Advanced Materials Modeling:

Molecular dynamics and statistical mechanics

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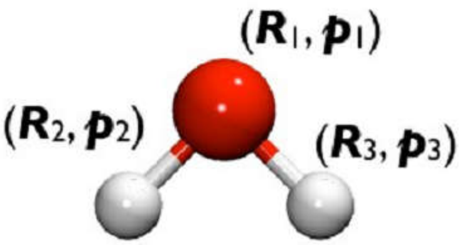
Molecular dynamics

- **Equations of motion (classical):**



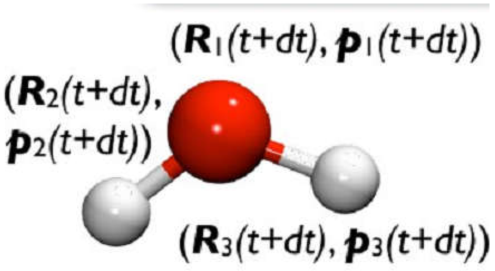
1) Assign initial $\boldsymbol{R}$ (positions) and $\boldsymbol{p}$ (momenta)

2) Evolve (numerically) Newton's equations of motion for a discrete time increment (requires evaluation of the forces)

$$\dot{\boldsymbol{p}} = \frac{d\boldsymbol{p}}{dt} = -\frac{\partial H(\boldsymbol{R},\boldsymbol{p})}{\partial \boldsymbol{R}}, \quad \dot{\boldsymbol{R}} = \frac{d\boldsymbol{R}}{dt} = \frac{\partial H(\boldsymbol{R},\boldsymbol{p})}{\partial \boldsymbol{p}}$$

$$H(\boldsymbol{R},\boldsymbol{p}) = \sum_I \frac{\boldsymbol{p}_I^2}{2M_I} + V(\boldsymbol{R}) \qquad \dot{\boldsymbol{p}}_I = -\nabla_I V = \boldsymbol{F}_I, \ \dot{\boldsymbol{R}}_I = \dot{\boldsymbol{p}}_I / M_I$$

$$M_I \ddot{\boldsymbol{R}}_I = \boldsymbol{F}_I$$



3) Assign new positions and momenta

Molecular dynamics - ensembles

- **Microcanonical (NVE)**

  Number of particles, Volume, and total Energy are conserved (natural ensemble to simulate MD, follows directly from Hamilton eqs. of motion)

- **Canonical (NVT)**

  Number of particles, Volume, and Temperature are conserved (system in contact with a heat bath)

- **NPT, NPH (Pressure, H - enthalpy)**

  For studying phase transitions

- **Grand-canonical (μVT)**

  For adsorption/desorption

Molecular dynamics – ensembles

Computer “experiment”:

equilibrate the system and measure

For adsorption/desorption

Molecular dynamics – solving eqns.

$$M_I \ddot{\boldsymbol{R}}_I = \boldsymbol{F}_I(\{\boldsymbol{R}\})$$

Many-body problem - need numeric solution (except in very special cases)

Simplest method: „forward Euler“:

$$R(t+\Delta t) = R(t) + \dot{R}(t)\Delta \mathrm{t} + \frac{1}{2}\ddot{R}(t)\Delta \mathrm{t}^2$$

Molecular dynamics – solving eqns.

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will not work!

1) is not time-reversible
2) suffers from energy drift
3) is numerically unstable (error $O(\Delta t^3)$ in R and $O(\Delta t^2)$ in $\dot{R}$)

Molecular dynamics – solving eqns.

- ❒ **(Basic) Verlet algorithm**

$$R(t+\Delta t) = R(t) + \frac{p(t)}{m}\Delta t + \frac{\overset{\text{Force}}{\enclose{circle}{\dot{p}(t)}}}{2m}\Delta t^2 + \overset{\text{Error } O(\Delta t^3)}{\cancel{\dddot{R}(t)\frac{\Delta t^3}{3!} + O(\Delta t^4)}}$$

Molecular dynamics – solving eqns.

❒ (Basic) Verlet algorithm

$$R(t+\Delta t) = R(t) + \frac{p(t)}{m}\Delta t + \frac{\overset{\text{Force}}{\boxed{\dot{p}(t)}}}{2m}\Delta t^2 + \overset{\text{Error } O(\Delta t^3)}{\cancel{\dddot{R}(t)\frac{\Delta t^3}{3!} + O(\Delta t^4)}}$$

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

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

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

1) is time-reversible
2) conserves energy
3) numerically stable

The first step ($R(t)$) is obtained from the Euler method

Molecular dynamics – solving eqns.

- **Instability of trajectories**

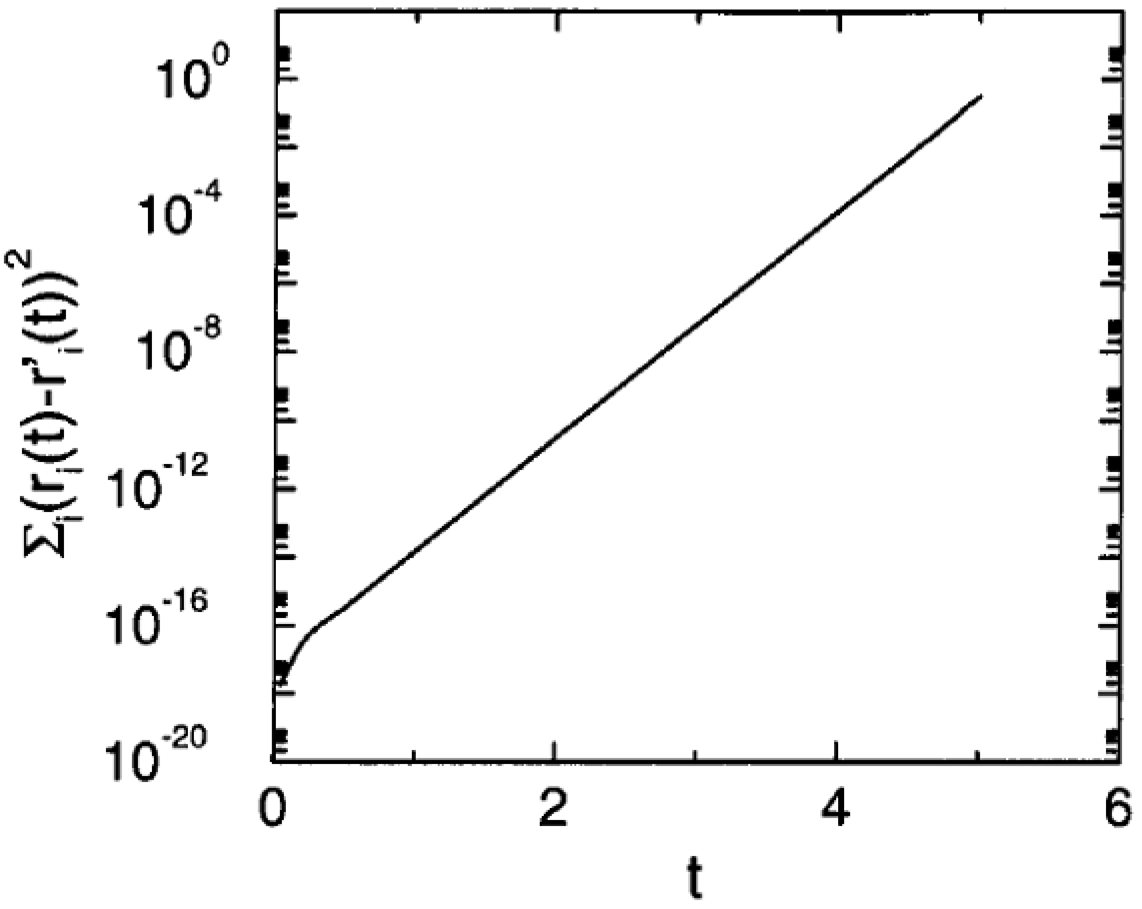
  Trajectories that differ very slightly in their initial conditions diverge exponentially → small discretization errors can lead to very different results:

$$\boldsymbol{R}(t) = f[\{\boldsymbol{R}\}(0), \{\boldsymbol{p}\}(0); t], \ \boldsymbol{R}'(t) = f[\{\boldsymbol{R}\}(0), \{\boldsymbol{p}\}(0) + \boldsymbol{\epsilon}; t]$$

$$|\boldsymbol{R}(t) - \boldsymbol{R}'(t)| \sim \boldsymbol{\epsilon} \exp(\lambda t)$$

Molecular dynamics – solving eqns.

- **Instability of trajectories**



Molecular dynamics – solving eqns.

- **Instability of trajectories**

Why should anyone believe in molecular dynamics simulations??

Molecular dynamics - solving eqns.

- **Instability of trajectories**

  Shadowing theorem: Although a numerically computed trajectory diverges exponentially from the true trajectory with the same initial coordinates, there exists an errorless trajectory with a slightly different initial condition that stays near ("shadows") the numerically computed one

  This is merely a hypothesis for any realistic many-body system (proven for some special cases)

  Does Verlet algorithm generate “shadow” trajectories?

Ott, E. Chaos in Dynamical Systems. New York: Cambridge University Press, pp. 18-19, 1993

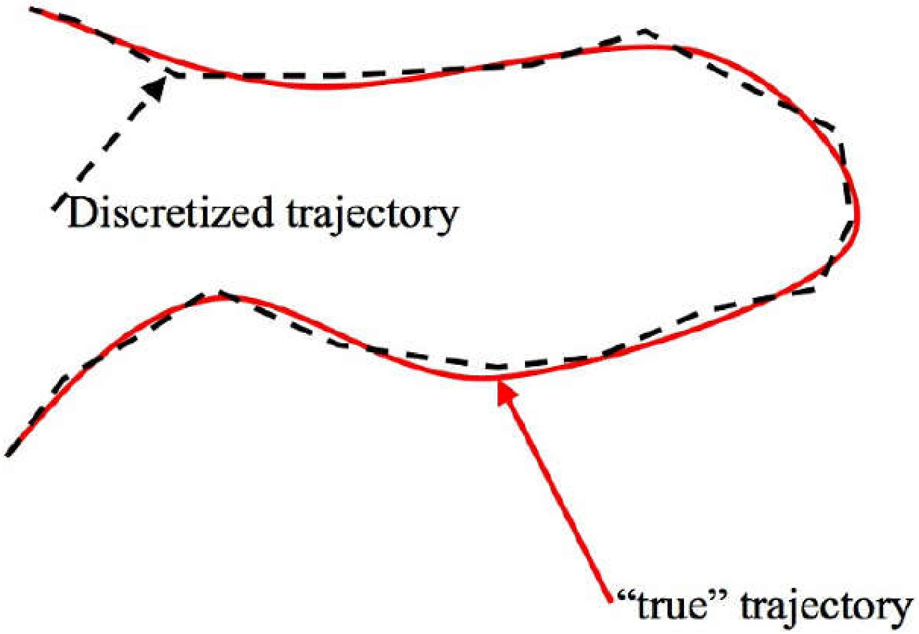
Molecular dynamics – solving eqns.

- **Principle of minimal action**

  A true trajectory minimizes the action:

$$\frac{\delta}{\delta x(t)} \int_{t_0}^{t_1} dt \left(\frac{mv^2}{2} - V\big(x(t)\big) \right) = 0$$

  Introducing discretization:



Molecular dynamics – solving eqns.

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Introducing discretization:

$$\frac{\partial}{\partial x_i} \sum_i \Delta t \left(\frac{m}{2} \frac{(x_{i+1} - x_i)^2}{\Delta t^2} - V(x_i) \right) = 0$$

$$2x_i - x_{i+1} - x_{i-1} - \frac{\Delta t^2}{m} \frac{\partial V(x_i)}{\partial x_i} = 0$$

But this is Verlet algorithm!

In fact, Verlet algorithm gives a trajectory that is an exact solution of Hamilton eqns with $\widetilde{H}(\Delta t) \rightarrow H$ when $\Delta t \rightarrow 0$

Molecular dynamics – uses

- **Statistical sampling**

Static equilibrium properties:

$$\langle A \rangle = \frac{1}{Z} \int d^{3N}R \int d^{3N}p e^{-\frac{H}{kT}} A(R,p)$$

Dynamic properties (correlation function):

$$\langle A(0)B(t) \rangle = \frac{1}{Z} \int d^{3N}R \int d^{3N}p e^{-\frac{H}{kT}} A(R,p,0)\, B(R,p,t)$$

It is difficult to calculate ensemble averages, but…

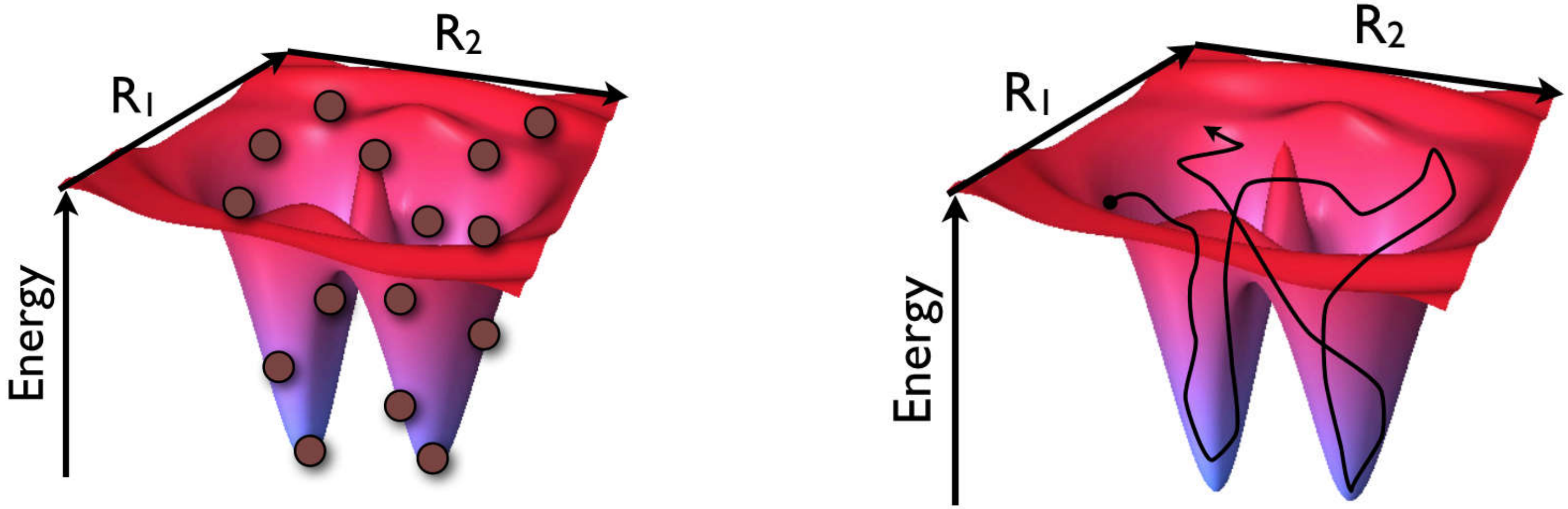
ergodic hypothesis → need only time average

