Density Functional Theory: from theory to Applications

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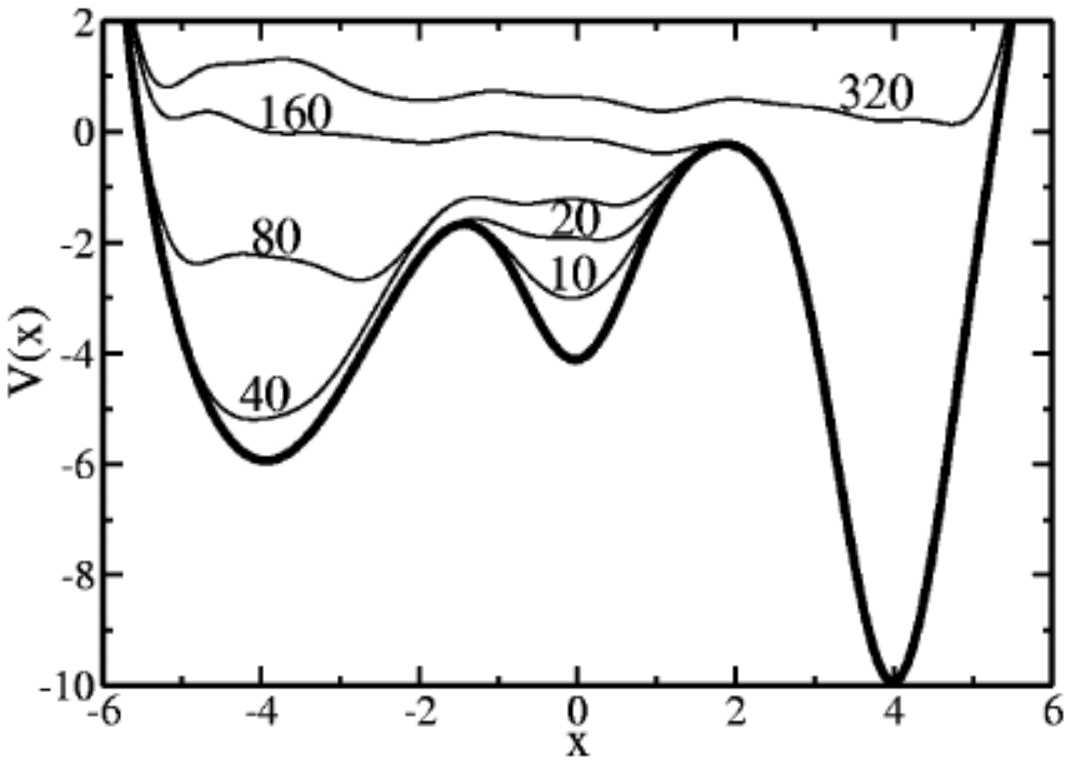
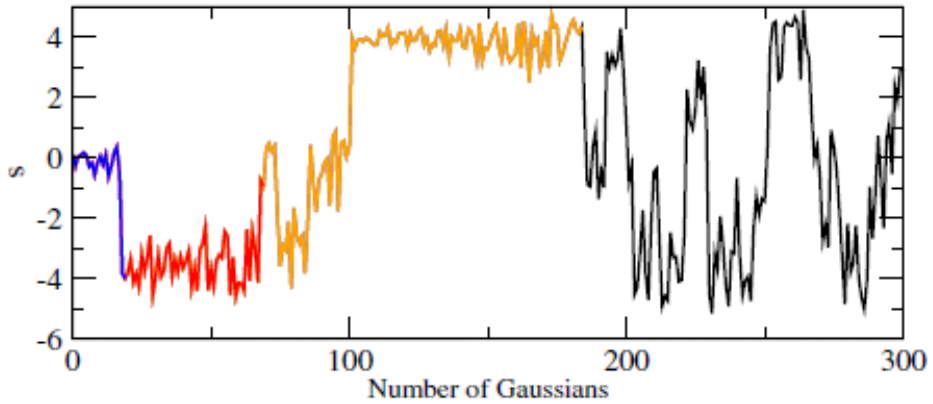
Sampling rare events and free energies: metadynamics

