Density Functional Theory: from theory to Applications

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Thermostats

- Thermostat on the electrons
- Nose'-Hoover chain thermostat

Imposing pressure: barostats

- Alternative approach for clusters

Sampling rare events and free energies: metadynamics

- Example: Alanine dipeptide
- Parrinello-Rahman & metadynamics
- Example: a tight binding model of Si

Zero or small electronic gaps: thermostatted electrons

- One way to (try to) overcome the problem in coupling of electronic and ionic dynamics is to thermostat also the electrons (Blöchl & Parrinello, PRB 1992)
- Thus electrons cannot heat up; if they try to, thermostat will adsorb the excess heat
- Target fictitious kinetic energy $E_{kin,0}$ instead of temperature
- Mass of thermostat to be selected appropriately:
  Too light: Adiabacity violated (electrons may heat up)
  Too heavy: Ions dragged excessively
- Note: Introducing the thermostat the conserved quantity changes

$$M_I \ddot{\mathbf{R}}_I(t) = -\frac{\partial}{\partial \mathbf{R}_I} < \Psi_0 | H_e^{KS} | \Psi_0 > -M_I \dot{R}_I \dot{x}_R \quad (1)$$

$$\mu \ddot{\phi}_i(t) = -H_e^{KS} \phi_i + \sum_j \Lambda_{ij} \phi_j - \mu \dot{\phi}_i \dot{x}_e \quad (2)$$

in blue are the frictious terms governed by the following equations:

$$Q_e \ddot{x}_e = 2 \left[\sum_i \mu \dot{\phi}^2 - E_{kin,0} \right] \quad (3)$$

$$Q_R \ddot{x}_R = 2 \left[\sum_I \frac{1}{2} M_I \dot{R}^2 - \frac{1}{2} g K_B T \right] \quad (4)$$

The masses Q_e and Q_R determines the time scale for the thermal fluctuations. The conserved quantity is now:

$$E_{tot} = \sum_I \frac{1}{2} M_I \dot{\mathbf{R}}_I^2 + \sum_i \mu < \dot{\phi}_i | \dot{\phi}_i > + < \Psi_0 | H_e^{KS} | \Psi_0 > + \frac{1}{2} Q_e \dot{x}_e^2 + 2 E_{kin,0} x_e + \frac{1}{2} Q_R \dot{x}_R^2 + g K_B T x_R \quad (5)$$

Standard Nose'-Hoover thermostat suffers from non-ergodicity problems for certain classes of Hamiltonian, so a closely related technique has been proposed, the Nose'-Hoover chain thermostat. For the nuclear part:

$$M_I \ddot{\mathbf{R}}_I = -\nabla E^{KS} - M_I \dot{\xi}_1 \dot{\mathbf{R}}_I \tag{6}$$

$$Q_1^n \ddot{\xi}_1 = \left[\sum_I M_I \dot{R}_I^2 - g K_B T \right] - Q_1^n \dot{\xi}_1 \dot{\xi}_2 \tag{7}$$

$$Q_k^n \ddot{\xi}_k = 2 \left[Q_{k-1}^n \dot{\xi}_{k-1}^2 - K_B T \right] - Q_k^n \dot{\xi}_k \dot{\xi}_{k+1} (1 - \delta_{kK}) \tag{8}$$

For the electronic part:

$$\mu \ddot{\phi}_i = -H_e^{KS} \phi_i + \sum_{ij} \Lambda_{ij} \phi_j - \mu \dot{\eta}_1 \dot{\phi}_i \tag{9}$$

$$Q_1^e \ddot{\eta}_1 = \left[\sum_i^{occ} \mu < \phi_i | \phi_i > - T_1^0 \right] - Q_1^e \dot{\eta}_1 \dot{\eta}_2 \tag{10}$$

$$Q_I^n \ddot{\eta}_I = 2 \left[Q_{I-1}^n \dot{\eta}_{I-1}^2 - \frac{1}{\beta_e} \right] - Q_I^e \dot{\eta}_I \dot{\eta}_{I+1} (1 - \delta_{IL}) \tag{11}$$

- Separate chains composed of K and L coupled thermostats are attached to the nuclear and electronic equations of motion, respectively
- Masses for the thermostats are chosen so that there overlap of the thermostat and system power spectra.

$$Q_1^n = \frac{gK_B T}{\omega_n^2}, \ \ldots \ Q_k^n = \frac{gK_B T}{\omega_n^2}, \tag{12}$$

$$Q_1^e = \frac{2T_e^0}{\omega_e^2}, \ \ldots \ Q_l^e = \frac{2T_e^0}{\omega_e^2} \tag{13}$$

- massive thermostatting method: NH chains for individual nuclear degree of freedom. Accelerate expensive equilibration periods

Energy and Momentum conservation

In micro-canonical classical molecular simulations the total energy and the total momentum are conserved.
In the case of thermostatted NVT simulations the constant of motion is:

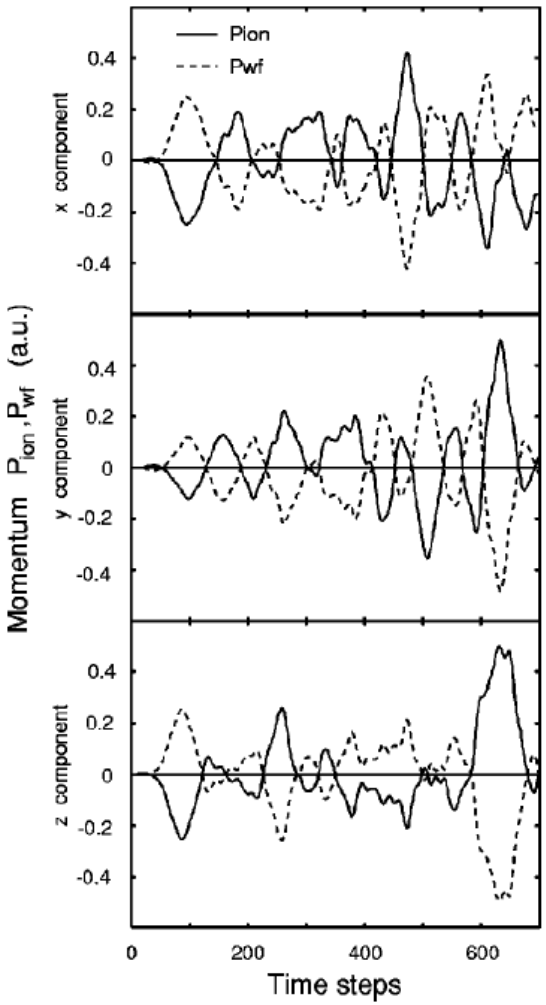
$$E_{cons}^{NVT} = \sum_{i}^{occ} \mu < \dot{\phi}_i | \dot{\phi}_i > + \sum_{I} \frac{1}{2} M_I \dot{\mathbf{R}}_I^2 + E^{KS}\left[\{\phi_i\}, \{\mathbf{R}_I\}\right] \quad (14)$$

$$+ \sum_{I=1}^{L} \frac{1}{2} Q_I^e \dot{\eta}_I^2 + \sum_{I=2}^{L} \frac{\eta_I}{\beta_e} + 2 T_e^0 \eta_1 + \sum_{k=1}^{K} \frac{1}{2} Q_k^n \dot{\xi}_k^2 + \sum_{k=2}^{K} K_b T \xi_k + g K_b T \xi_1 \quad (15)$$

In micro-canonical CPMD a generalized linear momentum is conserved:

$$\mathbf{P}_{CP} = \mathbf{P}_n + \mathbf{P}_e = \sum_{I} \mathbf{P}_I + \sum_{i}^{occ} \mu < \dot{\phi}_i | -\frac{1}{2} \nabla_r | \phi_i > + c.c. \quad (16)$$

where $\mathbf{P}_I = M_I \dot{\mathbf{R}}_I$.



