

# Lecture on First-principles Computations (27): The Ab-initio Molecular Dynamics

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# What is molecular dynamics (MD)?

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Molecular dynamics simulates the motions of atoms or molecules in real time according to the forces they experience.

In most cases, the atoms or molecules are treated as classical objects; they obey Newton's law:

$$M_I \ddot{\mathbf{R}}_I = \mathbf{F}_I; \quad \mathbf{F}_I = \mathbf{F}_I[\{\mathbf{R}_J\}] = - \frac{\partial U[\{\mathbf{R}_J\}]}{\partial \mathbf{R}_I}$$

Mass of atom  $I$

Potential energy surface (PES)

# Why molecular dynamics?

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- For many physical processes and properties, one needs to account for the nuclear motions in real time.
  - ❖ Phase transition between solids, liquids, and gases
  - ❖ Growth of crystals and thin films
  - ❖ Folding and unfolding of proteins
  - ❖ Diffusion of defects in bulk or adsorbates on surfaces
  - ❖ .....
- Provides a practical means for ensemble averages that bridge the macroscopic properties and the microscopic states

Ergodicity Assumption:

$$\langle A \rangle_{ensemble} = \langle A \rangle_{time} = \lim_{t \rightarrow \infty} \frac{1}{t} \int_0^t dt' A(t')$$

# Equilibrium thermodynamic properties

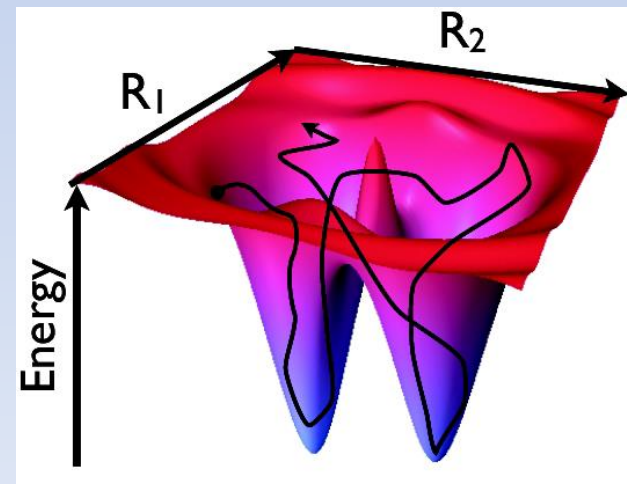
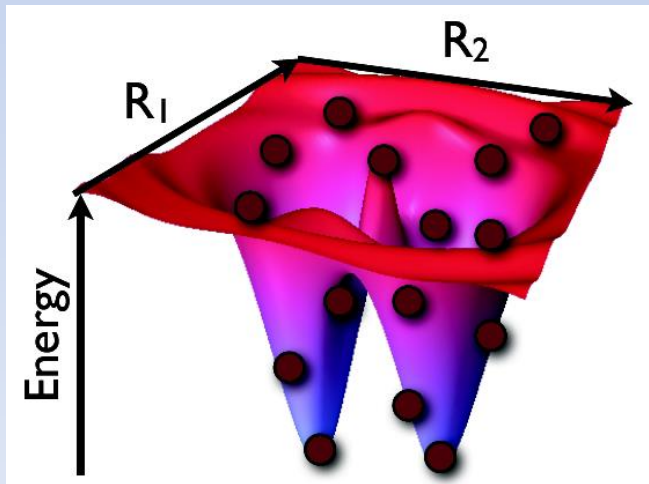
Description of a classical microscopic state:

$$(\mathbf{p}^N, \mathbf{R}^N) = \{\mathbf{p}_1, \mathbf{p}_2, \dots, \mathbf{p}_N; \mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_N\}$$

