends on the highest vibrational frequency (thus mass) of your system ($\omega \approx \sqrt{k/M}$)
  - Typically, choose a time step corresponding to ~1/(10ω_{max}) (femtosecond time scale)

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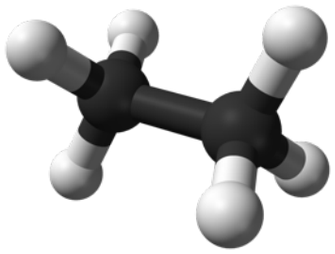
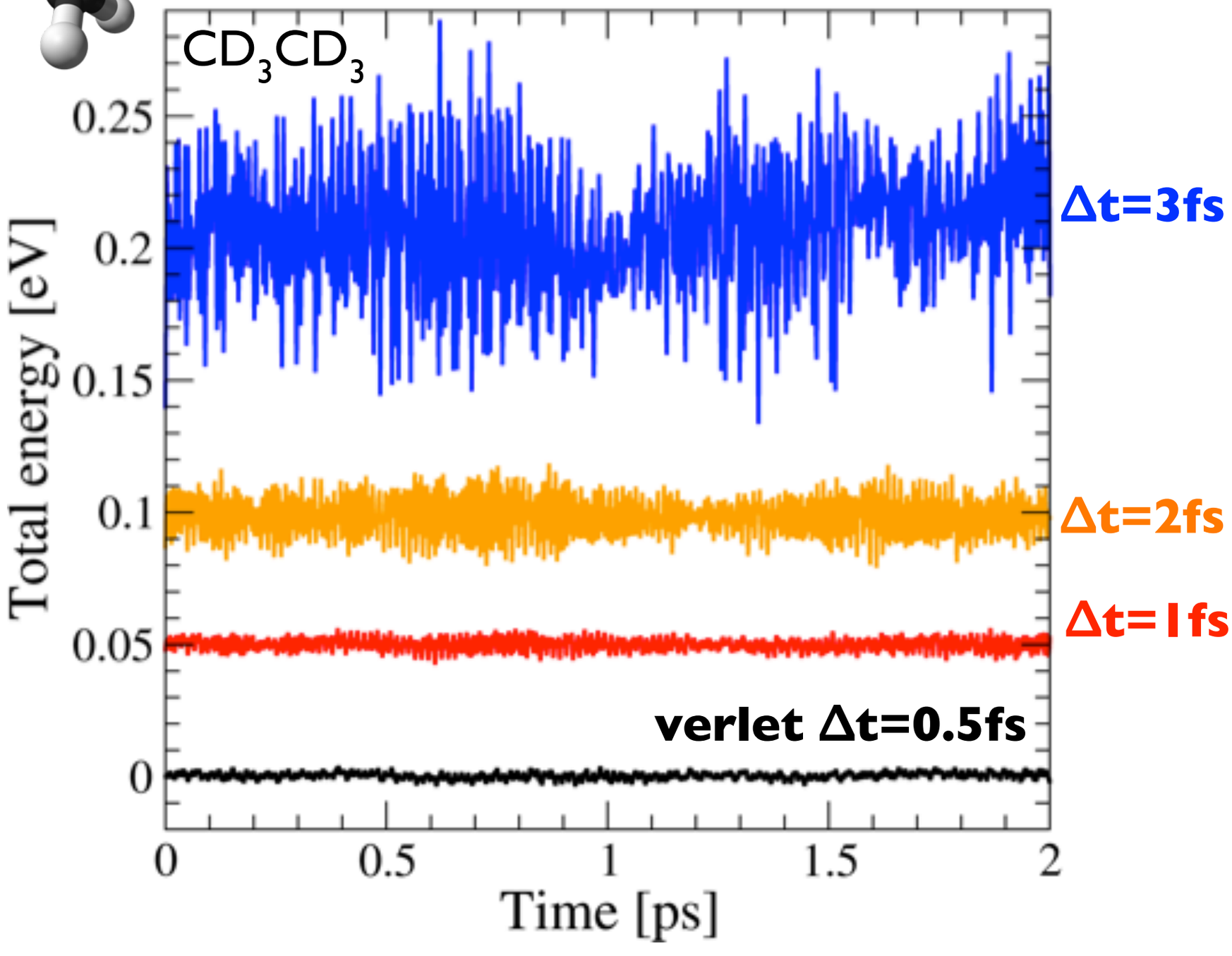


Energy fluctuations (arbitrary shifts)



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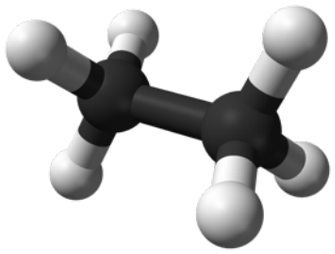

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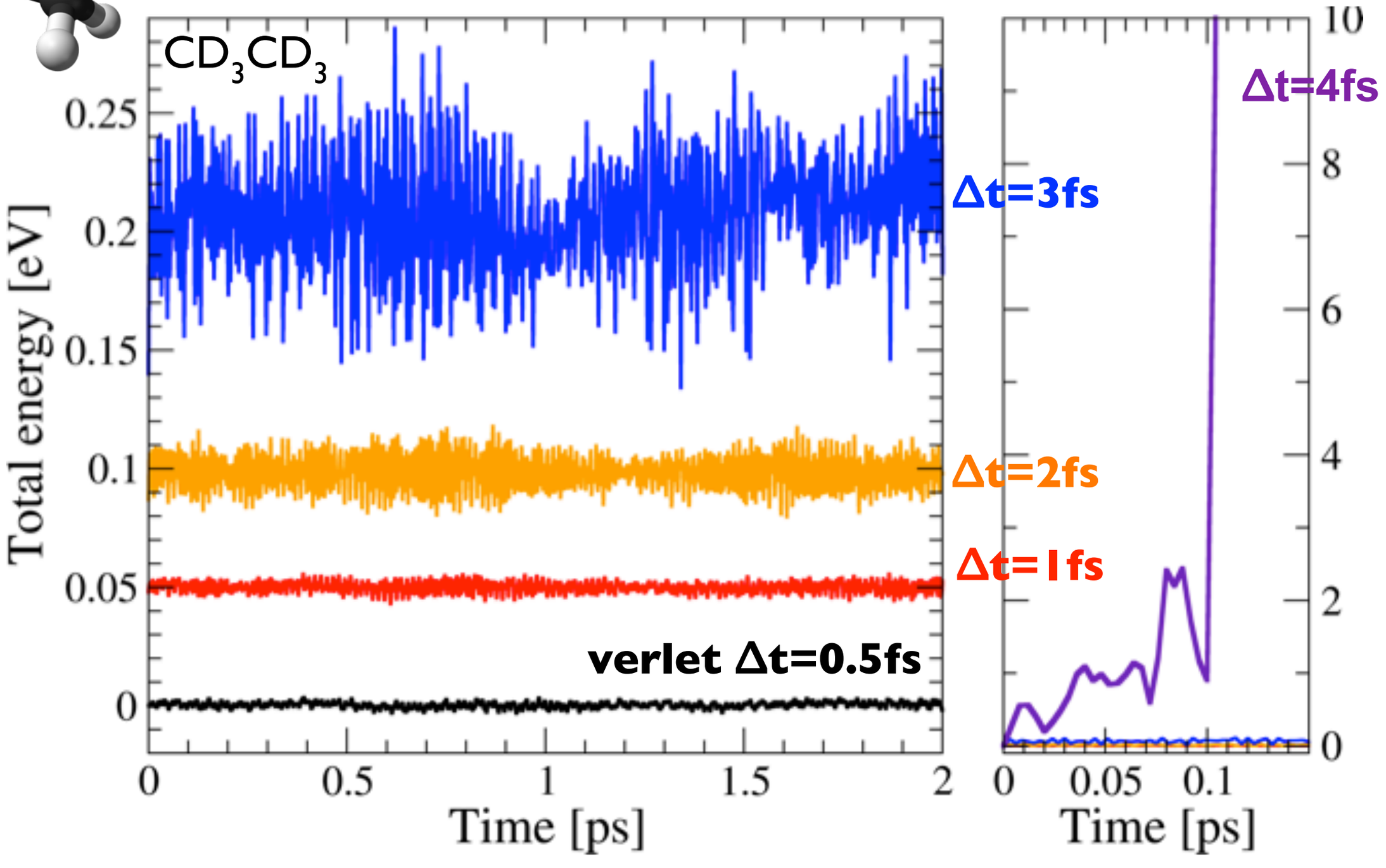

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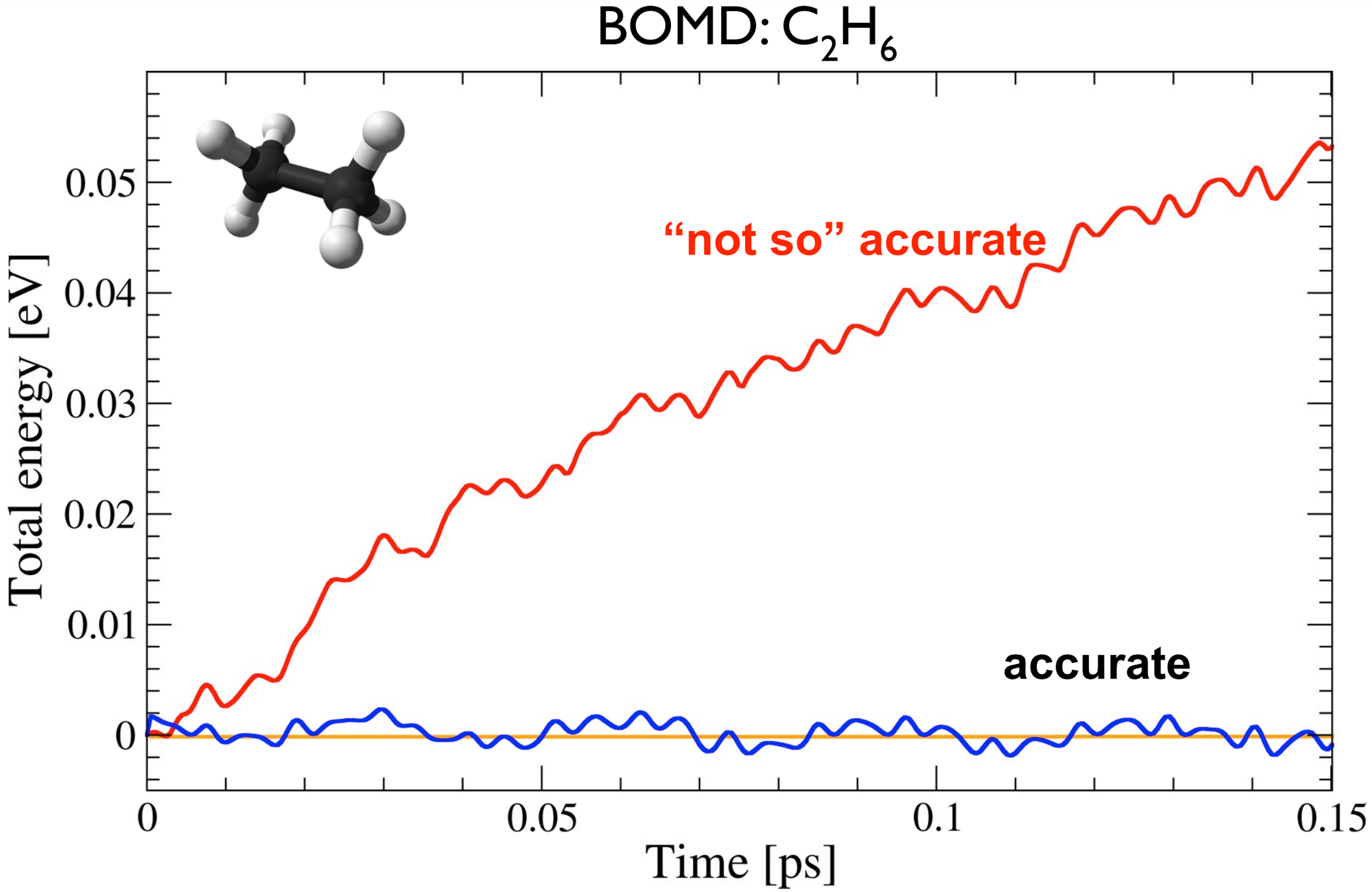