Time evolution of P_{ion} (solid line) and P_{wf} (dashed line) in the diamond structure of Si. From the upper panel, three components, x, y, z, are shown, respectively. (*Morishita and Nose'Phys Rev B , 59, 15126 (1999)*)

Imposing pressure: barostats

Original version from Andersen[1] devised to allow isotropic fluctuations in the volume of the supercell.
Variable cell approach: allows structural phase transition in solids at finite temperature. Parrinello-Rahman[2]
Built an extended Lagrangian with additional dynamical variables $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$, the primitive Bravais lattice vectors.
Using the $3X3$ matrix $\mathbf{h} = [\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3]$ which define the volume Ω, the scaled coordinates $\mathbf{S}$ are defined by $\mathbf{R}_I = \mathbf{h}\mathbf{S}_I$.
the normalized original orbitals are transformed according to:

$$\phi_i(\mathbf{r}) = \frac{1}{\Omega}\phi_i(\mathbf{s}) \tag{17}$$

The cell-variable extended Lagrangian is:

$$\begin{aligned}\mathcal{L} &= \sum_i \mu < \dot{\phi}(\mathbf{s})_i | \dot{\phi}_i(\mathbf{s}) > -E^{KS}[\{\phi_i\}, \{\mathbf{h}\mathbf{S}_I\}] \\ &+ \sum \Lambda_{ij}(< \phi_i(\mathbf{s}) | \phi_j(\mathbf{s}) > -\delta_{ij}) + \sum \frac{1}{2} M_I(\dot{\mathbf{S}}_I^T \mathbf{h}^T \mathbf{h} \dot{\mathbf{S}}_I) + \frac{1}{2} W Tr \dot{\mathbf{h}}^T \dot{\mathbf{h}} - p\Omega\end{aligned} \tag{18}$$

$$\mathcal{L} = \sum_i \mu < \dot{\phi}(\mathbf{s})_i | \dot{\phi}_i(\mathbf{s}) > - E^{KS}[\{\phi_i\}, \{\mathbf{h}\mathbf{S}_I\}] \quad (19)$$

$$+ \sum_{ij} \Lambda_{ij}(< \phi_i(\mathbf{s}) | \phi_j(\mathbf{s}) > - \delta_{ij}) + \sum_I \frac{1}{2} M_I(\dot{\mathbf{S}}_I^T \mathbf{h}^T \mathbf{h} \dot{\mathbf{S}}_I) + \frac{1}{2} W Tr \dot{\mathbf{h}}^T \dot{\mathbf{h}} - p\Omega$$

- nine additional degrees of freedom associated with lattice vectors of supercell $\mathbf{h}$.
- This constant-pressure CPMD reduce to constant-volume CPMD in the limit $\dot{\mathbf{h}} \rightarrow 0$ (apart from a constant term $p\Omega$
- W is the fictious mass that controls the timescale of the cell dynamics

The resulting equations of motion are:

$$M_I \ddot{S}_{I,u} = -\sum_{v=1}^{3} \frac{\partial E^{KS}}{\partial R_{I,v}} (\mathbf{h}^T)^{-1}_{v,u} - M_I \sum_{v=1}^{3}\sum_{s=1}^{3} \mathcal{G}^{-1}_{uv} \dot{\mathcal{G}}_{vs} \dot{S}_{I,s} \quad (20)$$

$$\mu \ddot{\phi}_i(\mathbf{s}) = -\frac{\partial E^{KS}}{\partial \phi^*_i(\mathbf{s})} + \sum_j \Lambda_{ij} \phi_j(\mathbf{s}) \quad (21)$$

$$W \ddot{h}_{uv} = \Omega \sum_{s=1}^{3} (\Pi^{tot}_{us} - p\delta_{us})(\mathbf{h}^T)^{-1}_{sv} \quad (22)$$

where the total stress tensor is:

$$\Pi^{tot}_{us} = \frac{1}{\Omega} \sum_I M_I (\dot{\mathbf{S}}_I^T \mathcal{G} \dot{\mathbf{S}}_I)_{us} + \Pi_{us} \quad (23)$$

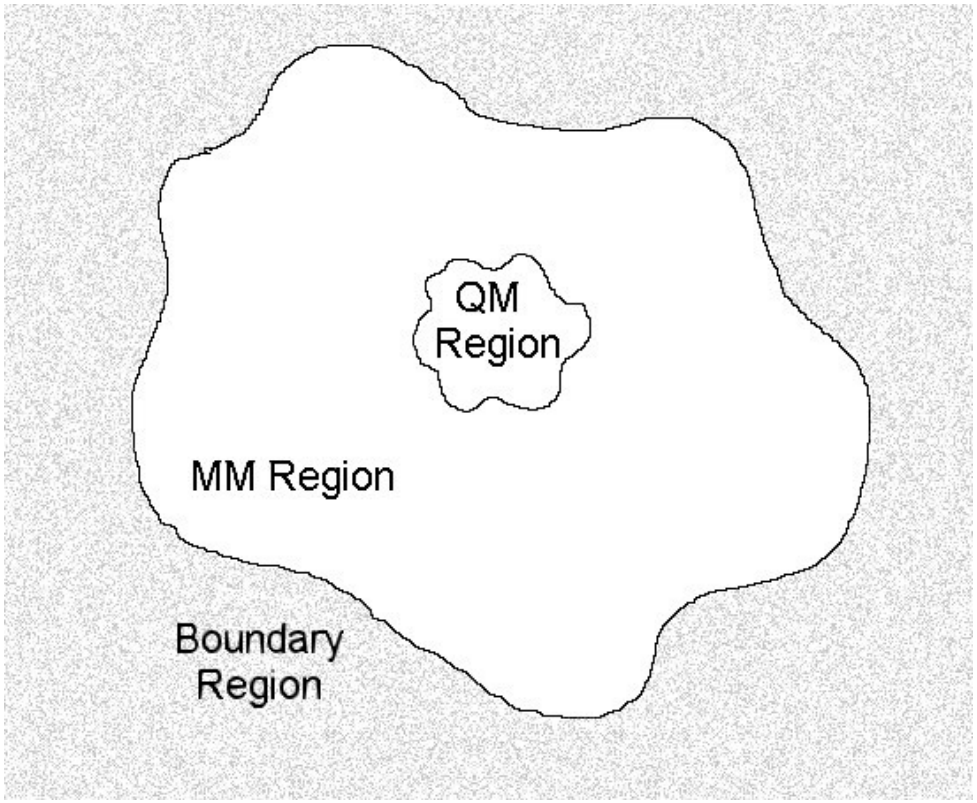
and Π_{us} is electronic stress tensor:

$$\Pi_{us} = -\frac{1}{\Omega} \sum_v \frac{\partial E_{tot}}{\partial h_{uv}} h^T_{vs} \quad (24)$$

- frictional feedback mechanism
- Parrinello-Rahman used in connection with metadynamics
- practical issue: basis set error, when using a fixed cutoff in plane wave with a varying cell

Alternative approach for clusters[3].

Idea: surrounding the finite cluster by a pressurizing medium described by N_L classical point particles.i (e.g. liquid of purely repulsive soft spheres).



[3] R. Martonak, C. Molteni and M. Parrinello, Comp Mat Science 20 (3-4) 2001, 293-299

Alternative approach for clusters[4].

Idea: surrounding the finite cluster by a pressurizing medium described by N_L classical point particles.i (e.g. liquid of purely repulsive soft spheres). The corresponding Lagrangian is:

$$\mathcal{L} = \sum_I \frac{1}{2} M_I \dot{\mathbf{R}}_I^2 + \sum_i \mu < \dot{\phi}(\mathbf{r})_i | \dot{\phi}_i(\mathbf{r}) > - E^{KS}[\{\phi_i\}, \{\mathbf{R}_I\}] \quad (25)$$

$$+ \sum_{ij} (< \phi(\mathbf{r})_i | \phi_j(\mathbf{r}) > - \delta_{ij}) + \sum_\alpha \frac{1}{2} M_\alpha \dot{\mathbf{X}}_\alpha^2 \quad (26)$$

$$+ - \sum_{I,\alpha} V_{C-L}(|\mathbf{R}_I - \mathbf{X}_\alpha|) - \sum_{\alpha<\beta} V_{L-L}(|\mathbf{X}_\alpha - \mathbf{X}_\beta|) \quad (27)$$

where M_α is the mass of a liquid particle at position $\mathbf{X}_\alpha$ and V_{C-L} and V_{L-L} are model pair potential to describe the cluster-liquid and the liquid-liquid interactions.

[4] R. Martonak, C. Molteni and M. Parrinello, Comp Mat Science 20 (3-4) 2001, 293-299

How is the pressure controlled?