Canonical ensemble

$$\begin{aligned}\langle A \rangle &= \frac{1}{Z} \int d^{3N} p \int d^{3N} R e^{-E(\mathbf{p}^N, \mathbf{R}^N)/\kappa_B T} A(\mathbf{p}^N, \mathbf{R}^N) \\ &= \lim_{t \rightarrow \infty} \frac{1}{t} \int_0^t dt' A(\mathbf{p}^N(t'), \mathbf{R}^N(t'))\end{aligned}$$

Classical trajectory



# Brief history of molecular dynamics (MD)

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- 1955, Alder and Wainwright  
interaction of hard spheres
- 1964, Rahman  
Liquid Argon (Lennard-Jones potential)
- 1974, Stillinger and Rahman  
Liquid water
- 1979, McCammon et al.  
Protein
- 1985, Car and Parrinello  
*ab initio* molecular dynamics



Classical MD

# Classical versus *ab initio* molecular dynamics

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- Classical molecular dynamics

The interatomic interactions are described by parameterized force field

$$U[\mathbf{R}^N] = \sum_{I=1}^N \sum_{J>I}^N v(\mathbf{R}_I, \mathbf{R}_J) + \dots \quad (\text{Non-bonding interaction})$$
$$+ \frac{1}{2} \sum_{\text{bonds}} k_{IJ}^R (R_{IJ} - R_{eq})^2$$
$$+ \frac{1}{2} \sum_{\text{bond angles}} k_{IJK}^\theta (\theta_{IJK} - \theta_{eq})^2 \quad (\text{Bonding interaction})$$

- *Ab initio* molecular dynamics

$$U[\mathbf{R}^N] = \sum_{I=1}^N \sum_{J>I}^N \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|} + E_{elec}(\mathbf{R}^N) \quad \leftarrow \text{From } ab \text{ initio methods, e.g., DFT}$$

# Classical versus *ab initio* molecular dynamics

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- Classical molecular dynamics (highly parameterized)
  - ❖ The force calculation is cheap =>  
Large system size, longer time scale  
( $nm - \mu m, ns - \mu s$ )
  - ❖ Suitable for describing processes that don't involve bonding breaking, e.g., protein folding, molecular recognition ...
- *Ab initio* molecular dynamics (no parameters)
  - ❖ Forces are expensive to obtain =>  
Smaller system size, shorter time scale  
( $0.1 - 1 nm, ps - ns$ )
  - ❖ Relevant for processes involving bonding breaking, or there is no good force field

# How to get the classical trajectory?

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1. Assign initial positions  $\mathbf{R}^N$  and momenta  $\mathbf{p}^N$  to atoms, choose short  $\Delta t$
2. Get force  $\mathbf{F}_I = -\nabla_I U[\mathbf{R}^N]$ , and acceleration  $\mathbf{a}_I = \mathbf{F}_I/M_I$
3. Move atoms  $\mathbf{R}_I^{(n+1)} = \mathbf{R}_I^{(n)} + \frac{\mathbf{p}_I^{(n)}}{M_I} \Delta t + \frac{1}{2} \mathbf{a}_I^{(n)} \Delta t^2$
4. Move time forward  $t \rightarrow t + \Delta t$
5. Go to 2, and repeat as long as you need



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However, simple minded algorithm like this, the discretization error cumulates, and long time MD becomes ill-conditioned (.e.g., the total energy is not conserved).

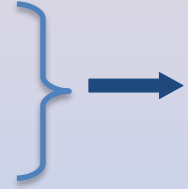
# The Verlet algorithm for integration

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Taylor expansion of  $\mathbf{R}(t)$

$$\mathbf{R}(t + \Delta t) = \mathbf{R}(t) + \mathbf{v}(t)\Delta t + \frac{1}{2}\mathbf{a}(t)\Delta t^2 + \frac{1}{3!}\ddot{\mathbf{R}}(t) + O(\Delta t^4)$$

$$\mathbf{R}(t - \Delta t) = \mathbf{R}(t) - \mathbf{v}(t)\Delta t + \frac{1}{2}\mathbf{a}(t)\Delta t^2 - \frac{1}{3!}\ddot{\mathbf{R}}(t) + O(\Delta t^4)$$



$$\mathbf{R}(t + \Delta t) = 2\mathbf{R}(t) - \mathbf{R}(t - \Delta t) + \mathbf{a}(t)\Delta t^2 + O(\Delta t^4)$$