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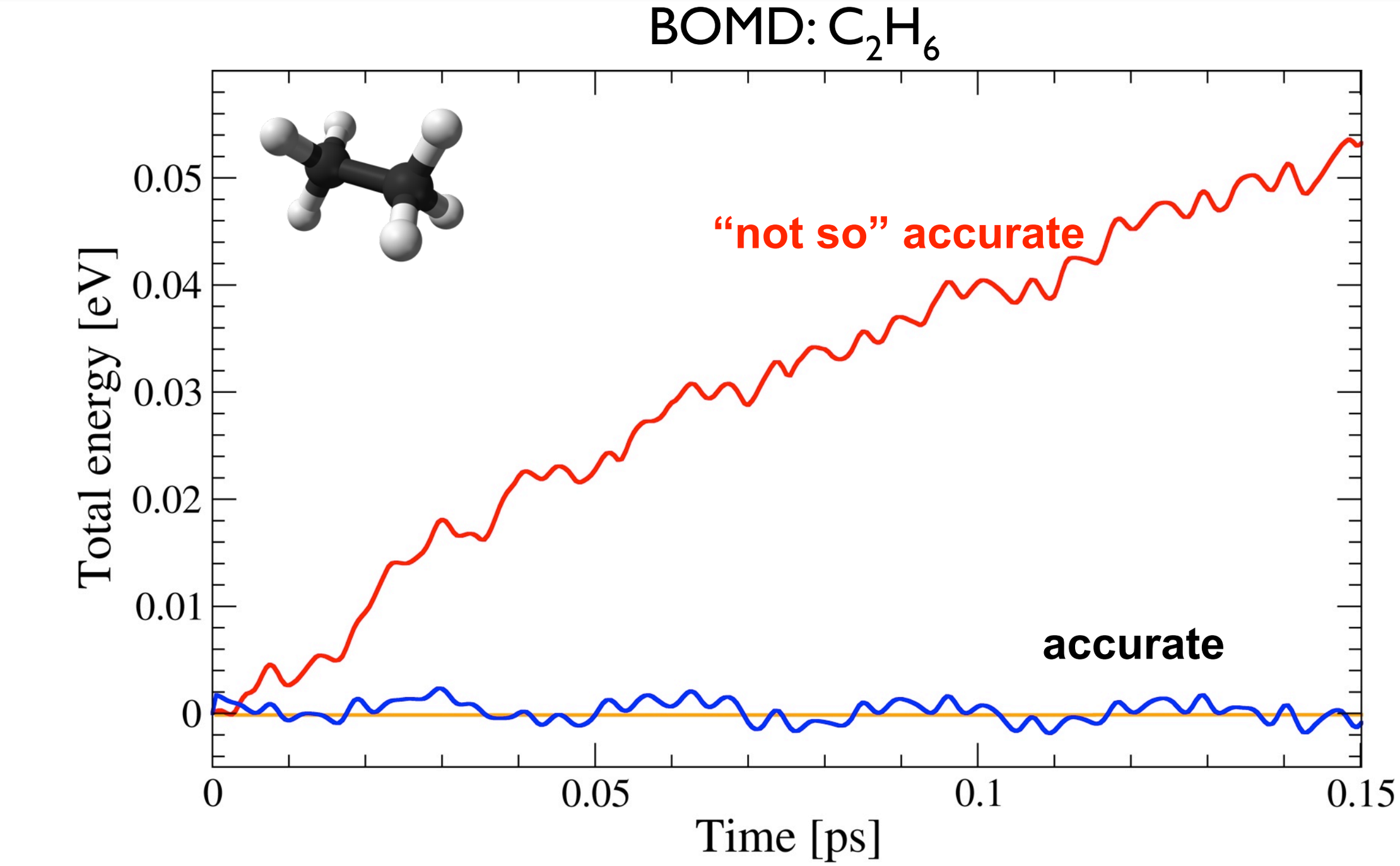

Many ways to make the self consistent loop "cheaper":

Car-Parrinello MD, Car-Parrinello-like BOMD, wave function extrapolation, ...

*T. Kühne, et al. PRL **98**, 066401 (2007); Steneteg et al., PRB **82**, 075110 (2010); others*

A bit about Car-Parrinello MD

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- Extended Lagrangian: add (fictitious) degrees of freedom for the electrons in the Lagrangian and solve coupled equations of motion

$$\mathcal{L} = \frac{1}{2}\left[\sum_I M_I \dot{\mathbf{R}}_I^2 + \mu \sum_i \int d\mathbf{r} |\dot{\phi}_i(\mathbf{r},t)|^2\right] - V(\phi,\phi^*;\mathbf{R}) + 2\lambda_{ij}\left[\int d\mathbf{r}\phi_i^*(\mathbf{r},t)\phi_j(\mathbf{r},t) - \delta_{ij}\right]$$

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Fictitious electron mass

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- Adiabatic separation: fictitious mass of the electrons need to be very small ⇒ smaller time step

- Electrons "follow" nuclei - avoids self consistency calculation at every step

How to get more realistic simulations?

- Some possibilities:

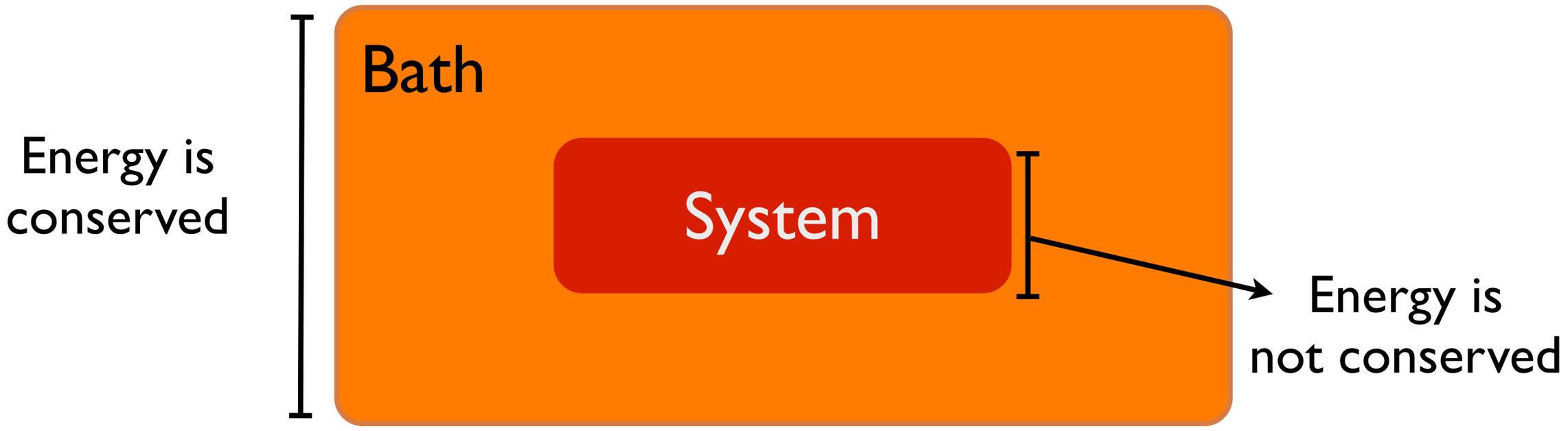
  - Simulate conditions that are experimentally accessible: control temperature and/or pressure

  - Nuclei are not classical particles:
    include their quantum nature in the simulations
    (Roberto Car, Tuesday 13.08.2013)

  - Enhance sampling of potential energy surface
    (Luca Ghiringhelli, Tuesday 13.08.2013)