Molecular dynamics – uses

- **Statistical sampling**

  It is difficult to calculate ensemble averages, but…

  ergodic hypothesis → need only time average



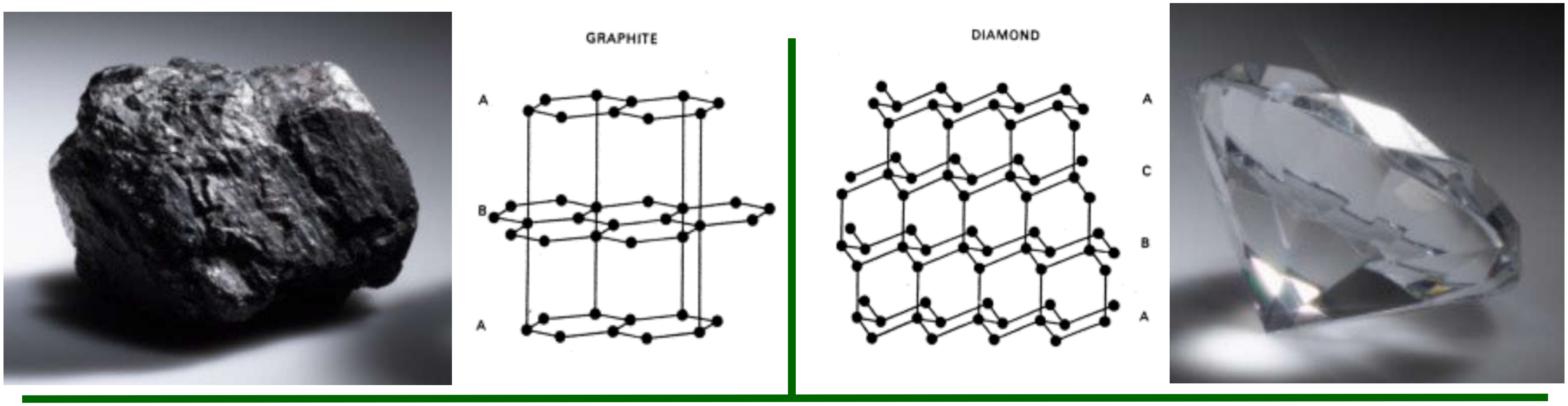
$$\langle A\rangle = \frac{1}{T}\int_0^T dt\, A(\boldsymbol{R}(t),\boldsymbol{p}(t))$$

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

Molecular dynamics – uses

- **Thermodynmic integration**

  How to accurately calculate phase transitions? Need to know accurate $\Delta F = F_B - F_A$



liquid

$$F = -kT\ln Z \qquad Z = \sum_R e^{-E(R)/kT}$$

Calculating F_A, then F_B, and taking difference is not accurate if phases are described by different PES E_A and E_B (e.g., different force fields)

Molecular dynamics – uses

- **Thermodynmic integration**

  How to accurately calculate phase transitions? Need to know accurate $\Delta F = F_B - F_A$

  Consider $$E_\lambda = E_A + \lambda(E_B - E_A)$$

$$F_\lambda = -kT\ln Z_\lambda \qquad Z_\lambda = \sum_R e^{-E_\lambda(R)/kT}$$

  Then

$$\Delta F(A \to B) = \int_0^1 \frac{\partial F_\lambda}{\partial \lambda} d\lambda = -\int_0^1 \frac{kT}{Z_\lambda}\frac{\partial Z_\lambda}{\partial \lambda} d\lambda = \int_0^1 \frac{1}{Z_\lambda}\sum_R \frac{\partial E_\lambda(R)}{\partial \lambda} e^{-E_\lambda(R)/kT}\, d\lambda$$

$$\Delta F(A \to B) = \int_0^1 \left\langle \frac{\partial E_\lambda}{\partial \lambda} \right\rangle d\lambda$$

Molecular dynamics – uses

- **Thermodynmic integration**

How to accurately calculate phase transitions? Need to know accurate $\Delta F = F_B - F_A$

$$E_\lambda = E_A + \lambda(E_B - E_A) \qquad \Delta F(A \to B) = \int_0^1 \left\langle \frac{\partial E_\lambda}{\partial \lambda} \right\rangle d\lambda$$

1) Sample E_λ at different values of λ
2) Calculate ensemble-averaged $\partial E_\lambda/\partial\lambda$
3) Integrate $\langle \partial E_\lambda/\partial\lambda \rangle$

→ Accurate free energies and phase transition conditions

Can be also used to calculate different contributions to free energy (e.g., harmonic versus anharmonic), and for an approximate versus accurate potential (force field versus DFT)

Molecular dynamics – uses

- **Statistical sampling**

  Example: absorption line-shape

$$I(\omega)\sim\omega^2\int dt e^{i\omega t}\langle \boldsymbol{D}(0)\cdot\boldsymbol{D}(t)\rangle$$

with $\boldsymbol{D}(t)$ - instantaneous dipole moment of the system

Can also calculate diffusion coefficients, thermal conductivity, viscosity

Molecular dynamics – uses

- ❒ **Statistical sampling**

  Example: thermal conductivity

  Heat current $\boldsymbol{J}$: $\boldsymbol{J} = \lambda \nabla T$

  Green-Kubo formula: $\lambda = \frac{1}{3VkT^2} \int_0^\infty \langle \boldsymbol{j}(0)\boldsymbol{j}(t) \rangle dt$

  where microscopic heat current $\boldsymbol{j}(t)$ is determined by

$$\boldsymbol{j}(t) = \sum_i \boldsymbol{v}_i \frac{1}{2}\left(mv_i^2 + \sum_j V\left(r_{ij}\right)\right) + \frac{1}{2}\sum_{i<j} \boldsymbol{r}_{ij} \left(\boldsymbol{F}_{ij} \cdot \left(\boldsymbol{v}_i + \boldsymbol{v}_j\right)\right)$$

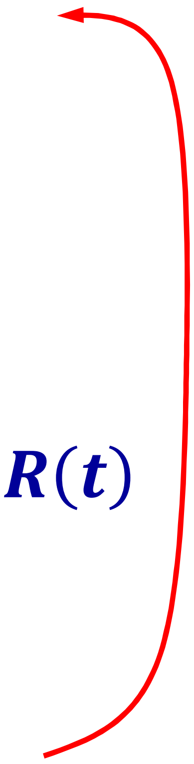
First-principles (ab initio) MD

- **Calculate forces from an *ab initio* potential $V(\{R\})$**

- **Different flavors**
  - Born-Oppenheimer MD
  - Car-Parrinello MD
  - Beyond Born-Oppenheimer MD (Ehrenfest, surface hopping)

- **Reachable time scales (by Born-Oppenheimer MD): tens of picoseconds to few nanoseconds**

Born-Oppenheimer MD in practice



- Specify initial $R(t_0)$ and $p(t_0)$
- Converge electronic structure via a self-consistent cycle
- Calculate forces
- Integrate the equations of motion to evolve $R(t)$ and $p(t)$
- Determine $R(t+\Delta\mathrm{t})$ and $p(t+\Delta\mathrm{t})$ and go to

Born-Oppenheimer MD in practice

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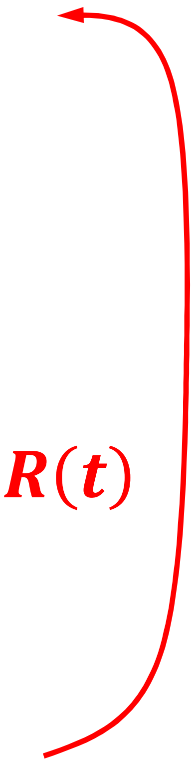
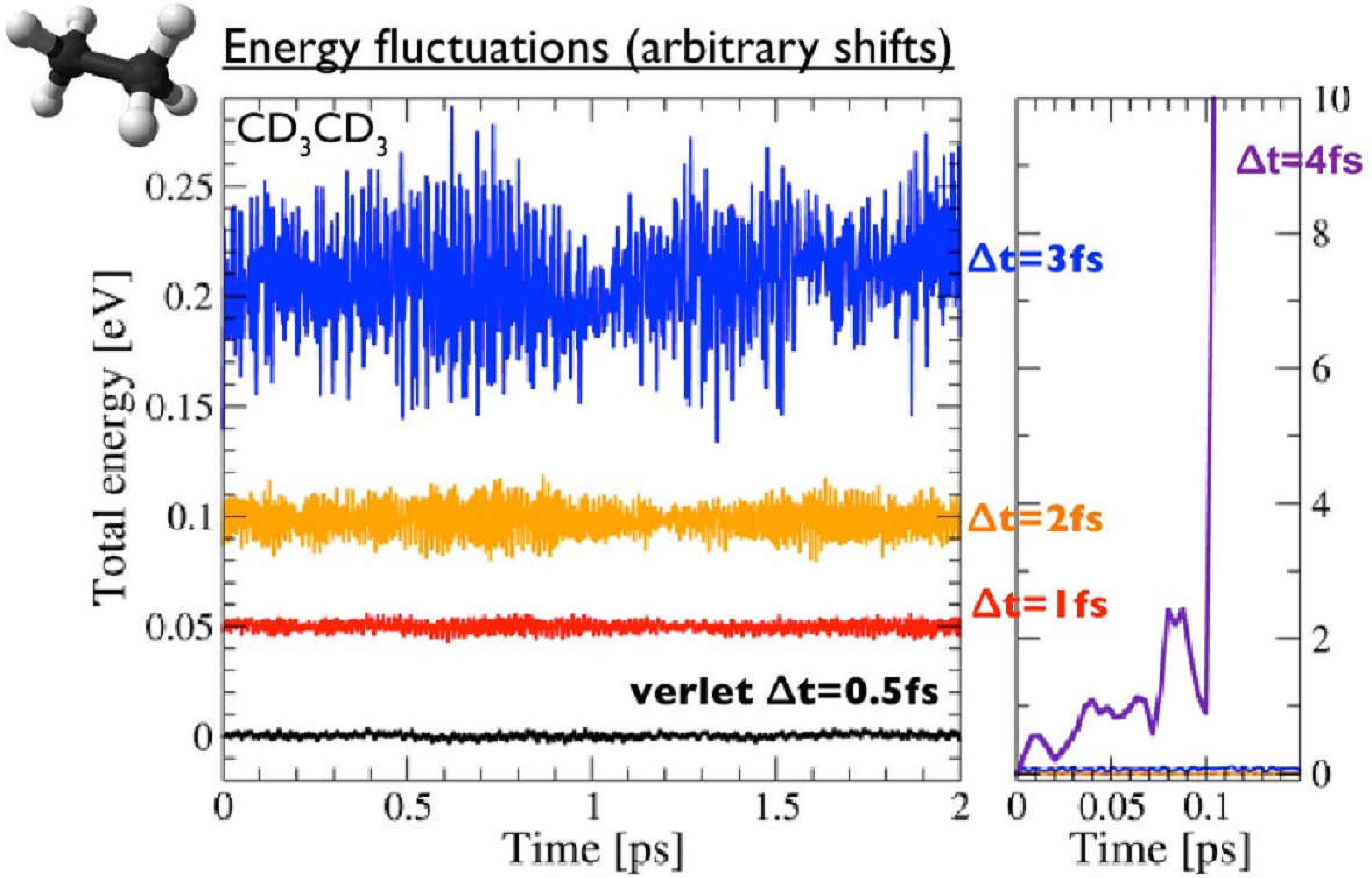
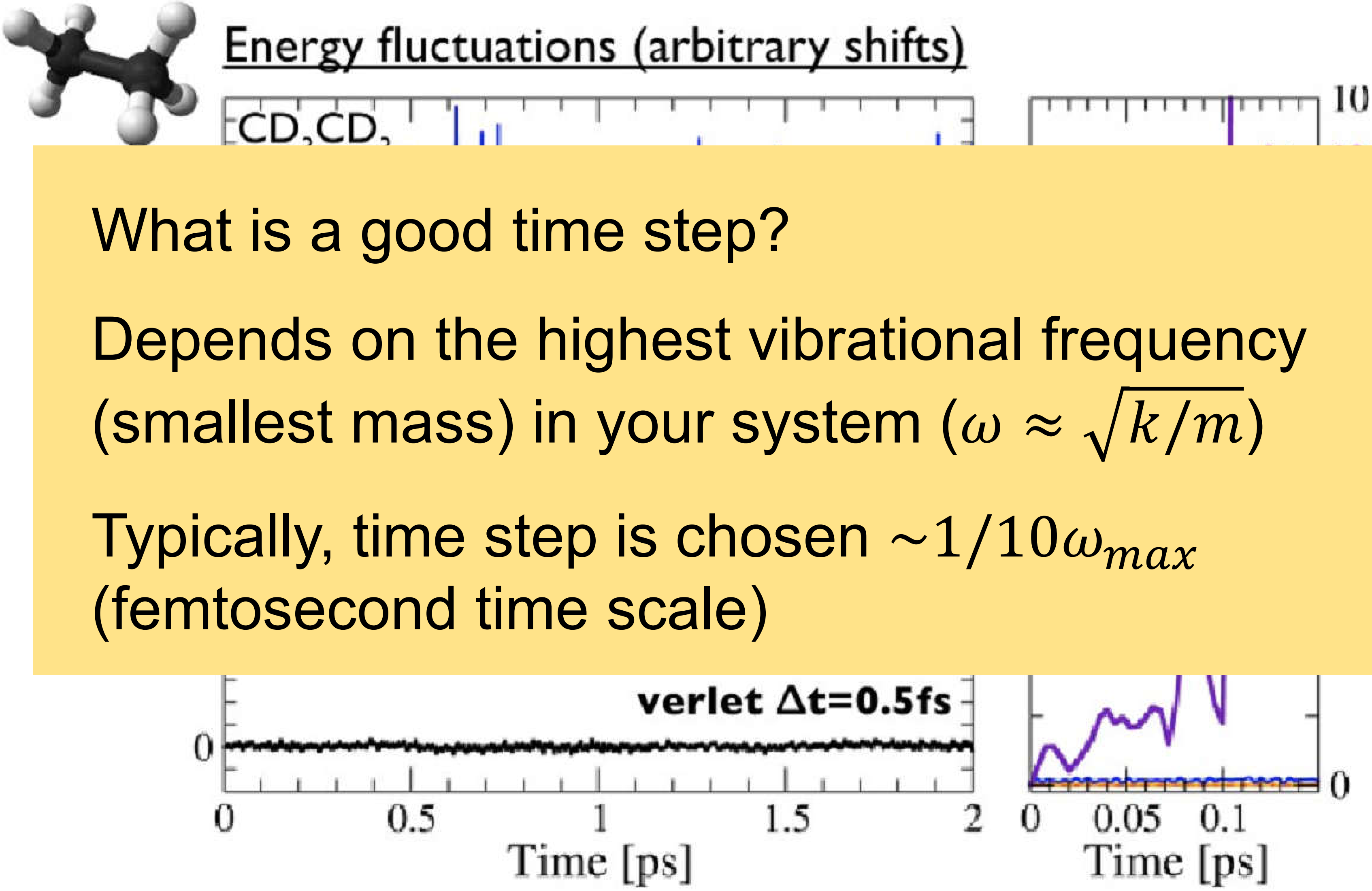