For purely repulsive soft spheres:

$$V_{L-L}(r) = \epsilon_{L-L}\left(\frac{\sigma_{L-L}}{r}\right)^{12} \tag{28}$$

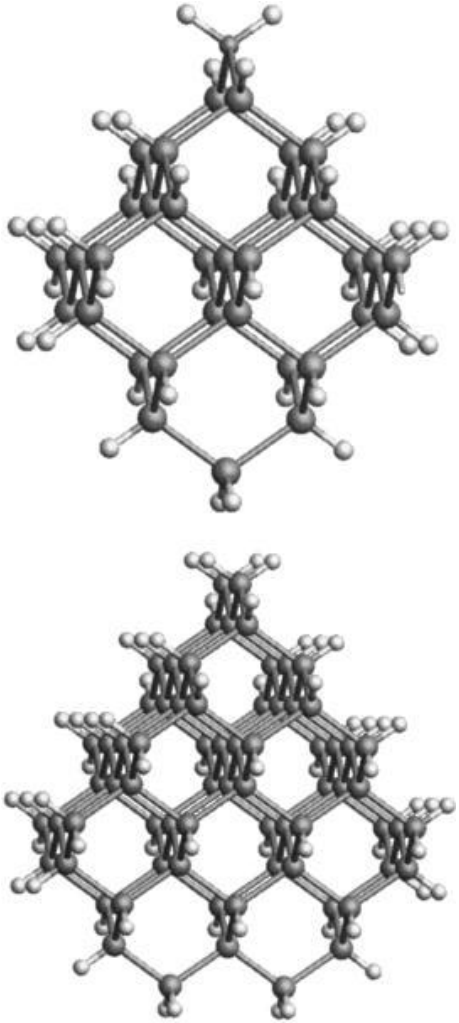
the equation of state gives:

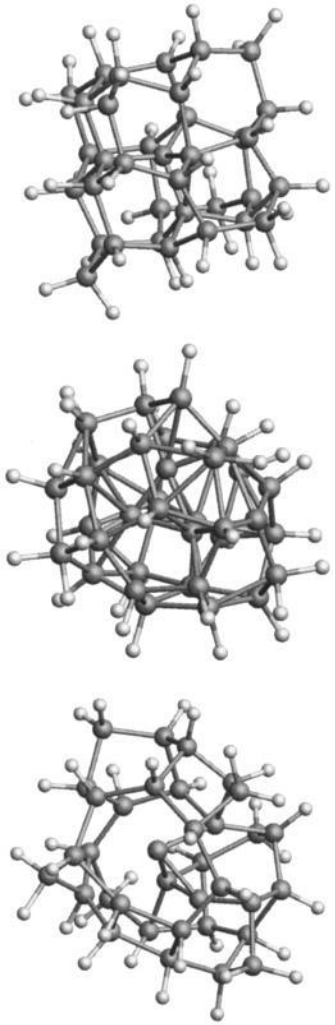
$$p = \frac{N_L K_B T}{\Omega_L}\xi(\tilde{\rho}) \tag{29}$$

where

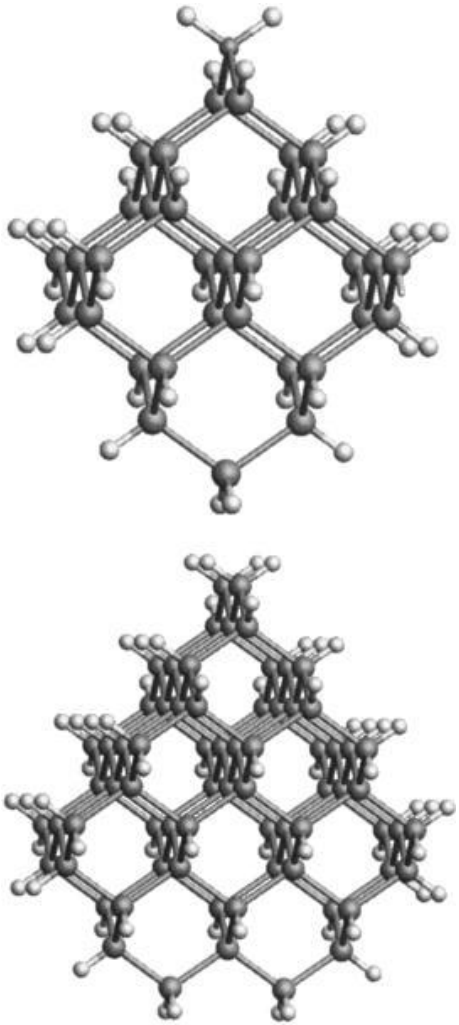
$$\xi(\tilde{\rho}) = \frac{N_L}{\Omega_L}\frac{\sigma_{L-L}^3}{\sqrt{2}}\left(\frac{\epsilon_{L-L}}{K_B T}\right)^{1/4} \tag{30}$$

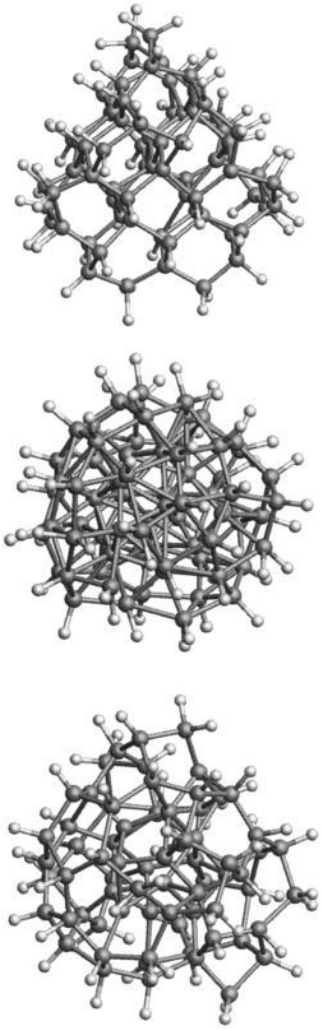
the pressure is adjusted tuning ϵ_{L-L}.





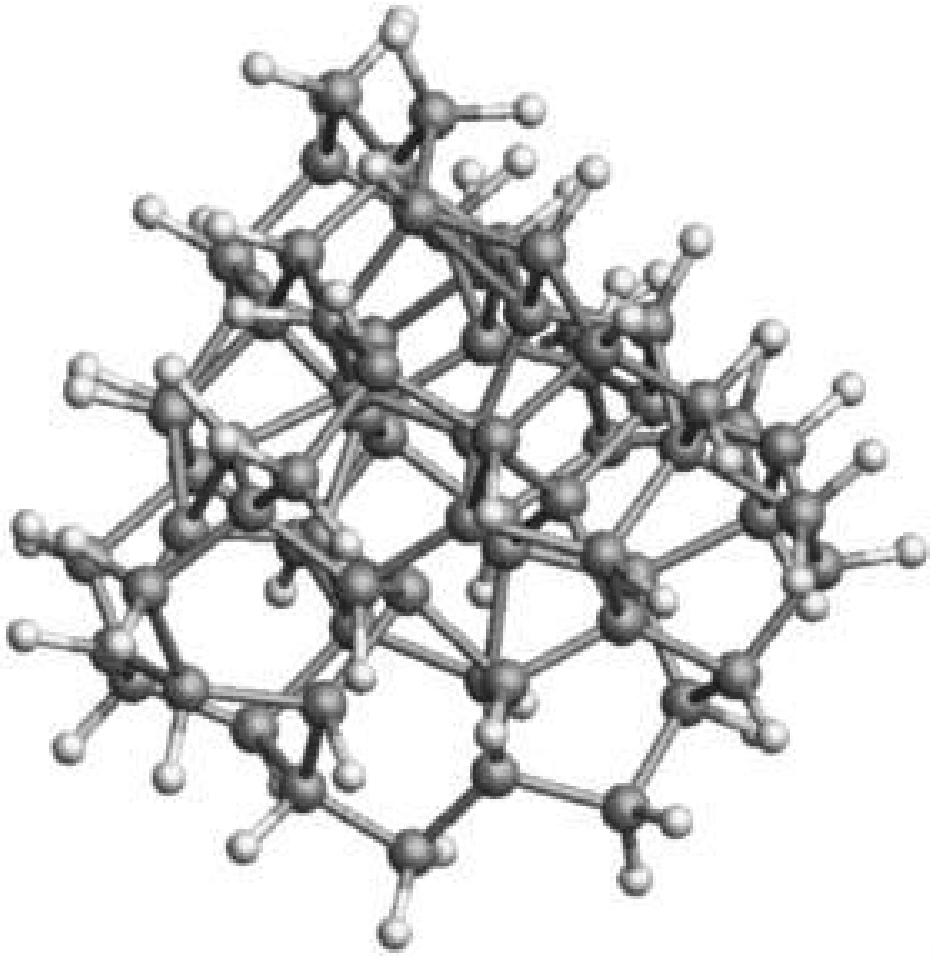
$Si_{35}H_{36}$ at 25 GPa (top), 35 GPa (center), and 5 GPa (after the pressure has been released, bottom).



