Ab initio Molecular Dynamics
Born-Oppenheimer and beyond
MD trajectories are chaotic (exponential divergence with respect to initial conditions), BUT....

With a good integrator (e.g., Verlet or velocity Verlet) the discrete trajectory, with the same initial and final point as the exact analytical one, can be made infinitely close to the latter (shadow theorem/hypothesis). So: the dynamical information are reliable.

What about the ensemble averages?

The ergodic theorem/hypothesis tells us that time and ensemble averages are equivalent (at the limit of infinite sampling time). Not true for all systems, though (indeed called non-ergodic).
Ab initio MD, general formalism

Schrödinger equation for a system of \( N \) nuclei and \( n \) electrons:

\[
\mathcal{H} \Xi(\mathbf{r}, \mathbf{R}; t) = i\hbar \frac{\partial}{\partial t} \Xi(\mathbf{r}, \mathbf{R}; t)
\]

\[\mathcal{H}(\mathbf{r}, \mathbf{R}) = \mathcal{T}(\mathbf{R}) + \mathcal{T}(\mathbf{r}) + \mathcal{V}(\mathbf{R}) + \mathcal{V}(\mathbf{r}, \mathbf{R}) + \mathcal{V}(\mathbf{r})\]

- \( \mathcal{T}(\mathbf{R}) = -\frac{\hbar^2}{2} \sum_{K=1}^{N} \frac{\nabla^2_K}{M_K} \) acts on nuclei
- \( \mathcal{T}(\mathbf{r}) = -\frac{\hbar^2}{2m_e} \sum_{k=1}^{n} \nabla^2_k \) acts on electrons

\[
\mathcal{V}(\mathbf{R}) = \frac{e^2}{4\pi\varepsilon_0} \sum_{K=1}^{N} \sum_{L>K}^{N} \frac{Z_K Z_L}{|\mathbf{R}_K - \mathbf{R}_L|}
\]

\[
\mathcal{V}(\mathbf{r}, \mathbf{R}) = -\frac{e^2}{4\pi\varepsilon_0} \sum_{K=1}^{N} \sum_{k=1}^{n} \frac{Z_K}{|\mathbf{r}_k - \mathbf{R}_K|}
\]

\[
\mathcal{V}(\mathbf{r}) = \frac{e^2}{4\pi\varepsilon_0} \sum_{k=1}^{n-1} \sum_{l>k}^{n} \frac{1}{|\mathbf{r}_k - \mathbf{r}_l|}
\]
Ab initio MD, general formalism

\[ H_{el}(r, R) = T(r) + V(R) + V(r, R) + V(r) \]

\[ H(r, R) = T(R) + H_{el}(r, R) \]

Suppose the solutions of the time independent electronic Schrödinger equation are known

\[ H_{el}(r, R)\phi_i(r, R) = E_i(R)\phi_i(r, R) \]

\[ \Xi(r, R; t) = \sum_i \phi_j(r, R)\chi_j(R, t) \]

\[ [T(R) + E_i(R)]\chi_i + \sum_j C_{ij}\chi_j = i\hbar \frac{\partial}{\partial t}\chi_i \]

\[ C_{ii} : \text{correction to the adiabatic eigenvalue of} \]

\[ C_{ij} \equiv \langle \phi_i | T(R) | \phi_j \rangle - \sum_K \frac{\hbar^2}{M_K} \langle \phi_i | \nabla_K | \phi_j \rangle \nabla_K \]
Ab initio MD, Born-Oppenheimer approximation

If all $C_{ij}$ are negligible:

$$\left[ T(R) + E_i(R) \right] \chi_i = i\hbar \frac{\partial}{\partial t} \chi_i$$

Adiabatic approximation (Born-Oppenheimer):

$$\Xi(r, R; t) \approx \phi_i(r, R) \chi_i(R, t)$$

Valid in many cases, but, notably, not for electron transfer, photoisomerisation, ...
Ab initio MD, semi-classical approach

\[ \mathcal{H}_{e1}(\mathbf{r}, \mathbf{R}(t)) \Phi(\mathbf{r}; t) = i \hbar \frac{\partial}{\partial t} \Phi(\mathbf{r}; t) \]