Born-Oppenheimer MD in practice



Energy fluctuations (arbitrary shifts)

Born-Oppenheimer MD in practice

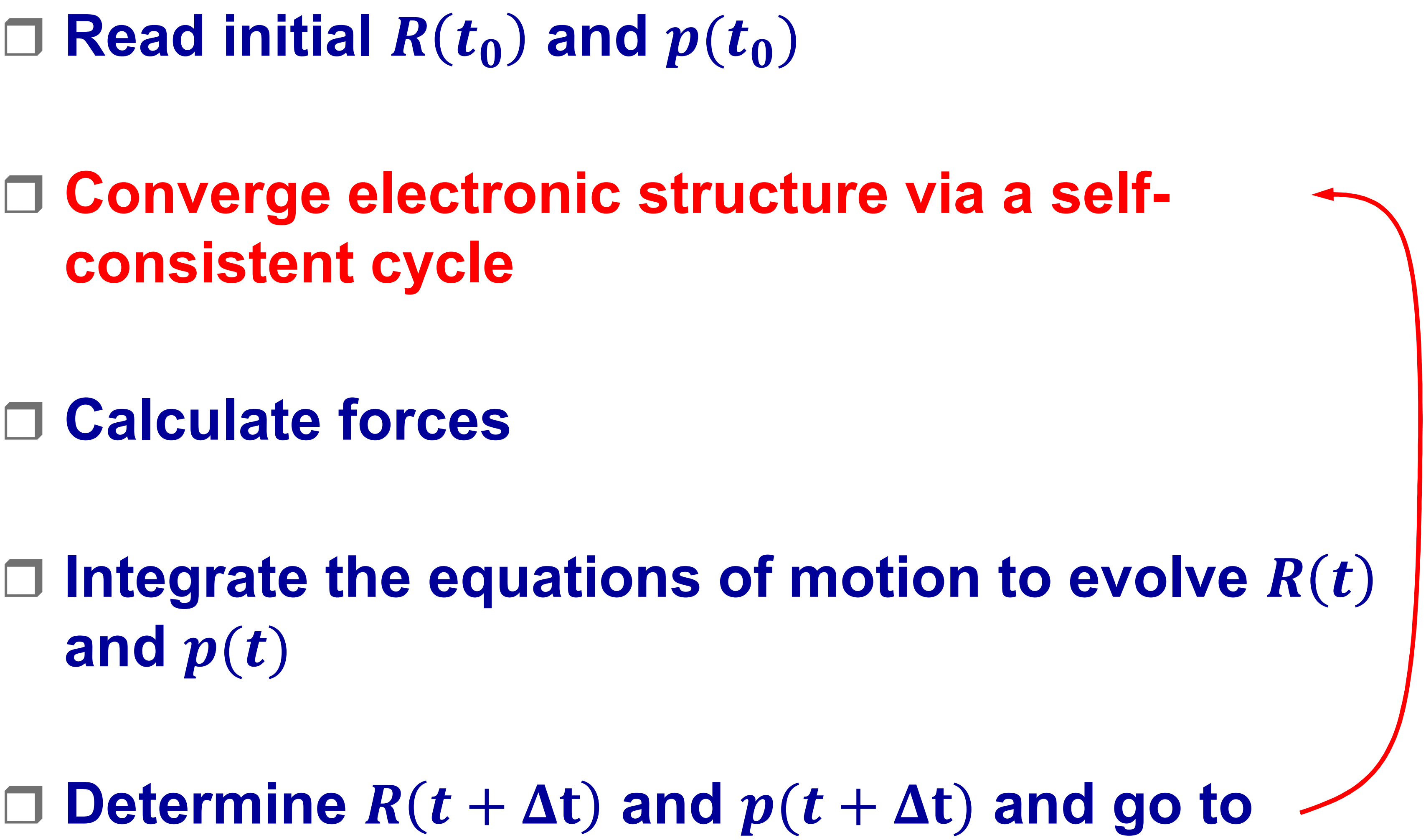


What is a good time step?

Depends on the highest vibrational frequency (smallest mass) in your system ($\omega \approx \sqrt{k/m}$)

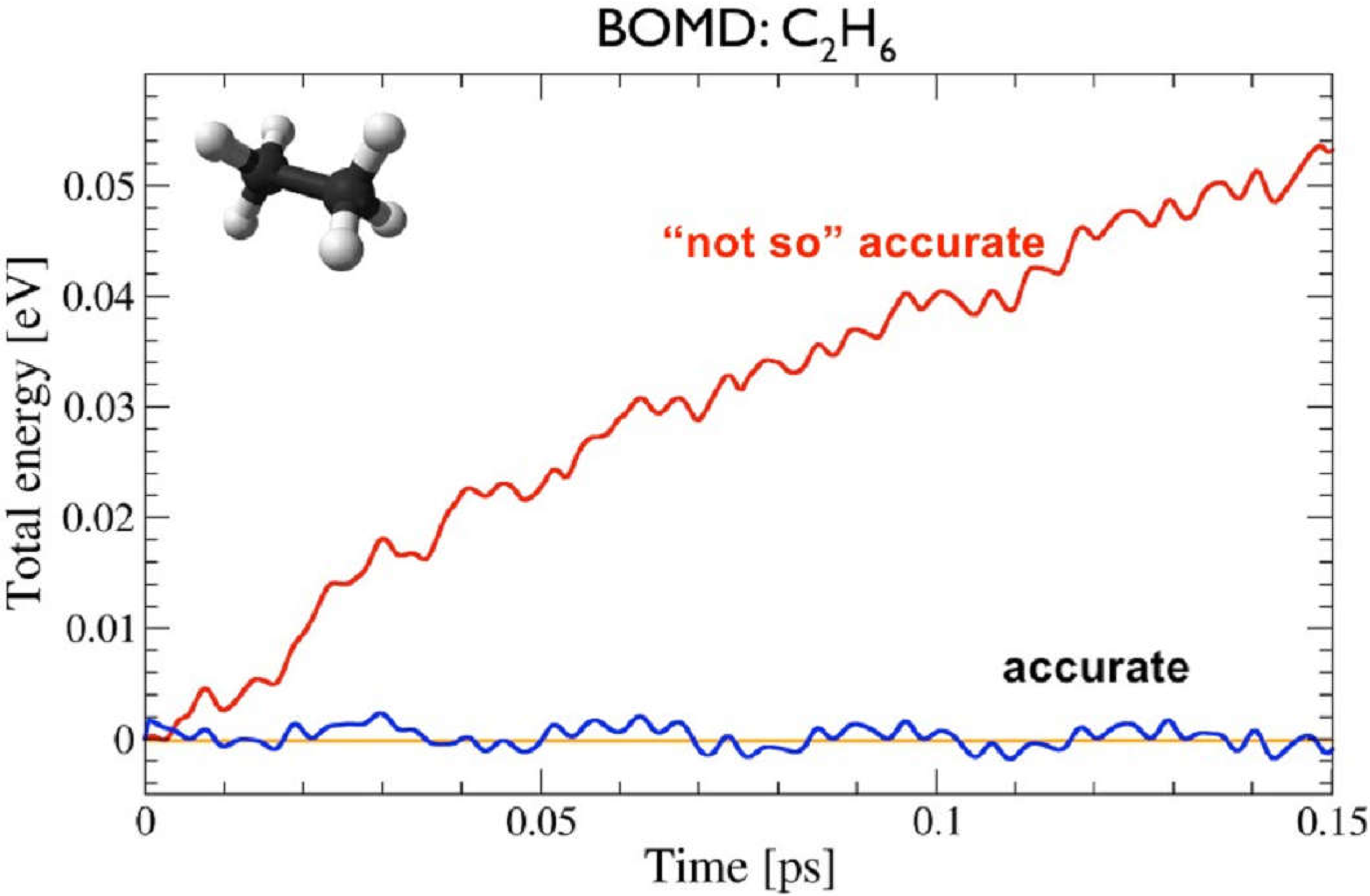
Typically, time step is chosen $\sim 1/10\omega_{max}$ (femtosecond time scale)

Born-Oppenheimer MD in practice



- **Read initial $R(t_0)$ and $p(t_0)$**
- **Converge electronic structure via a self-consistent cycle**
- **Calculate forces**
- **Integrate the equations of motion to evolve $R(t)$ and $p(t)$**
- **Determine $R(t+\Delta t)$ and $p(t+\Delta t)$ and go to**

Born-Oppenheimer MD in practice



Born-Oppenheimer MD in practice

❐ Car-Parinello MD

Self-consistent cycle is computationally expensive - can we avoid it? Yes, but with approximation

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

Lagrange multipliers

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

Fictitious electron mass

Kohn-Sham orbitals

satisfy constraints at each time step

$$M_I \ddot{\mathbf{R}}_I = -\nabla_I V(\phi, \phi^*; \mathbf{R})$$

$$\mu \ddot{\phi}_i = -\frac{1}{2}\frac{\delta V(\phi, \phi^*; \mathbf{R})}{\delta \phi_i^*} + \sum_j \phi_j \lambda_{ji}$$

Born-Oppenheimer MD in practice

- **Car-Parinello MD**

  Self-consistent cycle is computationally expensive - can we avoid it? Yes, but with approximation

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

  Adiabatic separation: electron “mass” needs to be very small → small time step (1/50 fs)

  Electrons “follow” nuclei: No self consistency needed (at each step)

Sampling canonical ensemble

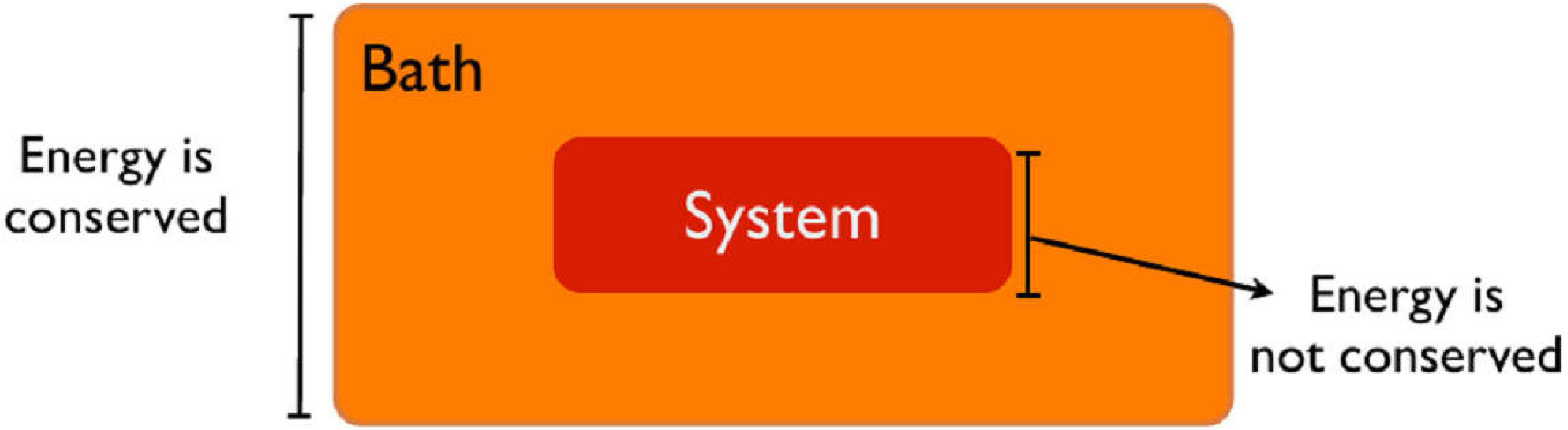
❐ Thermostats

The idea: couple the system to a heat bath

$$H = H^{\text{sys}} + H^{\text{bath}}$$

conserves energy

yields Maxwell-Boltzmann distribution of velocities for given *T*



Interesting because (i) experiments are usually done at constant T, (ii) better sampling of conformations

Sampling canonical ensemble

- **Thermostats**

  Andersen: every n time steps, replace velocity of a random particle by one drawn from a Maxwell-Boltzmann distribution at target temperature - canonical ensemble in the long-time limit, but slow equilibration, very sensitive to n, kinetics are not preserved (e.g., wrong diffusion coefficients)

  Berendsen: Re-scale velocities by $\sqrt{\left(1+\frac{\Delta t}{\tau}\left(\frac{T}{T(t)}-1\right)\right)}$ to approach the target temperature T ($T(t)=\frac{2\langle E_{\text{kinetic}}\rangle}{3k}$) - quick relaxation to target temperature, does not sample canonical ensemble

Sampling canonical ensemble

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  Nosé-Hoover: extended Hamiltonian (or Lagrangian)

$$\hat{H}_{NH} = \sum_I \frac{\boldsymbol{p}_I^2}{2M_I\eta^2} + V(\boldsymbol{R}) + \frac{p_\eta^2}{2Q} + 3NkT\ln(\eta)$$

fictitious oscillator

Sampling canonical ensemble

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fictitious oscillator

Momenta are damped by fictitious oscillator $\dot{\boldsymbol{p}}_I = F_I - \frac{p_\eta}{Q}\boldsymbol{p}_I$

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

Sampling canonical ensemble

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A microcanonical simulation in the extended system (including heat bath degrees of freedom) returns a canonical ensemble for the original system; deterministic (as opposed to stochastic)

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

Sampling canonical ensemble

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Q must be chosen carefully: too small Q → non-canonical, too large Q → large T fluctuations

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

Sampling canonical ensemble

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fictitious oscillator

Momenta are damped by fictitious oscillator $\dot{\boldsymbol{p}}_I = F_I - \frac{p_\eta}{Q}\boldsymbol{p}_I$

Ergodicity problems: system may be stuck in a region of phase space; solution: Nosé-Hoover chains (attach another fictitious oscillator to the first, and another to the second, etc.)