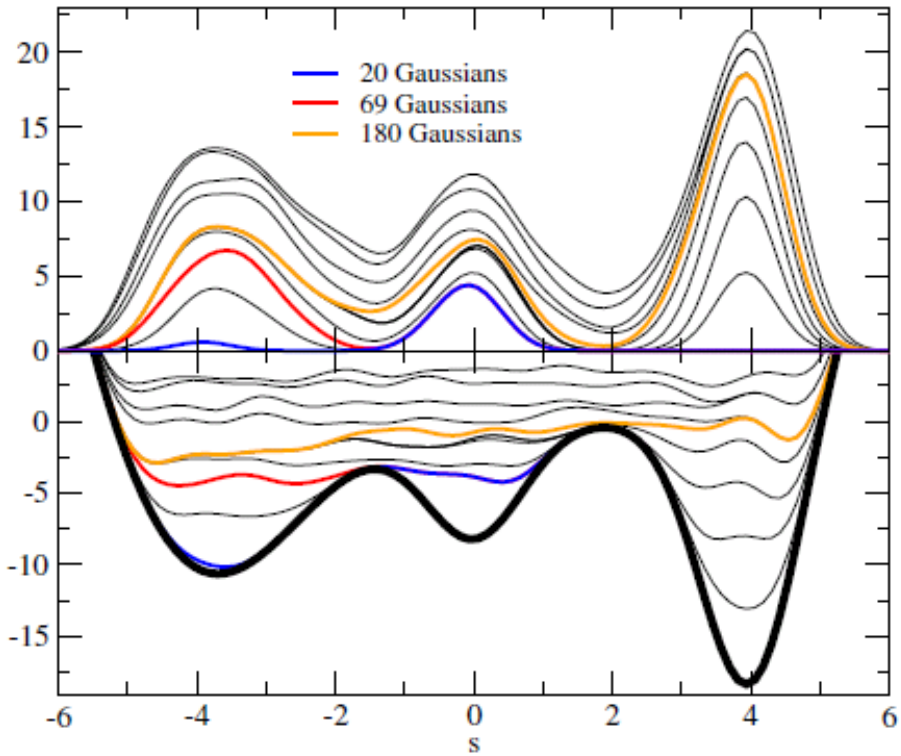
- Large barrier-activated processes
- time-dependent bias potential
- extended Lagrangian formalism
- Basic idea: during the MD dynamics preventing the system revisiting area in the configuration space where it has been in the past using a history dependent bias potential

- Laio A and Parrinello M 2002 Proc. Natl Acad. Sci. USA 99 12562.
- Iannuzzi M, Laio A and Parrinello M 2003 Phys. Rev. Lett. 90 238302.
- Ensing B, De Vivo M, Liu Z, Moore P, and Klein M, Acc. Chem. Res. 2006, 39, 73.
- Laio A and Gervasio FL, 2008 Rep. Prog. Phys. 71 126601