- No explicit use of velocity
- Straightforward, the storage requirement is modest
- The energy is conserved and the simulations are stable for long times
- The accuracy is moderate (smaller time step is required)

# The velocity Verlet algorithm

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$$\mathbf{R}(t + \Delta t) = \mathbf{R}(t) + \mathbf{v}(t)\Delta t + \frac{1}{2}\mathbf{a}(t)\Delta t^2$$

$$\mathbf{v}(t + \Delta t) = \mathbf{v}(t) + \frac{1}{2}[\mathbf{a}(t) + \mathbf{a}(t + \Delta t)]\Delta t$$

Equivalent to

$$\mathbf{v}(t + \Delta t/2) = \mathbf{v}(t) + \mathbf{a}(t) \Delta t/2$$

$$\mathbf{R}(t + \Delta t) = \mathbf{R}(t) + \mathbf{v}(t + \Delta t/2)\Delta t$$

$$\mathbf{v}(t + \Delta t) = \mathbf{v}(t + \Delta t/2) + \mathbf{a}(t + \Delta t) \Delta t/2$$

- Explicit evaluation of velocity
- Exactly time reversible
- Requiring one force evaluation per step
- The accuracy is high

# Timestep and accuracy of the integration

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What is a good timestep  $\Delta t$  ?

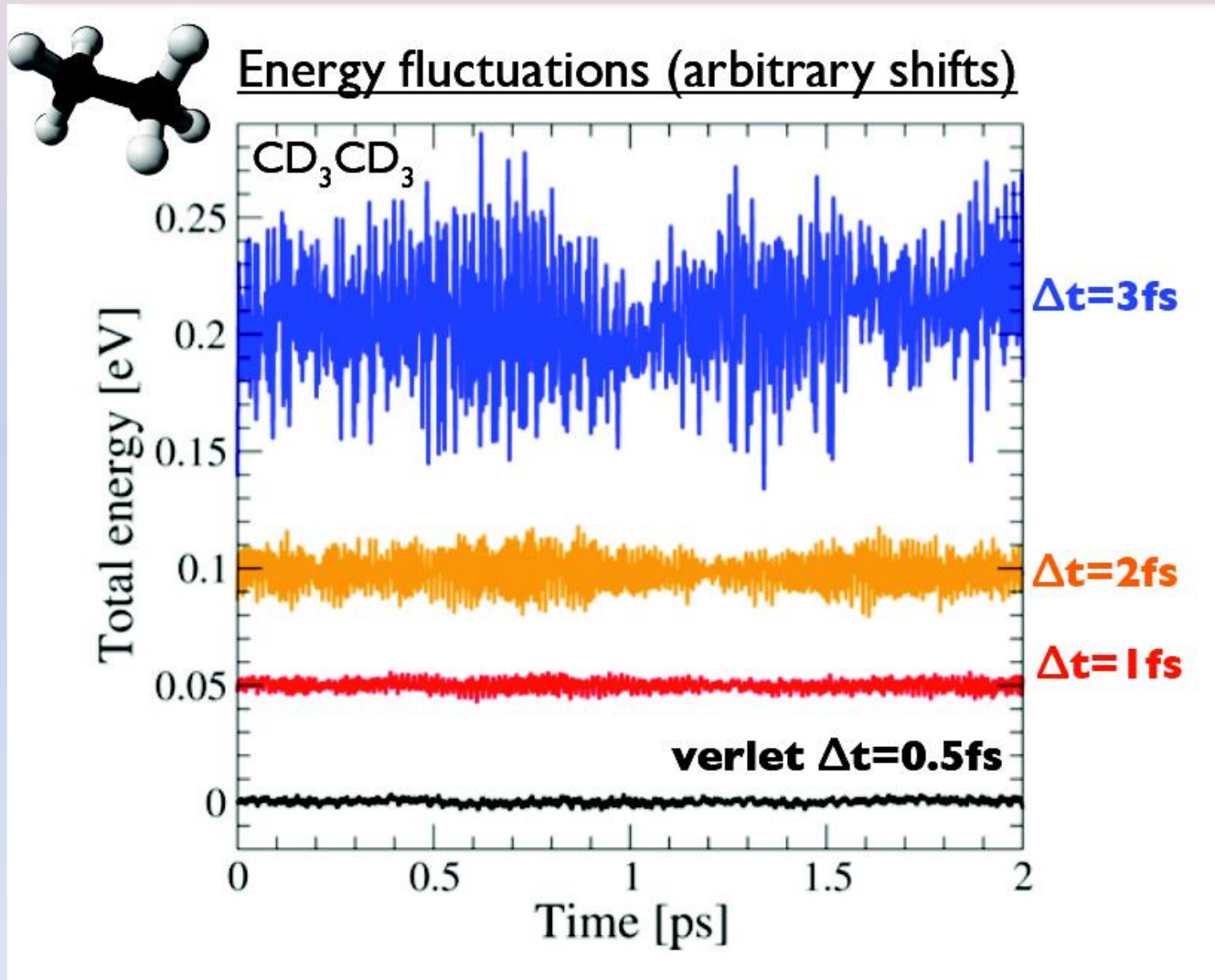
- Depending on the highest vibrational frequency of the system!