Temperature control: the canonical ensemble

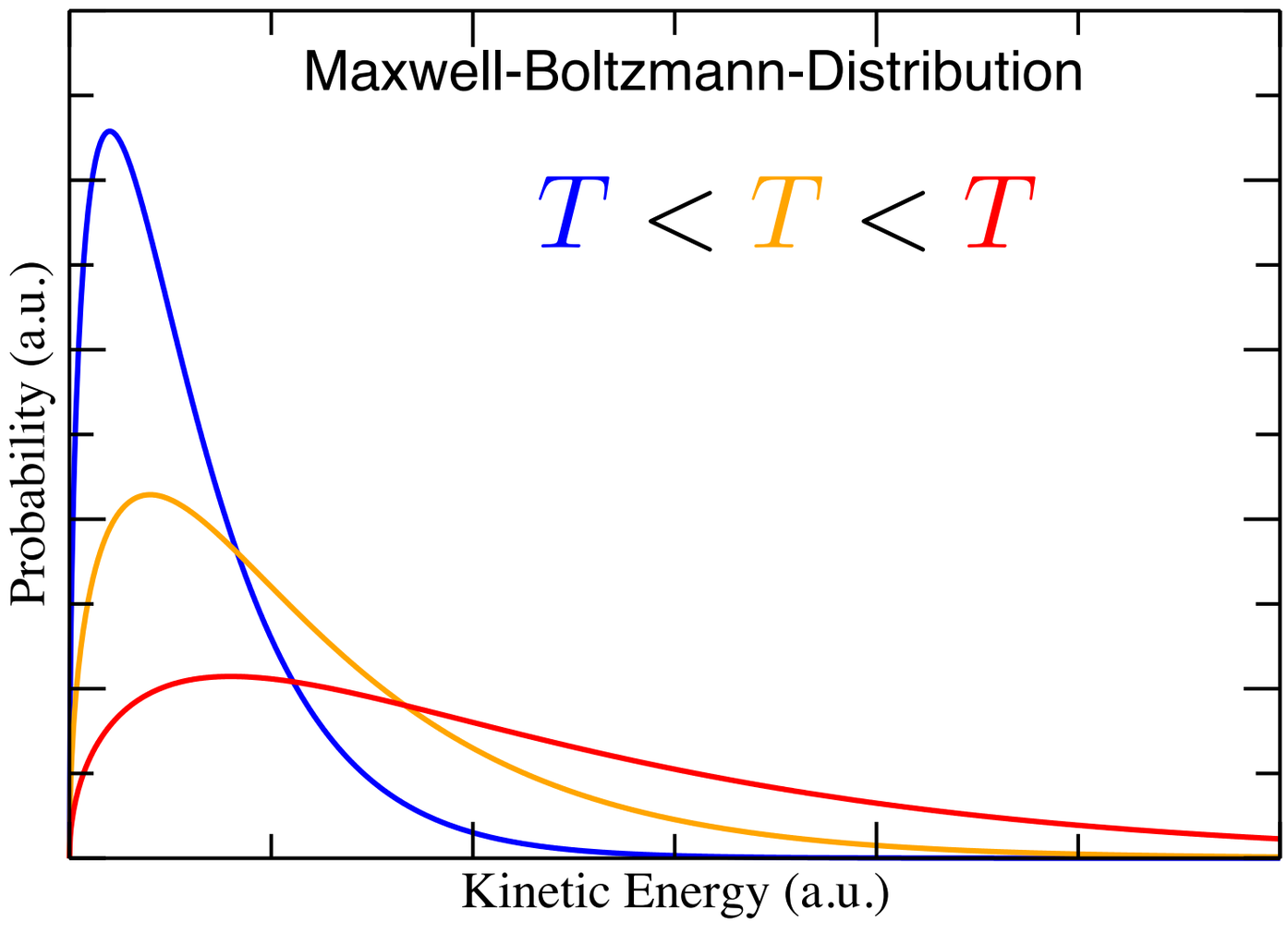
- The idea: couple the system to a thermostat (heat bath)
- Interesting because:
  - Experiments are usually done at constant temperature
  - Better modeling of conformational changes



Temperature definition

Probability distribution of the kinetic energy:

$$P(E_{kin}) \propto \exp(-E_{kin}/k_B T)$$



kinetic energy: $p^2/2M$

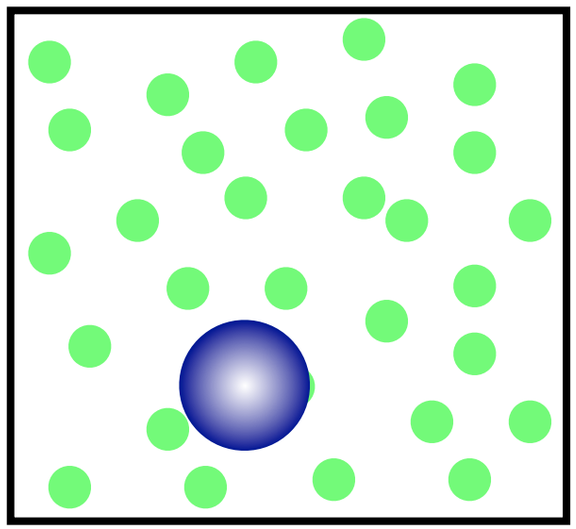
$$\langle T \rangle = \frac{2\langle E_{kin} \rangle}{3N k_B}$$

# of particles

Few words on newtonian vs. Langevin dynamics

Heavy(er) body in a solvent (or gas)

Newtonian dynamics



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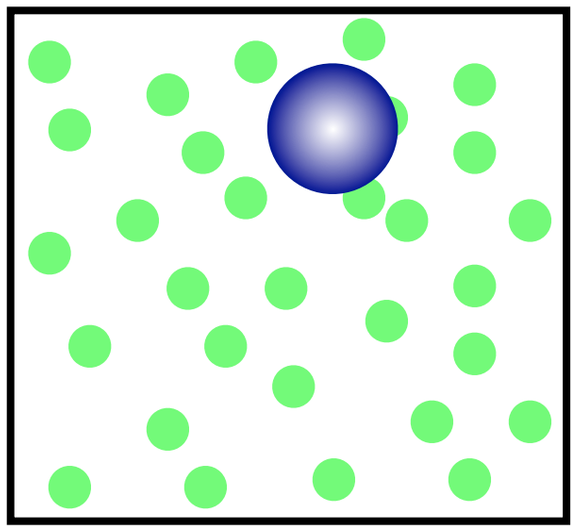

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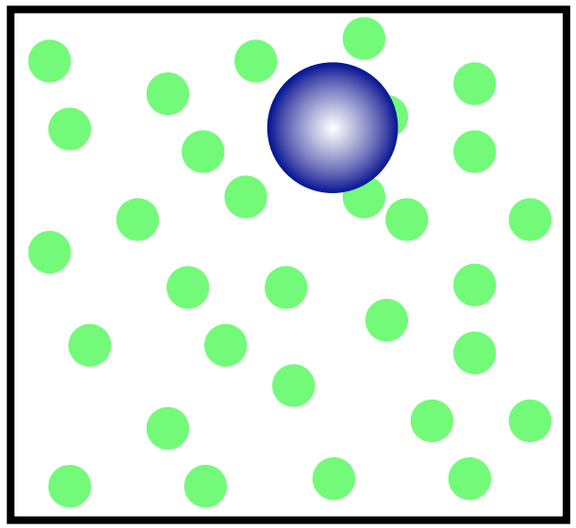

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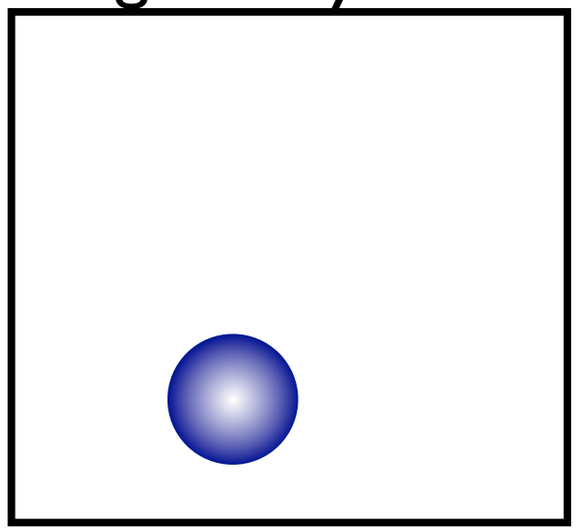
Langevin dynamics



$$\mathbf{F}_I = -\gamma \dot{\mathbf{R}}_I + \xi(t)$$

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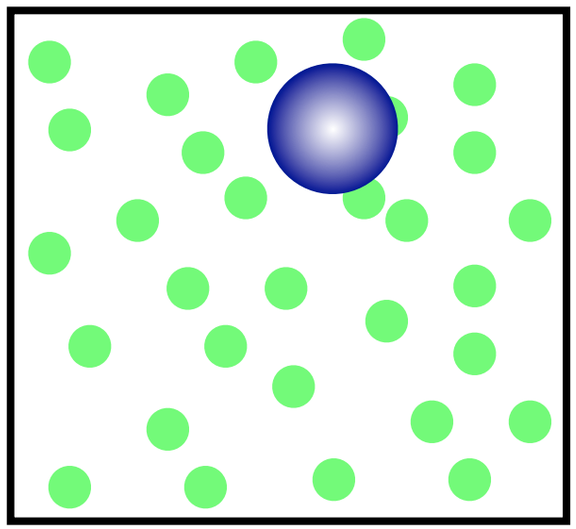

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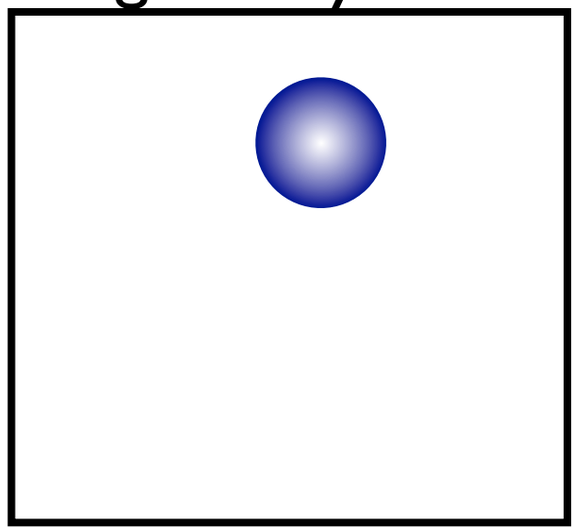

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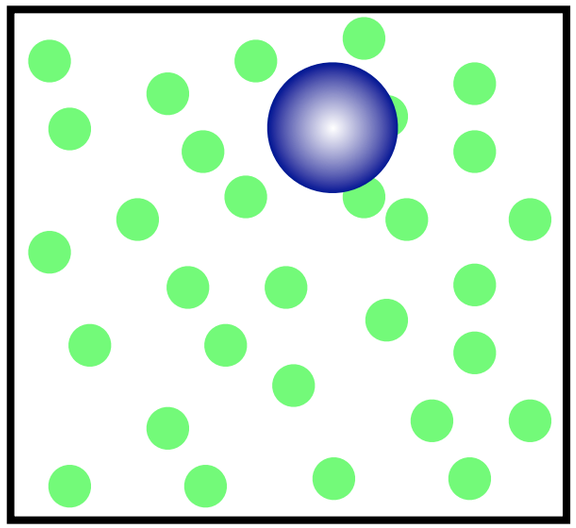

