

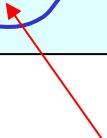
# Finite temperature properties of molecules and materials → ion dynamics

$$m_i \ddot{\mathbf{R}}_i(t) = \mathbf{F}_i(\mathbf{R}_1, \dots, \mathbf{R}_N) \quad i = 1, \dots, N$$

$$\mathbf{F}_i(\mathbf{R}_1, \dots, \mathbf{R}_N) = -\nabla_i E(\mathbf{R}_1, \dots, \mathbf{R}_N)$$

# BO approximation : “Separating” nuclei and electrons

---

$$\left\{ \hat{T}_N + \textcircled{E_e} + \hat{V}_{NN} \right\} \psi_N = E_{\text{TOT}} \psi_N$$


The nuclei move in a potential set up by the electrons.

**In summary :** The large difference between electron and nuclei masses allows us to approximate the total wavefunction as a product of nuclear and electronic wavefunctions. The electronic wave function is obtained by solving the electronic Schroedinger equation for a given set of nuclear coordinates:

and the electronic energy  $E_e$  contributes a potential term to the motion of the nuclei.

$$\hat{H}_e \psi_e(r, R) = \textcircled{E_e} \psi_e(r, R)$$

# Energy and forces in DFT/KS formulation can be used to derive the nuclear potential

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- In the Kohn-Sham formulation, DFT is a practical theory to compute static and dynamical properties of molecules and solids
- We can use forces derived from KS energy to derive nuclear potentials determined by the electrons
- **CLASSICAL approximation for the nuclear motion: we will solve Newton instead of Schroedinger equation for nuclear motion using molecular dynamics (MD)**
- In order to use **MD** we first need to learn about the technique in general terms; we'll then get back and use forces derived from KS total energy functionals to perform ***ab-initio* MD simulations.**

# Introduction to Molecular dynamics: general principles

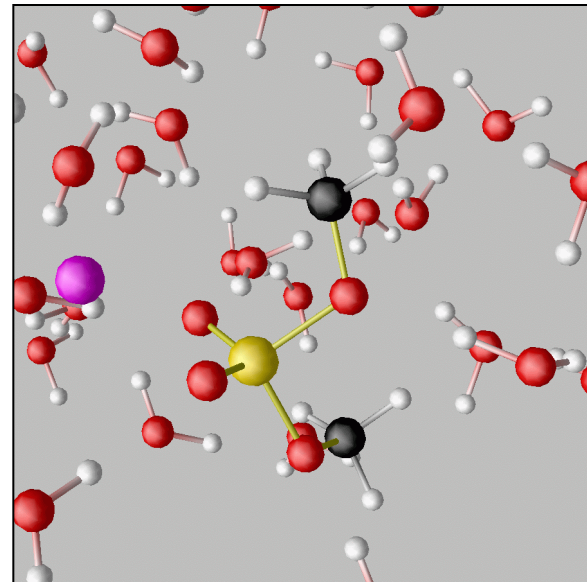
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- Integrate Newton's equations of motion for  $N$  atoms

$$m_i \ddot{\mathbf{R}}_i(t) = \mathbf{F}_i(\mathbf{R}_1, \dots, \mathbf{R}_N) \quad i = 1, \dots, N$$

$$\mathbf{F}_i(\mathbf{R}_1, \dots, \mathbf{R}_N) = -\nabla_i E(\mathbf{R}_1, \dots, \mathbf{R}_N)$$

Ergodic hypothesis and  
Statistical mechanics

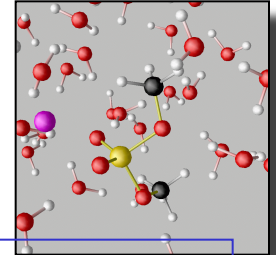


# Molecular dynamics: **Newtonian** equations of motion and determination of **trajectories** as a function of time.

- Integrate Newton's equations of motion for  $N$  atoms assuming ergodicity

$$m_i \ddot{\mathbf{R}}_i(t) = \mathbf{F}_i(\mathbf{R}_1, \dots, \mathbf{R}_N) \quad i = 1, \dots, N$$

$$\mathbf{F}_i(\mathbf{R}_1, \dots, \mathbf{R}_N) = -\nabla_i E(\mathbf{R}_1, \dots, \mathbf{R}_N)$$



Molecular dynamics is a technique to obtain trajectories of a given system obeying classical dynamics as a function of time. Time averages of the system's properties can be then calculated.

Molecular dynamics is a **deterministic method**, which means that the state of the system at any future time can be predicted from its current state.

At each step, the forces on the atoms are computed and combined with the current positions and velocities to generate new positions and velocities a short time ahead. The force acting on each atom is assumed to be constant during the time interval. The atoms are then moved to the new positions, an updated set of forces is computed and new dynamics cycle goes on.

