

Molecular Dynamics and Accelerated Molecular Dynamics

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Lecture 2

Tutorial Lecture Series
Institute for Pure and Applied Mathematics (IPAM)
UCLA
September 13-16, 2005

Acknowledgment: DOE/BES

Overall Outline

Day 1: Molecular dynamics methods

Day 2: Molecular dynamics methods

Day 3: Infrequent events, transition state theory, saddle finding, etc.

Day 4: Accelerated molecular dynamics methods

Overall Outline

Day 1: Molecular dynamics methods

Day 2: Molecular dynamics methods

- potentials
- thermostats
- maybe more

Day 3: Infrequent events, transition state theory, saddle finding, etc.

Day 4: Accelerated molecular dynamics methods

Interatomic potentials - beyond Lennard-Jones

Volume-dependent term

- embedded atom method (EAM) (fcc metals)

Bond covalency, angular terms

- Molecular mechanics potentials (proteins, DNA, polymers)
- Stillinger Weber (e.g., C, Si)
- Tersoff (e.g., C, Si)
- modified EAM (MEAM)
- bond-order potential (BOP)

Charge Transfer

- Rappe and Goddard
- Streitz and Mintmire

Ionic systems

- Buckingham form

Embedded Atom Method (EAM)

$$E_{tot} = \sum_i^N E_i$$

$$E_i = \frac{1}{2} \sum_j \phi(r_{ij}) + F(\bar{\rho}_i)$$

pair terms density term

$$\bar{\rho}_i = \sum_j \rho(r_{ij})$$

Also known as:

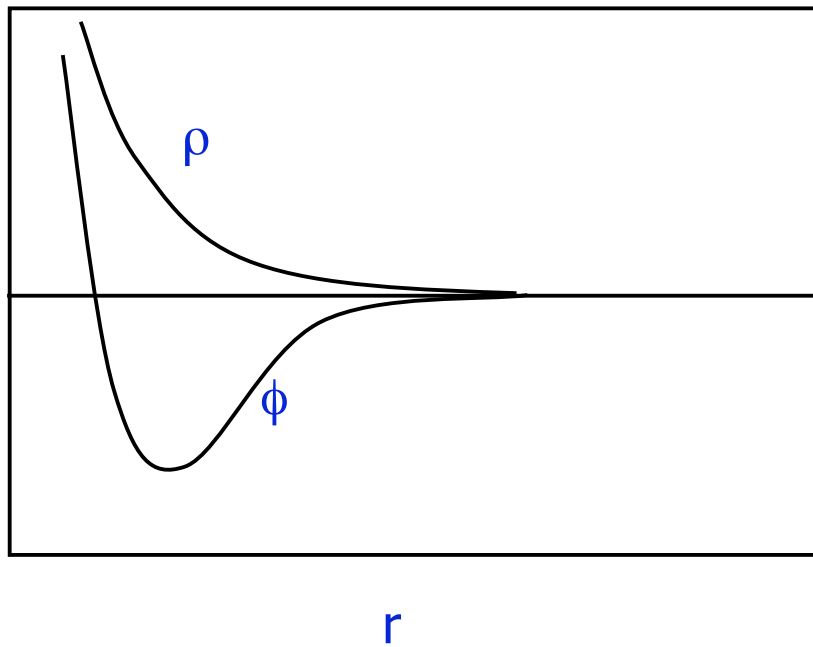
Effective medium theory (Norskov et al, 1980)
Embedded atom method (Daw and Baskes, 1983)
N-body potential (Finnis and Sinclair, 1984)
(second-moment approximation to tight binding)
Glue model (Ercolessi et al, 1986)
MD/MC CEM (DePristo and coworkers)

- Many-body potential for little more cost than pair potential
- Works especially well for fcc metals