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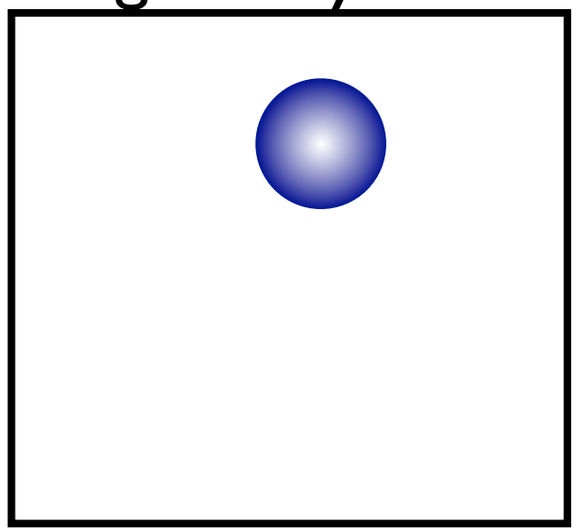

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friction

random force

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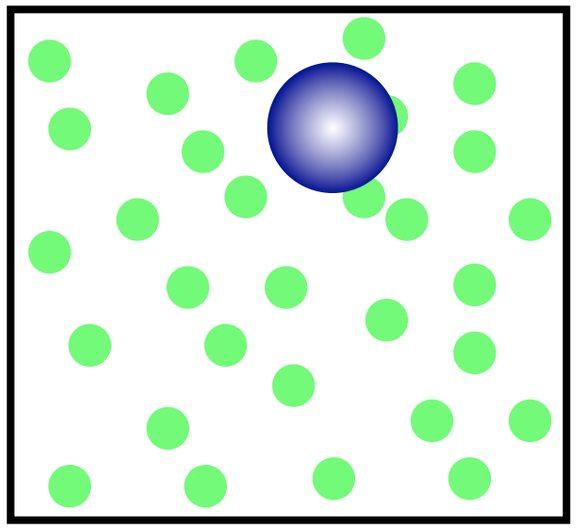

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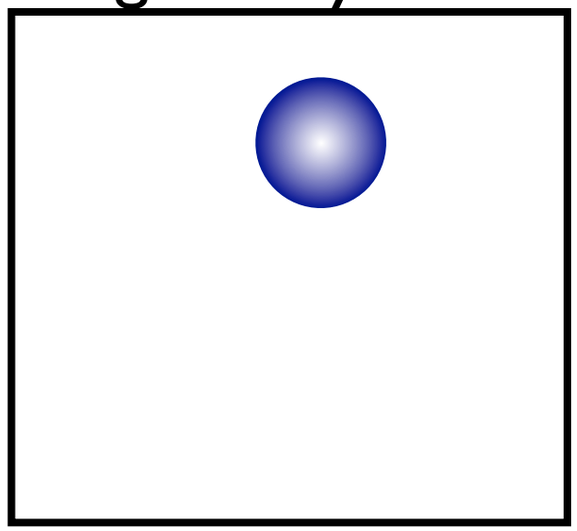

$$\mathbf{F}_I = -\gamma \dot{\mathbf{R}}_I + \xi(t)$$

friction *random force*

- In thermal equilibrium, drag of the friction and kicks of the random noise balance each other - Fluctuation Dissipation Theorem (FDT)

$$\langle \xi(t)\xi(0) \rangle = 2k_B T \gamma \delta(t)$$

No memory of past times
No frequency dependence (white noise)

How to model a thermostat: first ideas

- Temperature rescaling: Berendsen "thermostat"
  - Rescale velocities by a factor containing the ratio of target and instant temperature
  - Does not sample the canonical ensemble (wrong temperature distribution)
  - "Flying ice-cube" effect: rotations and translations acquire high E_{kin} and vibrations are frozen

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H. J. C. Berendsen, *et al. J. Chem. Phys.* **81** 3684 (1984)

- Simple stochastic idea: Andersen thermostat
  - At each n^{th} time-step, replace velocity of a random particle by one drawn from a Maxwell-Boltzmann distribution at target temperature
  - Not very efficient, no conserved quantity
  - Very sensitive on n

H. C. Andersen, *J. Chem. Phys.* **72**, 2384 (1980)

Nosé-Hoover thermostat

S. Nosé, *J. Chem. Phys.* **81**, 511 (1984) & W. G. Hoover, *Phys. Rev. A* **31**, 1695 (1985).

Extended Hamiltonian (or Lagrangian):

$$\mathcal{H}_{NH} = \sum_I \frac{\mathbf{p}_I^2}{2M_I} + V(\mathbf{R}) + \frac{p_\eta^2}{2Q} + 3Nk_BT\eta$$

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Original system

Fictitious Oscillator

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Original system — Fictitious Oscillator

- Momenta are damped by fictitious oscillator: $\dot{\mathbf{p}}_I = \mathbf{F}_I - \frac{p_\eta}{Q}\mathbf{p}_I$

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Original system | Fictitious Oscillator

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- Ergodicity problems - system may be stuck in a region of phase space
  - Possible solution: Nosé-Hoover chains
    Attach another fictitious oscillator to the first, and another to the second, and another to the third, ... (chain of fictitious oscillators)

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

Bussi-Donadio-Parrinello thermostat

G. Bussi, D. Donadio, and M. Parrinello, *J. Chem. Phys.* **126**, 014101 (2007).

Combine concepts from velocity rescaling (fast!) with concepts from stochastic thermostats (accurate!)

Target temperature follows a stochastic differential equation:

$$\frac{dT}{\bar{T}} = \left[1 - \frac{T(t)}{\bar{T}}\right]\frac{dt}{\tau} - 2\sqrt{\frac{T(t)}{3\bar{T}N\tau}}\xi(t)$$

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White noise

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Temperature rescaling

White noise

- Very successful thermostat, weakly dependent on relaxation time τ
- Pseudo-Hamiltonian is conserved

Bussi, Parrinello, *Phys. Rev. E* **75**, 056707 (2007)

Langevin (stochastic) thermostat

S. A. Adelman and J. D. Doll, *J. Chem. Phys.* **64**, 2375 (1976).

Model dynamics via the Langevin equation:

$$M_I \ddot{\mathbf{R}}_I = \mathbf{F}_I - \gamma_I \dot{\mathbf{R}}_I + \xi(t)$$

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- Sensitive on γ
  - For systems spanning a wide range of frequencies, how to achieve the "best" critical damping?
- Disturbs dynamics considerably

Colored noise thermostats

M. Ceriotti, G. Bussi, M. Parrinello, *JCTC* **2010**, 6, 1170-1180 (**http://gle4md.berlios.de/**)

Extremely flexible class of thermostats based on the Generalized Langevin Equation (GLE)

- Markovian (no memory) process in high dimensions

$$\begin{pmatrix} \dot{p} \\ \dot{\mathbf{s}} \end{pmatrix} = \begin{pmatrix} -V'(R) \\ 0 \end{pmatrix} - \mathbf{A}_p \begin{pmatrix} p \\ \mathbf{s} \end{pmatrix} + \mathbf{B}_p \left(\boldsymbol{\xi} \right)$$

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Friction and White Noise

- Non-Markovian process for the system (integrating out ***s***):

$$\dot{p} = F - \int_{-\infty}^{t} d\tau K(t-\tau) p(\tau) + \boldsymbol{\zeta}(t)$$

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Memory Kernel *Colored Noise*

Fluctuation Dissipation: $H(t) = \langle \zeta(t)\zeta(0) \rangle = k_B T K(t)$

Colored noise thermostats

M. Ceriotti, G. Bussi, M. Parrinello, *JCTC* **2010**, 6, 1170-1180 (**http://gle4md.berlios.de/**)

- Quite complex input matrices $\mathbf{A}_p$ (and $\mathbf{C}_p$), connected by:

$$\mathbf{A}_p\mathbf{C}_p + \mathbf{C}_p\mathbf{A}_p^T = \mathbf{B}_p\mathbf{B}_p^T$$

covariance matrix

- However, flexible:
  - For canonical sampling, $\mathbf{C}_p = \mathbf{I}\, k_B T$ and FDT is obeyed
  - For other samplings one can break FDT

- What can you model?
  - Nuclear quantum effects, excitation of single modes
  - Make "*Path Integral Molecular Dynamics*" computationally cheaper (see Roberto Car's talk)

Pressure control: Isobaric-isothermic ensemble

- Definition of pressure: $P = \frac{2}{V}\left(E_{kin} - \Gamma\right)$

$$\Gamma = -\frac{1}{2}\sum_I \mathbf{R_I} \cdot \mathbf{F}_I$$

- Similar schemes for barostats: pressure rescaling (Berendsen), extended Lagrangian (Parrinello-Rahman, Andersen), ...

  M. Parinello and A. Rahman, *J. Appl. Phys* **52**, 7182 (1981)

- Use thermostat together with a barostat to control pressure and temperature

Applications of AIMD

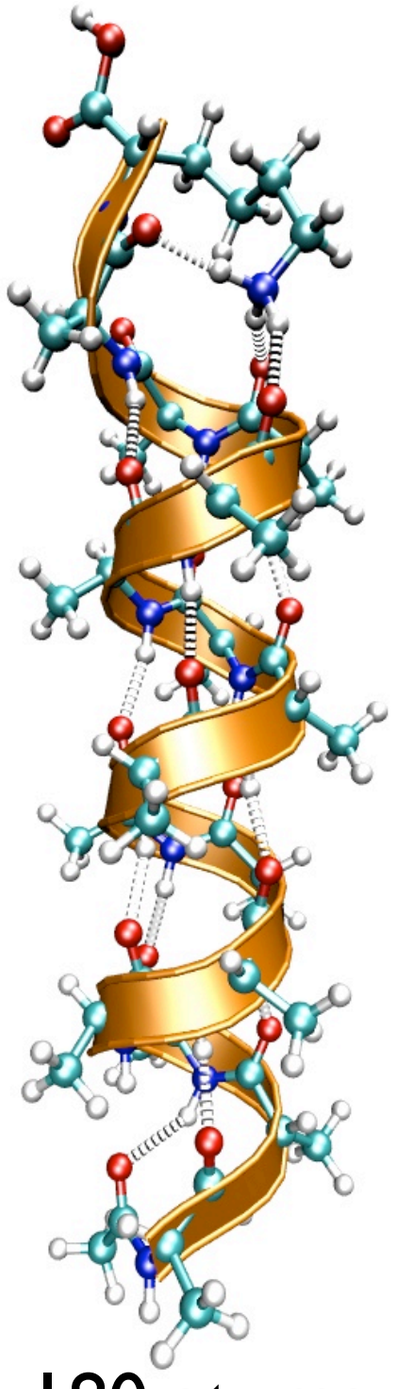
- Can be equally applied to solid-state, atoms, and molecules
- Phase transitions, diffusion coefficients, IR spectra, NMR, reaction paths, free energies of structures and reactions, etc.