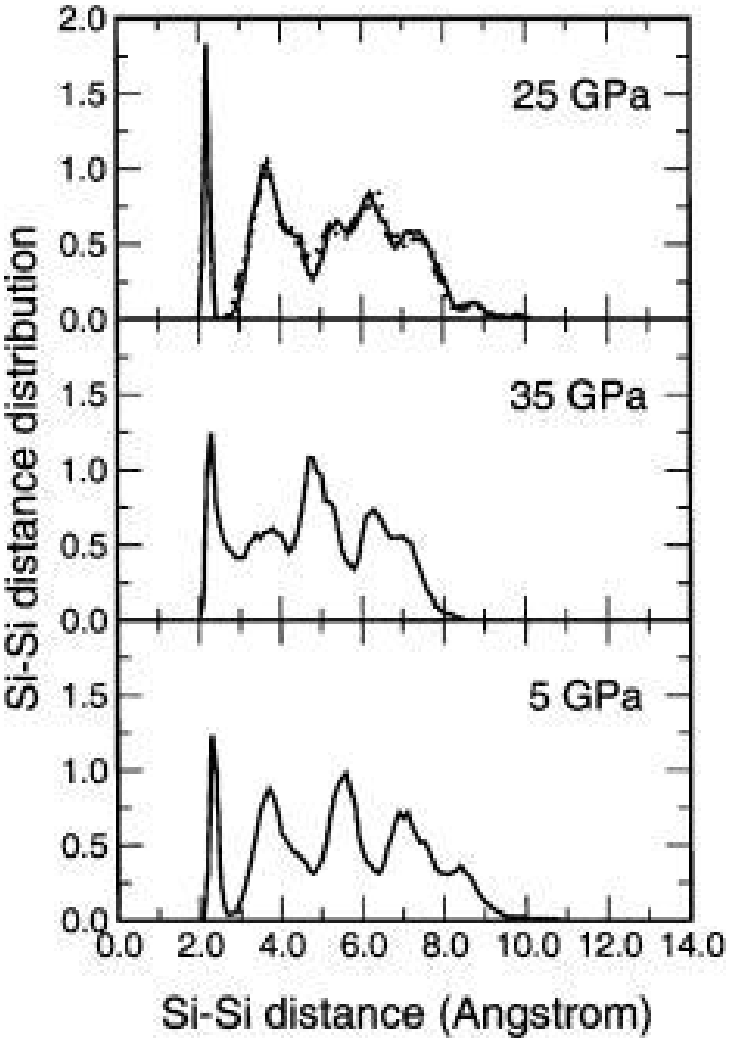


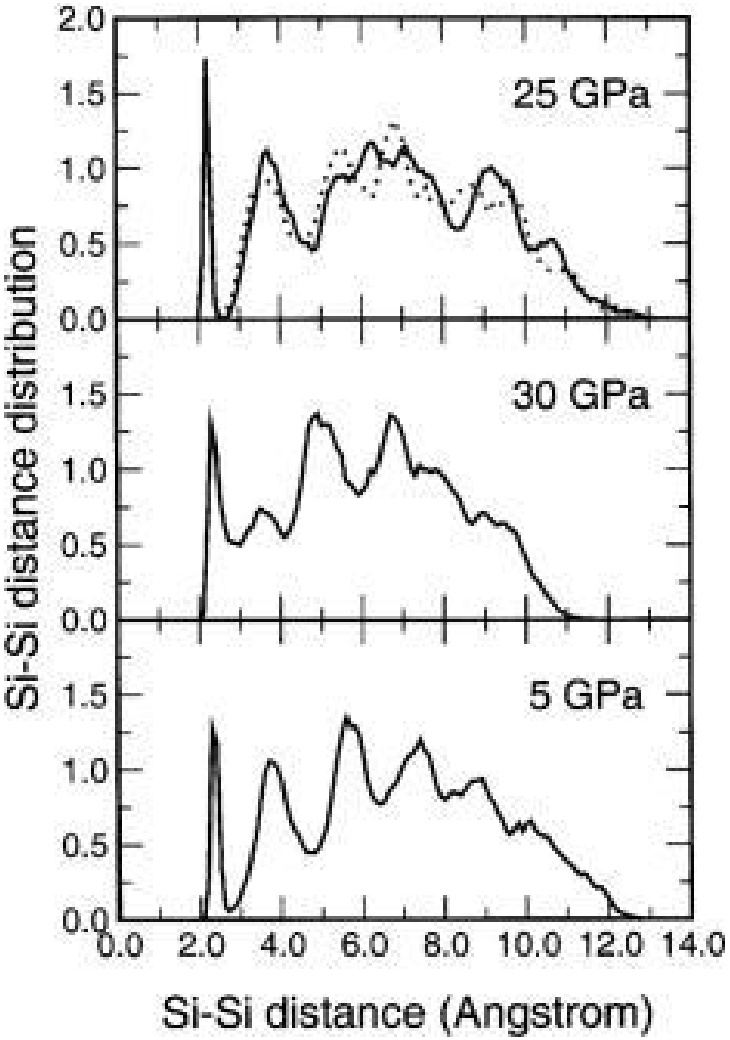
$Si_{71}H_{60}$ at 25 Gpa (top), 30 GPa (center), and 5 GPa (after the pressure has been released, bottom)

In both clusters, up to 25 GPa, a distorted but predominantly tetrahedral coordination is maintained, with no sign of a transformation to a different structure. This also holds for the case with the vacancy, even if with a higher degree of disorder.