Alder, B. J. and Wainwright, T. E. *J. Chem. Phys.* **27**, 1208 (1957) and *J. Chem. Phys.* **31**, 459 (1959)  
Rahman, A. *Phys. Rev.* **A136**, 405 (1964); Stillinger, F. H. and Rahman, A. *J. Chem. Phys.* **60**, 1545 (1974)  
McCammon, J. A., Gelin, B. R., and Karplus, M. *Nature (Lond.)* **267**, 585 (1977)

# Molecular Dynamics: assume **ergodicity** of the system

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Under the ergodic hypothesis, one can identify temporal and ensemble averages and thus compute thermodynamic properties of a given system, once the interatomic potential  $E$  is specified.

$$A_{ave} = \lim_{\tau \rightarrow \infty} \frac{1}{\tau} \int_{t=0}^{\tau} A(p^N(t), r^N(t)) dt$$



$$\langle A \rangle = \int \int dp^N dr^N A(p^N, r^N) \rho(p^N, r^N)$$

# Molecular Dynamics: The Beginning

THE JOURNAL OF CHEMICAL PHYSICS

VOLUME 31, NUMBER 2

AUGUST, 1959

## Studies in Molecular Dynamics. I. General Method\*

B. J. ALDER AND T. E. WAINWRIGHT

*Lawrence Radiation Laboratory, University of California, Livermore, California*

(Received February 19, 1959)

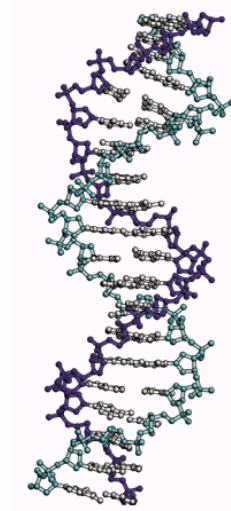
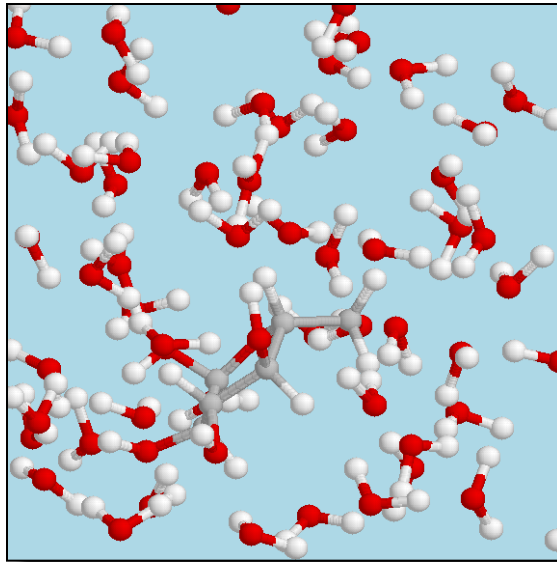
A method is outlined by which it is possible to calculate exactly the behavior of several hundred interacting classical particles. The study of this many-body problem is carried out by an electronic computer which solves numerically the simultaneous equations of motion. The limitations of this numerical scheme are enumerated and the important steps in making the program efficient on the computers are indicated. The applicability of this method to the solution of many problems in both equilibrium and nonequilibrium statistical mechanics is discussed.

Study of microscopic nature of liquids and solids (32 atoms).

Hard-sphere potentials were used.

# Where do the forces used in MD come from? How do we compute them?

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$$m_i \ddot{\mathbf{R}}_i(t) = \mathbf{F}_i(\mathbf{R}_1, \dots, \mathbf{R}_N) \quad i = 1, \dots, N$$

$$\mathbf{F}_i(\mathbf{R}_1, \dots, \mathbf{R}_N) = -\nabla_i E(\mathbf{R}_1, \dots, \mathbf{R}_N)$$



How do we get E???

**We can fit experiment(s) and derive a potential energy function or we can compute E by solving Schroedinger eq. for the electrons.**



# **Ab initio Molecular Dynamics**

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- **Simulating matter on the atomic scale.**
- **Compute trajectories of individual atoms.**
- **Use forces derived from Quantum Mechanics.**
- **Use only fundamental physical constants as input.**

# Classical vs ab initio molecular dynamics

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## Classical MD

**At each MD step:**

- Compute forces from a given model energy function (fitted to expt)
- Update atomic positions

**Millions of atoms**

## Ab initio MD

**At each MD step:**

- Solve the electronic structure problem
- Derive forces from electronic wavefunctions
- Update atomic positions

**Hundreds of atoms**

# How do we perform a MD simulation ?

---

- **Assign initial ionic configuration**

e.g., from x-ray crystallography or randomly chosen (usually not recommended)