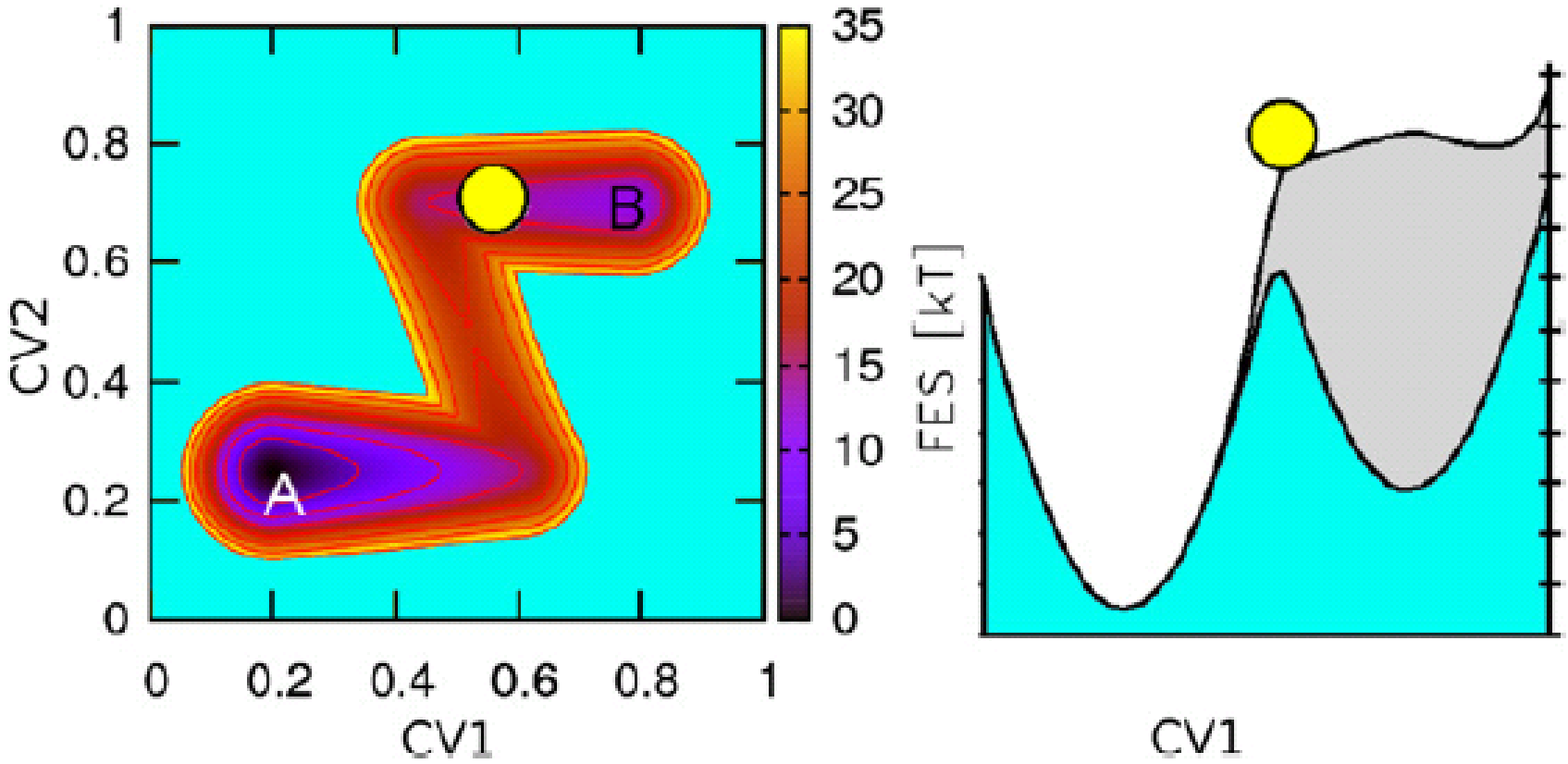


Filling a 1D model potential with hills, starting in the middle well. After 20 hills, the system escapes to the well on the left and so forth.


s
Number of Gaussians


20 Gaussians
69 Gaussians
180 Gaussians
s

It is crucial to introduce a small set of (scaled and dimensionless) collective variables $\mathbf{S} = \{S_1, ..., A_\alpha, ..., S_{N_s}\}$ defined in terms of the Cartesian coordinates of the nuclei $\mathbf{R} = \{\mathbf{R}_1, ..., \mathbf{R}_I, ..., \mathbf{R}_N\}$.
$N_s \ll N$
reduction of dimensionality makes possible the filling of minima with a manageable number of Gaussian.
Collective variables must include all relevant slow motions.


1
0.8
0.6
0.4
0.2
0
CV2
0
0.2
0.4
0.6
0.8
1
CV1
A
B
35
30
25
20
15
10
5
0
FES [kT]
CV1

The extended Lagrangian is:

$$\mathcal{L} = \mathcal{L}_{CP} + \sum_{\alpha=1}^{N_s} \frac{1}{2}\mu_\alpha^s \dot{s}_\alpha^2(t) - \sum_{\alpha=1}^{N_s} \frac{1}{2} k_\alpha \left[S_\alpha(\mathbf{R}(t)) - s_\alpha(t)\right]^2 + V(t,[s]) \quad (1)$$

where $\{\mathbf{s}_\alpha\}$ are the fictious variables;
third term is a restraining potential that keeps the instantaneous dynamic variables close to the collective variables $\mathbf{S}_\alpha$.
The time dependent potential is:

$$V(t,[\mathbf{s}]) = \int_{t_0}^{t} W(t') exp\left[-\frac{((s(t)-s(t'))^2}{2(\Delta s^\perp)^2}\right] dt' \quad (2)$$