$$\omega = \sqrt{k/M} \leftarrow \text{Mass}$$

  
Coupling constant

- Choose  $\Delta t \sim \frac{1}{10\omega_{max}}$  ( $10^{-15}s$  for typical molecules)
- The smaller  $\Delta t$  is, the more accurate (and more expensive) the simulation gets.

# Timestep and accuracy of the integration



# *Ab initio* molecular dynamics (AIMD)

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- Possible flavors of AIMD
  - ❖ Born-Oppenheimer MD
  - ❖ Car-Parrinello MD

- Times scales you can reach

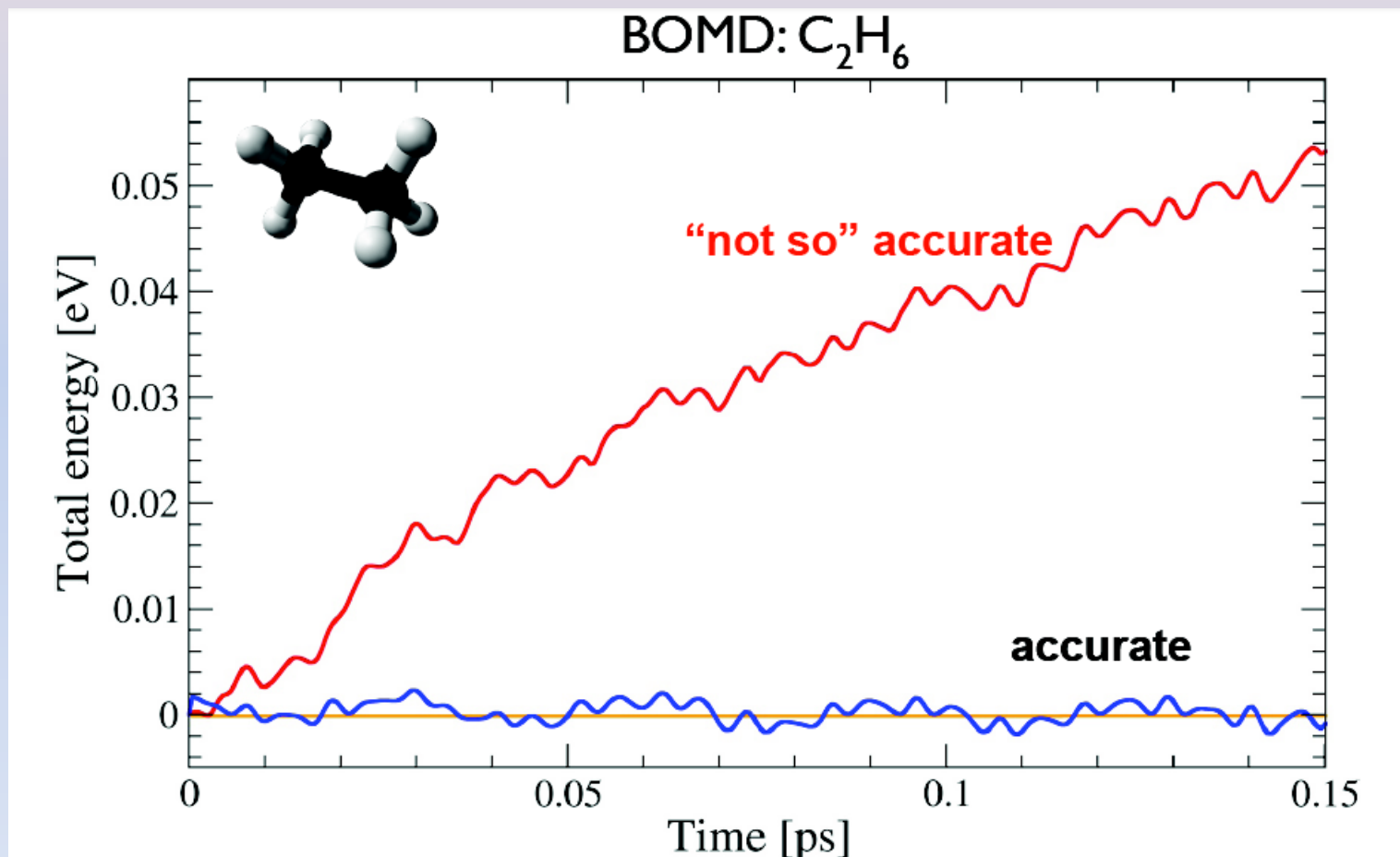
Hundreds of *ps* to 1 *ns*.

# Born-Oppenheimer MD (BOMD)

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- Assign initial  $\mathbf{p}^N(t_0), \mathbf{R}^N(t_0)$
- Converge the *ab initio* electronic structure calculation to self-consistency
- Evaluate the forces  $\mathbf{F}_I = -\frac{\partial U[\{\mathbf{R}_J\}]}{\partial \mathbf{R}_I}$
- Use a numerical integrator to evolve  $\mathbf{p}^N(t_0), \mathbf{R}^N(t_0)$
- Obtain  $\mathbf{p}^N(t_0 + \Delta t), \mathbf{R}^N(t_0 + \Delta t)$  and repeat

# Accurate electronic-structure calculation is needed in BOMD





# Car-Parrinello MD (CPMD)

The CPMD considers the motions of nuclei (described by classical variables  $\{\mathbf{R}_I\}$ ), and the motions of electrons (described by quantum variables  $\{\psi_i\}$ ) as one unified problem:

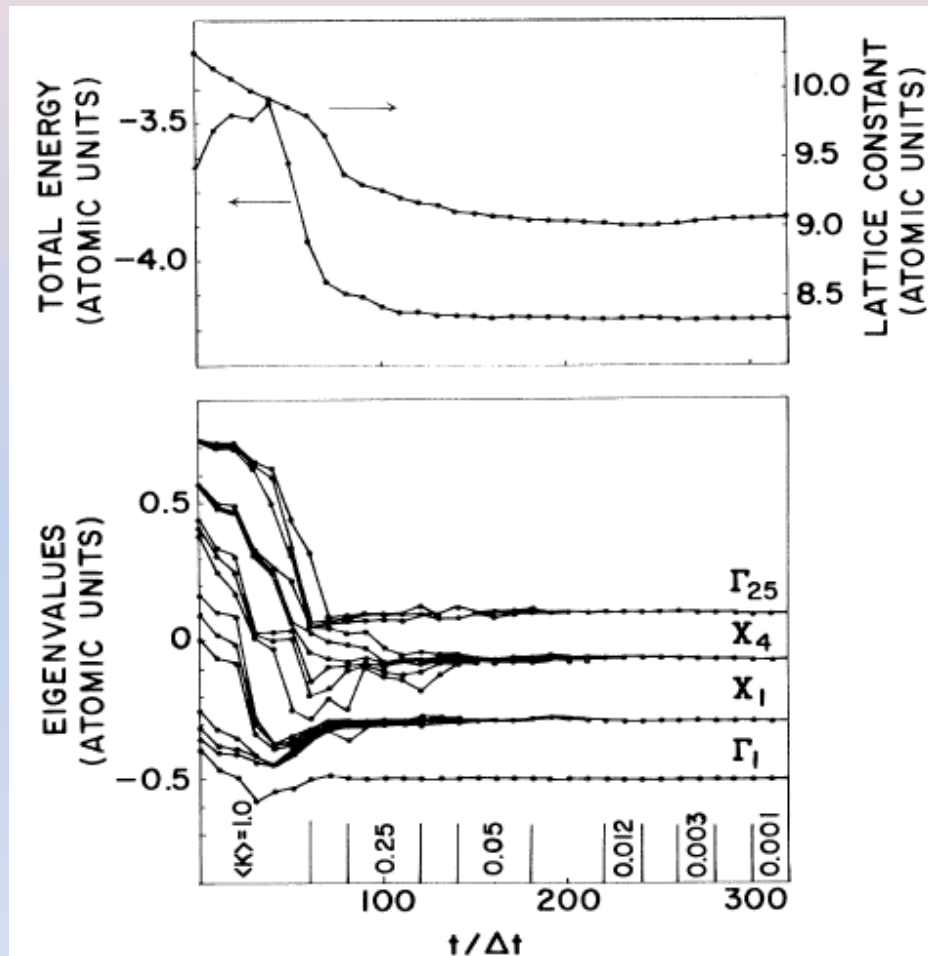
$$L = \sum_{i=1}^{N_e} \frac{1}{2} \mu \int d^3 r |\psi_i(\mathbf{r})|^2 + \sum_{I=1}^{N_{nuc}} \frac{1}{2} M_I \dot{\mathbf{R}}_I^2 - U[\psi_i, \mathbf{R}_I] \\ + \sum_{ij} \Lambda_{ij} \left[ \int d^3 r \psi_i^*(r) \psi_j(r) - \delta_{ij} \right]$$

$$\longrightarrow \mu \ddot{\psi}_i(\mathbf{r}, t) = - \frac{\delta U[\psi_i, \mathbf{R}_I]}{\delta \psi_i^*(\mathbf{r})} + \sum_j \Lambda_{ij} \psi_j(\mathbf{r}, t)$$

$$M_I \ddot{\mathbf{R}}_I = - \frac{\partial U[\psi_i, \mathbf{R}_I]}{\partial \mathbf{R}_I}$$

$\mu$ : Fictitious electronic mass

# Application of CPMD



R. Car and M. Parrinello, *Phys. Rev. Lett.* 55, 2471 (1985).

# Ensembles one can simulate

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- Microcanonical ( $NVE$ ) ensemble: particle numbers  $N$ , Volume  $V$ , and total energy  $E$  are conserved;

This is a natural ensemble for MD simulation, since it follows directly from the equation of motion of the Hamiltonian