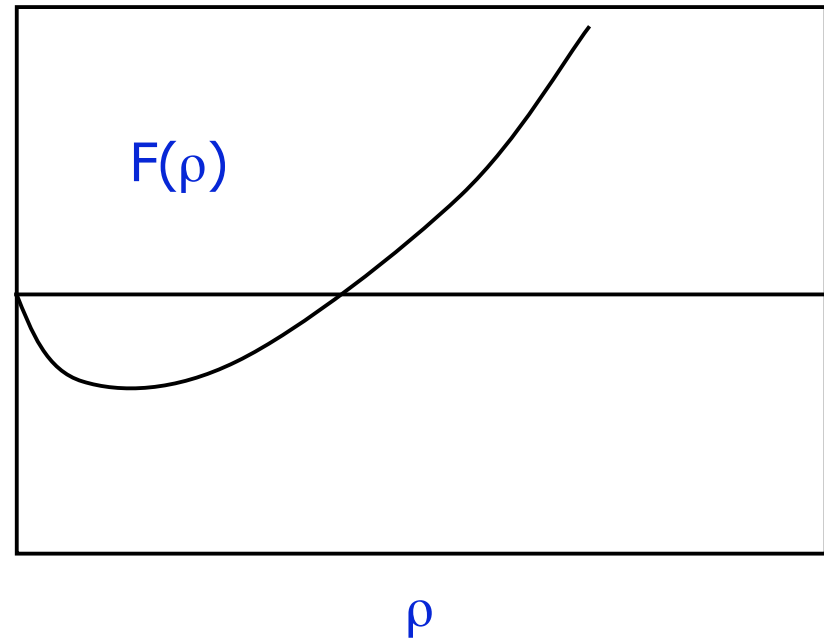
Embedded Atom Method (EAM)

$$E_i = \frac{1}{2} \sum_j \phi(r_{ij}) + F(\bar{\rho}_i) \quad \bar{\rho}_i = \sum_j \rho(r_{ij})$$

Typical shapes



ρ senses local density of atoms -- nearby atoms contribute most.



F has positive curvature -- first bonds are the strongest.

Embedded Atom Method (EAM)

Vacancy formation energy

pair potential predicts $E_{\text{vac}} = E_{\text{coh}}$

EAM fixes this

e.g., Ni: $E_{\text{coh}} = 4.45 \text{ eV}$, $E_{\text{vac}} = 1.6 \text{ eV}$

Elastic constants

pair potential gives $c_{12} = c_{44}$ (zero Cauchy pressure)

e.g., for Ni:

$c_{11} = 2.47 \text{ Mbar}$

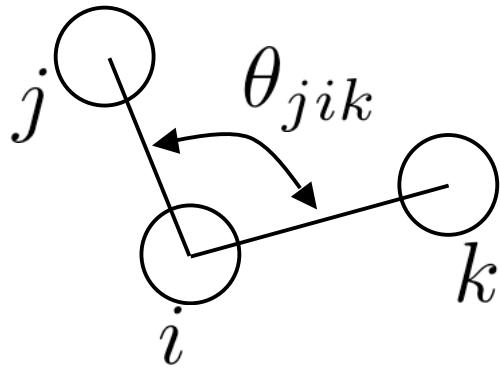
$c_{12} = 1.47 \text{ Mbar}$

$c_{44} = 1.25 \text{ Mbar}$

EAM has been fit to most fcc/bcc/hcp metals, but works best for "noble" metals Cu, Ag, Au, Ni, Pd, Pt

Angular Potentials

Simplest approach - explicit angular function



$$E_i = \sum_j \phi(r_{ij}) + \sum_{j,k} f(\theta_{jik})$$

Examples:

Keating (1966)

Stillinger-Weber (1985)

Biswas and Hamann (1987)

However, it is better to couple this angular dependence to a volume term...

Tersoff potential

J. Tersoff, Phys. Rev. B **37**, 6991 (1988)

Basic form:

$$E_i = \sum_j \phi_R(r_{ij}) + \sum_j B_{ij} \phi_A(r_{ij})$$

repulsive attractive

B_{ij} is the *bond order*, which depends on distances and angles to other atoms neighboring the i-j bond pair.

Tersoff form has been widely used for Si
Extended to C-H systems by Brenner (REBO).
And other systems.