The time dependent potential:

$$V(t,[\mathbf{s}]) = \int_{t_0}^{t} W(t') exp\left[-\frac{((s(t)-s(t'))^2}{2(\Delta s^{\perp})^2}\right] dt' \tag{3}$$

can be expressed in a discrete form as:

$$V(t,[\mathbf{s}]) \approx V(t,\{\mathbf{s}(t_i)\}) = \sum_{i=0}^{imax} W(t_i) exp\left[-\frac{((s(t)-s(t'))^2}{2(\Delta s^{\perp})^2}\right] \tag{4}$$

$$\times exp\left[-\frac{[(\mathbf{s}(t_{i+1})-\mathbf{s}(t_i))\cdot(\mathbf{s}(t)-\mathbf{s}(t_i))]^2}{2|\mathbf{s}(t_{i+1})-\mathbf{s}(t_i)|^4}\right] \tag{5}$$

$\Delta_s t$ is the meta-timestep ($\Delta_s t \gg \Delta t$)
$\Delta s^{\perp}$ is the width of the Gaussian orthogonal to the direction of motion in the **s**-space
$\Delta s^{\parallel}(t_i) = |\mathbf{s}(t_{i+1}) - \mathbf{s}(t_i)|$ is adapted to the surface topology
$W(t_i)$ is the height of the Gaussian can be fixed or adaptive.

the associated Euler-Lagrange equations are:

$$\frac{d}{dt}\frac{\partial \mathcal{L}}{\partial \dot{s}_\alpha} = \frac{\partial \mathcal{L}}{\partial s_\alpha} \quad (6)$$

$$\frac{d}{dt}\frac{\partial \mathcal{L}_{\mathcal{CP}}}{\partial \dot{\mathbf{R}}_I} = \frac{\partial \mathcal{L}_{\mathcal{CP}}}{\partial \mathbf{R}_I} \quad (7)$$

$$\frac{d}{dt}\frac{\partial \mathcal{L}_{\mathcal{CP}}}{\partial \dot{\phi}_i^*} = \frac{\partial \mathcal{L}_{\mathcal{CP}}}{\partial \phi_i^*} \quad (8)$$

- the trajectory that are generated do not reflect physical real time dynamics
- the fictious dynamics is used to explore the free energy landscape

- The adiabatic decoupling of the collective variable dynamics from the auxiliary electronic wave function dynamics requires additional attention to avoid deviation from the Born-Oppenheimer ground state.
- The meta timestep Δt_s (dropping rate of the Gaussian) must be larger than the ab initio molecular dynamics time-step Δt. Typically $\Delta t_s = 10 - 100 \Delta t$.

Metadynamics is used to map the free energy profile:

$$\mathcal{F}(\mathbf{s}) = -K_B T ln P(\mathbf{s}) \tag{9}$$

where

$$P(\mathbf{s}) = \frac{1}{\mathcal{Z}} \prod_{\alpha} [\delta(S_\alpha(\mathbf{R}) - s_\alpha)] \, exp\left[-\frac{E^{KS}(\mathbf{R})}{K_B T}\right] d\mathbf{R} \tag{10}$$

It can be shown that:

$$\Delta\mathcal{F}(\mathbf{s}) = -lim_{t\to\infty} V(t, \{\mathbf{s}(t_i)\}) \tag{11}$$

and the associated error can be estimated as:

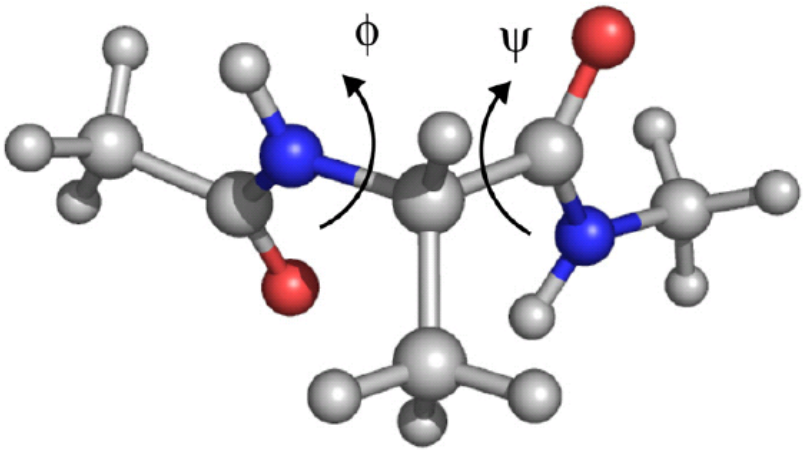
$$\epsilon \propto \sqrt{\frac{\bar{W}\Delta s^{\perp}}{\Delta_s t}} \tag{12}$$