Recent review:

B. Kirchner, Ph. J. di Dio, and J. Hutter, *Real-World Predictions from Ab Initio Molecular Dynamics Simulations*, Top. Curr. Chem., (2012), **307**, 109-154

Vibrational spectroscopy: Ac-Ala$_{15}$-LysH$^+$

α-helical Ac-Ala$_{15}$-LysH$^+$

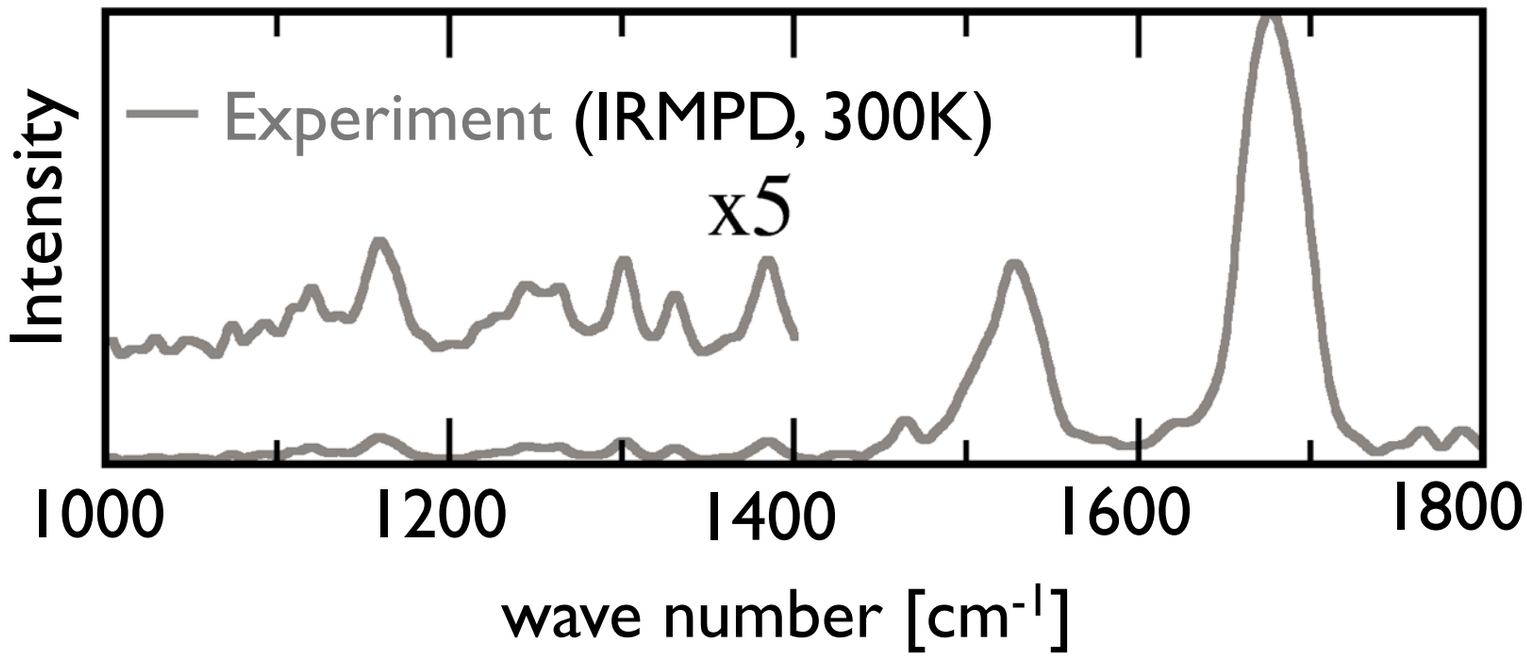


180 atoms

<u>Experiment</u>:
von Helden, Kupser, Bierau, Meijer, Molecular Physics, FHI Berlin

Infrared multiphoton dissociation spectroscopy, FELIX free electron laser

Room temperature



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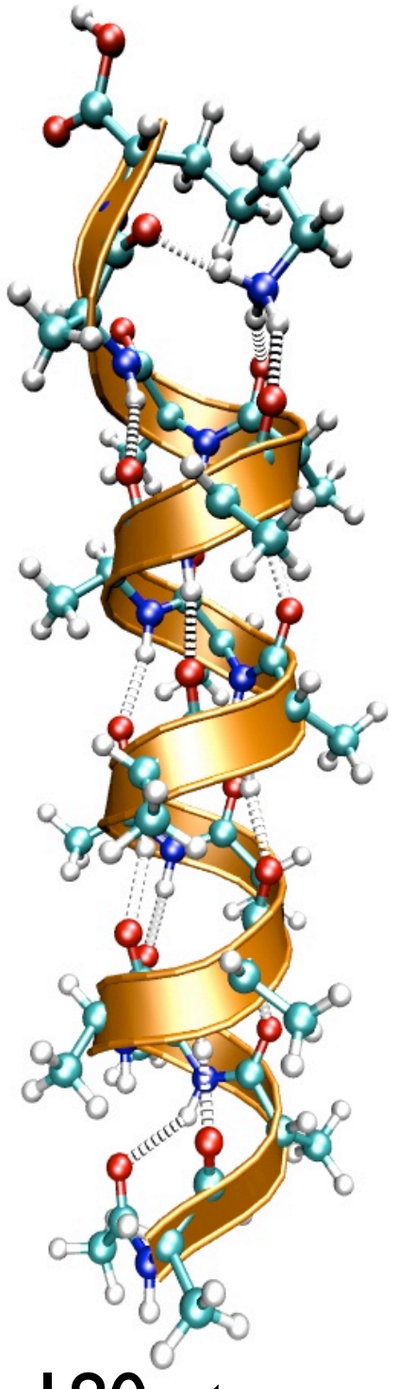

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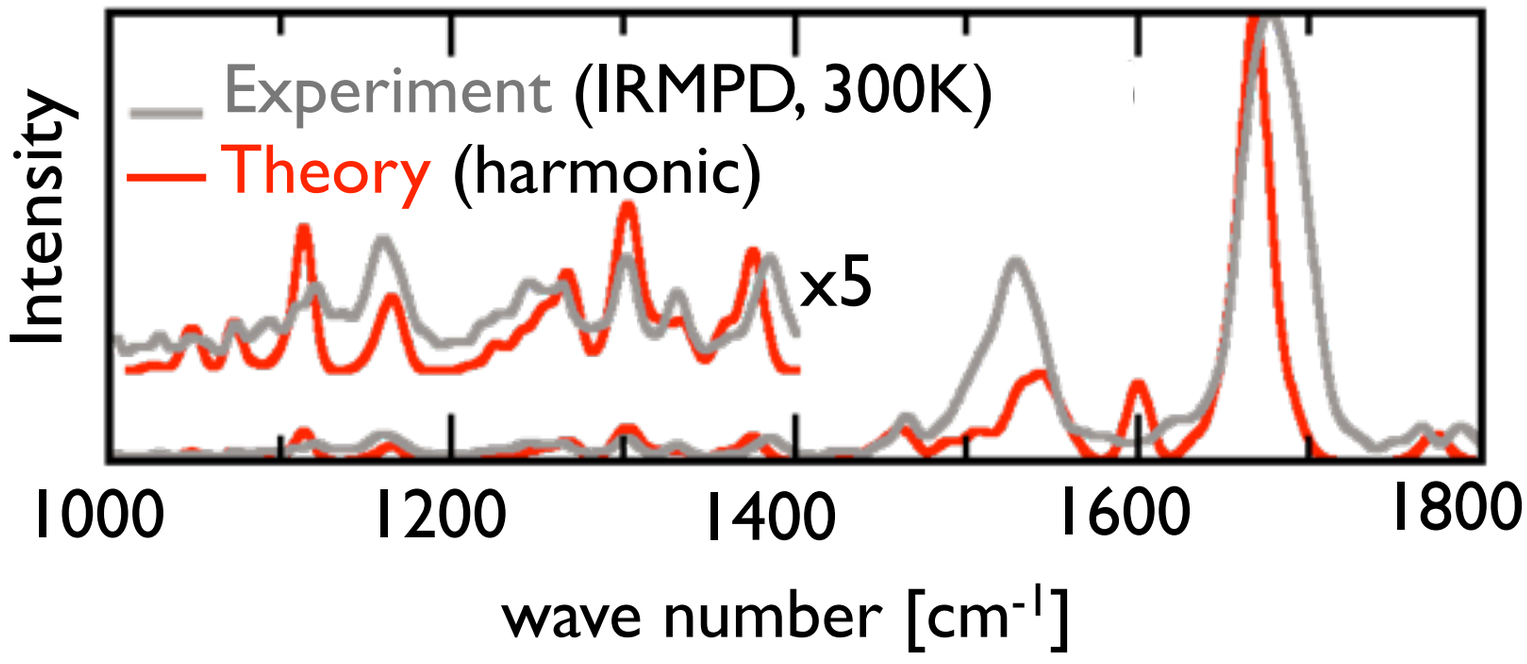

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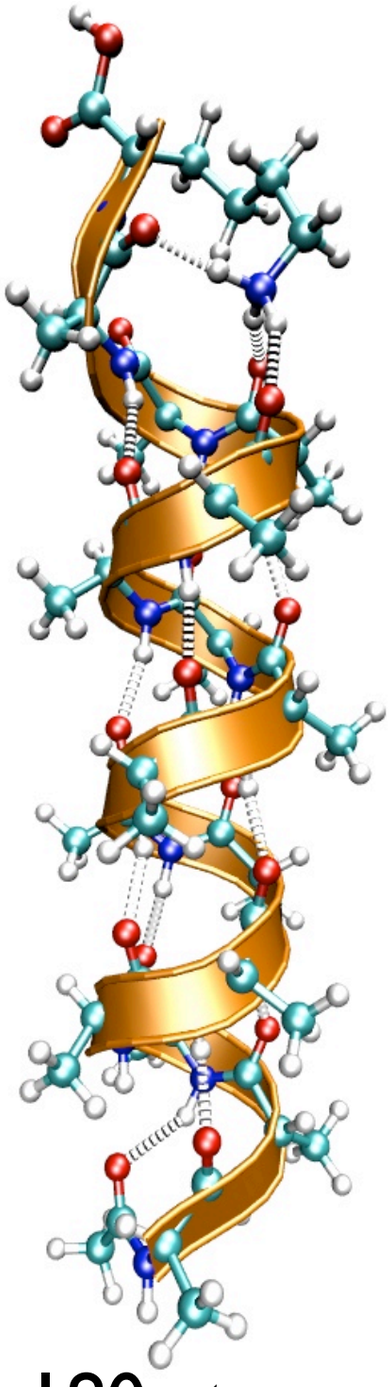