Modified embedded atom method (MEAM)

M.I. Baskes, Phys. Rev. B **46**, 2727 (1992).

$$E_i = \sum_j \phi(r_{ij}) + F \left[\sum_j \rho(r_{ij}) + \text{angular terms} \right]$$

Fit to many elements and alloys - reasonably successful.

Bond Order Potentials (BOP)

David Pettifor

Low-order moments to tight-binding (TB) electronic structure method.

Second moment ---> EAM (Finnis-Sinclair)

Higher moments give angular effects.

Infinite moments gives exact TB -- very appealing.

Protein systems

Total interactions = covalent interactions + “nonbond” interactions

Form is fairly simple.

Bonds cannot dissociate.

Very carefully fit parameter sets (e.g., Charmm, Amber, ...)

Sometimes water is included, sometimes not.

Protein systems

Covalent interactions:

$$E_{covalent} = E_{bond} + E_{angle} + E_{dihedral} + E_{improper}$$

$$E_{bond} = \sum_{bonds} \frac{1}{2} k_b (b - b_0)^2$$

$$E_{angle} = \sum_{angles} \frac{1}{2} k_\theta (\theta - \theta_0)^2$$

$$E_{dihedral} = \sum_{dihedrals} \frac{1}{2} V_n [1 + \cos(n\phi - \delta)]$$

Protein systems

“nonbonded” interactions:

$$E_{nonbond} = E_{electrostatic} + E_{LJ} + E_{polar}$$

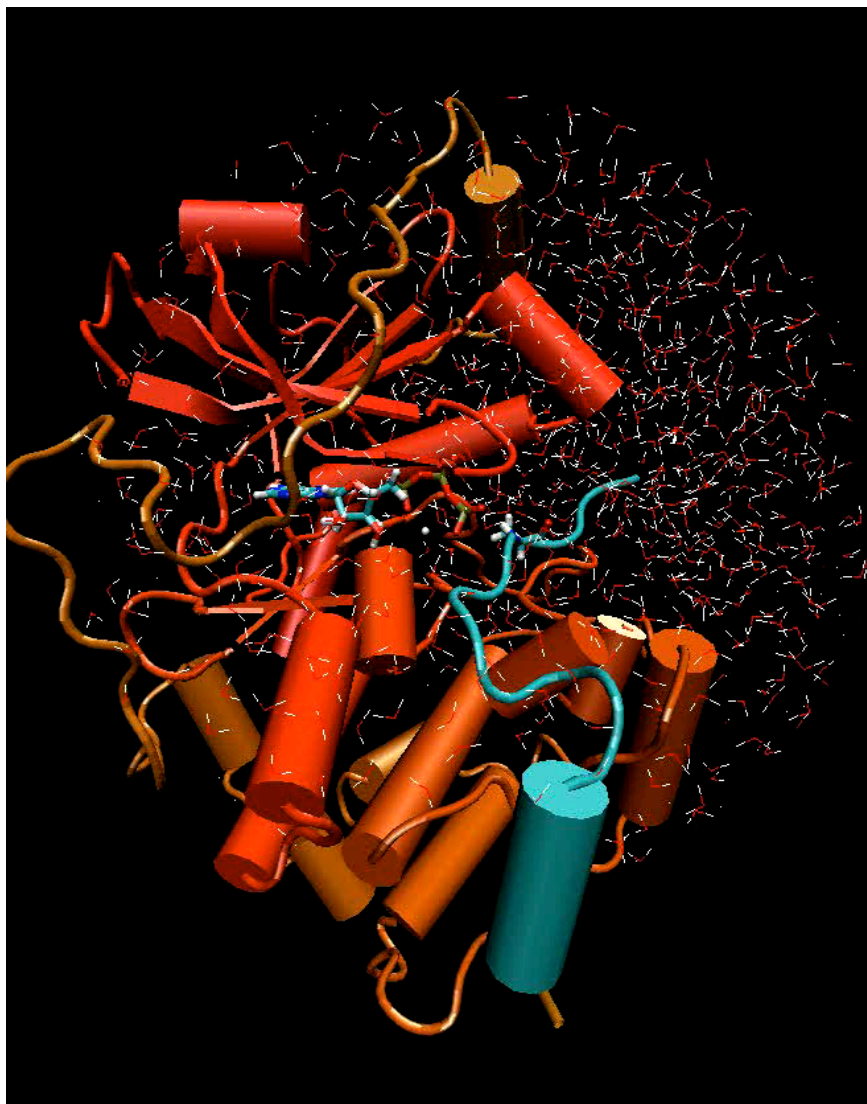
$$E_{electrostatic} = \frac{1}{4\pi\epsilon_0\epsilon} \sum_{i \neq j} \frac{q_i q_j}{r_{ij}}$$