- **Assign initial velocities**

At thermal equilibrium, the expected value of the kinetic energy of the system at temperature  $T$  is:

$$\langle E_{kin} \rangle = \frac{1}{2} \sum_{i=1}^{3N} m_i v_i^2 = \frac{1}{2} (3N) k_B T$$

This can be obtained by assigning the velocity components  $v_i$  from a random Gaussian distribution with mean 0 and standard deviation  $(k_B T/m_i)$ :

$$\langle v_i^2 \rangle = \frac{k_B T}{m_i}$$

# How do we perform a MD simulation ?

---

- For each time step:

- Compute the force on each atom:

*X: cartesian vector  
of the system*

$$F(X) = -\nabla E(X) = -\frac{\partial E}{\partial X}$$

- Solve Newton's 2<sup>nd</sup> law of motion for each atom, to get new coordinates and velocities: Use stepwise numerical integration

$$M \ddot{X} = F(X)$$

*M diagonal mass matrix*

- Store coordinates

- Stop

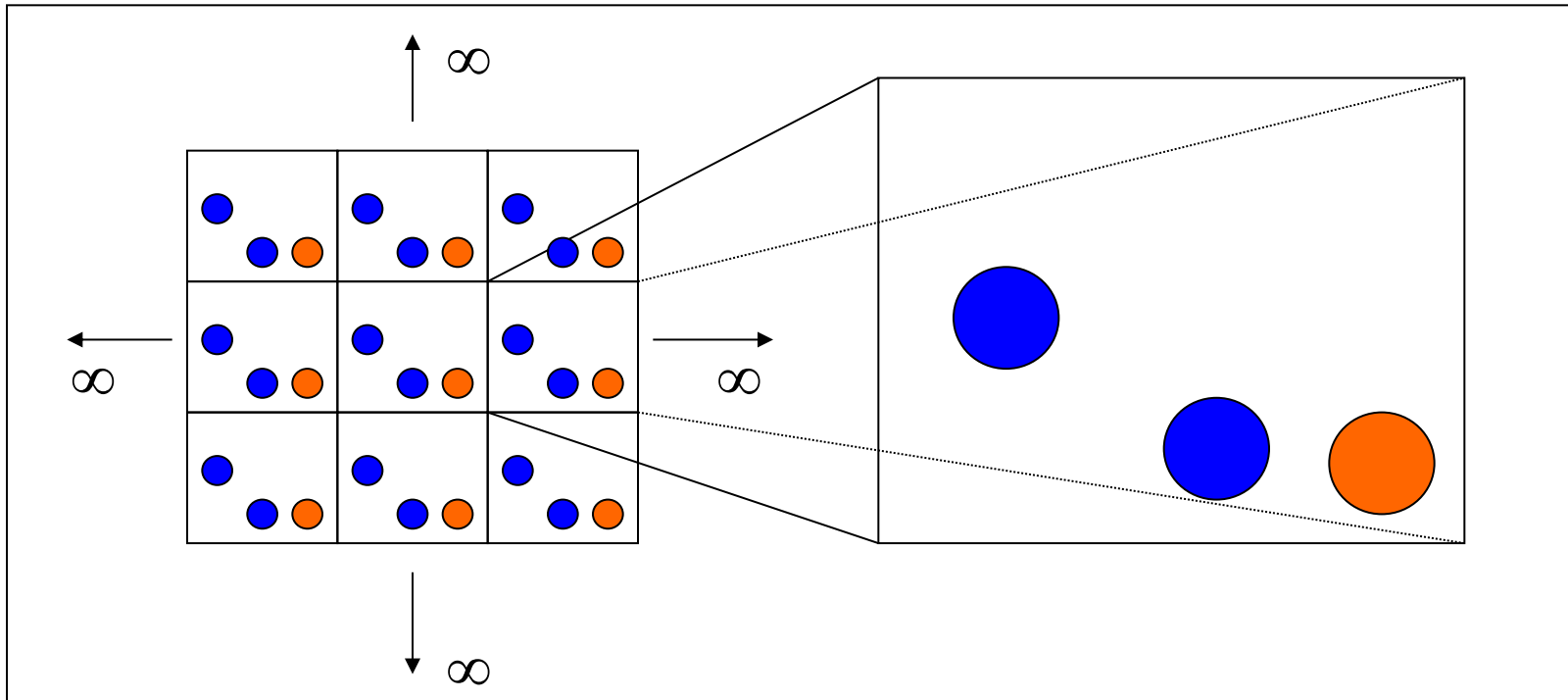
# Let's look at input for a MD simulation in detail

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- Determine or compute on the fly the **interaction energy  $E$**  between the particle of the system
- Choose number of particles, i.e. **size of simulation cell**
- Choose **algorithms to solve Newton equation of motion**
- **Statistical ensemble:**
  - Micro-canonical (NVE)
  - Constant T (NVT)
  - Constant P and T (NPT)