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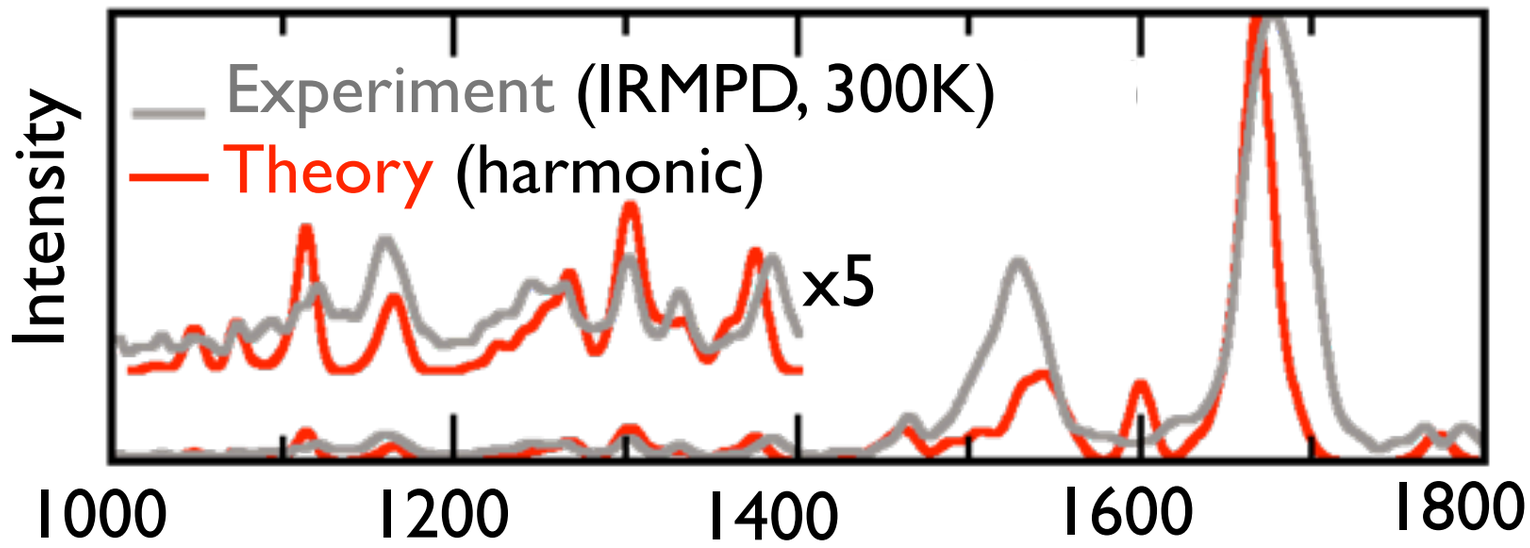

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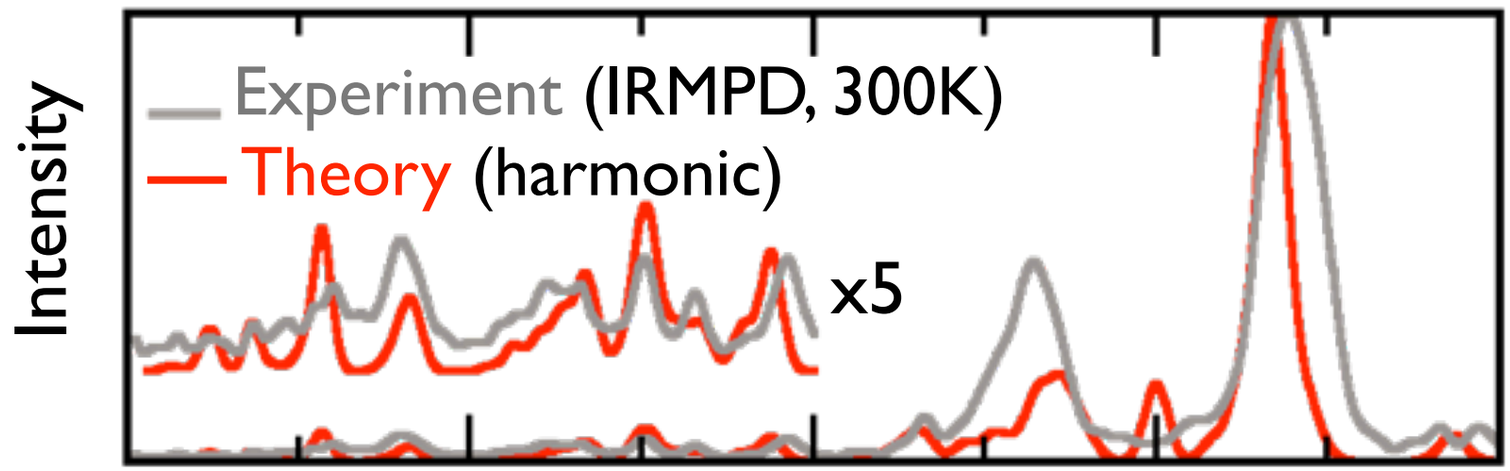
25 ps Born-Oppenheimer molecular dynamics, DFT-PBE+vdW

*M. Rossi, V. Blum, P. Kupser, G. von Helden, F. Bierau, K. Pagel, G. Meijer, and M. Scheffler, J. Phys. Chem. Lett. **1**, 3465 (2010)*

Theory: PBE+vdW, shifted, not scaled



$$I(\omega) \propto \omega^2 \int_{\infty}^{\infty} dt \, \underbrace{\langle \vec{M}(t) \cdot \vec{M}(0) \rangle}_{} \, e^{iwt}$$

dipole-dipole time correlation function

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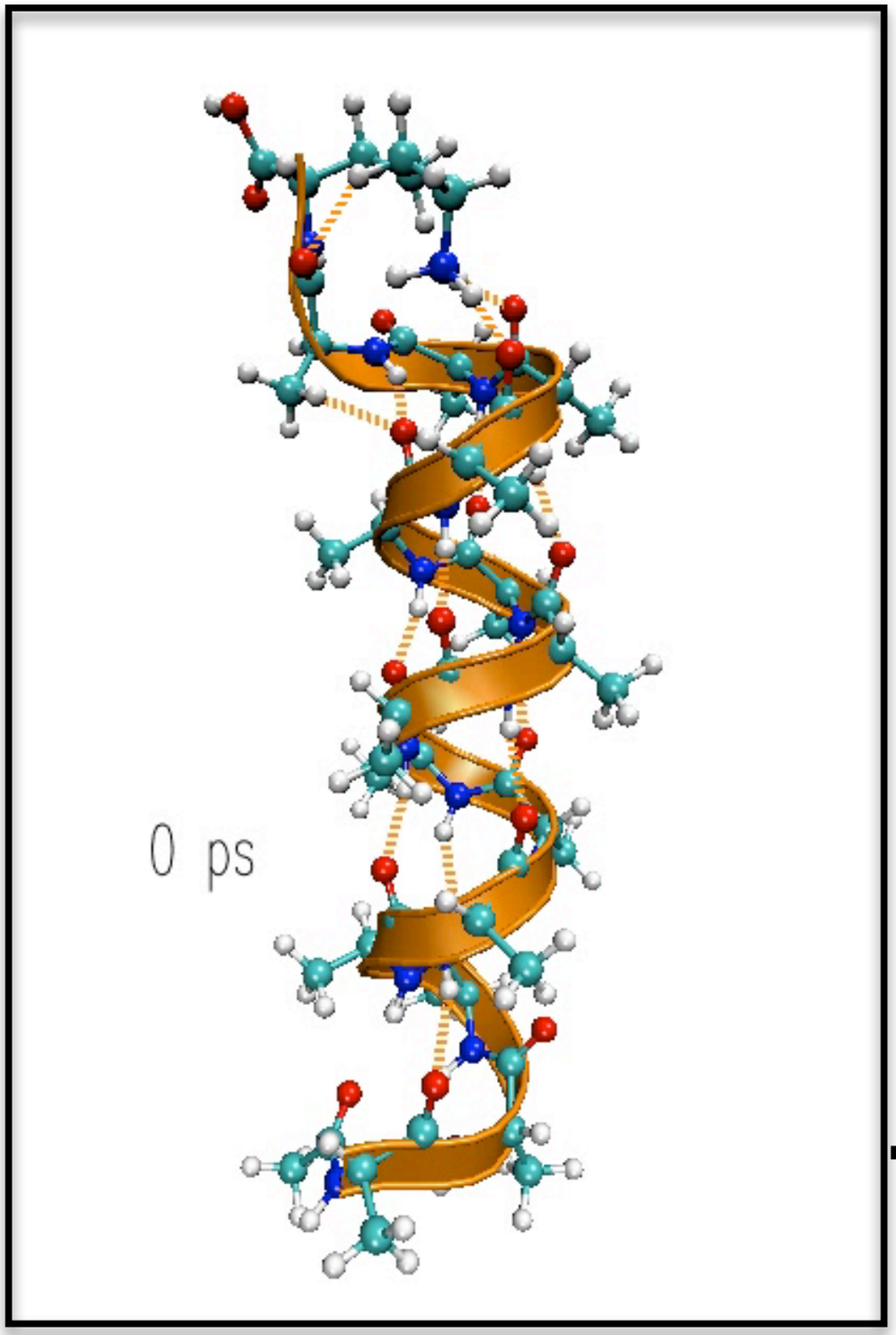

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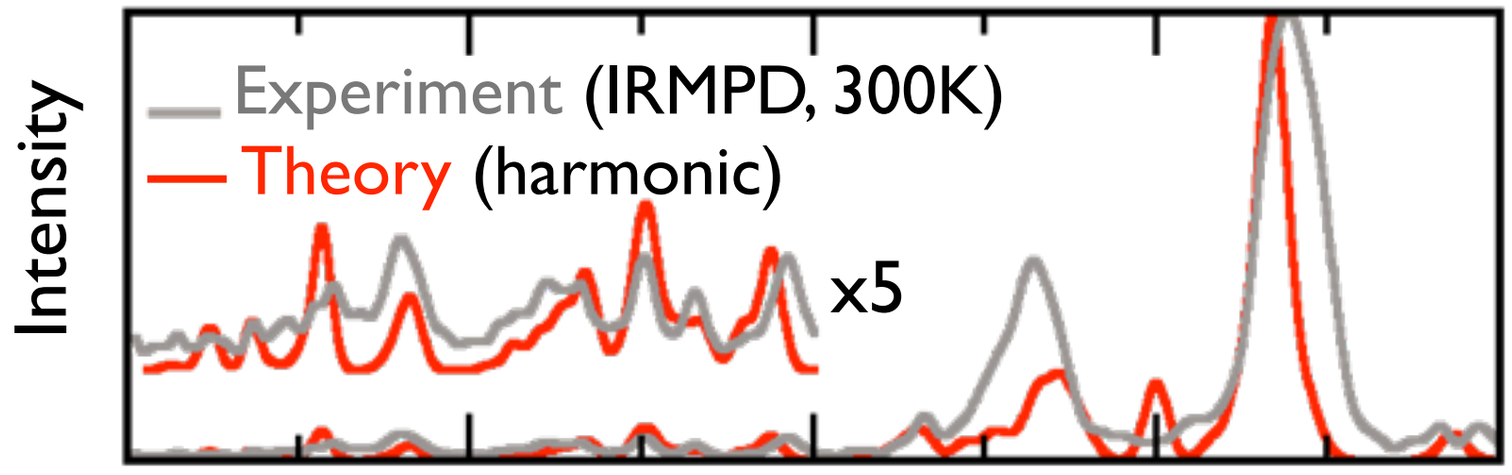