q_i, q_j = fractional charges

often omitted



Protein Kinase



- solvated by water (TIP3P)
- ~32000 atoms total
- 250 ps
- took a few days (1 processor)
- MD using Amber (Cornell et al force field, 1995 (parm 94))
- Only showing H₂O initially near protein
- Graphics using VMD
- Tube = alpha helix
- Arrow Ribbon = beta sheet

B. McMahon et al (~2003)

A.F. Voter, September, 2005 LAUR-05-8125

(250ps.mpg)

Los Alamos

Ionic systems

- Short-range Buckingham term

$$Ae^{-r/\rho} - \frac{C}{r^6}$$

- Long-range electrostatic term (full or partial charge)

$$\frac{q_i q_j}{r_{ij}}$$

- Efficient force evaluation requires either Ewald or fast-multipole techniques. (Much more complicated and expensive than simple pair potential with cutoff, but N-scaling can be achieved.)

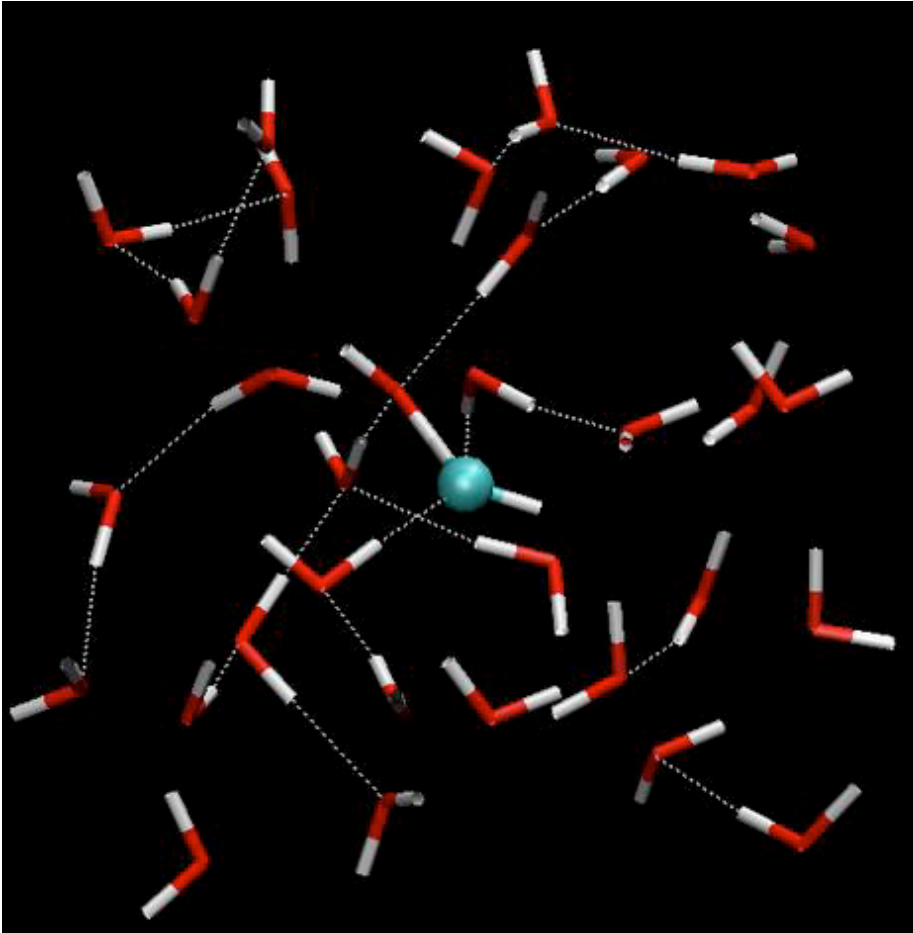
MD using forces from electronic structure calculations

Avoids the potential problem altogether

- no need to do a fit
- typically much more accurate

Very expensive -- typically can only do a few ps and not too many atoms (e.g., 10^1 - 10^2).