# Periodic Boundary Conditions and size of simulation cell

- Avoid surface effects; representative cell must include all relevant “bonds” and correlation.
- When molecules pass through one boundary another molecule enters the opposite boundary



# Finite difference integration: *advances the system by a small time step $\delta t$ during which forces are considered constant*

---

Expand Taylor series to second order:

$$\mathbf{r}(t + \delta t) = \mathbf{r}(t) + \mathbf{v}(t)\delta t + \frac{\mathbf{f}(t)}{2m}\delta t^2 + \mathcal{O}(\delta t^3)$$

$$\mathbf{v}(t + \delta t) = \mathbf{v}(t) + \frac{\mathbf{f}(t)}{m}\delta t + \frac{1}{2m} \frac{d\mathbf{f}(t)}{dt} \delta t^2 + \mathcal{O}(\delta t^3)$$

Computing  $d\mathbf{f}(t)/dt$  is something we may want to avoid (too costly, from a computational standpoint)

One thing we could do is to use the first equation to compute  $\mathbf{r}(t+\delta t)$ , and then compute  $\mathbf{v}(t+\delta t)$  from the new position as  $\mathbf{v}(t+\delta t)=[\mathbf{r}(t+\delta t)-\mathbf{r}(t)]/\delta t$

This is called the “Euler” algorithm and it is a complete disaster - catastrophic energy drifts and not reversible.

# Finite difference integration: an order $(\Delta t)^4$ algorithm

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- **Verlet algorithm** [  $a$  is acceleration:  $a = F/M$  ]

$$R(t+\Delta t) = R(t) + v(t)\Delta t + (1/2)a(t)\Delta t^2 \quad (1)$$

$$R(t-\Delta t) = R(t) - v(t)\Delta t + (1/2)a(t)\Delta t^2 \quad (2)$$

Summing these two equations yields

$$R(t+\Delta t) = 2R(t) - R(t-\Delta t) + a(t)\Delta t^2 \quad (3)$$

$$v(t+\Delta t) = v(t) + a(t)\Delta t + (1/2)b(t)\Delta t^2 \quad (4)$$

$$a(t+\Delta t) = a(t) + b(t)\Delta t \quad (5)$$

Plugging  $b(t)$  from (5) into (4) yields

$$v(t+\Delta t) = v(t) + (1/2)[a(t) + a(t+\Delta t)] \Delta t \quad (6)$$



# Finite difference integration: additional high order algorithms

- **Leap-frog algorithm**

$$R(t+\Delta t) = R(t) + v(t+(1/2)\Delta t) \Delta t$$

$$v(t+(1/2)\Delta t) = v(t-(1/2)\Delta t) + a(t) \Delta t$$

- **Beeman's algorithm**

$$R(t+\Delta t) = R(t) + v(t)\Delta t + (2/3)a(t)\Delta t^2 - (1/6)a(t-\Delta t)\Delta t^2$$

$$v(t+\Delta t) = v(t) + v(t)\Delta t + (1/3)a(t)\Delta t + (5/6)a(t)\Delta t - (1/6)a(t-\Delta t)\Delta t$$

# Choice of Time Step

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There are no hard and fast rules. In general, if  $\delta t$  is too small, not enough of phase space is explored, and if  $\delta t$  is too large, it will lead to instabilities in the integration

Typical time-steps fall in the range of 0.1-10 femtoseconds.

For a liquid, the time step should be small compared to the mean time between collisions.

For a flexible molecule, the time step should be no greater than 1/10 the time of the shortest period of motion.

Some examples\* ( $\delta t$  in seconds) :

- Atoms: translation,  $\delta t \sim 10^{-14}$
- Rigid Molecules: translation and rotation,  $\delta t \sim 5 \times 10^{-15}$
- Flexible Molecules: translation, rotation, torsion,  $\delta t \sim 2 \times 10^{-15}$
- Flexible Molecules & Flexible Bonds: translation, rotation, torsion, vibration,  $\delta t < 10^{-15}$

\* From “Molecular Modeling,” 2nd edition, A. Leach, Prentice Hall

# Comparison of different integration schemes

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- It turns out that the **Verlet algorithm** is nearly always the best choice.
  - It is very fast computationally
  - It requires little memory
  - Short-term energy conservation is decent
  - Long-term energy conservation is excellent
  - It is time-reversible
- Other, “Verlet-type” schemes, such as the “Leap-Frog” algorithm are also widely used.
- Higher order methods, such as the **“Predictor-Corrector”** scheme are less common. One can use larger time steps, but these algorithms suffer from being slower, requiring more storage, not being reversible, and needing to take differences of large numbers.

# Accuracy in MD

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The trajectory of a system is usually very sensitive to the initial conditions.

This means that two trajectories that are initially very close will diverge exponentially as time progresses.

If we consider the integration error as the source of an initial (small) difference, then we always have a simulated trajectory divergent from the “true” one.