**classical trajectory**

\[ \Phi(\mathbf{r}; t) = \sum_j a_j(t) \phi_j(\mathbf{r}, \mathbf{R}) e^{-\frac{i}{\hbar} \int E_j(\mathbf{R}) dt} \]

**adiabatic eigenfunctions**

\[ \dot{a}_i = - \sum_j a_j C_{ij} e^{-\frac{i}{\hbar} \int (E_j - E_i) dt} \]

\[ C_{ij} \equiv \langle \phi_i | \frac{\partial}{\partial t} | \phi_j \rangle \]

\[ |a_i(t)|^2 : \text{probability of finding the system in adiabatic state } i \text{ at time } t \]
**Ab initio MD, validity of the BO approximation**

![Diagram showing energy levels and characteristic lengths](image)

- **Characteristic length** $l$
- **Velocity of the nuclei** $v$
- **Time scale of electronic motion**
  \[ \Delta E = |E_1 - E_2| = \hbar \omega \]

- Passage time $\tau_p = \frac{l}{\dot{R}}$
- Electronic time scale $\tau_e = \frac{1}{\omega} = \frac{\hbar}{\Delta E}$

Massay parameter

\[ \xi = \frac{\tau_p}{\tau_e} = \frac{\Delta E l}{\hbar \dot{R}} \]
The system, when prepared in one adiabatic state $i$ stays there forever

$$\Phi(\mathbf{r}; t) = \sum_{j} a_j(t) \phi_j(\mathbf{r}, \mathbf{R}) e^{-\frac{i}{\hbar} \int E_j(\mathbf{R}) dt}$$

$$\Phi(\mathbf{r}; t) = \phi_i(\mathbf{r}, \mathbf{R}) e^{-\frac{i}{\hbar} \int E_i(\mathbf{R}) dt}$$

Nuclei move according to Newton's equations:

$$M_K \ddot{\mathbf{R}}_K = \mathbf{F}_K(\mathbf{R})$$

$$\mathbf{F}_K(\mathbf{R}) = -\nabla_K E_i(\mathbf{R})$$
Non adiabatic: mean field (Ehrenfest) dynamics

\[ E^{\text{eff}} = \langle \Phi | \mathcal{H}_{\text{el}} | \Phi \rangle = \sum_{i} |a_i|^2 E_i \]

The atoms evolve on an effective potential representing an average over the adiabatic states weighted by their state populations.

**Forces: Hellmann-Feynman theorem:**

\[ \nabla_K \langle \phi_i | \mathcal{H}_{\text{el}} | \phi_j \rangle = \nabla_K E_i \delta_{ij} \]

\[ = \langle \nabla_K \phi_i | \mathcal{H}_{\text{el}} | \phi_j \rangle + \langle \phi_i | \nabla_K \mathcal{H}_{\text{el}} | \phi_j \rangle + \langle \phi_i | \mathcal{H}_{\text{el}} | \nabla_K \phi_j \rangle \]

\[ = \langle \phi_i | \nabla_K \mathcal{H}_{\text{el}} | \phi_j \rangle + (E_j - E_i) d_{ji}, \]

\[ d_{ji} = \langle \phi_j | \nabla_K | \phi_i \rangle \quad \text{non-adiabatic coupling vectors} \]

\[ \langle \phi_i | \nabla_K \mathcal{H}_{\text{el}} | \phi_j \rangle = \nabla_K E_i \delta_{ij} - (E_j - E_i) d_{ji} \]

\[ \mathbf{F}_K = - \sum_{i} |a_i|^2 \nabla_K E_i + \sum_{i,j} a_i^* a_j (E_j - E_i) d_{ji} \]
Ehrenfest dynamics

- A system that was initially prepared in a pure adiabatic state will be in a mixed state when leaving the region of strong nonadiabatic coupling.

- The pure adiabatic character of the wavefunction cannot be recovered even in the asymptotic regions of configuration space.