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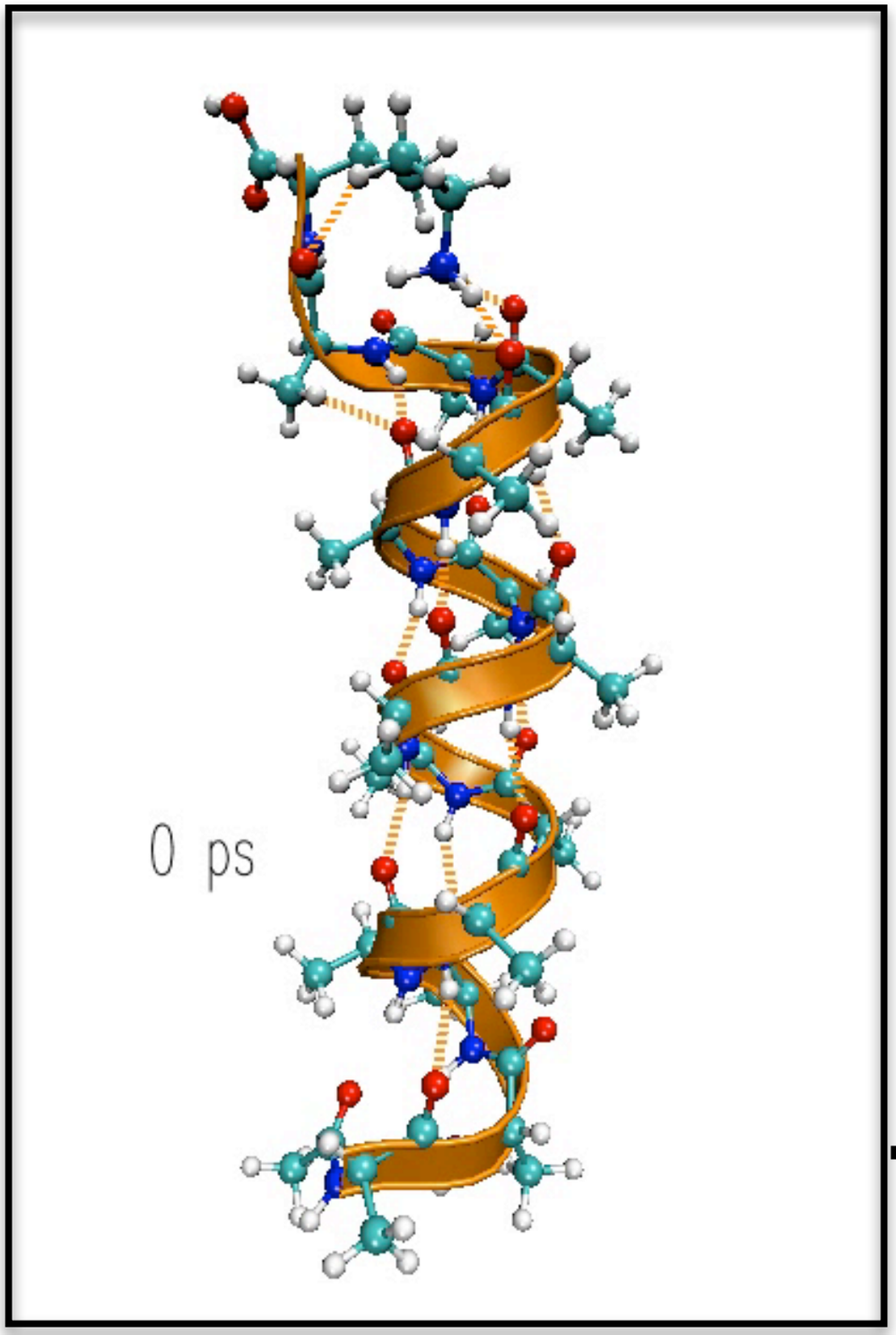

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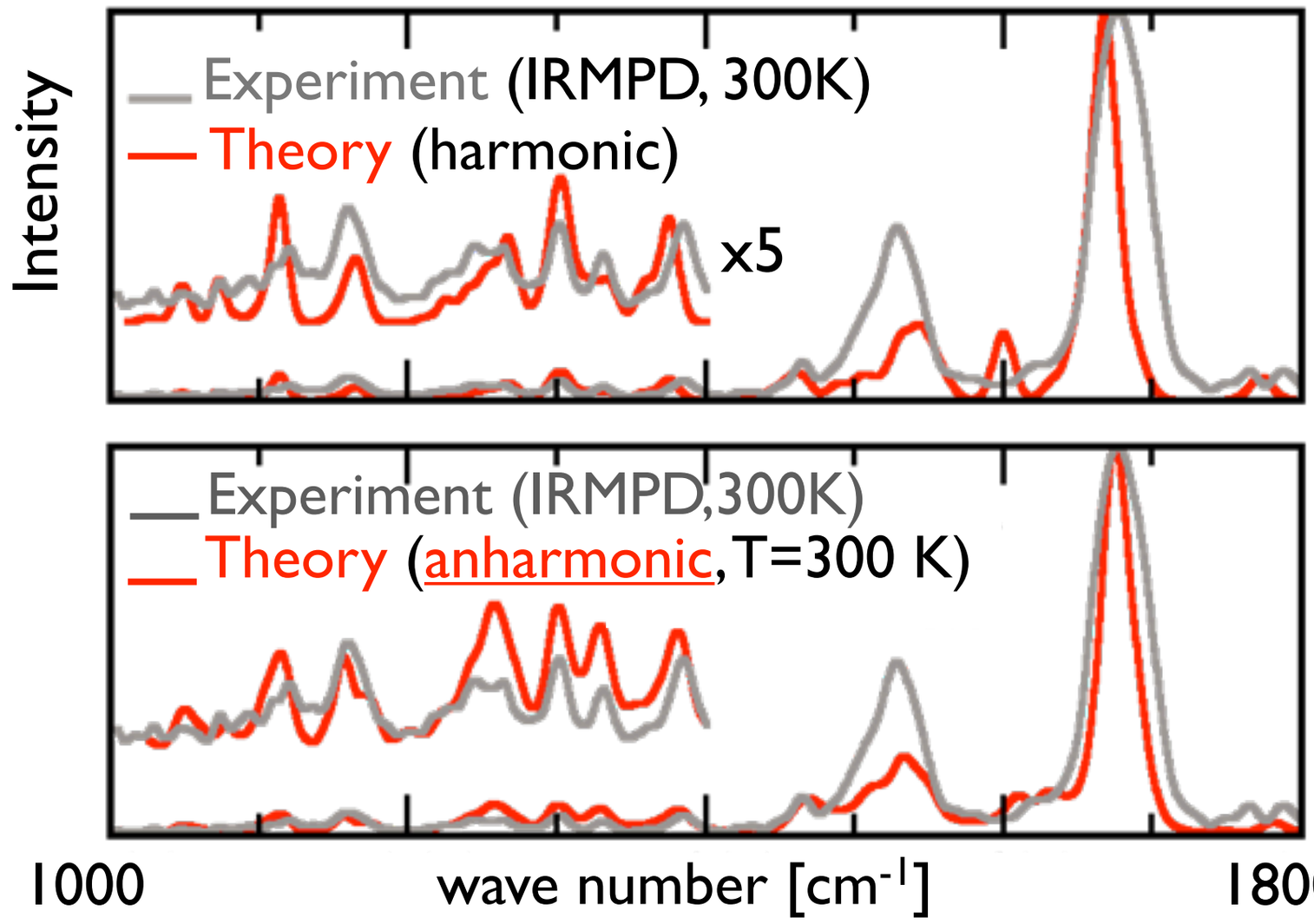

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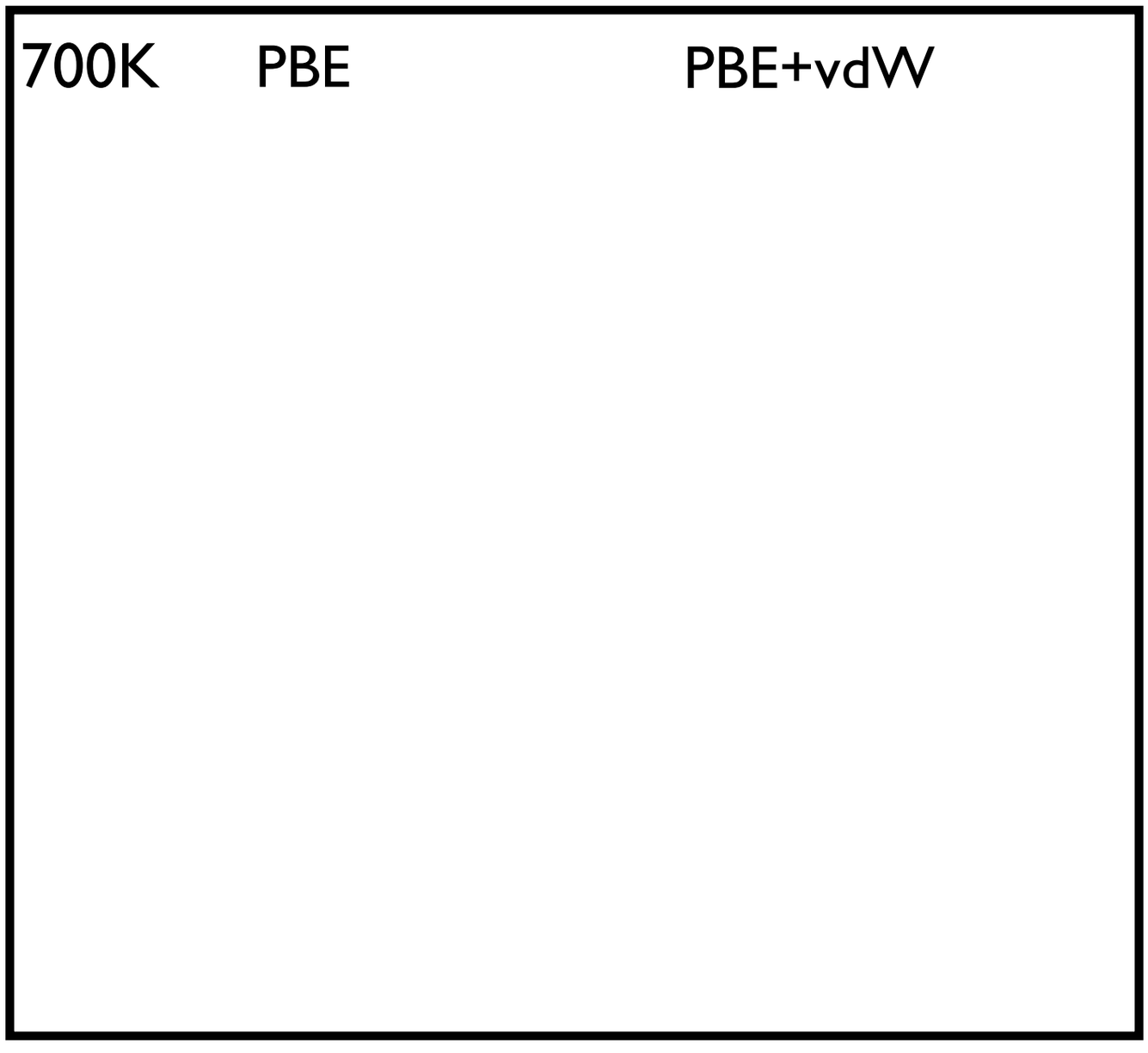
Quality of the approximation: vdW interactions