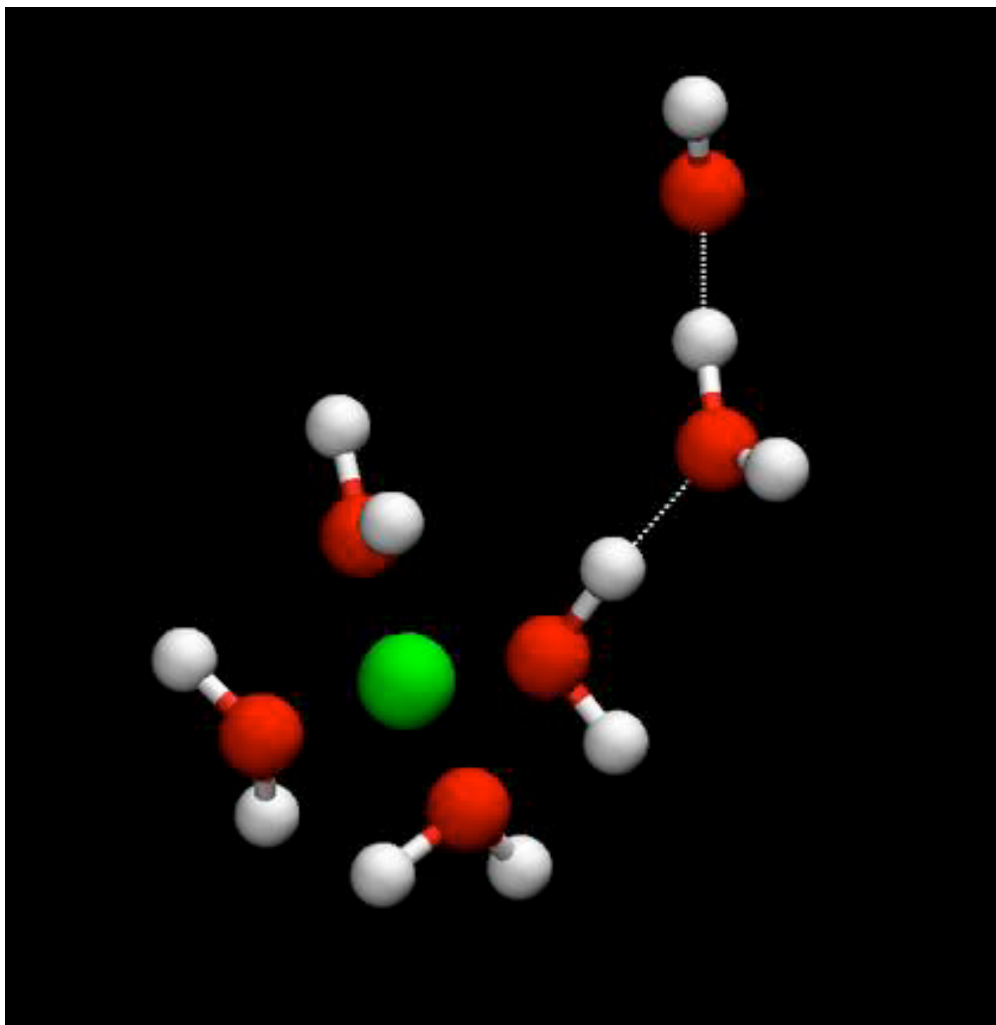
Hydration and mobility of DO^-



D. Asthagiri, L. R. Pratt, J. D. Kress, and M. A. Gomez, PNAS **101**, 7229 (2004).

- Simulation of DO^- in D_2O .
- Revised PBE (rPBE) functional and PAW treatment of electronic structure.
- Time-step = 0.5 fs.
- 32 water molecules.
- Hydroxide oxygen is colored cyan.
- Hydration structure of 3-waters consistent with theoretical predictions.
- Motion by hopping along hydrogen bonded chain.
- 20 fs between frames (1 ps total).