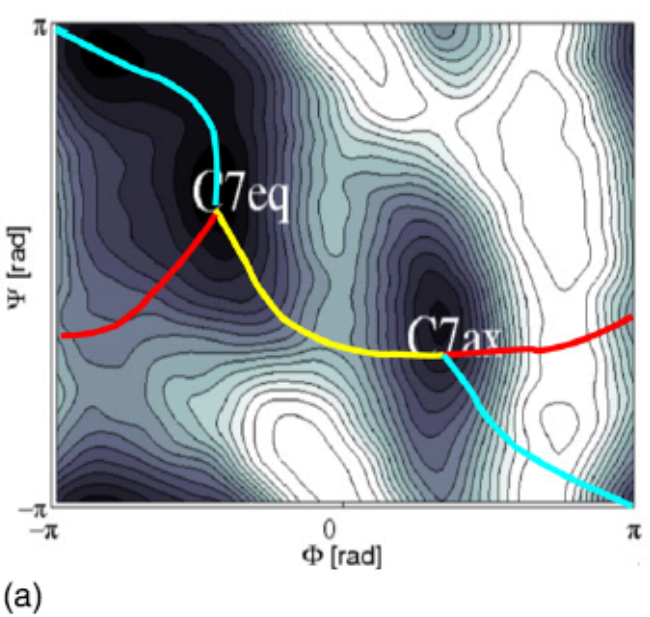
The error

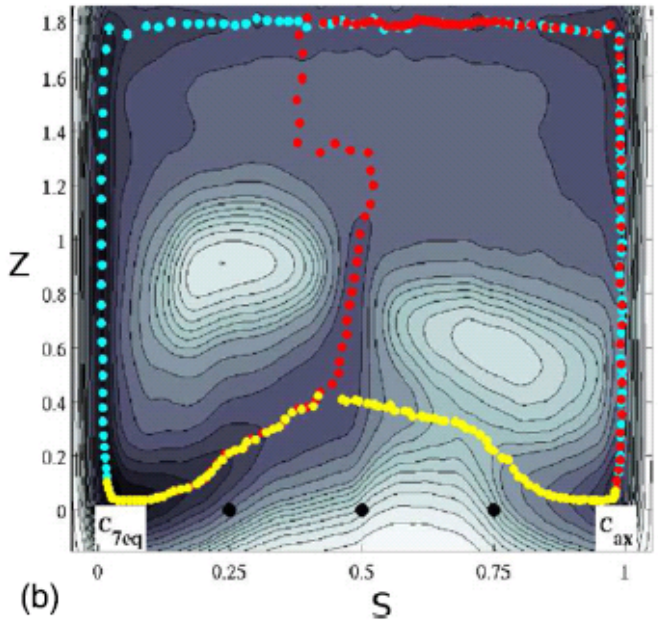
$$\epsilon \propto \sqrt{\frac{\bar{W}\Delta s^{\perp}}{\Delta_s t}}$$

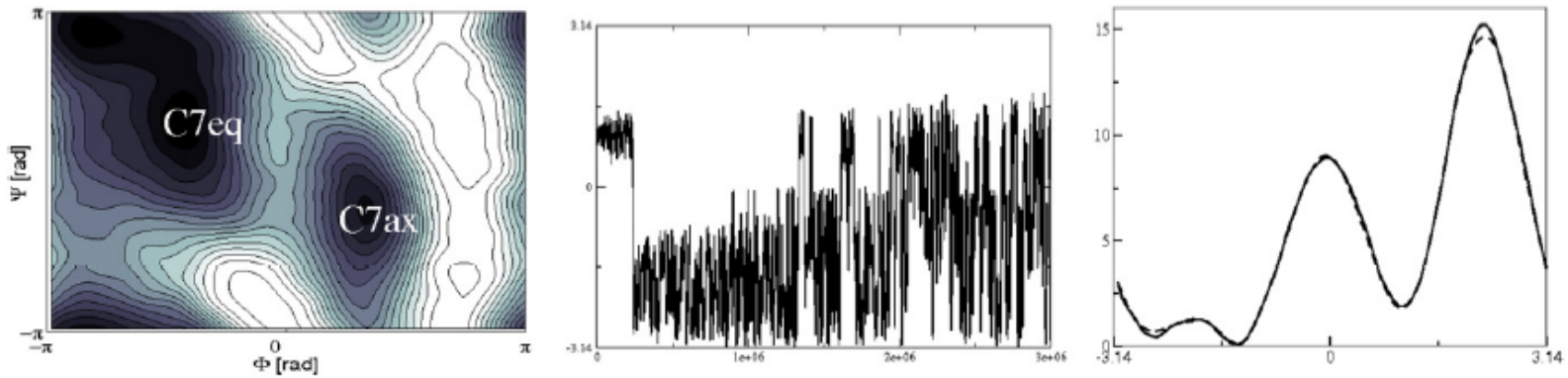
does not depend on μ_α^s and on k_α.
Recipe to choose metadynamics parameters: preliminary run without dropping Gaussians to estimate the fluctuations of the collective variables.