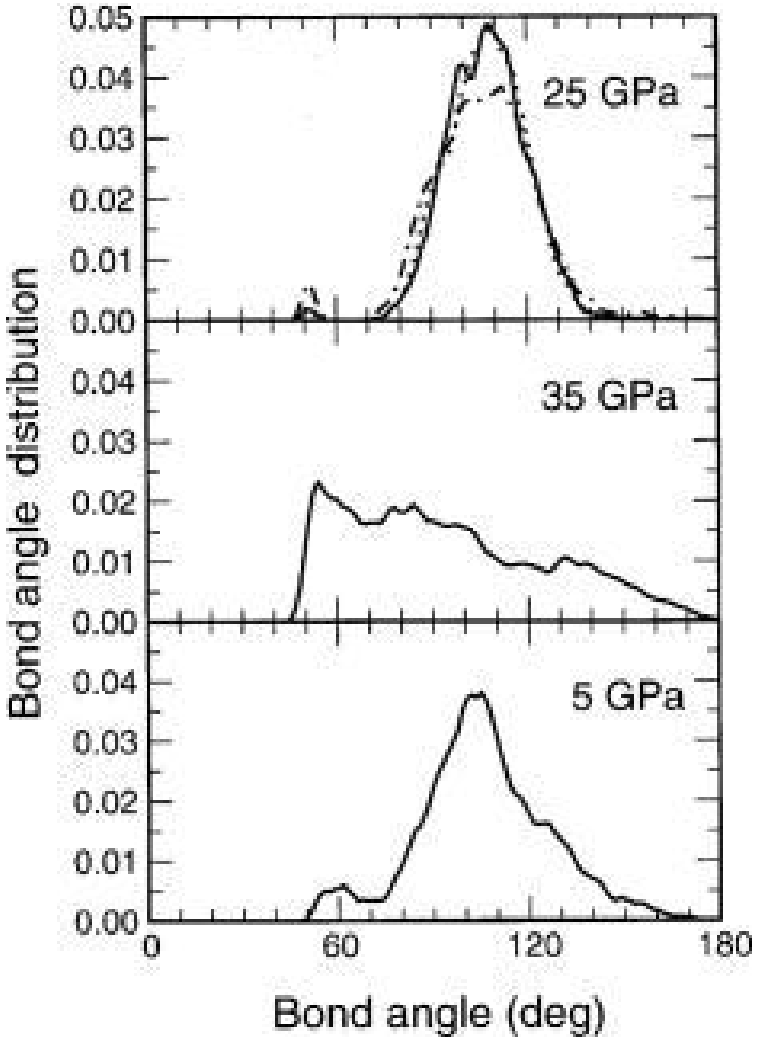


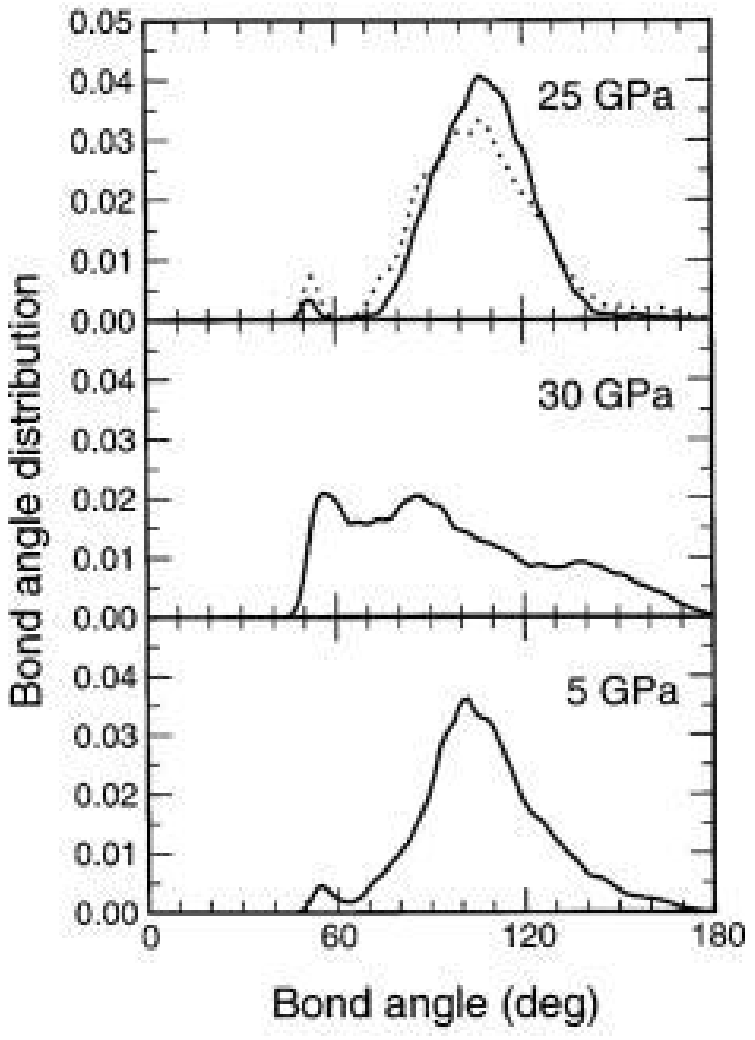
Dramatic structural transformation occurs for Si35H36 at 35 GPa and for Si71H60 at 30 GPa. Shape changes to roughly spherical and the tetrahedral coordination is no longer dominant. (In accord with exps.)



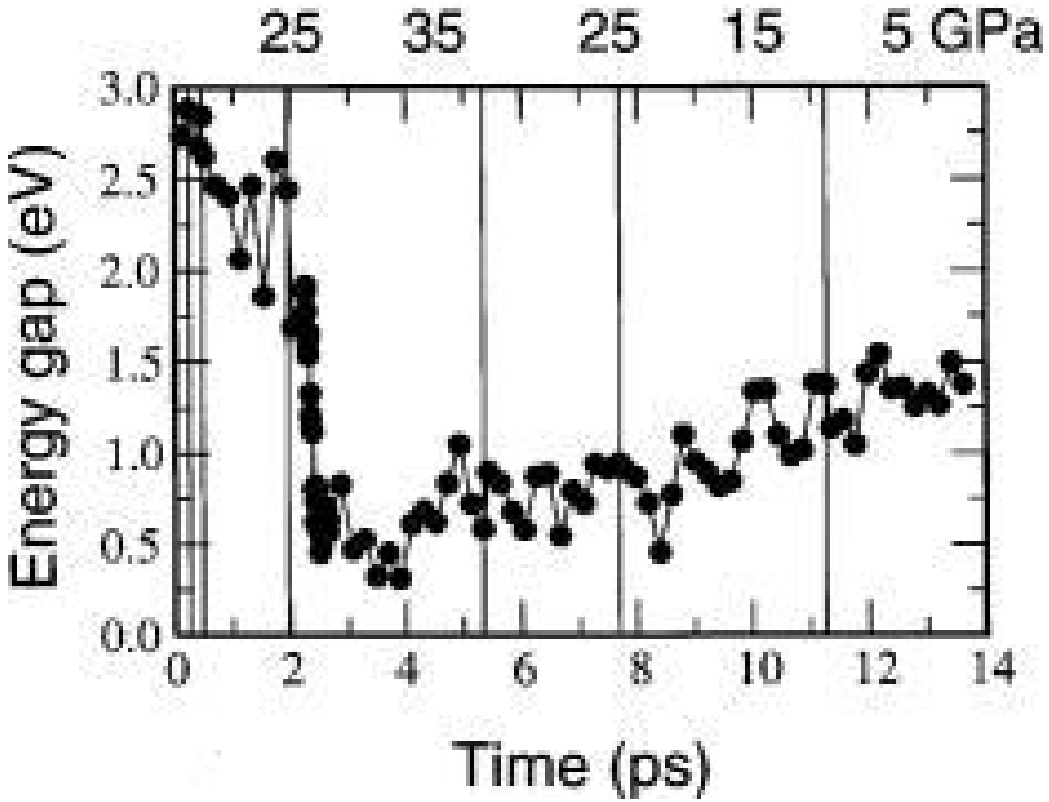


Distributions of the SiSi distances for Si71H60


Bond angle distribution
25 GPa
35 GPa
5 GPa
0.05
0.04
0.03
0.02
0.01
0.00
0
60
120
180
Bond angle (deg)


Bond angle distribution
25 GPa
30 GPa
5 GPa
0.05
0.04
0.03
0.02
0.01
0.00
0
60
120
180
Bond angle (deg)

The change in coordination and shape is accompanied by a change in the electronic properties.
There is a clear qualitative trend toward metallicity at high pressure.

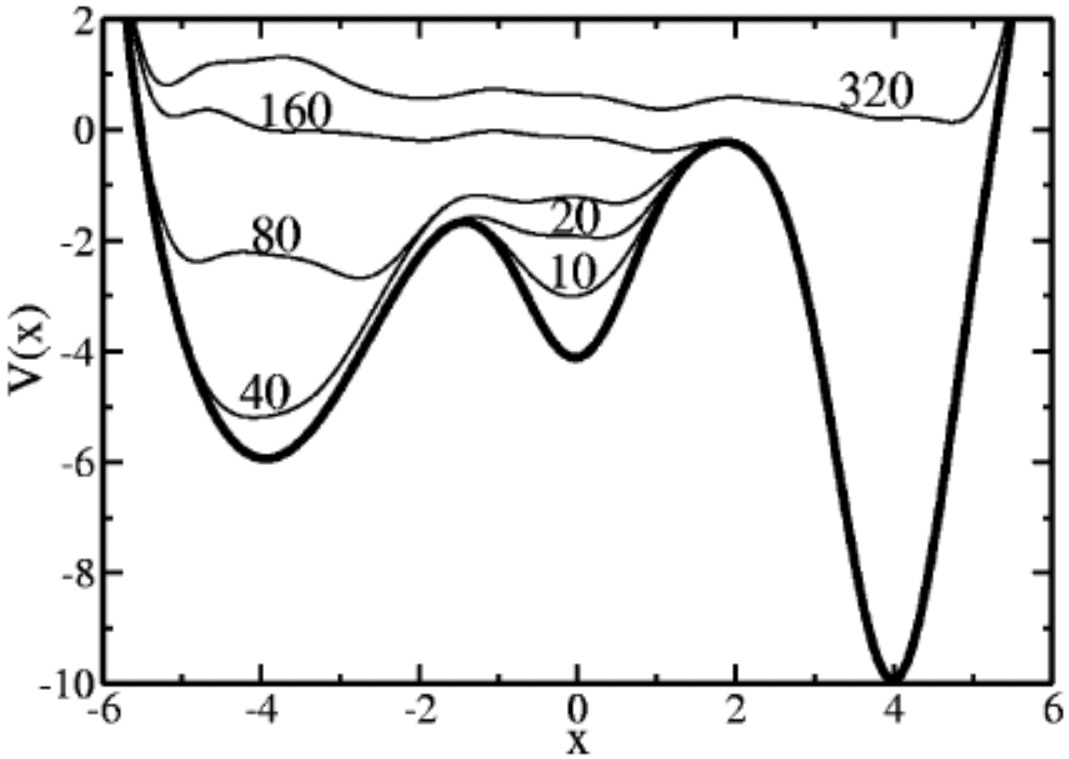


Time evolution of the KohnSham energy gap of Si35H36

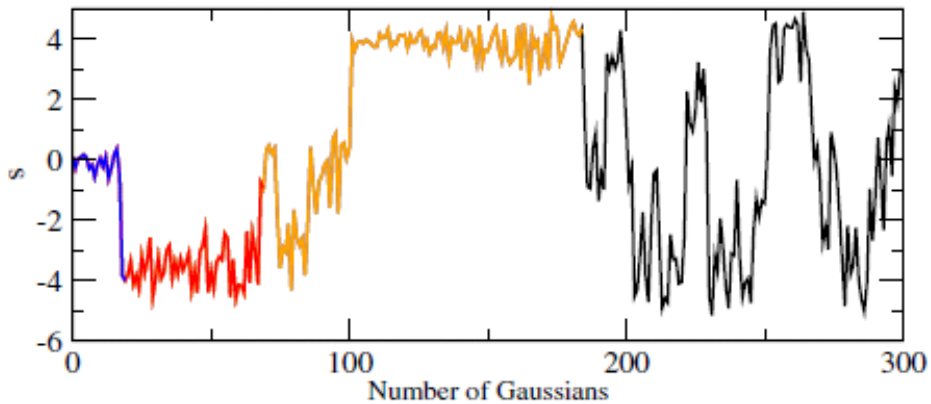
Sampling rare events and free energies: metadynamics