- The total wavefunction may contain significant contributions from adiabatic states that are energetically inaccessible.
Ehrnelfest dynamics, violation of microscopic reversibility.
Surface hopping (fewest switches)

Let there be $N$ trajectories:

$$N_i(t) = \rho_{ii}(t)N$$

$$\rho_{ij}(t) = a_i^*(t)a_j(t)$$

At a later time:

$$t' = t + \delta t$$

$$N_i(t') = \rho_{ii}(t')N$$

Supposing:

$$N_i(t') < N_i(t)$$

$$\delta N = N_i(t) - N_i(t') > 0$$

$$P_i(t, \delta t) = \frac{\delta N}{N} = \frac{\rho_{ii}(t) - \rho_{ii}(t')}{\rho_{ii}} \approx \frac{\dot{\rho}_{ii}\delta t}{\rho_{ii}}$$

$$\dot{\rho}_{ii} \approx \frac{\rho_{ii}(t') - \rho_{ii}(t)}{\delta t}$$
Surface hopping (fewest switches)

\[ \rho_{ii} = \frac{d}{dt} \left( a_i^* a_i \right) = a_i^* a_i + a_i^* a_i = (a_i^* a_i)^* + a_i^* a_i = 2 \Re (a_i^* a_i) \]

\[ \dot{a}_i = - \sum_j a_j C_{ij} e^{-\frac{i}{\hbar} \int (E_j - E_i) dt} \]

\[ \rho_{ii} = -2 \Re \left( \sum_j \rho_{ij} C_{ij} e^{-\frac{i}{\hbar} \int (E_j - E_i) dt} \right) \]

\[ P_i(t, \delta t) = \frac{2 \Re \left( \sum_j \rho_{ij} C_{ij} e^{-\frac{i}{\hbar} \int (E_j - E_i) dt} \right) \delta t}{\rho_{ii}} \]

\[ P_i(t, \delta t) = \sum_j P_{ij}(t, \delta t) \]

\[ P_{ij}(t, \delta t) = \frac{2 \Re \left( \rho_{ij} C_{ij} e^{-\frac{i}{\hbar} \int (E_j - E_i) dt} \right) \delta t}{\rho_{ii}} \]

Transition selected by using random numbers
Surface hopping (fewest switches)

Transition from $i$ to $k$ invoked if:

$$P_i^{(k)} < \zeta < P_i^{(k+1)}$$

Sum of the transition probabilities of the first $k$ states

$$P_i^{(k)} = \sum_j P_{ij}$$

Uniform random number Between 0 and 1
Photoisomerization of formaldimine
Photoisomerization of formaldimine

\[ R \rightarrow P \]

\[ R \rightarrow R \]
Suppose a fluid of polarizable molecules

\[ U = U_0 + U_{\text{pol}} \]

\[ U_{\text{pol}} = - \sum_i E_i \cdot \mu_i + \frac{1}{2\alpha} \sum_i (\mu_i)^2 \]

E.g., dipolar molecules:

\[ E_i = T_{ij} \cdot \mu_{i}^{\text{tot}} \rightarrow \text{permanent + induced dipole moment} \]

\[ \downarrow \text{dipole-dipole tensor} \]

Induced dipoles follow nuclei adiabatically and \( U_{\text{pol}} \) is always at its minimum:

\[ \mu_i = \alpha E_i \]

Iterative solution of (3N) linear equations?
Car-Parrinello MD, a classical system

Extended Lagrangian:

\[ \mathcal{L}(r^N, \mu^N) = \frac{1}{2} \sum_{i=1}^{N} m \dot{r}_i^2 + \frac{1}{2} \sum_{i=1}^{N} M \dot{\mu}_i^2 - \mathcal{U} \]

Equation of motion for dipoles:

\[ M \ddot{\mu}_i \equiv \frac{\partial \mathcal{L}}{\partial \mu_i} = -\frac{\mu_i}{\alpha} + E_i \]

Role of \( M \)?

\[ T_\mu \ll T_r \quad \quad M \ll m \]

Adiabaticity: two temperatures?

\[ T_\mu = \frac{1}{2} \sum_{i=1}^{N} M \dot{\mu}_i^2 \quad \quad T_r = \frac{1}{2} \sum_{i=1}^{N} m \dot{r}_i^2 \]
Car-Parrinello MD, the idea

Starting from minimized Kohn-Sham orbitals, define orbital velocities \( \{ \dot{\psi}_i(r) \} \) and kinetic energy:

\[
K_{\text{fict}} = \mu \sum_i \langle \dot{\psi}_i | \dot{\psi}_i \rangle
\]