Is this a devastating blow to molecular dynamics?

Not really - we're essentially interested in making *statistical predictions*, not in knowing *precisely* what will happen at a given condition in time.

# Simulating at constant T: simple rescaling

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Simplest way to modify  $T$ :

Temperature depends on velocities so correct the velocities every step to give desired temperature.

$$\langle E_{kin} \rangle = \frac{1}{2} \sum_{i=1}^{3N} m_i v_i^2 = \frac{1}{2} (3N) k_B T$$

Multiply by

$$\lambda = \sqrt{T_W / T(t)}$$

Where  $T_W$  is the temperature that you want and  $T(t)$  is the temperature at time  $t$ . **Simple, but crude and may inhibit equilibration.**

# Stochastic Collisions

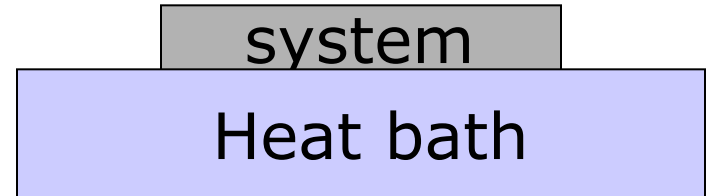
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- Influence the system temperature by reassigning the velocity of a random particle (a “collision”). An element of Monte-Carlo.
- The new velocity is from the Maxwell-Boltzmann distribution corresponding to the desired  $T_W$ .
- Between collisions sample a micro-canonical ensemble. It can be shown that overall the canonical ensemble is sampled.
- Collision frequency is important.
- Can also reassign some or all particle velocities.

# Simulating at constant T: the Berendsen scheme

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- Bath supplies or removes heat from the system as appropriate



- Exponentially scale the velocities at each time step by the factor  $\lambda$ :

$$\lambda = \sqrt{1 - \frac{\Delta t}{\tau} \left( 1 - \frac{T_{bath}}{T} \right)}$$

where  $\tau$  determines how fast the bath influences the system

*T: “kinetic” temperature*

Simple velocity rescaling and Berendsen's scheme do not sample the canonical ensemble

# Extended systems: Nosé thermostat

---

An extra degree of freedom  $s$  is introduced, which scales the real velocities and time step

$$\mathbf{v} = s \dot{\mathbf{r}}, \quad \delta t = s \delta t'$$

We then associate a kinetic and potential energy to  $s$  ( $f$  is the number of degrees of freedom in the system)

$$V_s = (f + 1)kT_W \ln s, \quad K.E._s = \frac{1}{2} Q \dot{s}^2$$

$Q$  measures coupling between reservoir and system. It should not be too high (slow flow) or too low (oscillations).

It can be shown that the partition function of this system is

$$Z = \frac{1}{(f + 1)} \left( \frac{2\pi Q}{kT} \right)^{1/2} \exp(E / kT) Z_c$$

Method allows one to sample the canonical ensemble



# NoséThermostat

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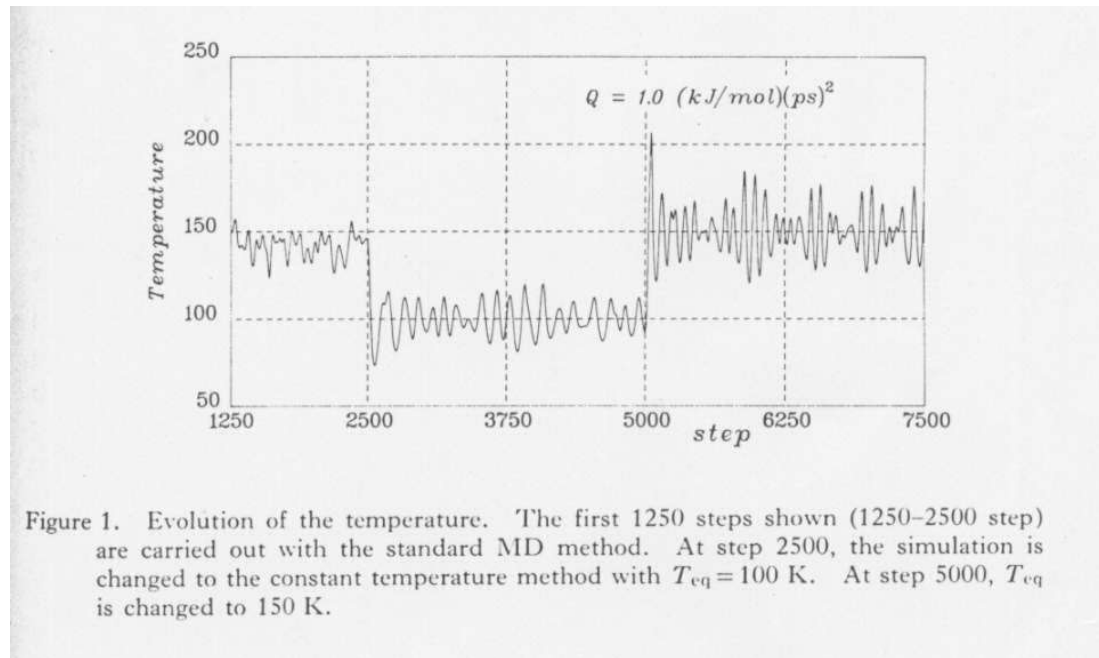
$$\left\langle A\left(\frac{\mathbf{p}}{s}, \mathbf{r}\right) \right\rangle = \langle A(\mathbf{p}', r) \rangle_c$$

for a given property  $A$ .