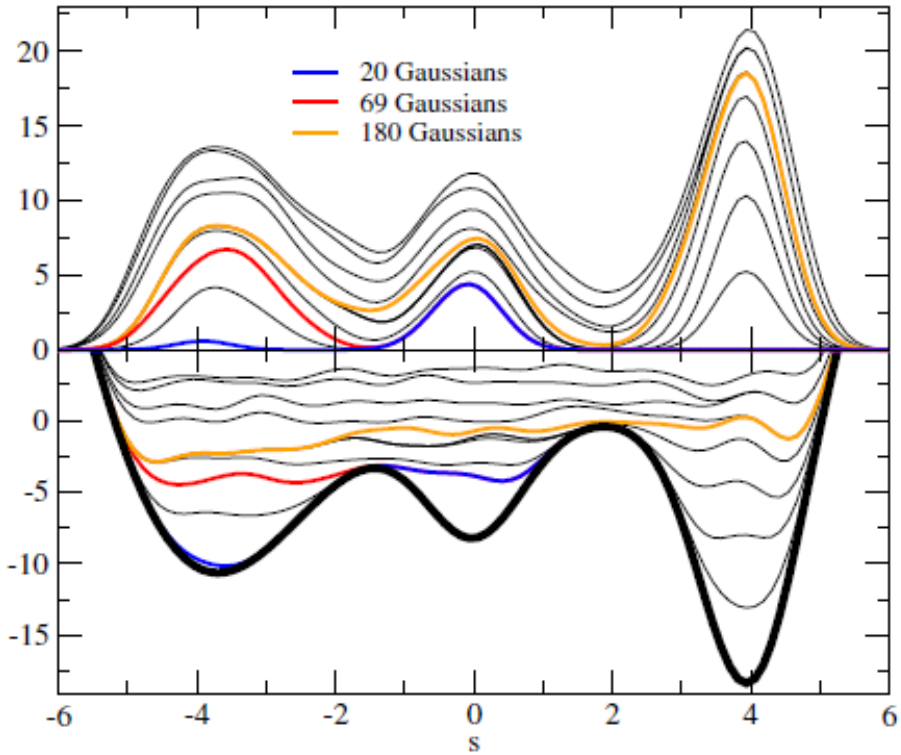
- Large barrier-activated processes
- time-dependent bias potential
- extended Lagrangian formalism
- Basic idea: during the MD dynamics preventing the system revisiting area in the configuration space where it has been in the past using a history dependent bias potential

- 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

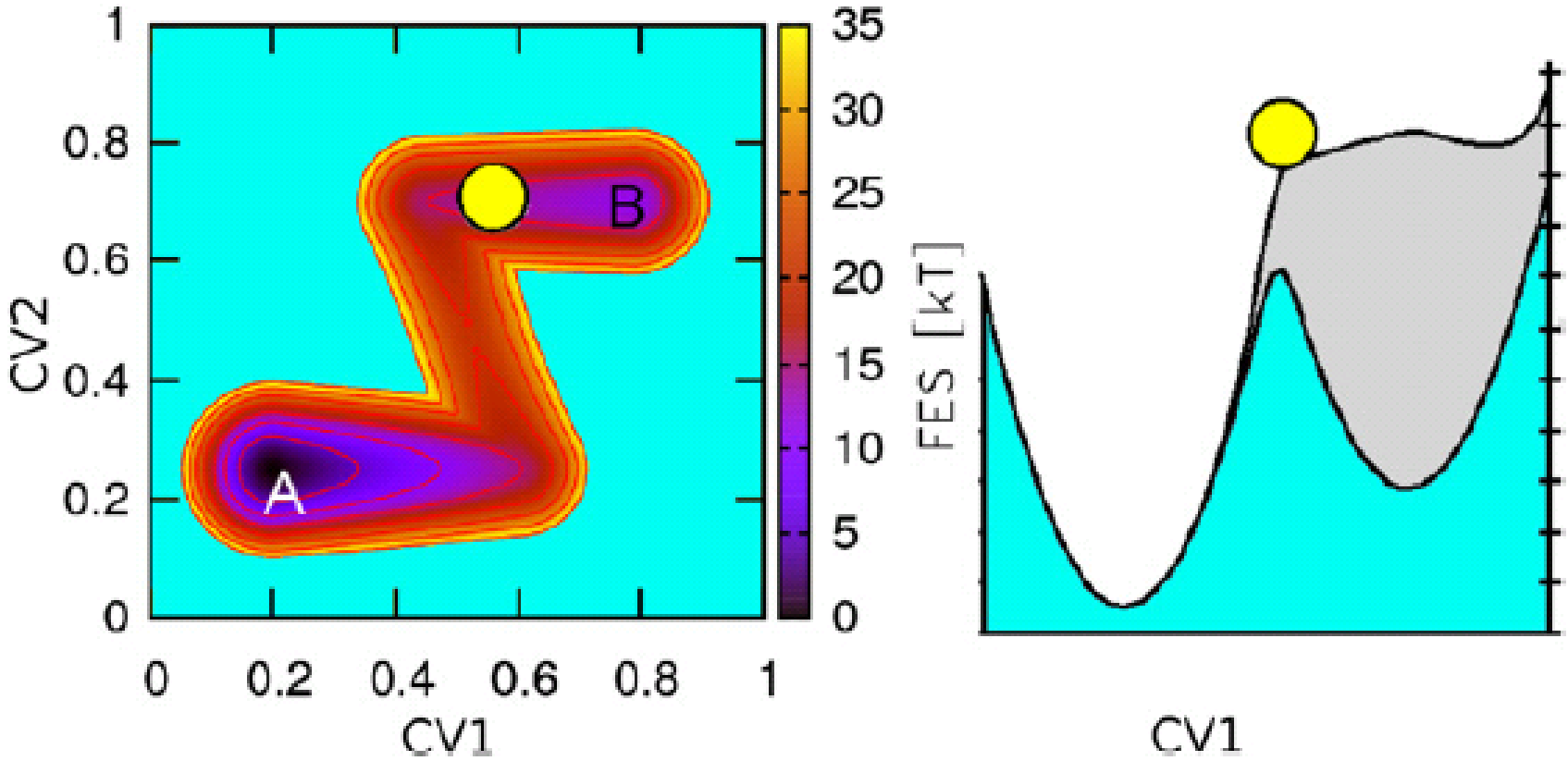


Filling a 1D model potential with hills, starting in the middle well. After 20 hills, the system escapes to the well on the left and so forth.


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.


CV2
CV1
A
B
FES [kT]
CV1

The extended Lagrangian is:

$$\mathcal{L} = \mathcal{L}_{CP} + \sum_{\alpha=1}^{N_s} \frac{1}{2}\mu_\alpha^s \dot{s}_\alpha^2(t) - \sum_{\alpha=1}^{N_s} \frac{1}{2} k_\alpha \left[S_\alpha(\mathbf{R}(t)) - s_\alpha(t)\right]^2 + V(t,[s]) \quad (31)$$

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:

$$V(t,[\mathbf{s}]) = \int_{t_0}^{t} W(t') exp\left[-\frac{((s(t)-s(t'))^2}{2(\Delta s^\perp)^2}\right] dt' \quad (32)$$

The time dependent potential:

$$V(t,[\mathbf{s}]) = \int_{t_0}^{t} W(t') exp\left[-\frac{((s(t)-s(t'))^2}{2(\Delta s^{\perp})^2}\right] dt' \tag{33}$$

can be expressed in a discrete form as:

$$V(t,[\mathbf{s}]) \approx V(t,\{\mathbf{s}(t_i)\}) = \sum_{i=0}^{imax} W(t_i) exp\left[-\frac{((s(t)-s(t'))^2}{2(\Delta s^{\perp})^2}\right] \tag{34}$$

$$\times exp\left[-\frac{[(\mathbf{s}(t_{i+1})-\mathbf{s}(t_i))\cdot(\mathbf{s}(t)-\mathbf{s}(t_i))]^2}{2|\mathbf{s}(t_{i+1})-\mathbf{s}(t_i)|^4}\right] \tag{35}$$

$\Delta_s t$ 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:

$$\frac{d}{dt}\frac{\partial \mathcal{L}}{\partial \dot{s_\alpha}} = \frac{\partial \mathcal{L}}{\partial s_\alpha} \quad (36)$$

$$\frac{d}{dt}\frac{\partial \mathcal{L}_{\mathcal{CP}}}{\partial \dot{\mathbf{R}}_I} = \frac{\partial \mathcal{L}_{\mathcal{CP}}}{\partial \mathbf{R}_I} \quad (37)$$

$$\frac{d}{dt}\frac{\partial \mathcal{L}_{\mathcal{CP}}}{\partial \dot{\phi}_i^*} = \frac{\partial \mathcal{L}_{\mathcal{CP}}}{\partial \phi_i^*} \quad (38)$$