Equations of motion:

\[
\begin{align*}
\frac{d}{dt} \left( \frac{\delta L}{\delta \dot{\psi}_i^*(r)} \right) - \frac{\delta L}{\delta \psi_i^*(r)} &= 0 \\
\frac{d}{dt} \left( \frac{\partial L}{\partial \dot{R}_I} \right) - \frac{\partial L}{\partial R_I} &= 0
\end{align*}
\]

In practice wrt the coefficients of the chosen basis set

\[
\begin{align*}
\mu \ddot{\psi}_i(r) &= -\frac{\delta}{\delta \psi_i^*(r)} E[\{\psi\}, R] + \sum_j \Lambda_{ij} \psi_j(r) \\
M_I \ddot{R}_I &= -\nabla_I E[\{\psi\}, R]
\end{align*}
\]

Lagrange multipliers
Car-Parrinello MD, the algorithm

Initial conditions: \( \{|\psi_i(0)\rangle\} \) \( \{\dot{\psi}_i(0)\rangle\} \) \( \mathbf{R}(0) \) \( \dot{\mathbf{R}}(0) \)

Update velocities \((\Delta t/2)\)

\[
|\dot{\psi}_i^{(1)}(0)\rangle = |\dot{\psi}_i(0)\rangle + \frac{\Delta t}{2\mu} |\varphi_i(0)\rangle \quad i = 1, \ldots, \frac{N_e}{2}
\]

\[
\mathbf{R}_I(\Delta t/2) = \mathbf{R}_I(0) + \frac{\Delta t}{2M_I} \mathbf{F}_I(0) \quad I = 1, \ldots, N
\]

Update positions \((\Delta t)\)

\[
|\tilde{\psi}_i\rangle = |\psi_i(0)\rangle + \Delta t|\dot{\psi}_i^{(1)}\rangle \quad i = 1, \ldots, \frac{N_e}{2}
\]

\[
\mathbf{R}_I(\Delta t) = \mathbf{R}_I(0) + \Delta t\dot{\mathbf{R}}_I(\Delta t/2) \quad I = 1, \ldots, N
\]

Constraint?

\[
X_{ij} = (\Delta t^2 / 2\mu) \Lambda_{ij}
\]

\[
\langle \psi_i(\Delta t)|\psi_j(\Delta t)\rangle = \delta_{ij} \quad |\psi_i(\Delta t)\rangle = |\tilde{\psi}_i\rangle + \sum_j X_{ij} |\psi_j(0)\rangle
\]
Iterative solution:

\[
X_{n+1} = \frac{1}{2} \left[ I - A + X_n (I - B) + (I - B^\dagger) X_n^\dagger - X_n^2 \right]
\]

Starting from: \( X_0 = \frac{1}{2} (I - A) \)

\[
|\dot{\psi}_i^{(2)}\rangle = |\dot{\psi}_i^{(1)}\rangle + \frac{1}{\Delta t} \sum_j X_{ij} |\psi_j(0)\rangle
\]

\[
|\dot{\psi}_i^{(3)}\rangle = |\dot{\psi}_i^{(2)}\rangle + \frac{\Delta t}{2\mu} |\varphi_i(\Delta t)\rangle \quad i = 1, \ldots, \frac{N_e}{2}
\]

\[
\dot{R}_I(\Delta t) = \dot{R}_I(\Delta t/2) + \frac{\Delta t}{2M_I} F_I(\Delta t) \quad E[\{\psi\}, R] = \varepsilon[\{\psi\}, R]
\]

\[
\langle \psi_i(\Delta t) | \dot{\psi}_j(\Delta t) \rangle + \langle \dot{\psi}_i(\Delta t) | \psi_j(\Delta t) \rangle = 0
\]

\[
|\psi_i(\Delta t)\rangle = |\psi_i^{(3)}\rangle + \sum_j Y_{ij} |\psi_i(\Delta t)\rangle 
\]

\[
Y = -\frac{1}{2} (C + C^\dagger) \quad C_{ij} = \langle \psi_i(\Delta t) | \dot{\psi}_i^{(3)} \rangle
\]
Car-Parrinello MD, the algorithm (summary)

Velocities:

1. \( |\dot{\psi}_i^{(1)}(0)\rangle = |\dot{\psi}_i(0)\rangle + \frac{\Delta t}{2\mu} |\varphi_i(0)\rangle \)