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

Sampling canonical ensemble

- **Thermostats**

  Bussi-Donadio-Parrinello: target temperature follows a stochastic differential equation:

$$\frac{dT}{\bar{T}} = \underset{\text{Temperature rescaling}}{\boxed{\left[1 - \frac{T(t)}{\bar{T}}\right]\frac{dt}{\tau}}} - \underset{\text{White noise}}{\boxed{2\sqrt{\frac{T(t)}{3\bar{T}N\tau}}\,\xi(t)}} \qquad T(t) = \frac{2\langle E_{\text{kinetic}}\rangle}{3k}$$

  Very successful thermostat, weakly dependent on τ

  Pseudo-Hamiltonian is conserved

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

NPT ensemble

- **Barostats**

  Define instantaneous internal pressure:

$$P = \frac{2}{3V}\left(E_{\text{kinetic}} + \frac{1}{2}\sum_I \boldsymbol{R}_I \cdot \boldsymbol{F}_I\right)$$

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

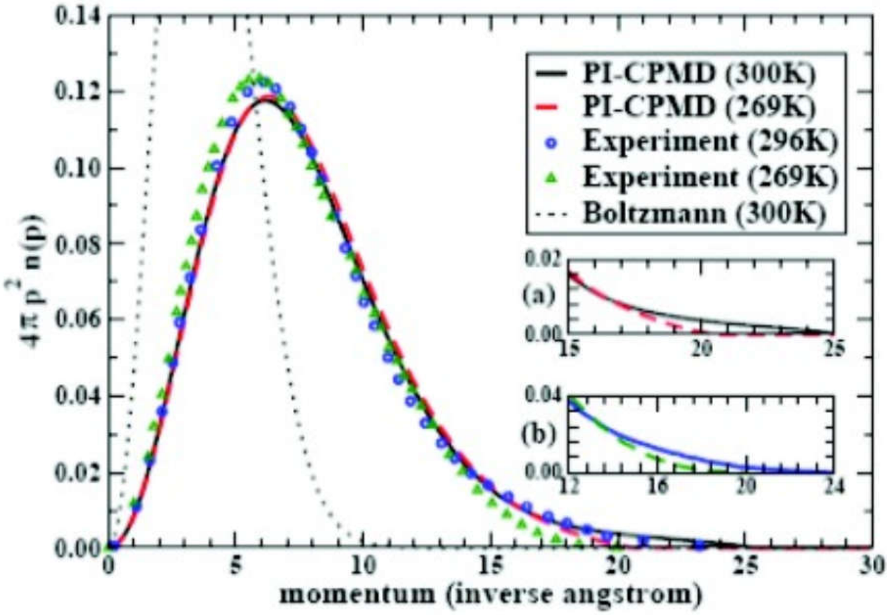
M. Parinello and A. Rahman, J. Appl. Phys 52, 7182 (1981)

Use thermostat together with a barostat to control temperature and pressure

Quantum nuclei

- ❐ **Why is this important?**

  Protons in water and ice



Classical Distribution: $n(p) \propto e^{-p^2/(2mk_BT)}$

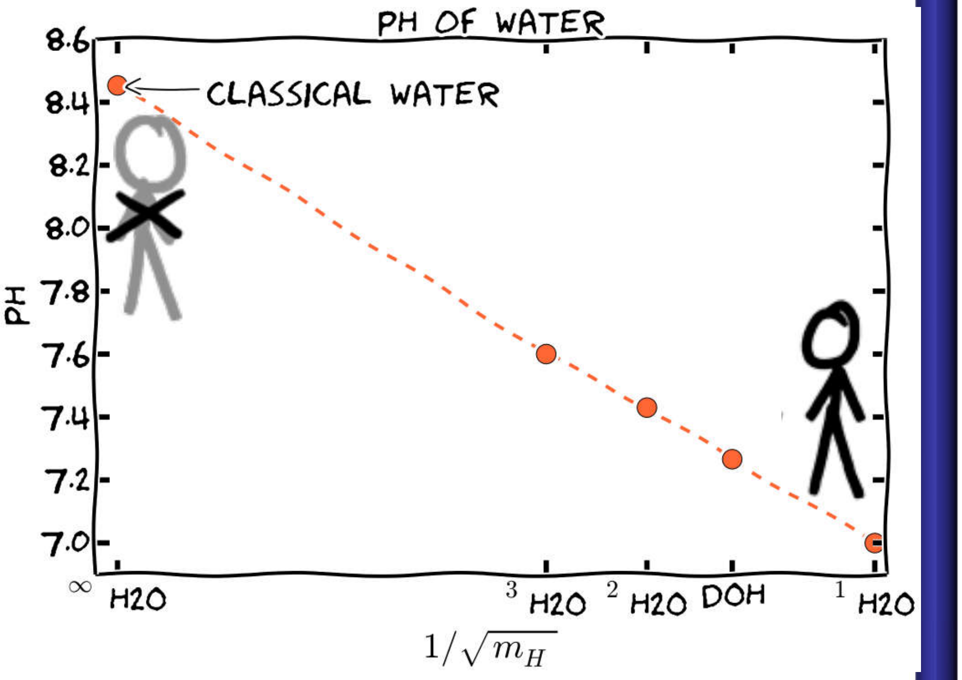


figure courtesy of Mariana Rossi

Path integral simulations: J. Morrone, RC, *PRL* 2008

Experiment: deep inelastic neutron scattering (DINS), G. Reiter et al., *Braz. J. Phys* 2004

Quantum nuclei

❒ When is this important?

- Relation between thermal De Broglie wavelength Λ and interparticle spacing l

$$\Lambda = \frac{h}{\sqrt{2\pi m k_B T}}$$

$$\Lambda \gg l$$

Low temperature, low mass
⇒ nuclear quantum effects important

$$\Lambda \ll l$$

High temperature, high mass
⇒ classical Boltzmann statistics are fine

Species	T(K)	Λ(Å)	Species	T(K)	Λ(Å)
e	300	43.03	He	4	4.35
H	300	1.00	Li	100	0.66
He	300	0.50	Cu	10	0.69
Li	300	0.38			

Systems approximately harmonic ⇒ $\frac{\hbar\omega}{k_B T} \gg 1$ ⇒ quantum (vibration dominated by ZPE)

T=300K corresponds to $\omega \approx 208\text{cm}^{-1}$ ⇒ vibrations (much) above are influenced by ZPE

Quantum nuclei

- **Path integral MD**

Quantum canonical partition function ($\beta = 1/kT$):

$$Z(\beta) = \int dx \langle x | \, e^{-\beta(\hat{T}+\hat{V})} | x \rangle$$

configuration coordinate

eigenstates of position operator ($\hat{V}|x\rangle = V(x)|x\rangle$)

$\hat{V}$ and $\hat{T}$ do not commute → use Trotter decomposition

$$Z(\beta) = \lim_{P\to\infty} \int dx \langle x | \Omega^P | x \rangle \qquad \Omega = e^{-\frac{\beta\hat{V}}{2P}} e^{-\frac{\beta\hat{T}}{P}} e^{-\frac{\beta\hat{V}}{2P}}$$

Quantum nuclei

❐ Path integral MD

Quantum canonical partition function ($\beta = 1/kT$):

$$Z(\beta) = \lim_{P\to\infty} \int dx \langle x|\Omega^P|x\rangle \qquad \Omega = e^{-\frac{\beta\hat{V}}{2P}} e^{-\frac{\beta\hat{T}}{P}} e^{-\frac{\beta\hat{V}}{2P}}$$

$$\int dx \big|x\rangle\langle x\big| = \hat{1} \rightarrow Z(\beta) = \lim_{P\to\infty} \int \prod_i dx_i \, \langle x_1|\Omega|x_2\rangle\langle x_2|\Omega|x_3\rangle \ldots \langle x_P|\Omega|x_1\rangle$$

Calculate the matrix elements $(\hat{\boldsymbol{V}}|\boldsymbol{x}\rangle = \boldsymbol{V}(\boldsymbol{x})|\boldsymbol{x}\rangle)$:

$$\langle x_i|\Omega|x_{i+1}\rangle = \langle x_i|e^{-\frac{\beta\hat{V}}{2P}} e^{-\frac{\beta\hat{T}}{P}} e^{-\frac{\beta\hat{V}}{2P}}|x_{i+1}\rangle$$
$$= e^{-\frac{\beta V(x_i)}{2P}} \langle x_i|e^{-\frac{\beta\hat{T}}{P}}|x_{i+1}\rangle e^{-\frac{\beta V(x_{i+1})}{2P}}$$

Quantum nuclei

❐ Path integral MD

Quantum canonical partition function ($\beta = 1/kT$):

$$Z(\beta) = \lim_{P\to\infty} \int dx \langle x|\Omega^P|x\rangle \qquad \Omega = e^{-\frac{\beta\hat{V}}{2P}} e^{-\frac{\beta\hat{T}}{P}} e^{-\frac{\beta\hat{V}}{2P}}$$

$$\int dx|x\rangle\langle x| = \hat{1} \rightarrow Z(\beta) = \lim_{P\to\infty} \int \prod_i dx_i \,\langle x_1|\Omega|x_2\rangle\langle x_2|\Omega|x_3\rangle \ldots \langle x_P|\Omega|x_1\rangle$$

$$\begin{aligned}\langle x_i|\Omega|x_{i+1}\rangle &= \langle x_i|e^{-\frac{\beta\hat{V}}{2P}} e^{-\frac{\beta\hat{T}}{P}} e^{-\frac{\beta\hat{V}}{2P}}|x_{i+1}\rangle \\ &= e^{-\frac{\beta V(x_i)}{2P}} \langle x_i|e^{-\frac{\beta\hat{T}}{P}}|x_{i+1}\rangle e^{-\frac{\beta V(x_{i+1})}{2P}}\end{aligned}$$

$$\int dp|p\rangle\langle p| = \hat{1} \rightarrow \langle x_i|e^{-\frac{\beta\hat{T}}{P}}|x_{i+1}\rangle = \int dp\, \langle x_i|p\rangle \left\langle p\middle|e^{-\frac{\beta\hat{T}}{P}}\middle|x_{i+1}\right\rangle$$

eigenstates of momentum operator ($\hat{T}|p\rangle = (p^2/2m)|p\rangle$)

Quantum nuclei

❒ Path integral MD

Matrix elements:

$$\int dp|p\rangle\langle p| = \hat{1} \rightarrow \langle x_i|e^{-\frac{\beta\hat{T}}{P}}|x_{i+1}\rangle = \int dp\,\langle x_i|p\rangle\left\langle p\middle|e^{-\frac{\beta\hat{T}}{P}}\middle|x_{i+1}\right\rangle$$

eigenstates of momentum operator ($\hat{T}|p\rangle = (p^2/2m)|p\rangle$)

$$\langle x|p\rangle = \frac{1}{\sqrt{2\pi\hbar}}e^{\frac{ipx}{\hbar}} \rightarrow$$

$$\langle x_i|e^{-\frac{\beta\hat{T}}{P}}|x_{i+1}\rangle = \int dp\,\langle x_i|p\rangle\left\langle p\middle|e^{-\frac{\beta\hat{T}}{P}}\middle|x_{i+1}\right\rangle = \frac{1}{\sqrt{2\pi\hbar}}\int dp\,e^{-\frac{\beta p^2}{2mP}}e^{ip(x_i-x_{i+1})/\hbar}$$

$$= \left(\frac{mP}{2\pi\beta\hbar^2}\right)^{1/2}\exp\left[-\frac{mP}{2\beta\hbar^2}(x_i-x_{i+1})^2\right]$$

Quantum nuclei

- ❐ **Path integral MD**

  Matrix elements:

$$Z(\beta) = \lim_{P\to\infty} \int \prod_i dx_i \, \langle x_1|\Omega|x_2\rangle\langle x_2|\Omega|x_3\rangle \ldots \langle x_P|\Omega|x_1\rangle$$

$$\langle x_i|\Omega|x_{i+1}\rangle = e^{-\frac{\beta V(x_i)}{2P}} \langle x_i|e^{-\frac{\beta \hat{T}}{P}}|x_{i+1}\rangle e^{-\frac{\beta V(x_{i+1})}{2P}}$$

$$\langle x_i|e^{-\frac{\beta \hat{T}}{P}}|x_{i+1}\rangle = \left(\frac{mP}{2\pi\beta\hbar^2}\right)^{1/2} \exp\left[-\frac{mP}{2\beta\hbar^2}(x_i - x_{i+1})^2\right]$$

$$\langle x_i|\Omega|x_{i+1}\rangle = \left(\frac{mP}{2\pi\beta\hbar^2}\right)^{1/2} \exp\left[-\frac{mP}{2\beta\hbar^2}(x_i - x_{i+1})^2 - \frac{\beta}{2P}(V(x_i) + V(x_{i+1}))\right]$$

Quantum nuclei

- ❒ **Path integral MD**

  Partition function:

$$Z(\beta) = \lim_{P\to\infty} Z_P(\beta),$$

$$Z_P(\beta) = \left(\frac{mP}{2\pi\beta\hbar^2}\right)^{P/2} \int dx_1 \dots dx_P \exp\left[-\beta U_{eff}(x_1, \dots x_P)\right]$$

$$U_{eff}(x_1, \dots x_P) = \sum_{i=1}^{P} \left[\frac{1}{2} m \left(\frac{\sqrt{P}}{\beta\hbar}\right)^2 (x_i - x_{i+1})^2 + \frac{1}{P} V(x_i)\right]_{x_{P+1}=x_1}$$

Quantum nuclei

❐ Path integral MD

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$$Z(\beta) = \lim_{P\to\infty} Z_P(\beta),$$

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No momenta?!? No problem!

fictitious momenta and masses

$$\tilde{Z}_P(\beta) = \left(\frac{mP}{2\pi\beta\hbar^2}\right)^{P/2} \int \prod_{i=1}^{P} dp_i \int \prod_{i=1}^{P} dx_i \exp\left[-\beta\left(\sum_{i=1}^{P} \frac{p_i^2}{2M_i} + U_{eff}(x_1, \dots x_P)\right)\right]$$

Quantum nuclei

❒ Path integral MD

Partition function:

$$Z(\beta) = \lim_{P\to\infty} Z_P(\beta),$$

$$Z_P(\beta) = \left(\frac{mP}{2\pi\beta\hbar^2}\right)^{P/2} \int dx_1 \ldots dx_P \exp\left[-\beta U_{eff}(x_1, \ldots x_P)\right]$$

$$\tilde{Z}_P(\beta) = \left(\frac{mP}{2\pi\beta\hbar^2}\right)^{P/2} \int \prod_{i=1}^{P} dp_i \int \prod_{i=1}^{P} dx_i \exp\left[-\beta\left(\sum_{i=1}^{P} \frac{p_i^2}{2M_i} + U_{eff}(x_1, \ldots x_P)\right)\right]$$

Gaussians are easy to integrate →

$$\tilde{Z}_P(\beta) = \prod_{i=1}^{P} \left(\frac{2\pi M_i}{\beta}\right)^{\frac{P}{2}} Z_P(\beta)$$

a constant at fixed *T* →

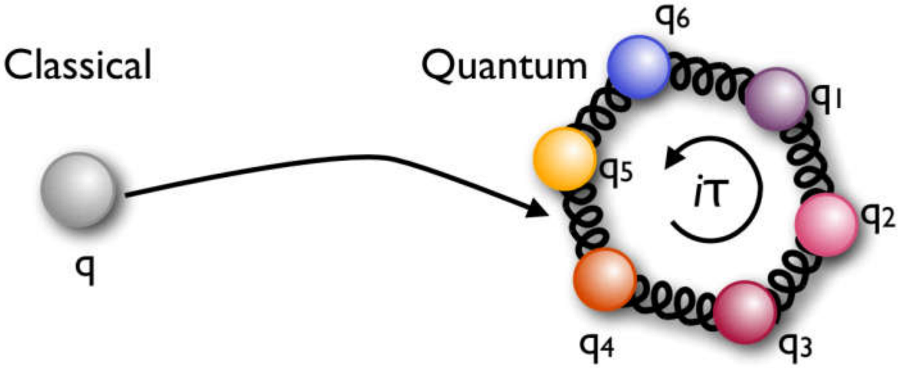
Quantum nuclei

- **Path integral MD**

  Sampling the effective potential:

$$\tilde{Z}_P(\beta) = \left(\frac{mP}{2\pi\beta\hbar^2}\right)^{P/2} \int \prod_{i=1}^{P} dp_i \int \prod_{i=1}^{P} dx_i \exp\left[-\beta\left(\sum_{i=1}^{P} \frac{p_i^2}{2M_i} + U_{eff}(x_1, \ldots x_P)\right)\right]$$

$$U_{eff}(x_1, \ldots x_P) = \sum_{i=1}^{P} \left[\frac{1}{2} m \left(\frac{\sqrt{P}}{\beta\hbar}\right)^2 (x_i - x_{i+1})^2 + \frac{1}{P} V(x_i)\right]_{x_{P+1}=x_1}$$