- 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:

$$\mathcal{F}(\mathbf{s}) = -K_B T ln P(\mathbf{s}) \tag{39}$$

where

$$P(\mathbf{s}) = \frac{1}{\mathcal{Z}} \prod_{\alpha} [\delta(S_\alpha(\mathbf{R}) - s_\alpha)] \, exp\left[-\frac{E^{KS}(\mathbf{R})}{K_B T}\right] d\mathbf{R} \tag{40}$$

It can be shown that:

$$\Delta\mathcal{F}(\mathbf{s}) = -lim_{t\to\infty} V(t, \{\mathbf{s}(t_i)\}) \tag{41}$$

and the associated error can be estimated as:

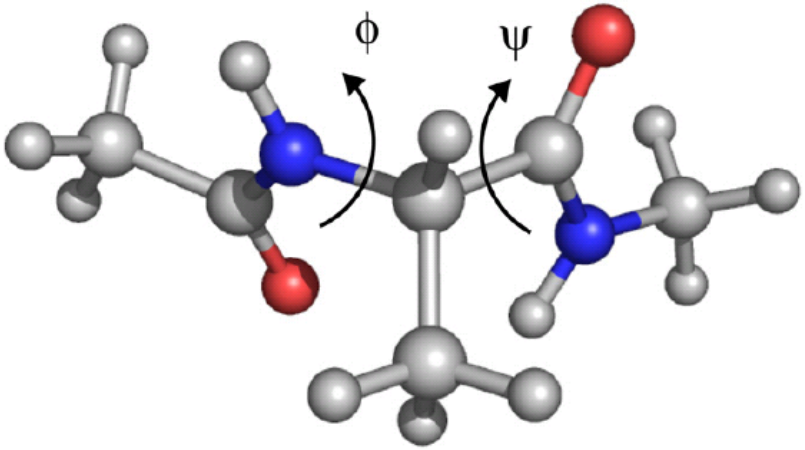
$$\epsilon \propto \sqrt{\frac{\bar{W}\Delta s^{\perp}}{\Delta_s t}} \tag{42}$$

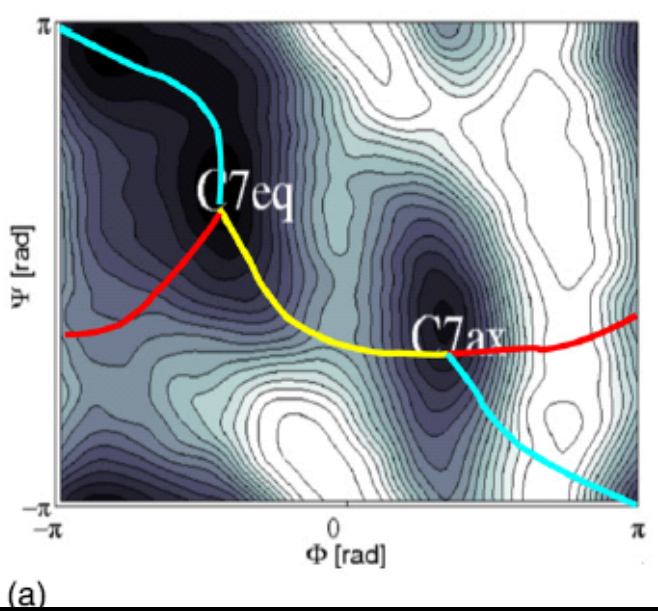
The error

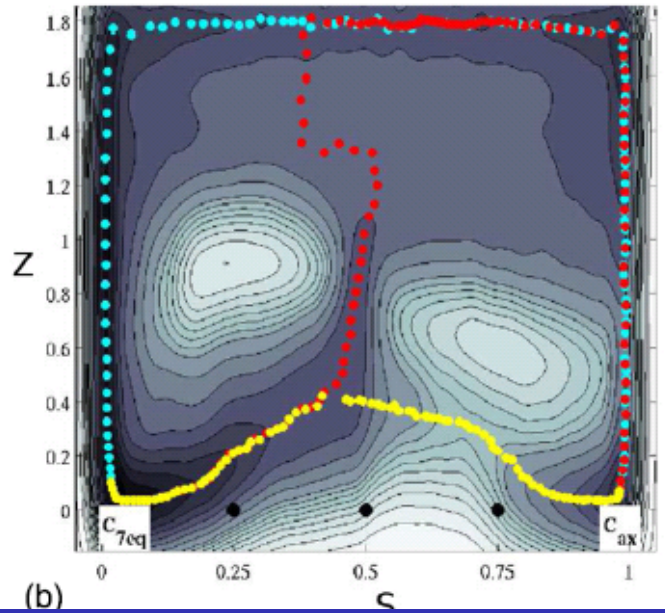
$$\epsilon \propto \sqrt{\frac{\bar{W}\Delta s^{\perp}}{\Delta_s t}}$$

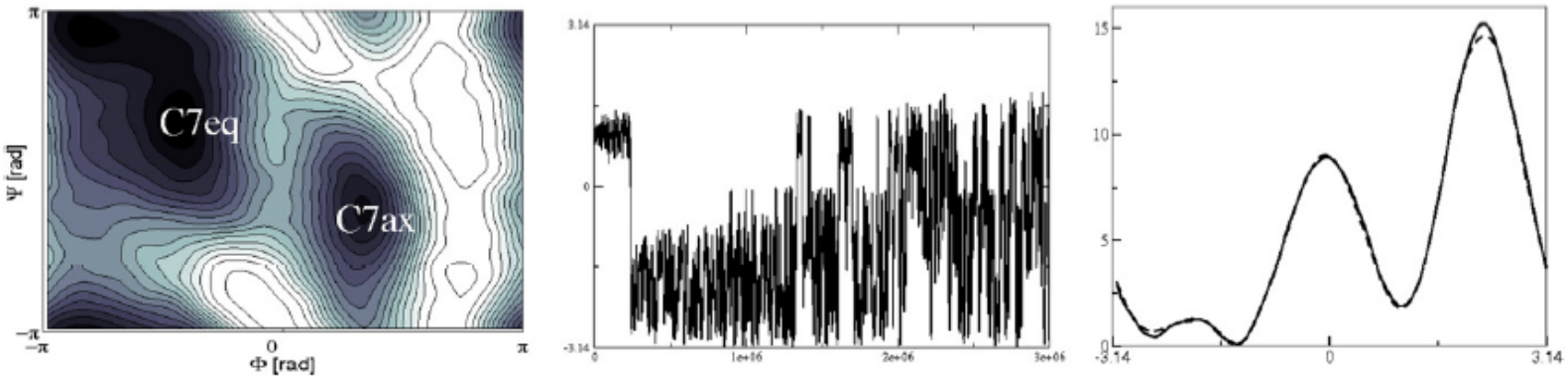
does not depend on μ_α^s and on k_α.
Recipe to choose metadynamics parameters: preliminary run without dropping Gaussians to estimate the fluctuations of the collective variables.

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

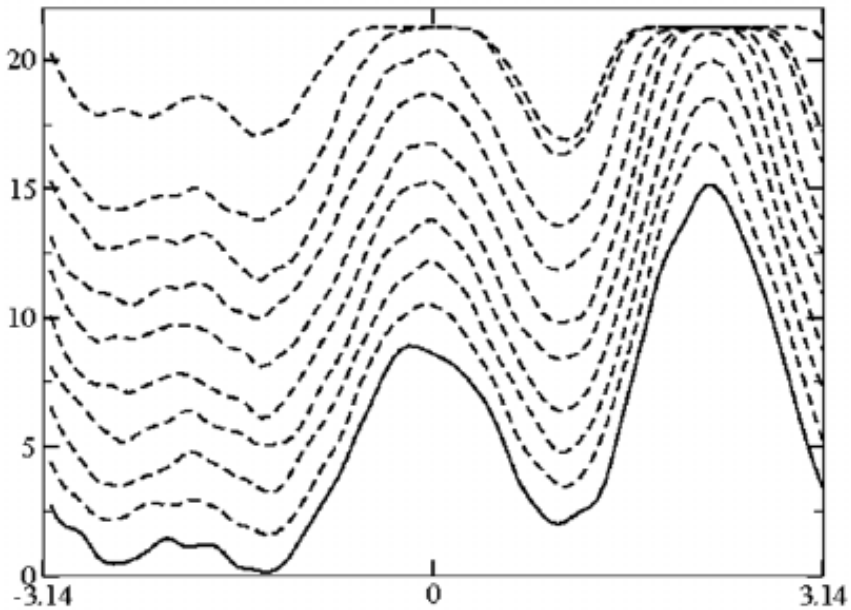








The initial configuration corresponds to a C7ax conformation. As the history-dependent potential is added, the fluctuations of ψ increase, until the system fills the free energy basin to reach a C7eq conformation. After approximately 0.8 ns, the added potential has mostly filled the two energy basins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