**Note that the total momentum and total angular momentum deviate from canonical values by  $O(1/N)$ .**

# Example of application of Nosé Thermostat

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**System of 108 argon atoms.**

***S. Nosé Mol. Phys. 52, 255 (1984).***

# Hoover Thermostat

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Start with the Nosé method and redefine the time variable

$$dt_{old} = s dt_{new}$$

Thus eliminate  $s$  from equations of motion

$$\dot{\mathbf{p}} = \mathbf{f} - \xi \mathbf{p}, \xi = \frac{p_s}{Q}, \dot{\xi} = \frac{fk}{Q} (T(t) - T_W)$$

Hoover thermostat samples a canonical ensemble

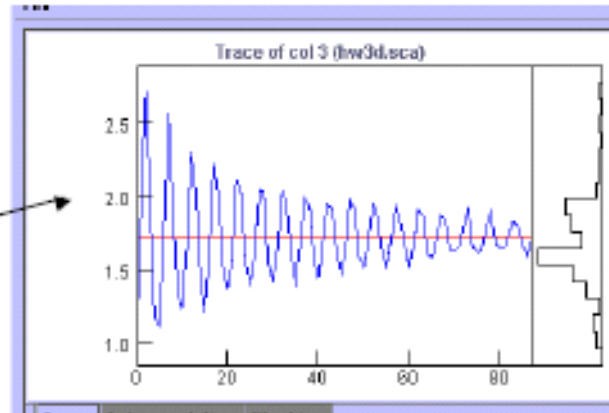
*S. Nose, J. Chem. Phys. 81, 511 (1984); Mol. Phys. 52, 255 (1984).*

*W. Hoover, Phys. Rev. A31, 1695 (1985).*

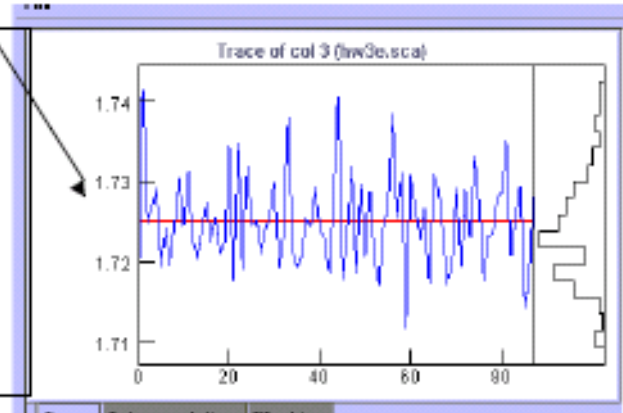
# Effect of thermostat

System T fluctuates but  
how quickly?

Q=1



Q=100

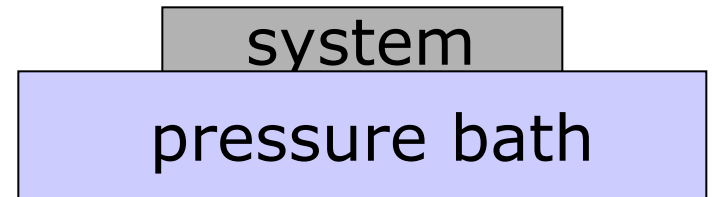


```
DIMENSION 3
TYPE argon 256 48.
POTENTIAL argon argon 1 1. 1. 2.5
DENSITY 1.05
TEMPERATURE 1.15
TABLE_LENGTH 10000
LATTICE 4 4 4 4
SEED 10
WRITE_SCALARS 25
NOSE 100.
RUN MD 2200 .05
```

# Simulating at constant P: Berendsen scheme

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- Couple the system to a pressure bath
- Exponentially scale the volume of the simulation box at each time step by a factor  $\lambda$ :



$$\lambda = 1 - \kappa \frac{\Delta t}{\tau_P} (P - P_{bath}) \quad \text{where} \quad P = \frac{2}{3v} \left( E_{kin} + \sum_{i=1}^N x_i \cdot F_i \right)$$

where  $\kappa$  : isothermal compressibility

$\tau_P$  : coupling constant

$v$  : volume

$x_i$ : position of particle  $i$

$F_i$  : force on particle  $i$

# Andersen Barostat

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- Variables are scaled.
  - The ‘piston’ has its own kinetic and potential energies.
- $$\mathbf{r} = V^{1/3} \mathbf{r}', \dot{\mathbf{r}} = V^{1/3} \dot{\mathbf{r}}'$$

$$K_V = \frac{1}{2} \underset{\uparrow}{Q} \dot{V}^2, PE_V = P_W V$$

$Q$  measures coupling between reservoir and system. It should not be too high (slow flow) or too low (oscillations).