Deprotonation of $\text{Be}[\text{H}_2\text{O}]_4^{2+}$ in the presence of HO^-



- $\text{Be}[\text{H}_2\text{O}]_4^{2+}$ pKa = 3.5
- Deprotonation hastened in simulation by adding a HO^-
- VASP simulation with PW91 functional and US-PP.
- 32 Waters + Be^{2+} ion.
- Time-step = 0.5 fs.
- Deprotonation happens within 250 fs.
- Only crucial water molecules shown for clarity.
- 2.5 fs between frames.

D. Asthagiri and L. R. Pratt, CPL **371**, 613 (2003)

Fitting an Interatomic Potential

- Experimental data usually limited
- First-principles data provides information unavailable from experiment
- Fitting to forces (Ercolessi-Adams, 1994) -- very powerful -- $3N$ observables for each calculation.
- Be sure to test against information not in fit
- Plan on being patient and persistent, and hope for good luck!

Evaluating equilibrium properties

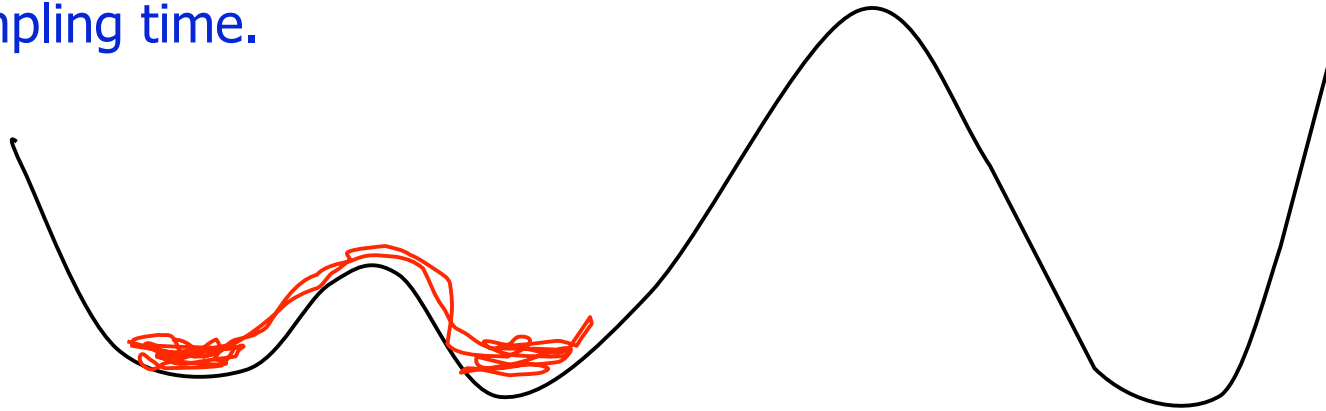
$$\begin{aligned}\langle A \rangle &= \frac{1}{t} \int_0^t A(t') dt' \pm c/\sqrt{t} \\ &= \frac{1}{n_{step}} \sum_i^{n_{step}} A[\mathbf{x}(t_i), \mathbf{p}(t_i)]\end{aligned}$$

Assumes:

- system has been run long enough to properly sample the phase space
- that the system is ergodic (i.e, that it can sample the phase space fully)

Enhanced Sampling Methods

Often, high barriers prevent system from fully sampling the configuration space we care about in our limited sampling time.



If we care about *equilibrium* (not dynamic) properties, we can play tricks to speed up the sampling without corrupting those properties.

- umbrella sampling (importance sampling)
- parallel tempering
- multicanonical sampling
- hybrid Monte Carlo
- many other specialized methods

What ensemble is MD?

An energy-conserving trajectory gives results for a *microcanonical* (N,V,E) ensemble (i.e., fixed N, volume, and total energy).