- Evidence from gas-phase experiment [*Kohtani, Jones, Schneider, Jarrold, JACS* ***126****, 7420 (2004)*] that the Ac-Ala_{15}-$LysH^+$ **α-helix** is stable up to ≈ 700 K
- Can DFT-PBE and DFT-PBE+vdW reproduce this high temperature stability?



A. Tkatchenko, M. Rossi, V. Blum, J. Ireta, and M. Scheffler, Phys. Rev. Lett. ***106****, 118102 (2011)*

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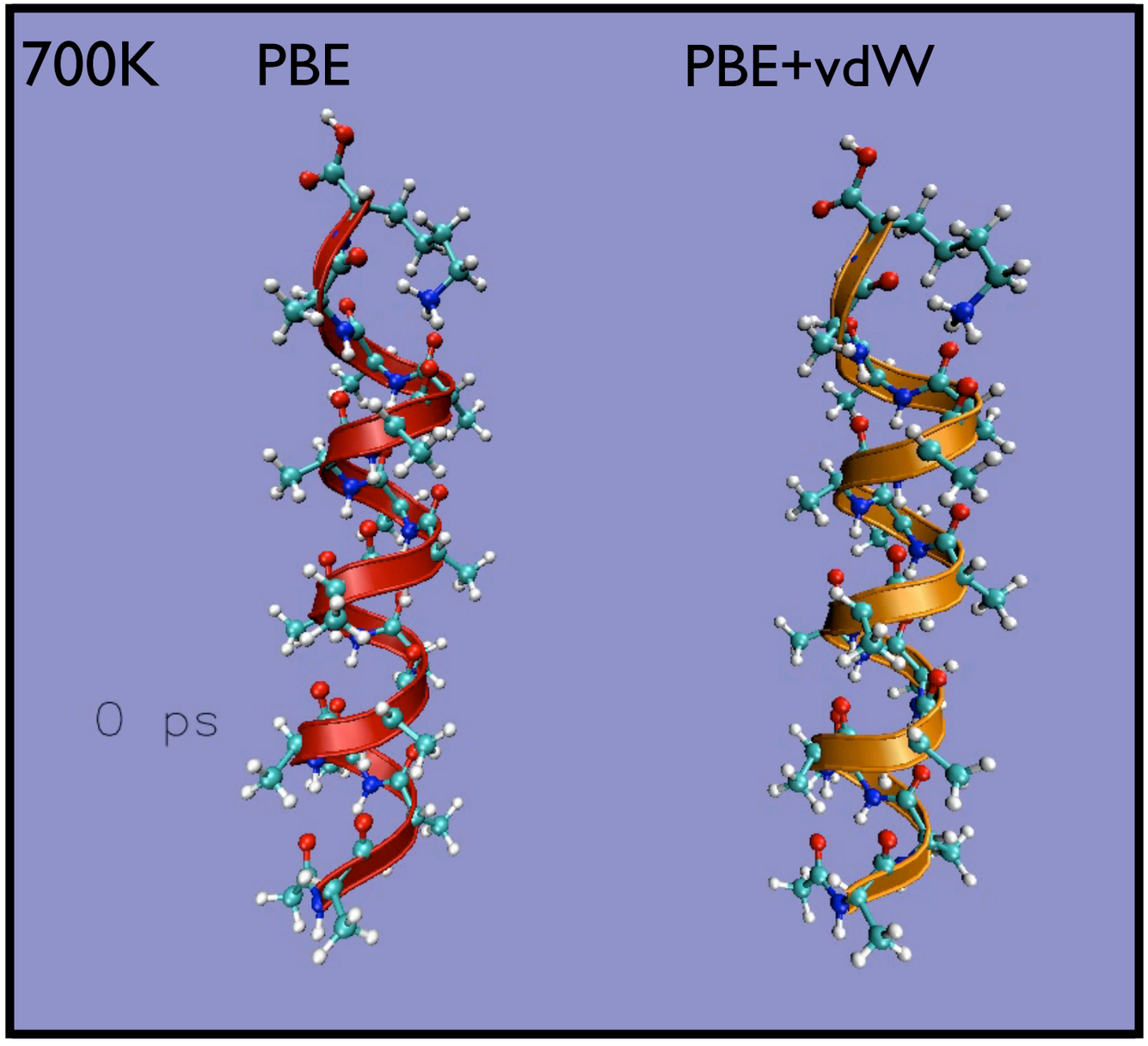
- Evidence from gas-phase experiment [*Kohtani, Jones, Schneider, Jarrold, JACS* ***126****, 7420 (2004)*] that the Ac-Ala_{15}-$LysH^+$ **α-helix** is stable up to ≈ 700 K
- Can DFT-PBE and DFT-PBE+vdW reproduce this high temperature stability?



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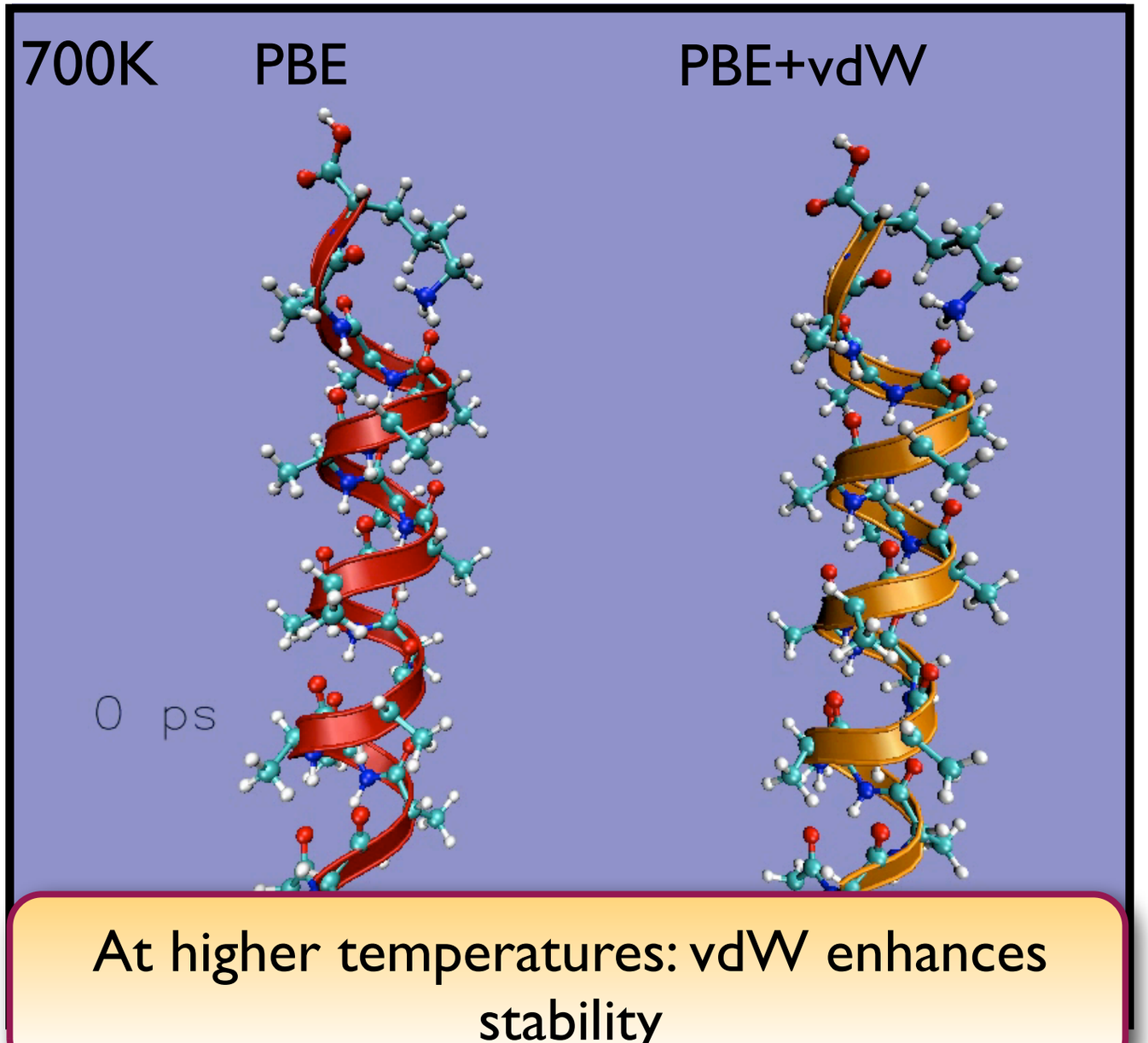

At higher temperatures: vdW enhances stability

A. Tkatchenko, M. Rossi, V. Blum, J. Ireta, and M. Scheffler, Phys. Rev. Lett. ***106****, 118102 (2011)*

References (books)

Understanding Molecular Simulation: From Algorithms to Applications
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Statistical Mechanics: Theory and Molecular Simulation
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Thank you!