Quantum nuclei

❒ Path integral MD

Sampling the effective potential:

$$\tilde{Z}_P(\beta) = \left(\frac{mP}{2\pi\beta\hbar^2}\right)^{P/2} \int \prod_{i=1}^{P} dp_i \int \prod_{i=1}^{P} dx_i \, \exp\left[-\beta\left(\sum_{i=1}^{P}\frac{p_i^2}{2M_i} + U_{eff}(x_1,\dots x_P)\right)\right]$$

$$U_{eff}(x_1,\dots x_P) = \sum_{i=1}^{P}\left[\frac{1}{2}m\left(\frac{\sqrt{P}}{\beta\hbar}\right)^2 (x_i - x_{i+1})^2 + \frac{1}{P}V(x_i)\right]_{x_{P+1}=x_1}$$

Evolve several images of the system (“beads”) connected by springs

Each bead evolves at temperature $P \cdot T$

P is determined by how “quantum” the system is

$P > \beta\hbar\omega_{max}$ (typically between 10 and 100)

Monte Carlo (random) sampling

- ❐ **Calculation of integrals numerically**

  Consider a multidimensional integral: $I[f] = \int_{\Omega} f(\boldsymbol{X}) d^M X$

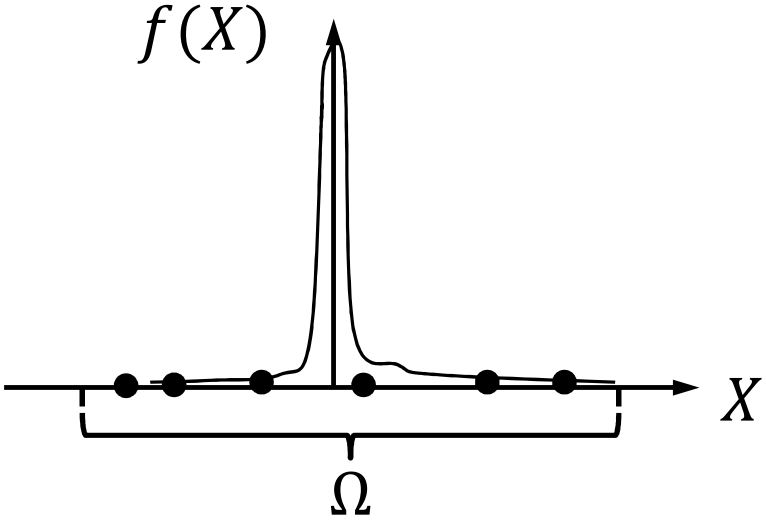
  How to calculate it numerically? 1) Choose a regular grid in Ω. However, for a very modest sampling of 10 points per direction, we need to calculate $f(\boldsymbol{X})$ at 10^M points - not practical for $M > 10$

  2) Choose points in Ω randomly - the "curse of dimensions" is alleviated

  Is a uniform distribution of the random points a good choice?

Monte Carlo (random) sampling

- **Calculation of integrals numerically**



$$I[f] = \int_{\Omega} f(\mathbf{X})\, d^M X$$

Obviously, in this case uniform sampling is not the best choice: the error in $I[f]$ converges very slowly with number of samples N:

$$\delta I \approx \Omega\sqrt{\frac{Var(f)}{N}},\; Var(f) = \frac{1}{N-1}\sum_{i=1}^{N}\left(f(\mathbf{X}_i) - \frac{1}{N}\sum_{j=1}^{N} f(\mathbf{X}_j)\right)^2$$

variance

Monte Carlo (random) sampling

- **Importance sampling**

  Perform a trivial transformation:

$$I[f] = \int_\Omega f(\boldsymbol{X}) d^M X = \int_\Omega \frac{f(\boldsymbol{X})}{w(\boldsymbol{X})} w(\boldsymbol{X}) d^M X$$

  If $w(\boldsymbol{X}) \geq 0$, $\int_\Omega w(X) d^M X = 1$, this looks like an expectation value of $f(\boldsymbol{X})/w(\boldsymbol{X})$ for $\boldsymbol{X}$ distributed according to probability density $w(\boldsymbol{X})$:

$$I[f] \approx \frac{1}{N} \sum_{i=1}^{N} \frac{f(\boldsymbol{X}_i)}{w(\boldsymbol{X}_i)}, \; w(\boldsymbol{X}) \rightarrow \boldsymbol{X}_i$$

  This gives freedom to minimize the variance by a proper choice of $w(\boldsymbol{X})$. In particular, if $w(\boldsymbol{X}) = Cf(\boldsymbol{X})$, the variance is zero. In practice, $w(\boldsymbol{X}) \approx Cf(\boldsymbol{X})$ is a very good choice (importance sampling)

Monte Carlo (random) sampling

❐ Importance sampling

Perform a trivial transformation:

$$I[f] \approx \frac{1}{N}\sum_{i=1}^{N}\frac{f(\boldsymbol{X}_i)}{w(\boldsymbol{X}_i)},\ w(\boldsymbol{X}) \to \boldsymbol{X}_i$$

How to generate $\{\boldsymbol{X}_i\}$ according to $w(\boldsymbol{X})$?

Metropolis algorithm: (1) generate a set of $\boldsymbol{X}_i$; (2) choose randomly a displacement $\Delta\boldsymbol{X}_i$ for each i; (3) replace $\boldsymbol{X}_i$ with $\boldsymbol{X}_i' = \boldsymbol{X}_i + \Delta\boldsymbol{X}_i$ with the probability:

$$P_{accept}(\boldsymbol{X}_i \to \boldsymbol{X}_i') = \min\left(1, \frac{w(\boldsymbol{X}_i')}{w(\boldsymbol{X}_i)}\right)$$

(4) continue until convergence

Metropolis, Rosenbluth, Rosenbluth, Teller, Teller, J. Chem. Phys. 21, 1087 (1953)

Monte Carlo (random) sampling

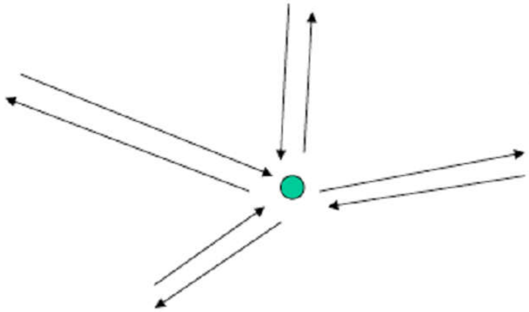
- **Calculation of integrals numerically**

$$P_{accept}(\boldsymbol{X}_i \to \boldsymbol{X}_i') = \min\left(1, \frac{w(\boldsymbol{X}_i')}{w(\boldsymbol{X}_i)}\right)$$

This follows from detailed balance in equilibrium:

$$w(\boldsymbol{X}_i)P(\boldsymbol{X}_i \to \boldsymbol{X}_i') = w(\boldsymbol{X}_i')P(\boldsymbol{X}_i' \to \boldsymbol{X}_i)$$

Detailed balance is sufficient (although not necessary) for equilibrium:



$$\sum_{\boldsymbol{X}_i'} w(\boldsymbol{X}_i)P(\boldsymbol{X}_i \to \boldsymbol{X}_i') = \sum_{\boldsymbol{X}_i'} w(\boldsymbol{X}_i')P(\boldsymbol{X}_i' \to \boldsymbol{X}_i)$$

Metropolis, Rosenbluth, Rosenbluth, Teller, Teller, J. Chem. Phys. 21, 1087 (1953)

Monte Carlo sampling – applications

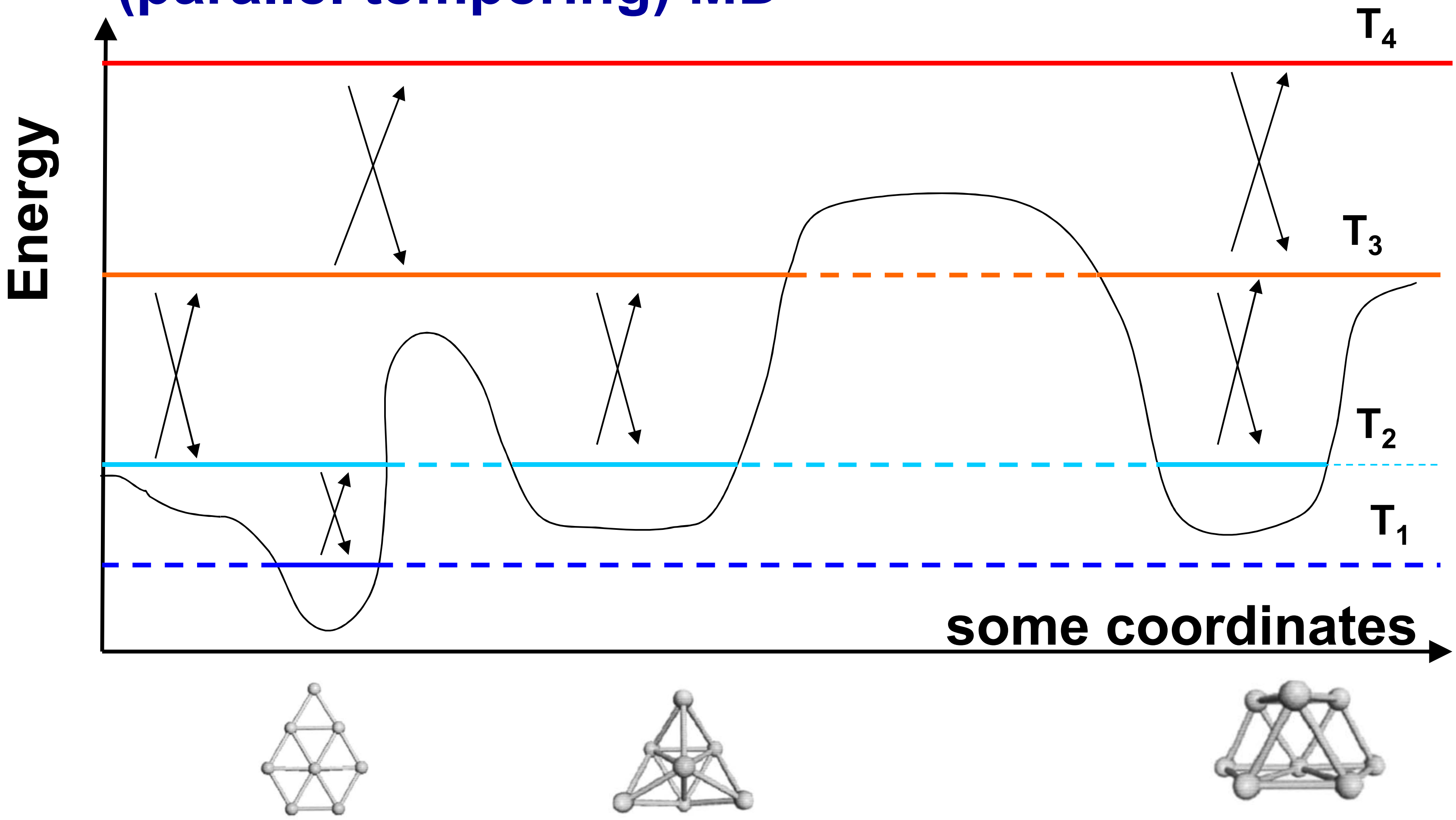
- **Computing statistical averages**

$$\langle A\rangle = \frac{\int d^{3N}R \int d^{3N}p\; A(\boldsymbol{R},\boldsymbol{p})e^{-H(\boldsymbol{R},\boldsymbol{p})/kT}}{\int d^{3N}R \int d^{3N}p\; e^{-H(\boldsymbol{R},\boldsymbol{p})/kT}}$$

$\frac{e^{-\frac{H(\boldsymbol{R},\boldsymbol{p})}{kT}}}{\int d^{3N}R \int d^{3N}p\; e^{-H(\boldsymbol{R},\boldsymbol{p})/kT}}$ is a natural choice for $w(\boldsymbol{X})$ for Monte Carlo integration of thermodynamic averages (easily extendable to ensembles other than canonical; kinetic energy integral can often be taken analytically)

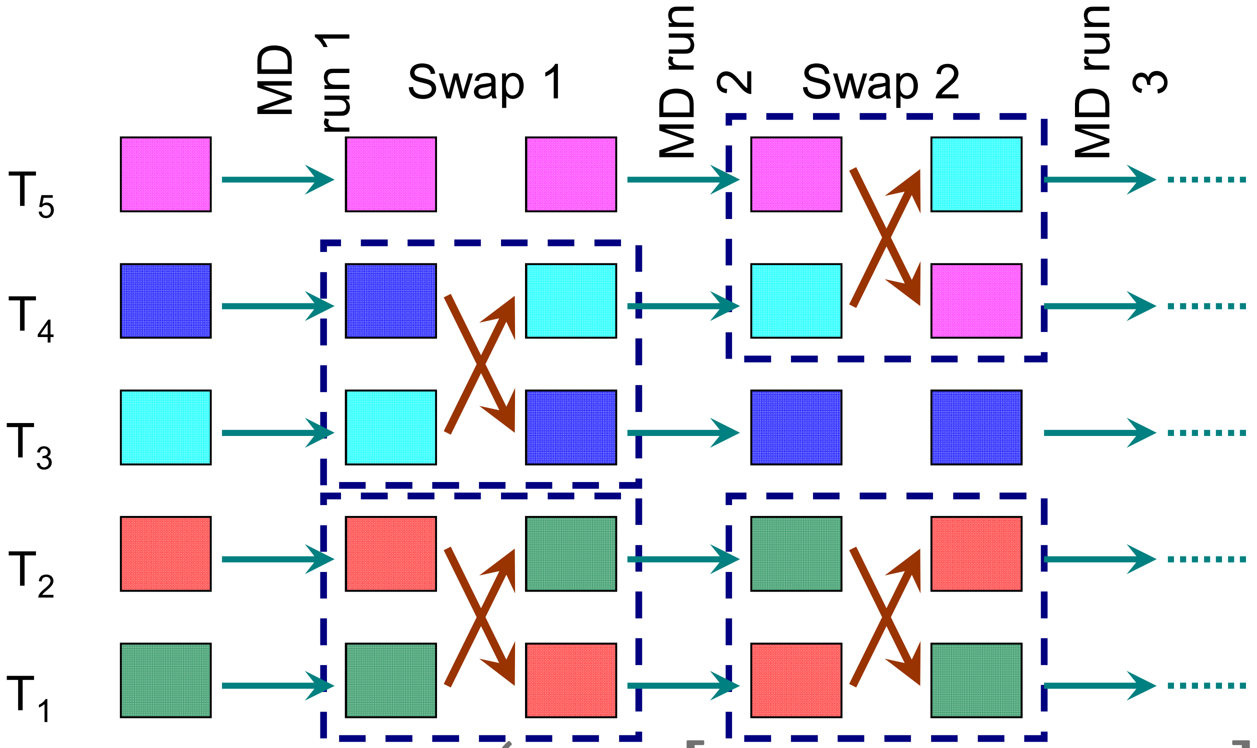
Monte Carlo sampling – applications

- Combining MD and MC - replica-exchange (parallel tempering) MD



Monte Carlo sampling – applications

- **Replica-exchange (parallel tempering) MD**

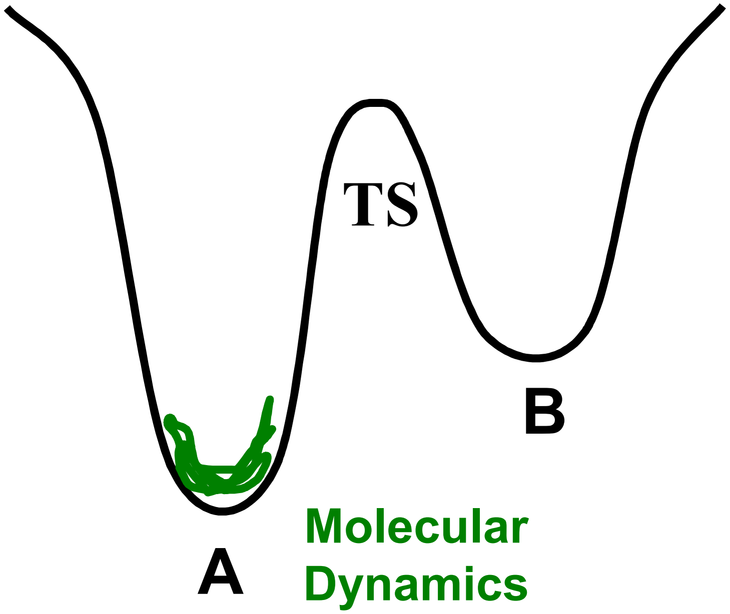


Swap probability $\min\left(1, \exp\left[(E_i - E_j)\left(\frac{1}{kT_i} - \frac{1}{kT_j}\right)\right]\right)$ This ensures canonical ensemble at each temperature