More typically, we are interested in a thermal ensemble, such as the *canonical* (N,V,T) ensemble (fixed N, volume, and temperature):

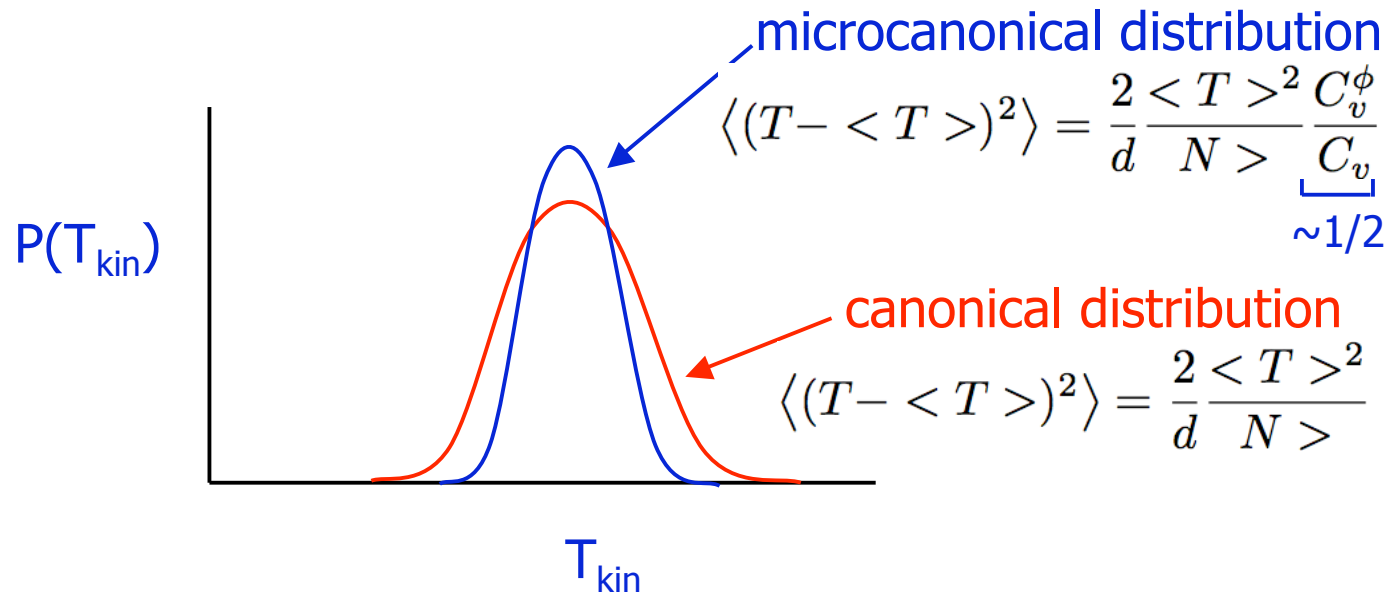
$$p(x) \propto \exp(-V(x)/kT)$$

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Thermostats

<u>Thermostat</u>	<u>Brief description</u>	
<u>canonical?</u> <u>Gaussian</u>	K.E. fixed to match correct T	no
Berendsen	momenta dragged up or down towards correct T	no
Nose-Hoover	extra degree of freedom acts as thermal reservoir	in principle, but caution!
Nose-Hoover chain (...(((NH)NH)NH...		yes-probably
Langevin	noise + frictional drag balances to give correct T	yes
Andersen	occasionally re-randomize momenta	yes

Berendsen Thermostat

Berendsen et al, J. Chem. Phys. 81, 3684 (1984).

$$\frac{dv}{dt} = \frac{F}{m} + \frac{1}{2\tau} \left(\frac{T}{T_{kin}} - 1 \right) v$$

Drags kinetic temperature towards the correct value.

Simple.

Robust.

But note that this has to give a T_{kin} distribution even narrower than the microcanonical one, so it cannot be right.