- It can be shown that the time average of the trajectories derived using the Andersen barostat equals the isoenthalpic-isobaric ensemble average to  $O(N^{-2})$ .

# Constant Temperature and Pressure (combining Nose and Andersen formulations)

---

For example in the Hoover formulation:

$$\dot{\mathbf{p}} = \mathbf{f} - \chi \mathbf{p} - \xi \mathbf{p}$$

$$\dot{\mathbf{p}} = \mathbf{f} - \chi \mathbf{p} - \xi \mathbf{p}, \chi = \dot{V} / 3V, \dot{\chi} = (P(t) - P_W)V / \tau^2 kT_W$$

- *Unit cell shape can also change.*

- System can switch between crystal structures.

- Method is very useful in studying the transitions between crystal structures.

- *Dynamics is unrealistic*: Just because a system can fluctuate from one structure to another does not mean that probability is high for it to happen.

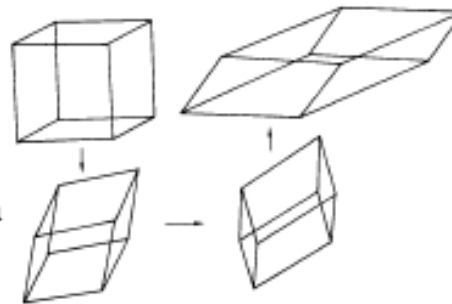


Fig. 7.3 Changing box-shape.

# Which Method?

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- **Scaling is simple and easy and in the simplest case requires no parameters. Convergence may be a problem; does not sample canonical/isobaric/isobaric-isothermal ensemble. Good for equilibration purposes.**
- **Stochastic approach is more stable than scaling but leads to a method which is no longer deterministic.**
- **Extended system methods are more complex and require choice of parameters. Nosé-Hoover thermostats enable the canonical ensemble to be sampled.**