Metadynamics

- **Sampling rough potential-energy surfaces**

  The time scale for evolving from A → B is much larger than practically accessible MD time scales (<1 ns)

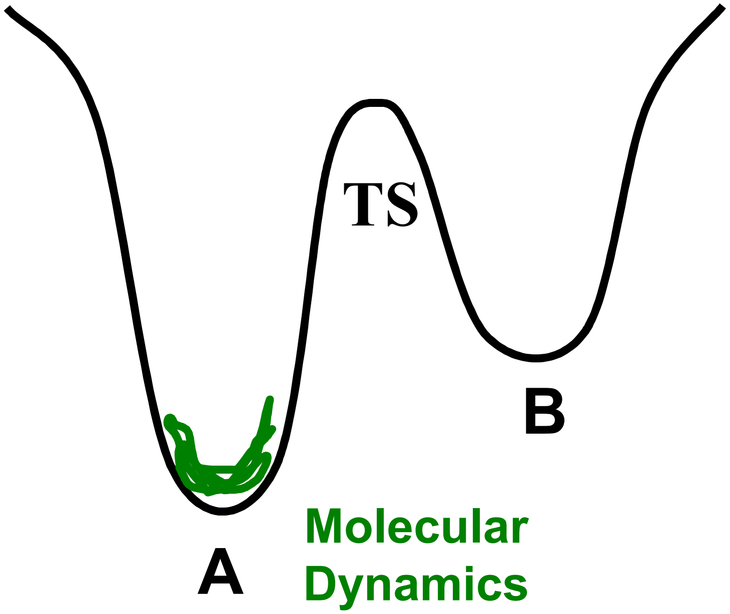


For example, a small protein folds in 10^{-4} s → 10^{11} time steps (~1 fs)

Metadynamics

- **Sampling rough potential-energy surfaces**

  The time scale for evolving from A → B is much larger than practically accessible MD time scales (<1 ns)

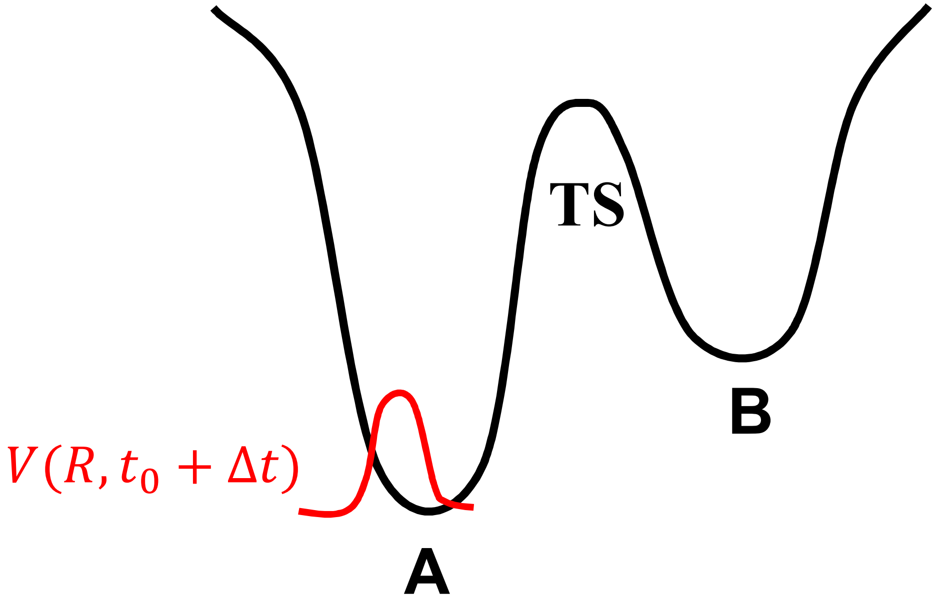


Idea: Introduce a bias potential to push the system out of the local minima

Metadynamics

- ❐ **Sampling rough potential-energy surfaces**

  The time scale for evolving from A → B is much larger than practically accessible MD time scales (<1 ns)



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A. Barducci, M. Bonomi and M. Parrinello, WIREs Comput Mol Sci 1, 826 (2011)

Metadynamics

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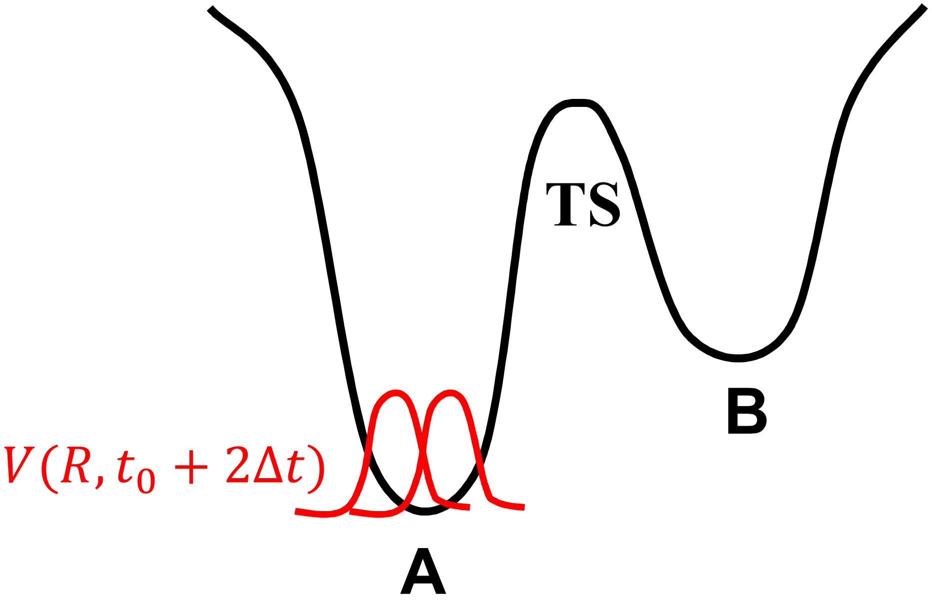

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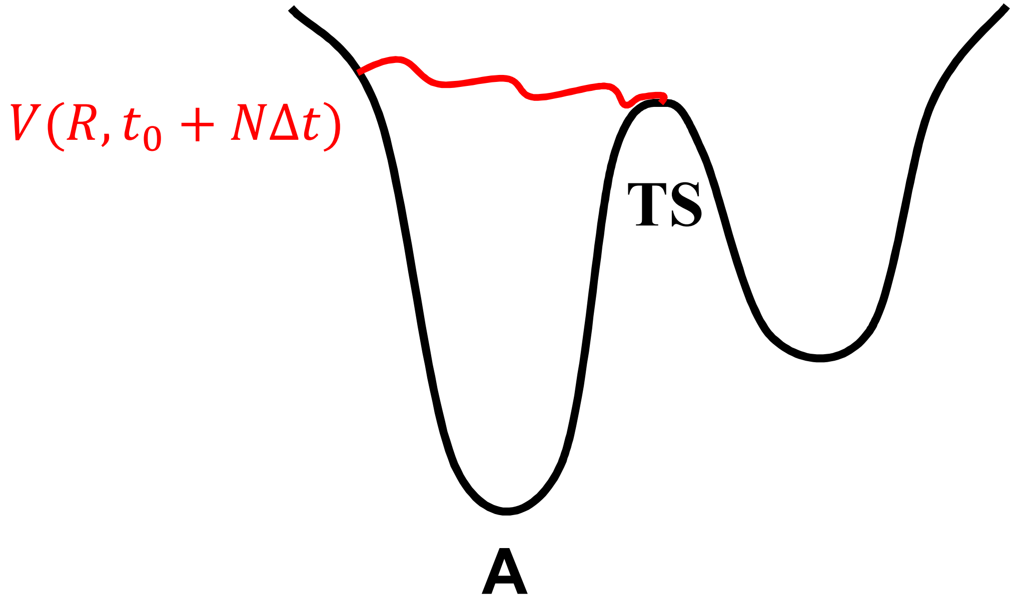

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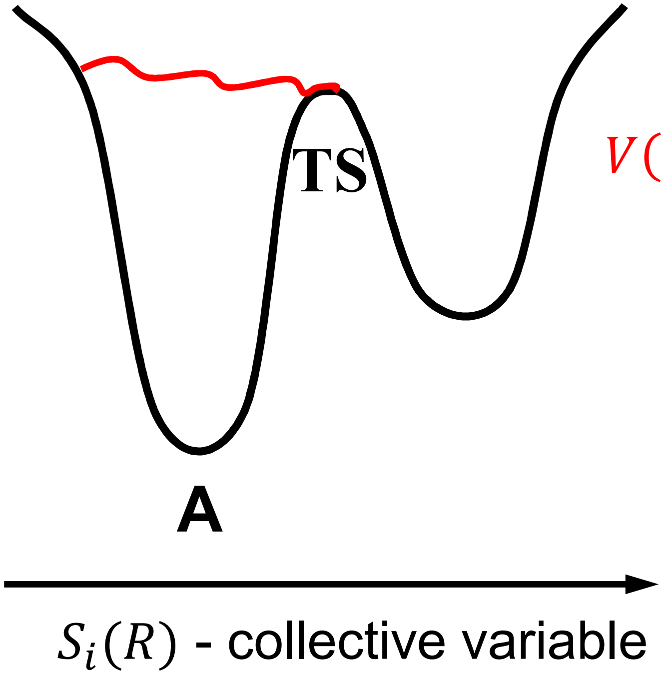

$$V(S,t) = \int_{t_0}^{t} dt'\omega \exp\left(-\sum_i \frac{\left(S_i(R) - S_i\left(R(t')\right)\right)^2}{2\sigma_i^2}\right)$$

Add a Gaussian every time step at every visited point on PES (continuous direct metadynamics)

A. Barducci, M. Bonomi and M. Parrinello, WIREs Comput Mol Sci 1, 826 (2011)

Metadynamics

- **Sampling rough potential-energy surfaces**

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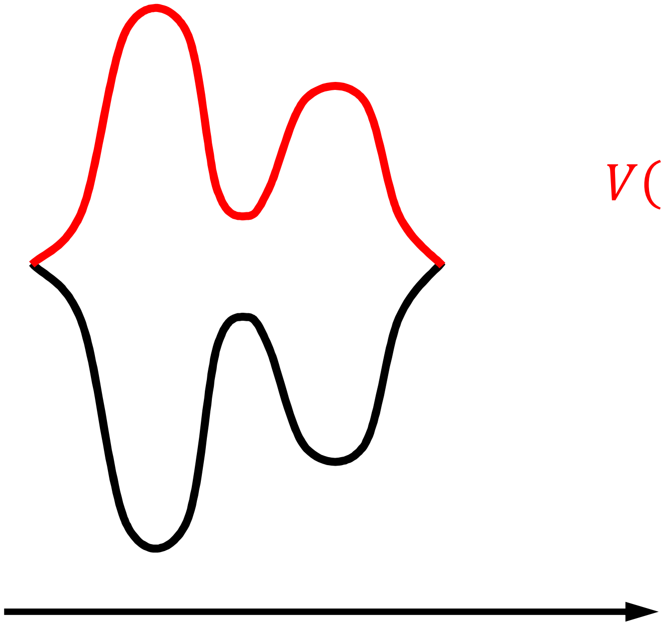


$S_i(R)$ - collective variable

collective variables

$$V(S,t) = \int_{t_0}^{t} dt'\,\omega \exp\left(-\sum_i \frac{\left(S_i(R) - S_i\left(R(t')\right)\right)^2}{2\sigma_i^2}\right)$$

Add a Gaussian every time step at every visited point on PES (continuous direct metadynamics)

The "magic" (in fact, rigorously proven):

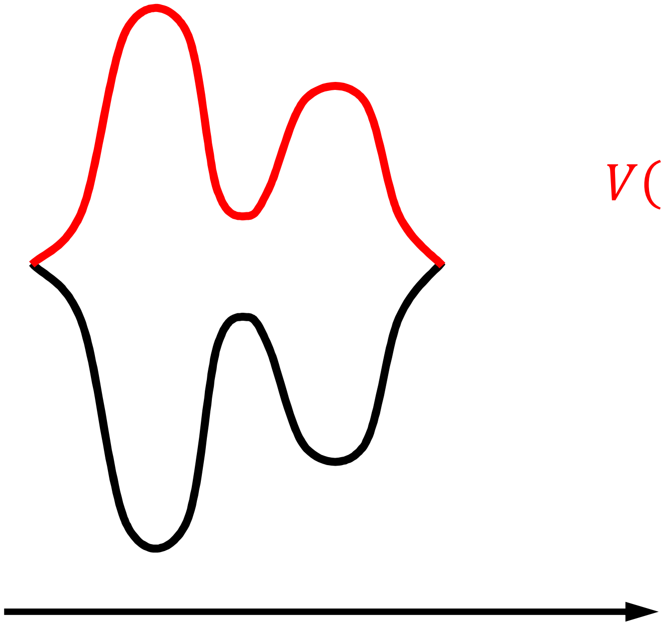
$$\boldsymbol{V(S, t \to \infty) = -F(S) + \mathrm{constant}}$$