2. \( \dot{\mathbf{R}}_I(\Delta t/2) = \dot{\mathbf{R}}_I(0) + \frac{\Delta t}{2M_I} \mathbf{F}_I(0) \)

3. \( |\dot{\psi}_i^{(2)}\rangle = |\dot{\psi}_i^{(1)}\rangle + \frac{1}{\Delta t} \sum_j X_{ij} |\psi_j(0)\rangle \)

4. \( |\dot{\psi}_i^{(3)}\rangle = |\dot{\psi}_i^{(2)}\rangle + \Delta t \frac{\mu}{2\mu} |\varphi_i(\Delta t)\rangle \)

5. \( \dot{\mathbf{R}}_I(\Delta t) = \dot{\mathbf{R}}_I(\Delta t/2) + \frac{\Delta t}{2M_I} \mathbf{F}_I(\Delta t) \)

6. \( |\psi_i(\Delta t)\rangle = |\dot{\psi}_i^{(3)}\rangle + \sum_j Y_{ij} |\dot{\psi}_i(\Delta t)\rangle \)

Positions:

2. \( |\tilde{\psi}_i\rangle = |\psi_i(0)\rangle + \Delta t |\dot{\psi}_i^{(1)}\rangle \)

3. \( \mathbf{R}_I(\Delta t) = \mathbf{R}_I(0) + \Delta t \dot{\mathbf{R}}_I(\Delta t/2) \)

3. \( |\psi_i(\Delta t)\rangle = |\tilde{\psi}_i\rangle + \sum_j X_{ij} |\psi_j(0)\rangle \)
Molecular dynamics: summary of extended systems and applications of Born-Oppenheimer MD
REMINDER, RELIABILITY OF MD

MD trajectories are chaotic (exponential divergence with respect to initial conditions), BUT....

With a good integrator (e.g., Verlet or velocity Verlet) the discrete trajectory, with the same initial and final point as the exact analytical one, can be made infinitely close to the latter (shadow theorem/hypothesis). So: the dynamical information are reliable.

What about the ensemble averages?

The ergodic theorem/hypothesis tells us that time and ensemble averages are equivalent (at the limit of infinite sampling time). Not true for all systems, though (indeed called non-ergodic).
Summary of extended systems: NVT (Nosé)

Lagrangian: \[ \mathcal{L}_{\text{Nose}} = \sum_{i=1}^{N} \frac{m_i}{2} s^2 \dot{r}_i^2 - U(r^N) + \frac{Q}{2} \dot{s}^2 - \frac{L}{\beta} \ln s \]

Conjugated momenta:

\[ p_i \equiv \frac{\partial \mathcal{L}}{\partial \dot{r}_i} = m_i s^2 \dot{r}_i \]

\[ p_s \equiv \frac{\partial \mathcal{L}}{\partial \dot{s}} = Q \dot{s} \]

Hamiltonian

\[ \mathcal{H}_{\text{Nose}} = \sum_{i=1}^{N} \frac{p_i^2}{2m_i s^2} + U(r^N) + \frac{p_s^2}{2Q} + L \ln s \]

\[ \ddot{r}_i = \frac{p_i}{m_i} \]

\[ \ddot{p}_i = -\frac{\partial U(r^N)}{\partial r_i} - \xi p_i \]

Eq. of motion:

\[ \dot{\xi} = \left( \sum_i \frac{p_i^2}{m_i} - \frac{L}{\beta} \right) / Q \]

\[ \frac{\dot{s}}{s} = \frac{d \ln s}{dt} = \xi. \]
Summary of extended systems: NPH (Andersen)

\[ P = \begin{pmatrix} P_{xx} & P_{xy} & P_{xz} \\ P_{yx} & P_{yy} & P_{yz} \\ P_{zx} & P_{zy} & P_{zz} \end{pmatrix} \]

\[ P = \frac{\operatorname{Tr}(P)}{3} \]

\[ E_{V,\text{kin}} = \frac{1}{2} Q \dot{V}^2 \]

\[ E_{V,\text{pot}} = P_{\text{md}} V \]

\[ \mathbf{r}_i = V^{1/3} \mathbf{s}_i \]

\[ \mathbf{v}_i = V^{1/3} \dot{s}_i \]