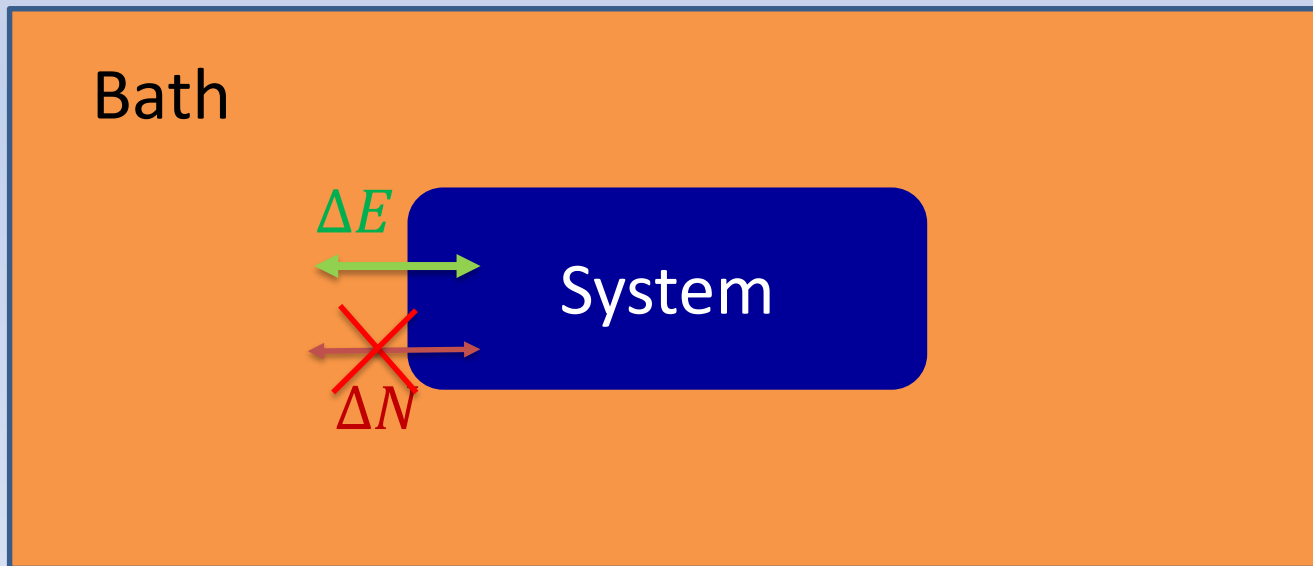
- Canonical ( $NVT$ ) ensemble: particles number  $N$ , Volume  $V$ , and Temperature  $T$  are conserved;

The system is in contact with a heat bath.

- Isothermic-Isobaric ( $NPT$ ) ensemble: particle number  $N$ , Pressure  $P$ , and Temperature  $T$  are conserved;

# The canonical ensemble

- The canonical ensemble is simulated by coupling the system to a thermostat (heat bath).
- This is a more realistic situation (than the NVE ensemble) since experiments are usually done at a given temperature.



Energy of the total system is conserved.

# The Nosé-Hoover thermostat

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

Extended Hamiltonian:

$$H = \underbrace{\sum_I \frac{\mathbf{p}_I^2}{2M_I s^2} + U(\{\mathbf{R}_I\})}_{\text{Physical system}} + \underbrace{\frac{p_s^2}{2Q} + gk_B T \ln(s)}_{\text{Fictitious Oscillator}}$$

- The momenta are damped by fictitious oscillator:  $\dot{\mathbf{p}}_I = F_I - \frac{p_s}{Q} \mathbf{p}_I$
- When the fictitious variable  $s$  is integrated out, the equilibrium distribution function of the original system in canonical ensemble.
- Ergodicity problems– system may get stuck in a region of the phase space  
Possible solution: Nosé-Hoover chains

Attach a chain of fictitious oscillators to the original one.

# Reference (books)

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- D. Frenkel and B. Smith, *Understanding Molecular Simulations: From Algorithms to Applications*
- M. Tuckerman, *Statistical Mechanics: Theory and Molecular Simulation*
- D. Mark and J. Hutter, *Ab initio molecular dynamics*