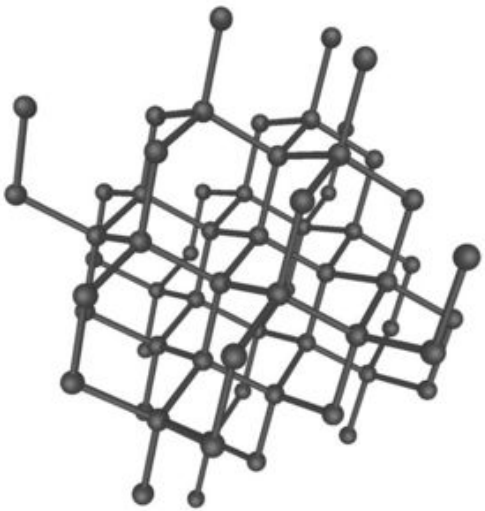
Parrinello-Rahman & metadynamics

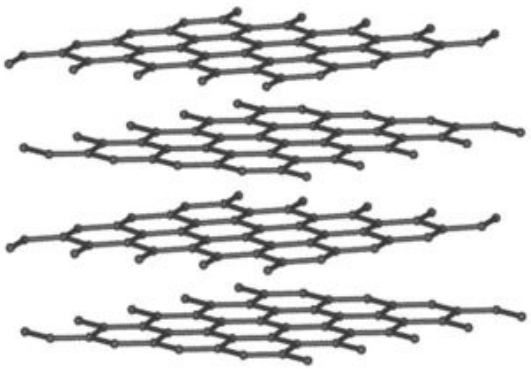
- In the Parrinello-Rahman method the box is allowed to change its shape in order to comply with a new structure.
- Often the system has to cross a significant barrier in order to transform from one structure to another. One possibility: overpressurize the system close to the point of mechanical instability.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

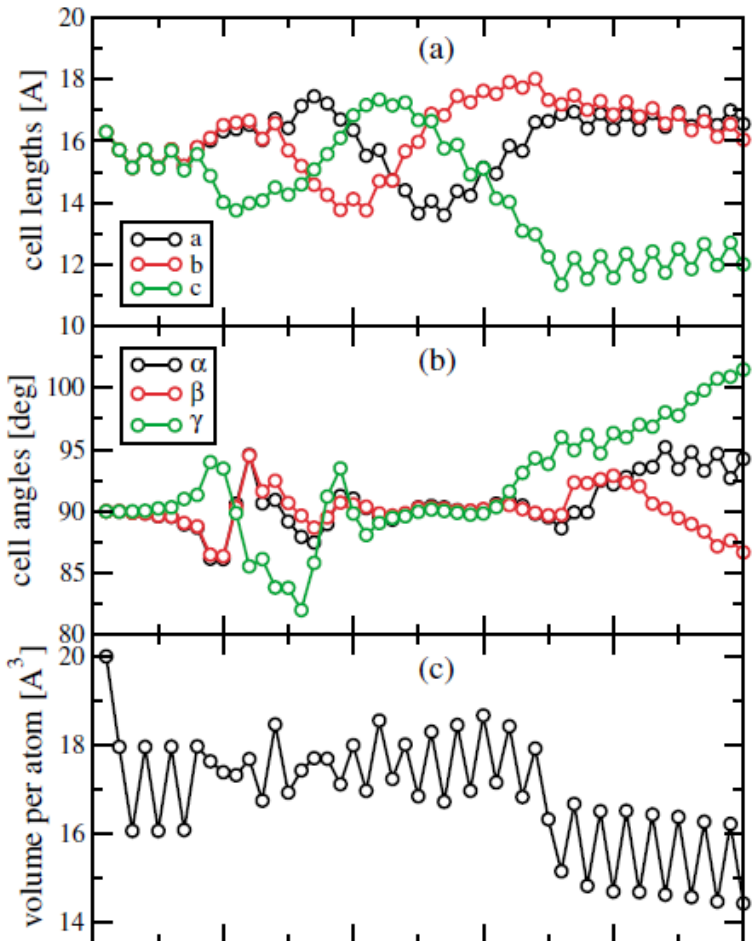
R. Martonak, A. Laio, and M. Parrinello, Phys. Rev. Lett. 90, 075503 (2003)

Example: a tight binding model of Si

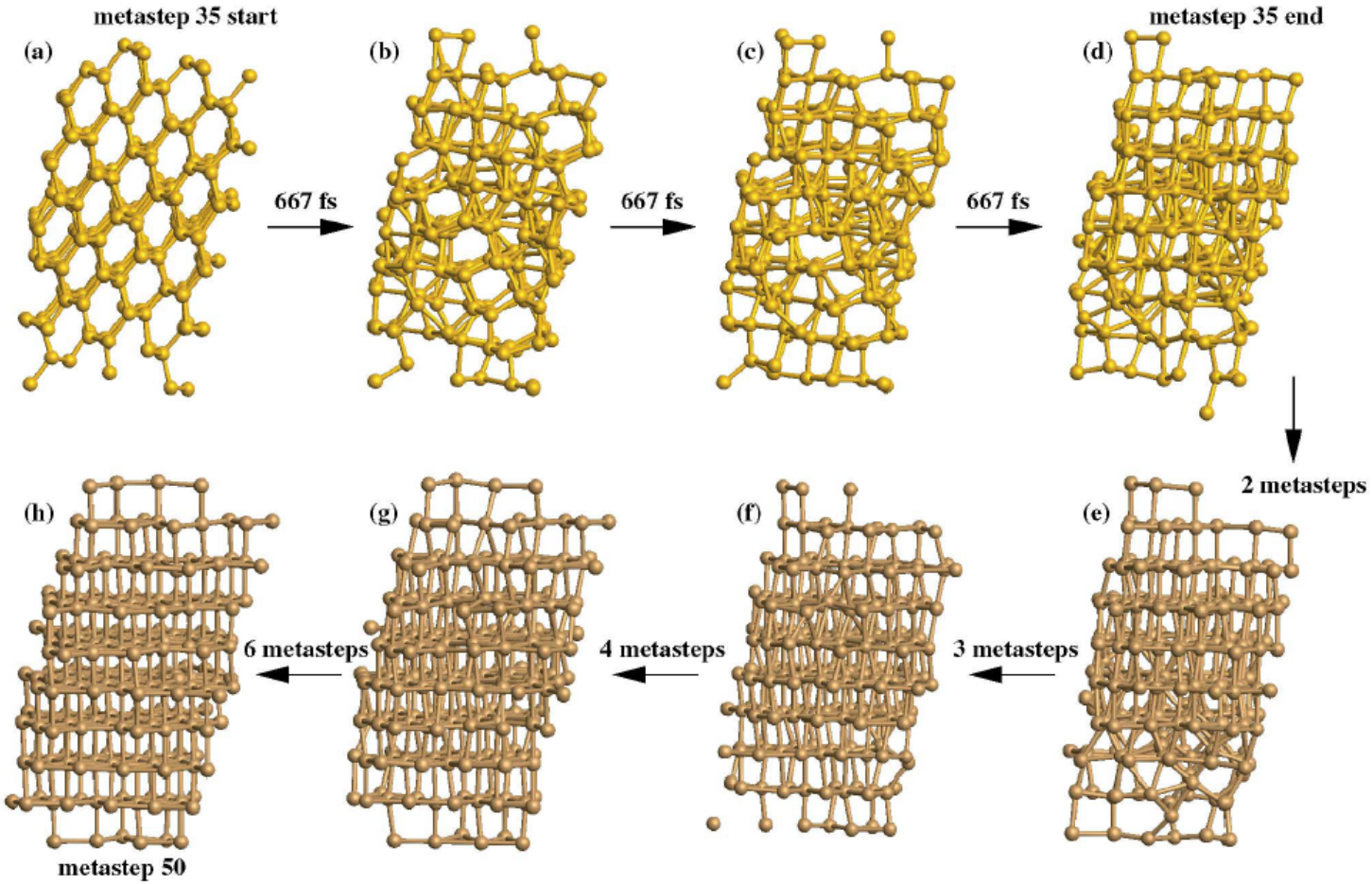
The tight-binding parametrization captures some of the main features of the Si phase diagram and provides a convenient test model.
A supercell of 216 atoms is used and only the Γ point of the Brillouin zone is considered.
At P=1 atm the equilibrium structure is the diamond, the two high-pressure phases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