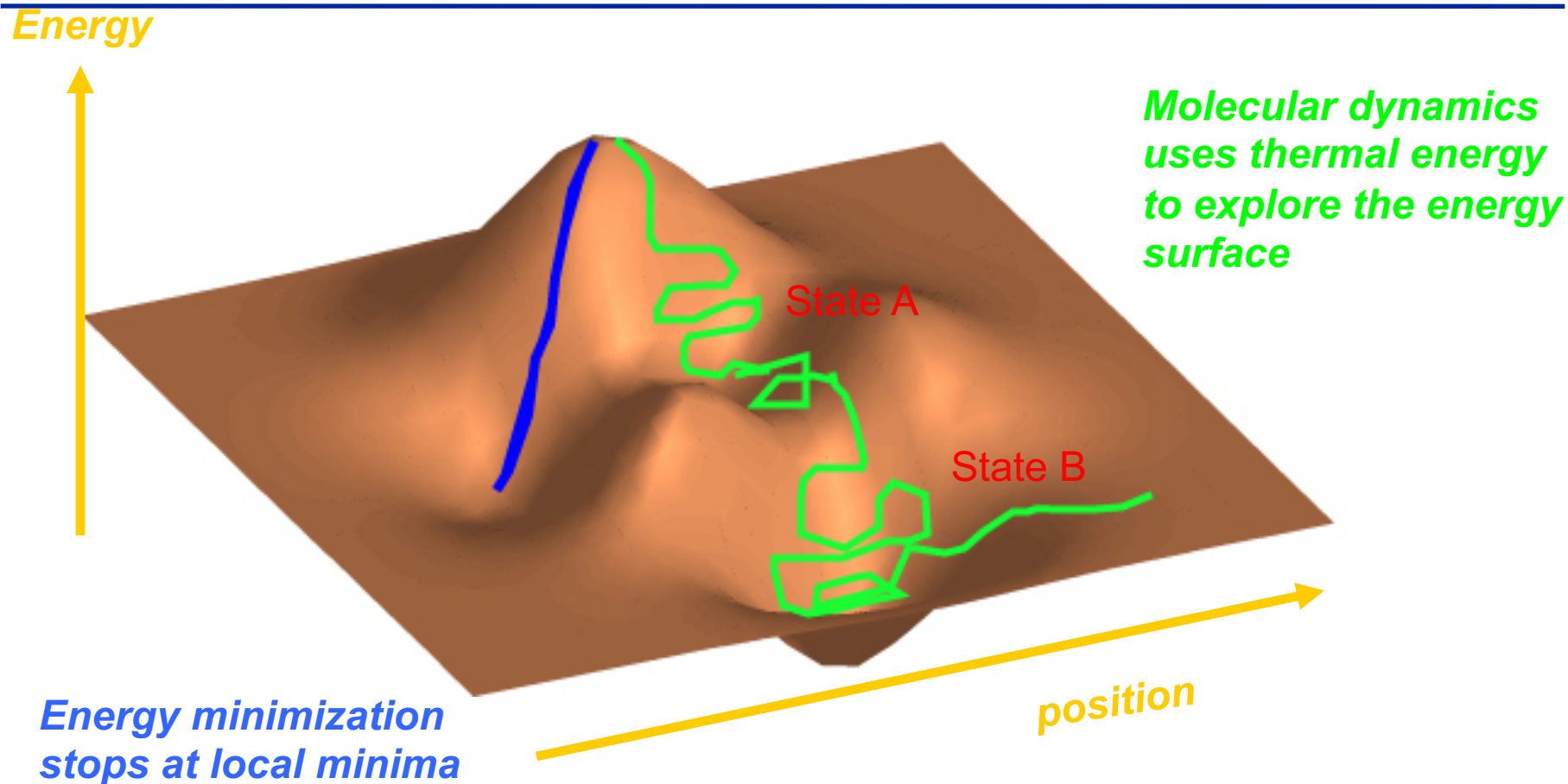


# Constant T and/or P: Summary

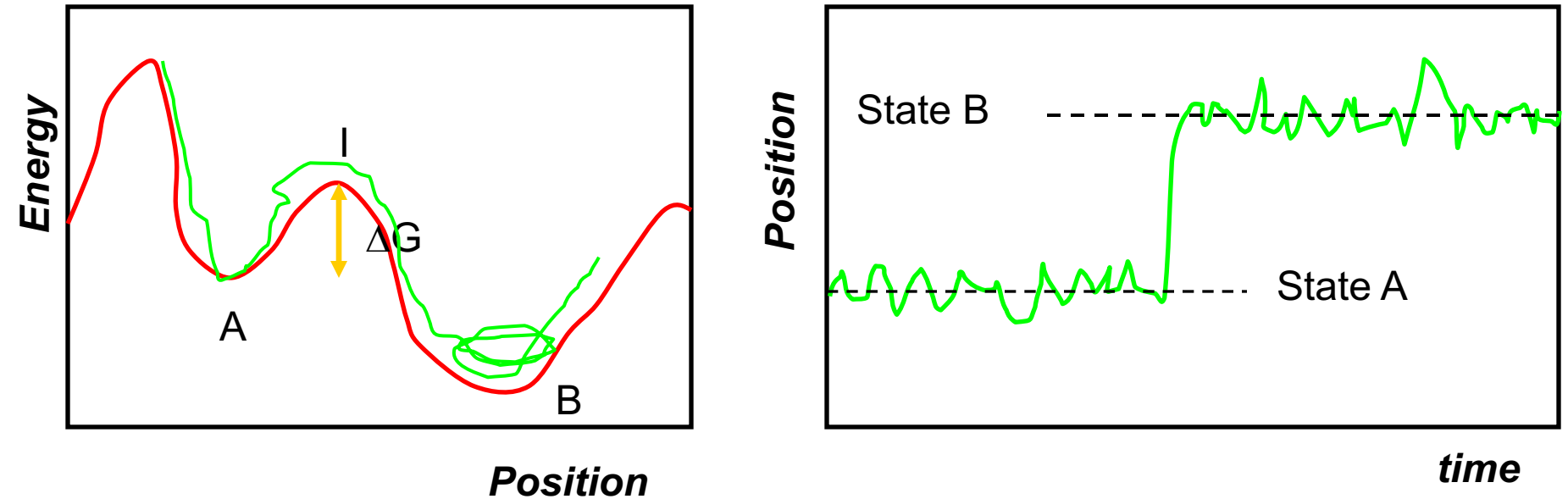
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- One may want to constrain/choose temperature and/or pressure in a molecular dynamics simulation
- The temperature can be fixed by a) scaling the velocities (partially or completely); b) changing some or all of the velocities of the particles to a randomly selected member of the Maxwell-Boltzmann distribution of the desired  $T$ , c) couple the system to a heat bath
- Analogous methods exist to chose/maintain a constant pressure.
- Combinations of methods can be used to simulate a system at constant temperature and pressure.

# MD as a tool for minimization



# Crossing energy barriers



The actual transition time from A to B is very quick (a few pico seconds).

What takes time is waiting. The average waiting time for going from A to B can be expressed as:

$$\tau_{A \rightarrow B} = C e^{\frac{\Delta G}{kT}}$$