A. Barducci, M. Bonomi and M. Parrinello, WIREs Comput Mol Sci 1, 826 (2011)

Metadynamics

- ❐ **Sampling rough potential-energy surfaces**

  Idea: Introduce a bias potential to push the system out of the local minima



$S_i(R)$ - collective variable

$$V(S,t) = \int_{t_0}^{t} dt' \omega \exp\left(-\sum_i \frac{\left(S_i(R) - S_i\left(R(t')\right)\right)^2}{2\sigma_i^2} \right)$$

$$\boldsymbol{V(S, t \to \infty) = -F(S) + \mathbf{constant}}$$

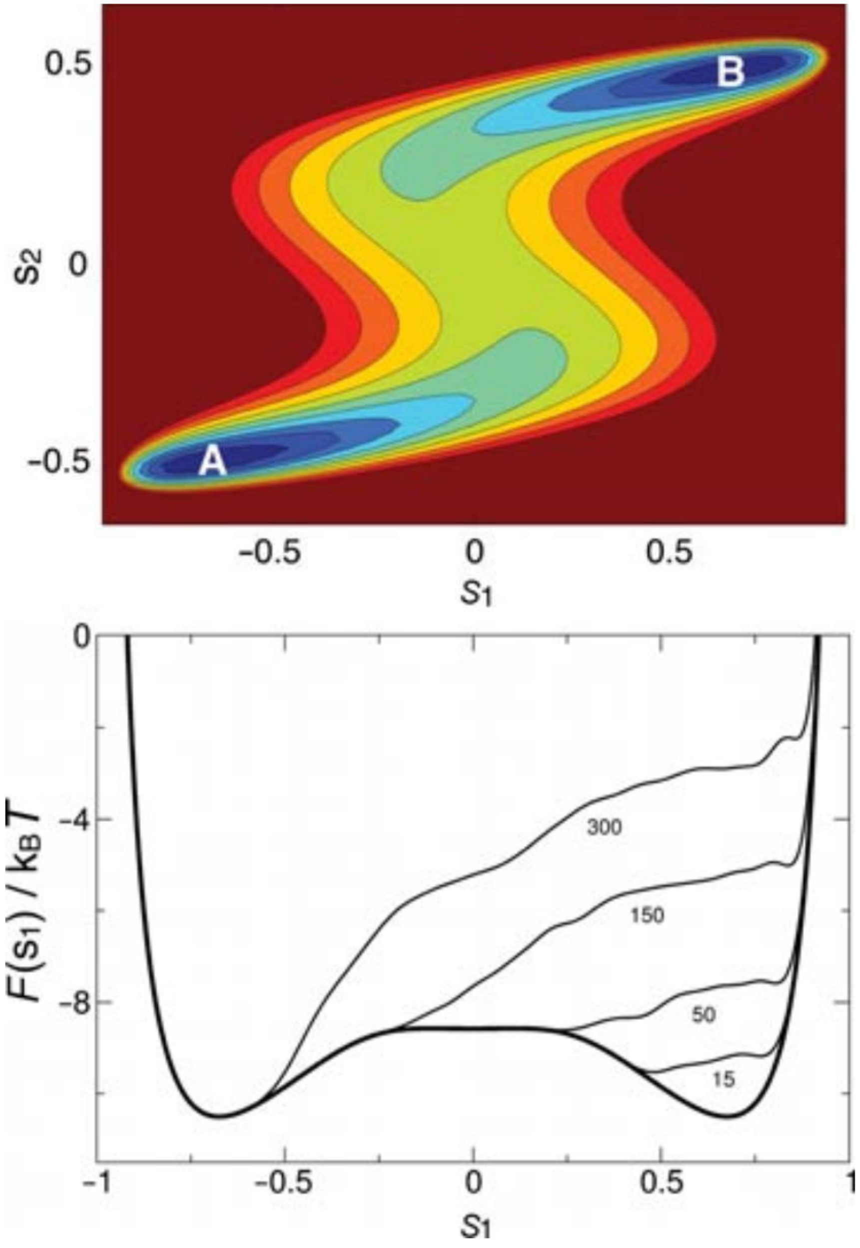
To reduce oscillations around $F(S)$: decrease Gaussian deposition rate with time (well-tempered metadynamics)

A. Barducci, M. Bonomi and M. Parrinello, WIREs Comput Mol Sci 1, 826 (2011)

Metadynamics

- ❒ **Collective variables**

  “Identifying a set of CVs
  appropriate for describing
  complex processes
  is far from trivial”



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Metadynamics

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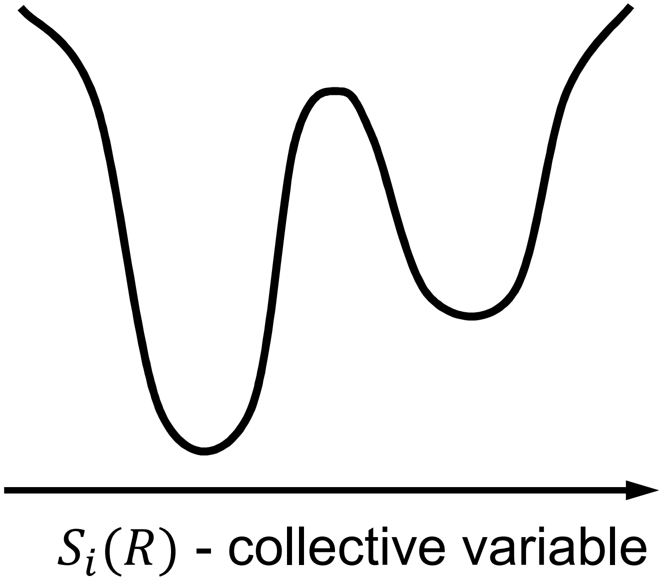


$S_i(R)$ - collective variable

1) $S(R) = R$ - inefficient for complex PES

2) Principal component analysis of data from a preliminary sampling

3) Along reaction coordinate (NEB) plus distance from the path

A. Barducci, M. Bonomi and M. Parrinello, WIREs Comput Mol Sci 1, 826 (2011)

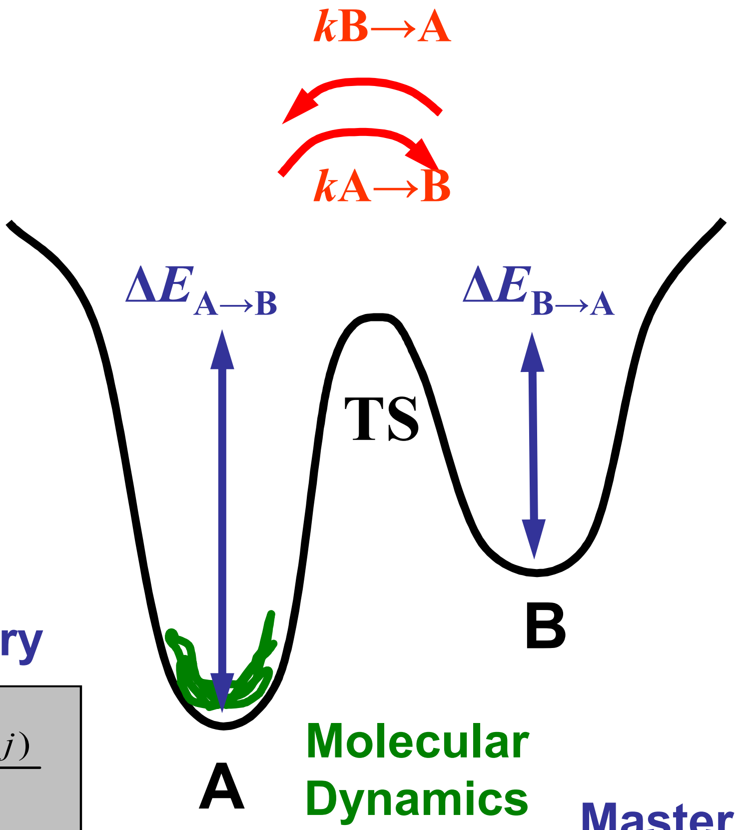
Metadynamics

- ❐ **Applications**
  1) Predicting equilibrium crystal structures at a given thermodynamics condition
  2) Diffusion
  3) Solid-liquid interface free energy (difficult to measure experimentally)
  4) Chemical reactions
  5) Protein folding

A. Barducci, M. Bonomi and M. Parrinello, WIREs Comput Mol Sci 1, 826 (2011)

Monte Carlo sampling - applications

- Reaction kinetics - kinetic MC (kMC)



Transition State Theory

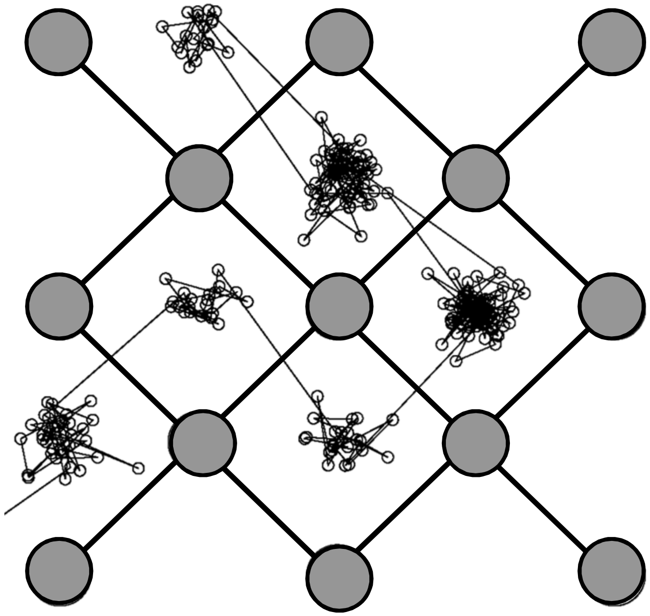
$$k_{i\to j} = \left(\frac{k_B T}{h}\right)\frac{Z_{TS(i\to j)}}{Z_i} = \Gamma_o \exp\left(\frac{-\Delta E_{i\to j}}{k_B T}\right)$$

Master equation

$$\frac{dP_i(t)}{dt} = -\sum_j k_{i\to j} P_i(t) + \sum_j k_{j\to i} P_j(t)$$

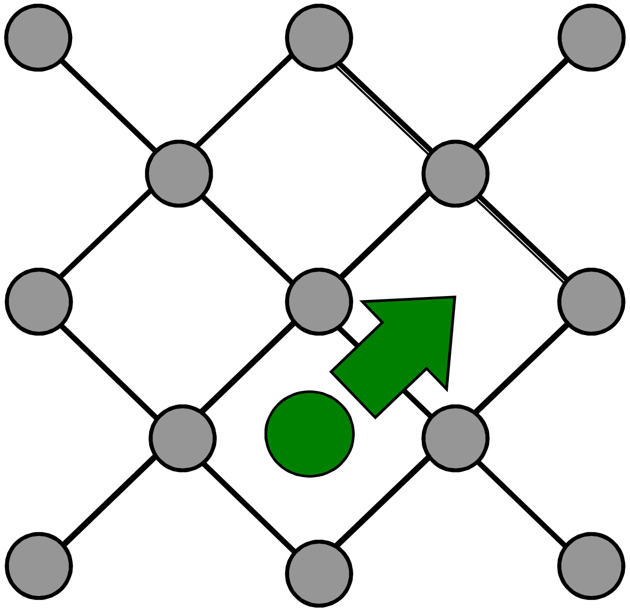
Monte Carlo sampling – applications

- Reaction kinetics - kinetic MC (kMC)



Molecular Dynamics:
the whole trajectory

***ab initio* MD:**
up to 50 ps



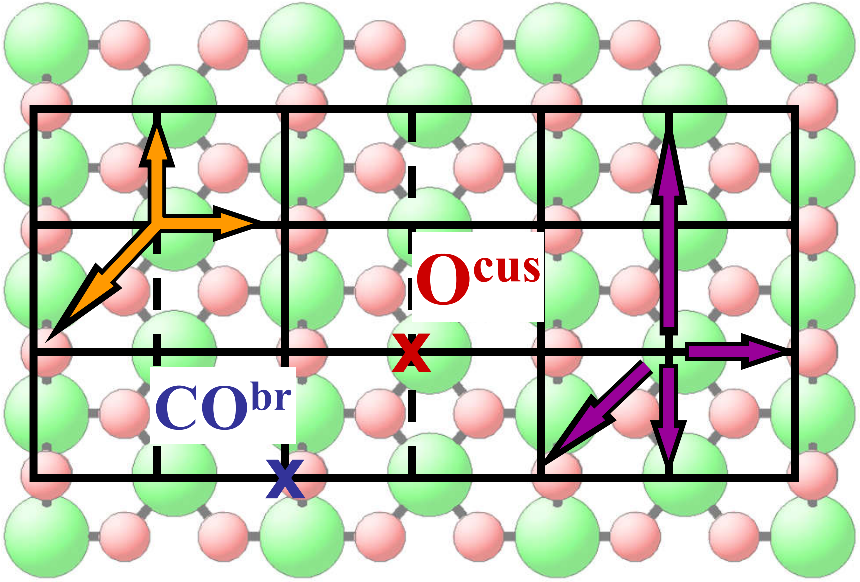
Kinetic Monte Carlo:
coarse-grained hops

***ab initio* kMC:**
up to minutes

Monte Carlo sampling – applications

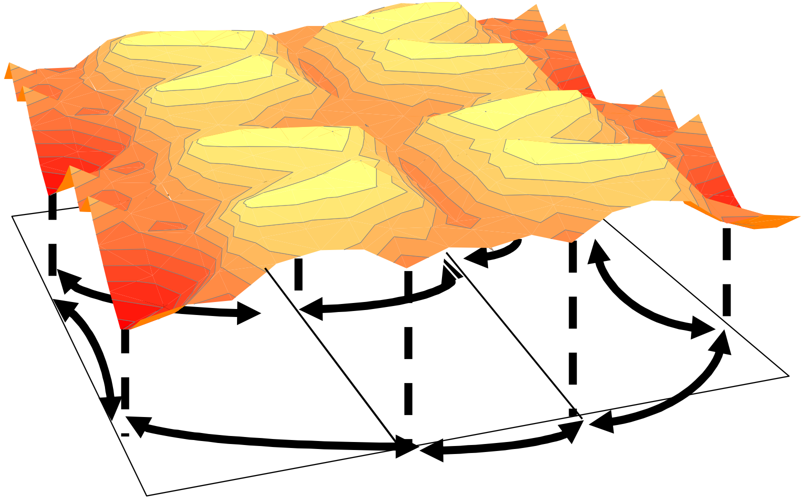
- **Crucial ingredients of kMC**

$$\frac{dP_i(t)}{dt} = -\sum_j k_{i\to j} P_i(t) + \sum_j k_{j\to i} P_j(t)$$



1) Elementary processes

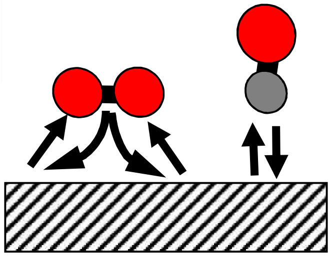
Fixed process list vs. „on-the-fly“ kMC
Lattice vs. off-lattice kMC