\[ \ddot{s}_i = \frac{f_i}{m_i V^{1/3}} - \frac{2}{3} \frac{\ddot{s}_i \dot{V}}{V} \]

\[ \dot{V} = \frac{P(t) - P_{\text{md}}}{Q} \]

\[ H = E_{\text{kin}}(\mathbf{R}) + E_{\text{pot}}(\mathbf{R}) + E_{V,\text{kin}} + E_{V,\text{pot}} \]
Summary of extended systems: NPH (Parrinello-Rahman)

\[ V = \det \mathbf{H} = \mathbf{a} \cdot (\mathbf{b} \times \mathbf{c}) \]

\[ \mathbf{r}_i = \mathbf{Hs}_i \]

\[ E_{\text{pot},V} = PV \]

\[ E_{\text{kin},V} = \frac{1}{2} Q \text{Tr}(\dot{\mathbf{H}}^T \dot{\mathbf{H}}) \]

\[ \ddot{\mathbf{s}}_i = \frac{\mathbf{H}^{-1} \mathbf{f}_i}{m} - \mathbf{G}^{-1} \dot{\mathbf{G}} \dot{\mathbf{s}} \]

\[ \mathbf{G} = \mathbf{H}^T \mathbf{H} \]

\[ \ddot{\mathbf{H}} = \frac{(\mathbf{P} - 1 P_{md}) V (\mathbf{H}^{-1})^T}{Q} \]

\[ \mathbf{H} = E_{\text{kin}}(\mathbf{R}) + E_{\text{pot}}(\mathbf{R}) + E_{V,\text{kin}} + E_{V,\text{pot}} \]
Summary of extended systems: on-the-fly optimization

Car-Parrinello MD

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

\[ \mu \ddot{\psi}_i (r) = -\frac{\delta}{\delta \psi_i^* (r)} E[\{\psi\}, R] + \sum_j \Lambda_{ij} \psi_j (r) \]

\[ M_I \ddot{R}_I = -\nabla_I E[\{\psi\}, R] \]

Classical example: polarizable fluid

\[ \mathcal{L}(r^N, \mu^N) = \frac{1}{2} \sum_{i=1}^N m_i \dot{r}_i^2 + \frac{1}{2} \sum_{i=1}^N M \dot{\mu}_i^2 - \mathcal{U} \]

\[ M \dot{\mu}_i \equiv \frac{\partial \mathcal{L}}{\partial \mu_i} = -\frac{\mu_i}{\alpha} + E_i \]
Application of plain MD: nature of liquid C

Galli et al. Science 1990

\[ P = \left\langle -\frac{\partial E}{\partial \Omega} \right\rangle + \rho_d k_B T \]

\[ \frac{dP}{dT} = \frac{S_\ell - S_s}{\Omega_\ell - \Omega_s} \]

**Fig. 1.** Pressure (\(P\)) as a function of temperature (\(T\)) in the solid and liquid phases of C. We obtained the liquid at 9000 K by heating the 8000 K sample (see text), whereas we generated the liquid at 7500 K by cooling down the 9000 K system.

**Fig. 2.** Evolution of the pressure (\(P\)) operator (A) and mean squared displacement (\(r^2\)) of the atoms relative to the initial configuration (B), as a function of simulation time. Arrows indicate the onset of diffusive behavior (see text).
Application of plain MD: nature of liquid C


5000 K

DOS (states/eV cell)

Conduction Bands

Cubic Diamond

Hexagonal Diamond

Valence Bands

LMTO Calculation
Dynamics of Dissociative Chemisorption: Cl₂/Si(111)-(2×1)

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(Received 1 February 1993)

We report the first simulation of a surface chemical reaction performed with the ab initio molecular dynamics approach. A set of trajectories with different initial conditions has been generated for single Cl₂ molecules impinging on the Si(111)-2×1 surface with incident translational energy of 1 eV. We observe a high probability of dissociation, triggered by active sites on the π-bonded chains, and accompanied by a large surface response and local rehybridization effects.

Initial @ Collision Final (400fs)

Trajectory 1

Trajectory 2

Kinetic energy: 1 eV

Trajectory 3

Trajectory 4

Trajectory 5
Application of plain MD: solvation of DMSO in water

Kirchner and Hutter,
J. Chem. Phys. 2004

32 water molecules + 1 DMSO @ 320 K