The metadynamics method can be used with different Hamiltonian, e.g. in conjunction with classical force-field based MD.

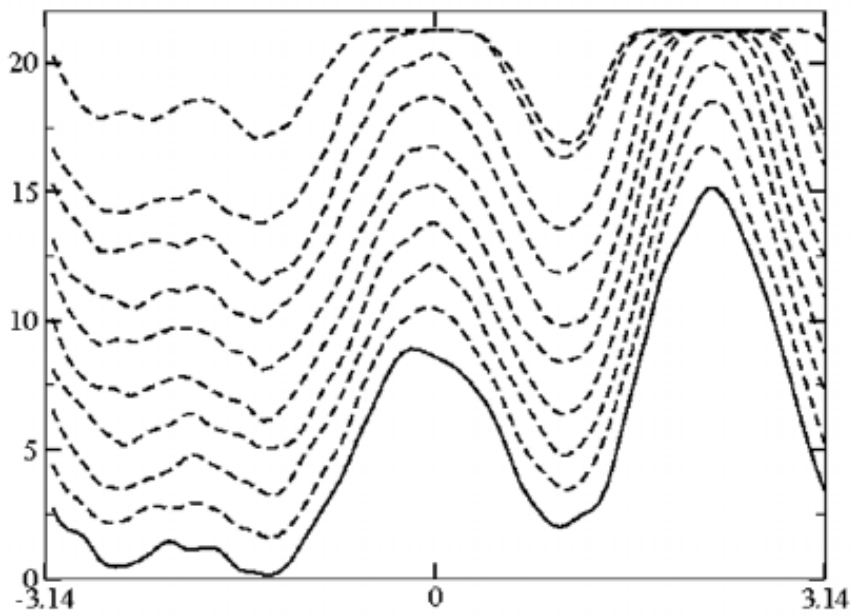








The initial configuration corresponds to a C7ax conformation. As the history-dependent potential is added, the fluctuations of ψ increase, until the system fills the free energy basin to reach a C7eq conformation. After approximately 0.8 ns, the added potential has mostly filled the two energy basins and the CV starts to show a diffusive behavior, visiting repeatedly the two basins.



Accumulated profiles at 0.8 ns intervals. It can be seen that after 2.4 ns the profile has reached an almost complete convergence.

In conclusion, a metadynamics run requires

- Equilibrate the system by normal molecular dynamics
- Choose the collective variables, taking into account (i) the performance of metadynamics is optimal with two or three variables. One variable is practically equivalent to thermodynamic integration.
- Choose the metadynamics parameters, keeping in mind that: (i) width(s) chosen by monitoring the value of standard deviation the CV(s) in a finite temperature run. (ii) height W and the time Δt_s are not independent: the accuracy is determined by their ratio.
- Check the convergence of the results: the history-dependent potentials evaluated at different times must be approximately similar.