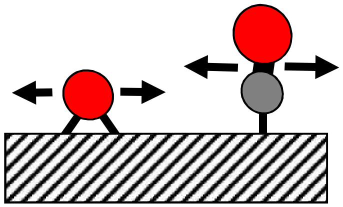


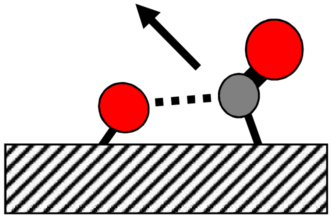
2) Process rates

PES accuracy
Reaction rate theory

Monte Carlo sampling - applications







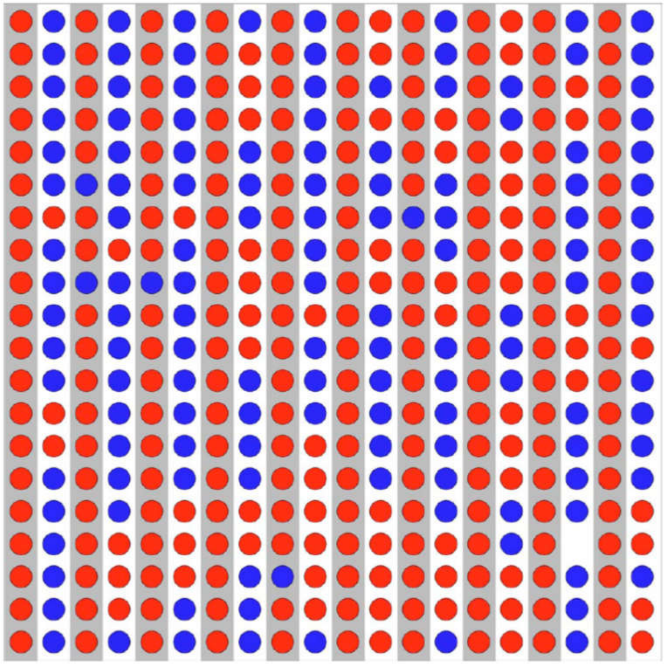
Adsorption:	CO - unimolecular, O_2 – dissociative no barrier rate given by impingement $k \approx S_0 p/(2\pi m k_B T)$
Desorption:	CO – 1st order, O_2 – 2nd order out of DFT adsorption well (= barrier) prefactor from detailed balance
Diffusion:	hops to nearest neighbor sites site and element specific barrier from DFT (TST) prefactor from DFT (hTST)
Reaction:	site specific immediate desorption, no readsorption barrier from DFT (TST) prefactor from detailed balance

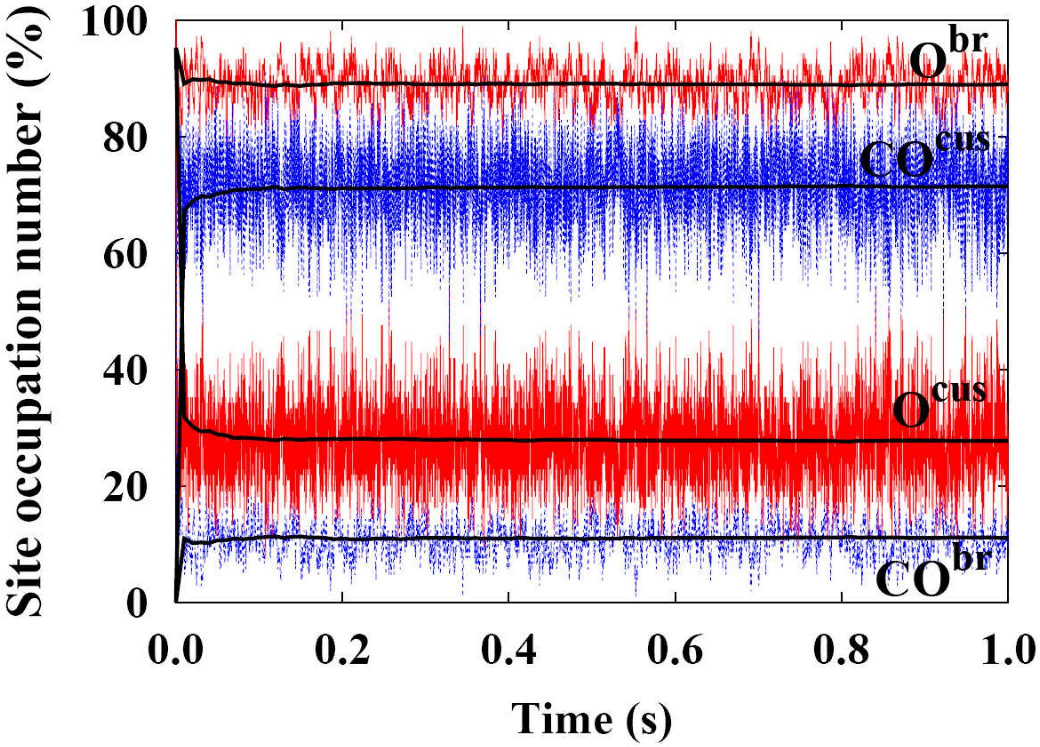
26 elementary processes
considered

K. Reuter and M. Scheffler, Phys. Rev. B 73, 045433 (2006)

Monte Carlo sampling – applications

T = 600 K p_{O2} = 1 atm p_{CO} = 7 atm





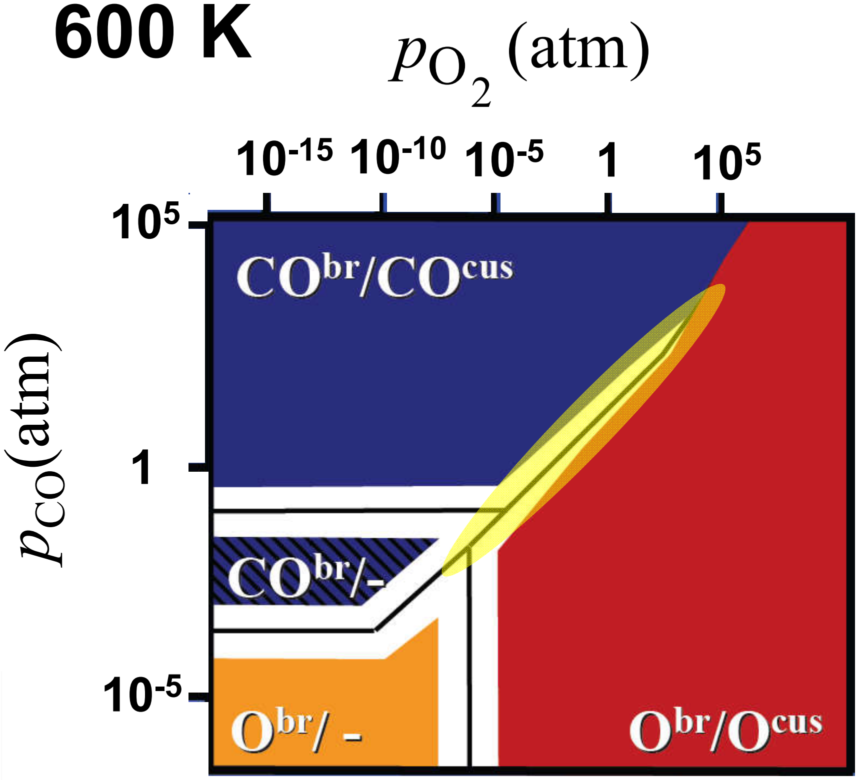
K. Reuter, D. Frenkel and M. Scheffler, Phys. Rev. Lett. 93, 116105 (2004)

K. Reuter, C. Stampfl, and M. Scheffler, Handbook of materials modeling, part A. Methods, p. 149, Springer, Berlin (2005)

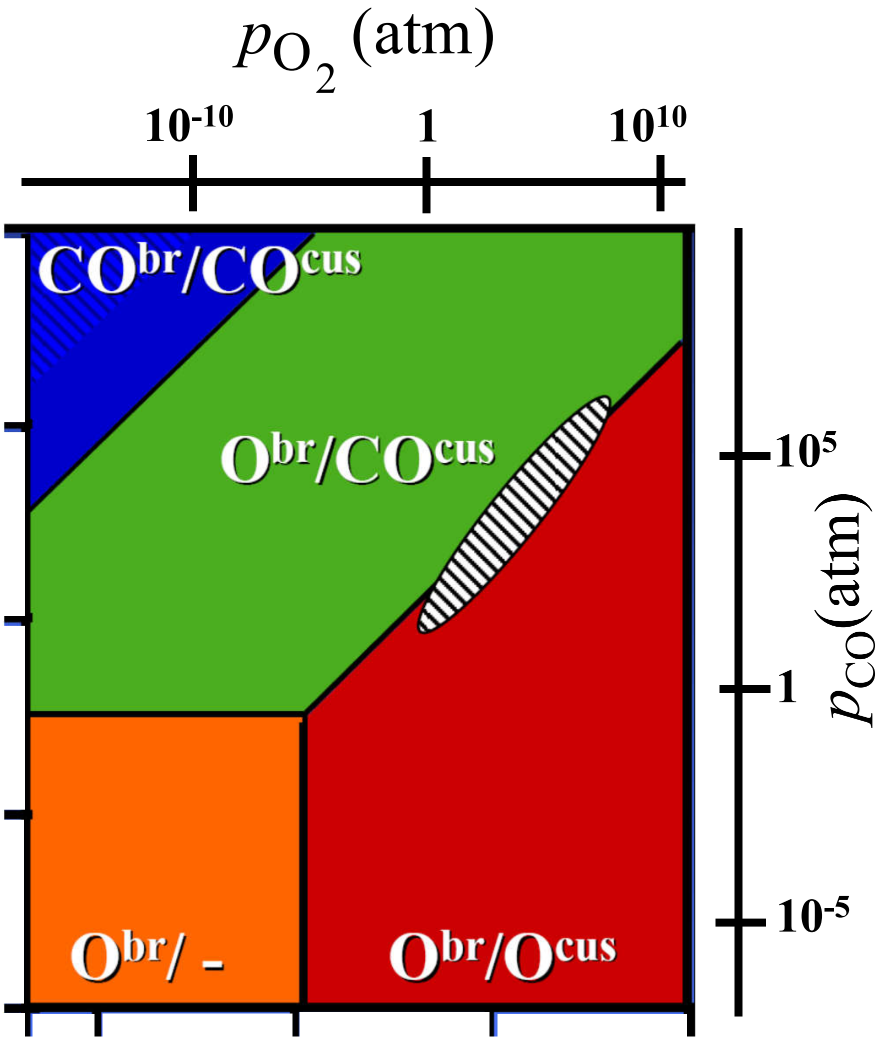
Monte Carlo sampling – applications

❒ **kMC phase diagrams**

600 K



kinetics

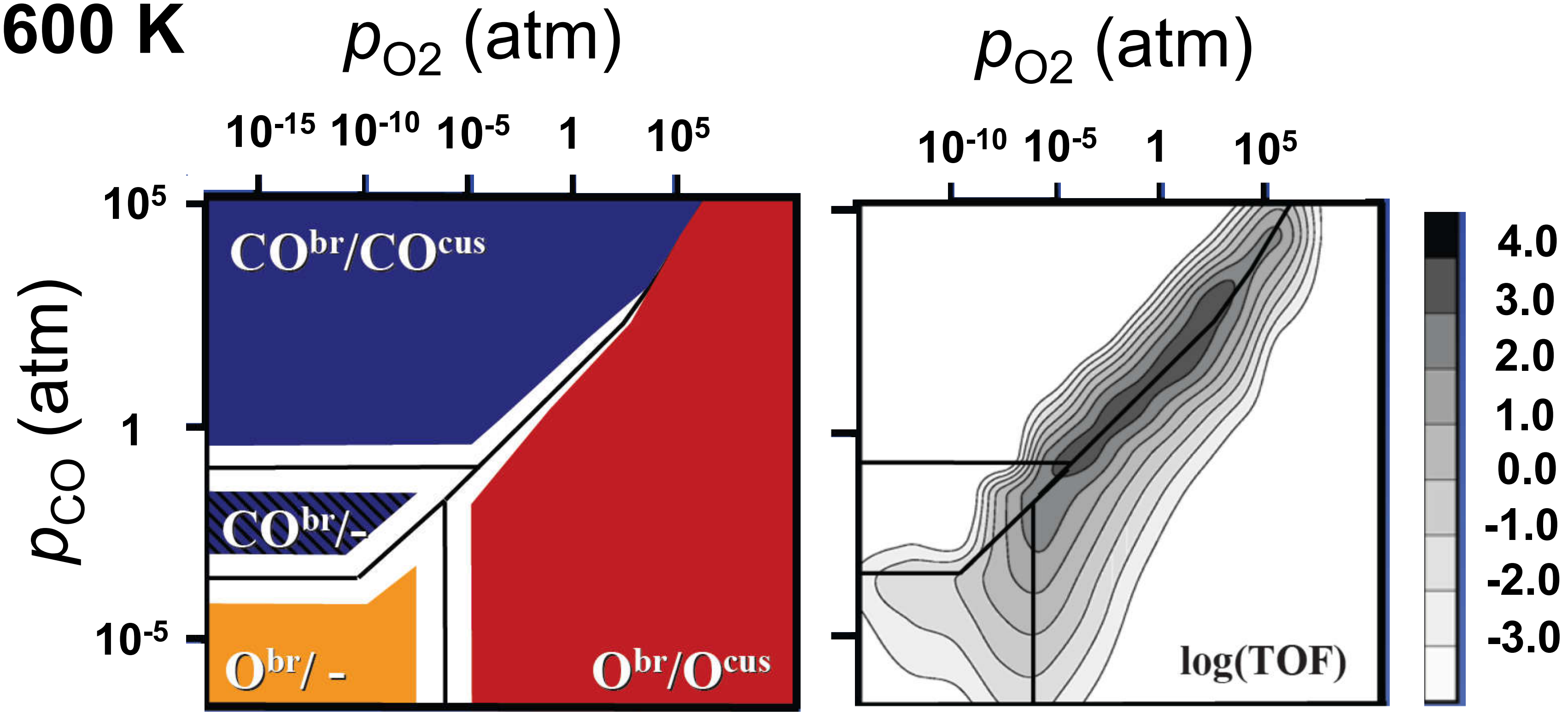


thermodynamics

Monte Carlo sampling - applications

- ❒ **(p_{O2}, p_{CO})-map of catalytic activity**

600 K



K. Reuter, D. Frenkel and M. Scheffler, Phys. Rev. Lett. 93, 116105 (2004)

Conclusions

- ❒ **Molecular dynamics - system dynamics at finite *T***

  enslemble average from time average, diffusion coefficients, thermal conductivity, viscosity

- ❒ **Monte Carlo - clever random walks**

  calculating integrals by random sampling, ensemble averages, electronic problem, long-time kinetics

- ❒ **Combined - replica-exchange (parallel tempering) MD**

  better sampling of configurational space