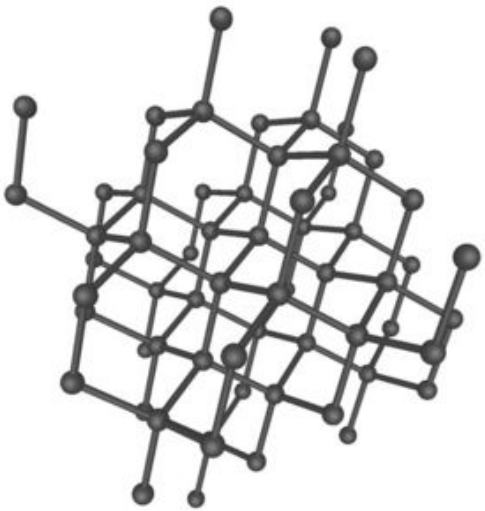
Parrinello-Rahman & metadynamics

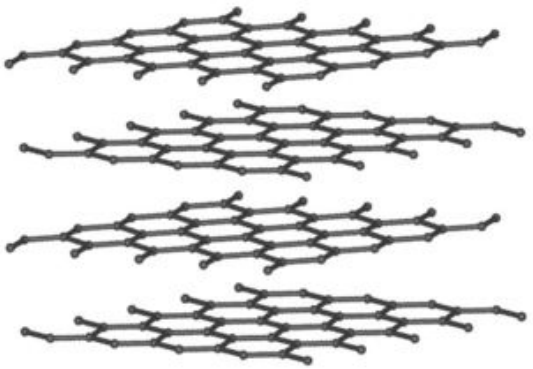
- In the Parrinello-Rahman method the box is allowed to change its shape in order to comply with a new structure.
- Often the system has to cross a significant barrier in order to transform from one structure to another. One possibility: overpressurize the system close to the point of mechanical instability.
- PR can be combined with metadynamics to explore the Gibss free energy landscape
- 6 independent components of h now represent collective coordinates

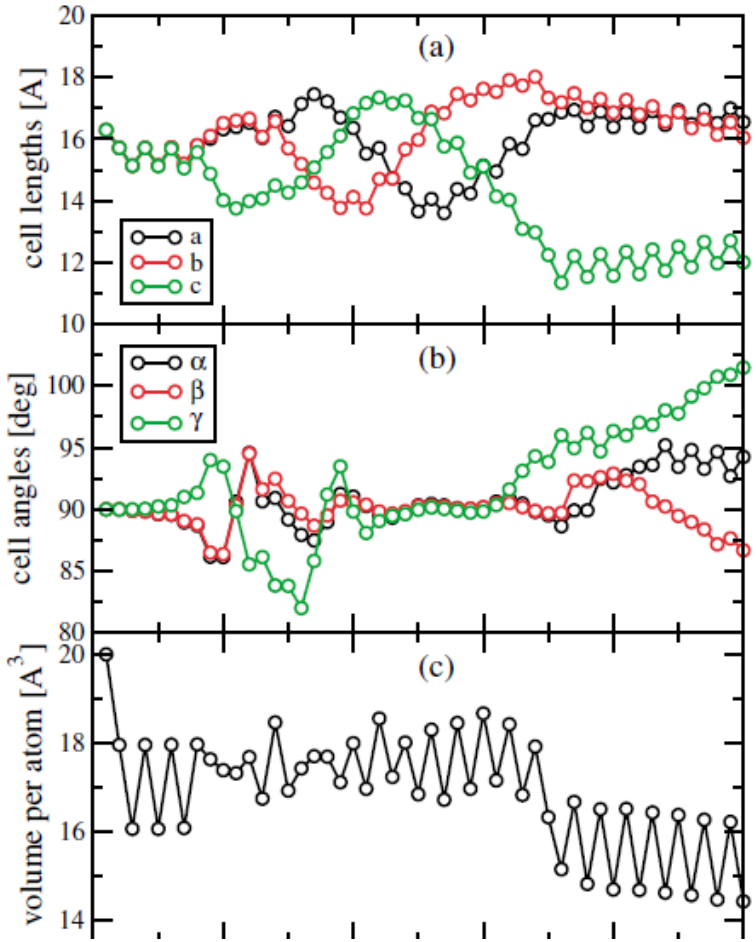
R. Martonak, A. Laio, and M. Parrinello, Phys. Rev. Lett. 90, 075503 (2003)

Example: a tight binding model of Si

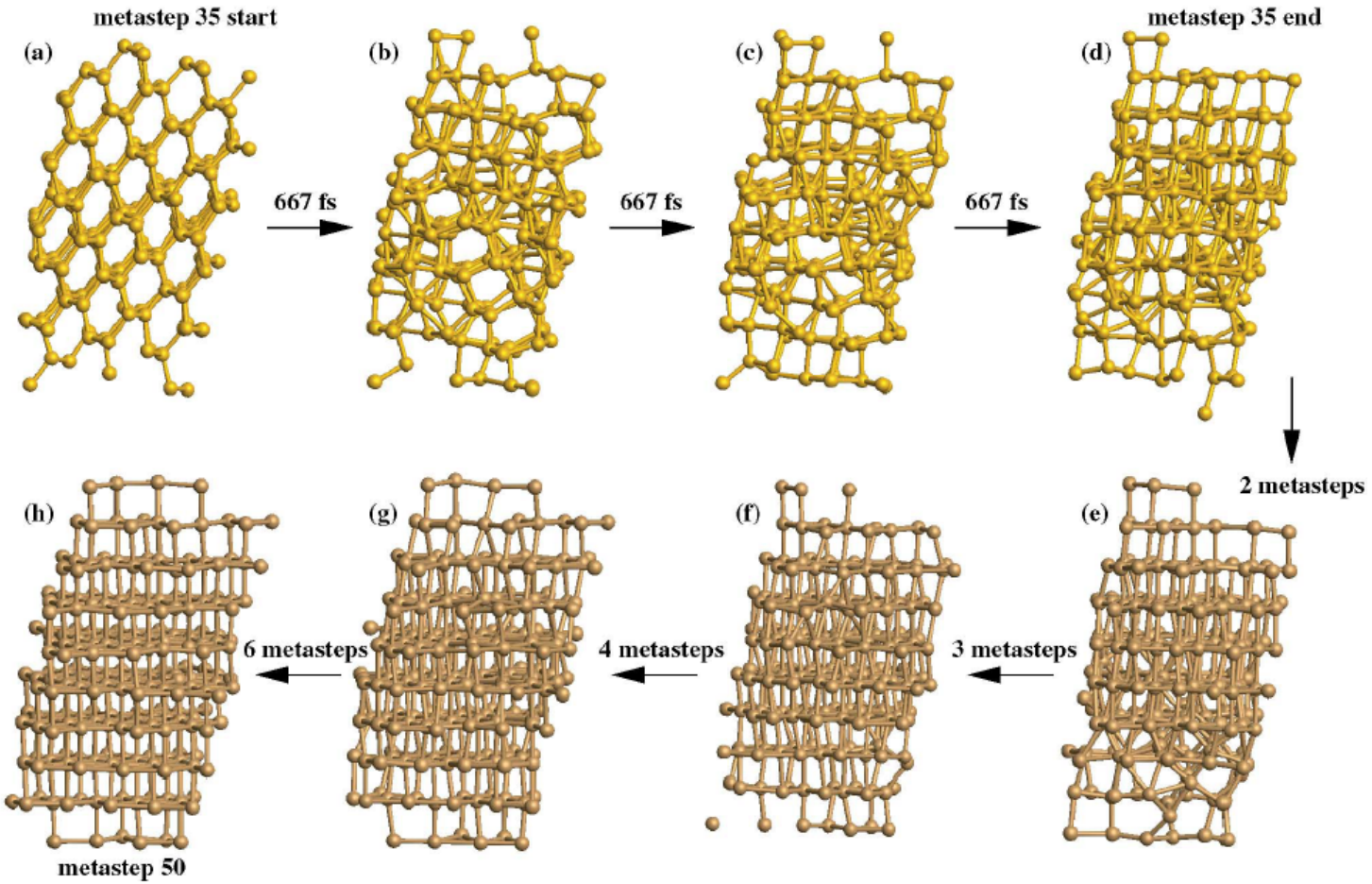
The tight-binding parametrization captures some of the main features of the Si phase diagram and provides a convenient test model.
A supercell of 216 atoms is used and only the Γ point of the Brillouin zone is considered.
At P=1 atm the equilibrium structure is the diamond, the two high-pressure phases are the β-tin (metastable) and simple hexagonal (SH).







At metastep 35 there is a phase transition: the system had made a transition to the SH structure, whose parameters are $a = 2.61\mathring{A}$ and $c = 2.48\mathring{A}$.


metastep 35 start
(a)
667 fs
(b)
667 fs
(c)
667 fs
(d)
metastep 35 end
2 metasteps
(e)
3 metasteps
(f)
4 metasteps
(g)
6 metasteps
(h)
metastep 50