Berendsen Thermostat

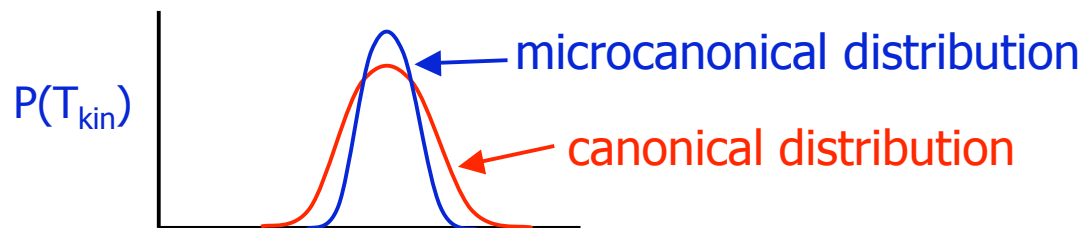
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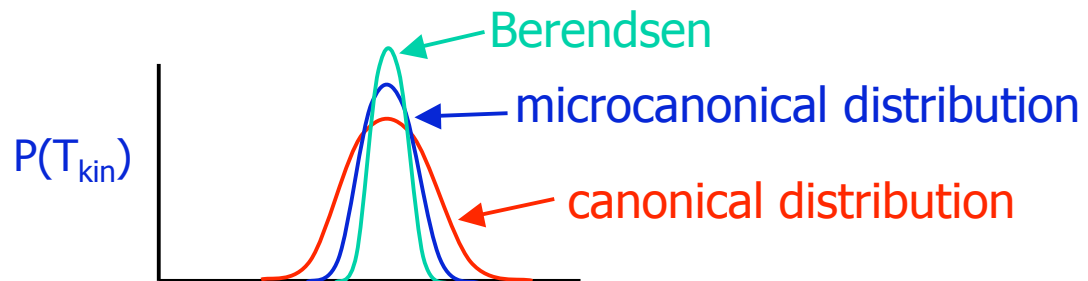
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Nose-Hoover Thermostat

Deterministic.

Add one new variable, s , to equations of motion, and scale momenta by $1/s$. With mass Q , s acts as a thermal reservoir.

Built on elegant formalism proposed by Nose (1984), in which microcanonical dynamics on this extended system is shown to give canonical properties.

However, in some cases, the extended system is not ergodic, becoming trapped in subspace -- dangerous as a thermostat.

Nose-Hoover chain

Martyna, Klein, and Tuckerman (1992)

Improve ergodicity in Nose-Hoover by thermostating the thermostat variable, and then thermostating that one, and so on.

Langevin Thermostat

Each particle (i) moves as if it is immersed in a bath of much smaller particles (i.e., a viscous fluid). They continuously jostle the particle (giving the $A_i(t)$ noise term in the force) and provide a viscous drag force proportional to the velocity ($-\alpha_L v$):

$$\ddot{x}_i = \underbrace{-\frac{1}{m} \frac{\partial V}{\partial x_i}}_{\text{force}} \underbrace{- \alpha_L \dot{x}_i}_{\text{drag}} + \underbrace{\frac{A_i(t)}{m}}_{\text{noise}},$$

Given the coupling strength α_L and the temperature T , the noise strength is given by

$$\langle A_i(t) A_j(t + \Delta t) \rangle = 2\alpha_L m k_B T \delta(\Delta t) \delta_{ij}$$

Langevin Thermostat

Langevin dynamics samples from canonical ensemble --
i.e., the behavior is properly thermal for temperature T .

Can be shown to be ergodic.

Andersen Thermostat

H.C. Andersen, J. Chem. Phys. **72**, 2384 (1980).

Stochastic.

Procedure:

Occasionally “kick” the system, by assigning fresh momenta to all the atoms (or one atom chosen at random) from a Boltzmann distribution.

Coupling strength α_A is the kick rate. (i.e., kick if $r < \alpha_A \Delta t$)

While a Langevin trajectory, over time, drifts away from the “perfect” (energy conserving) path due to noise and drag, the Andersen trajectory is perfectly energy conserving until it abruptly (at Poisson intervals) changes direction. Both give canonical distribution at large t .

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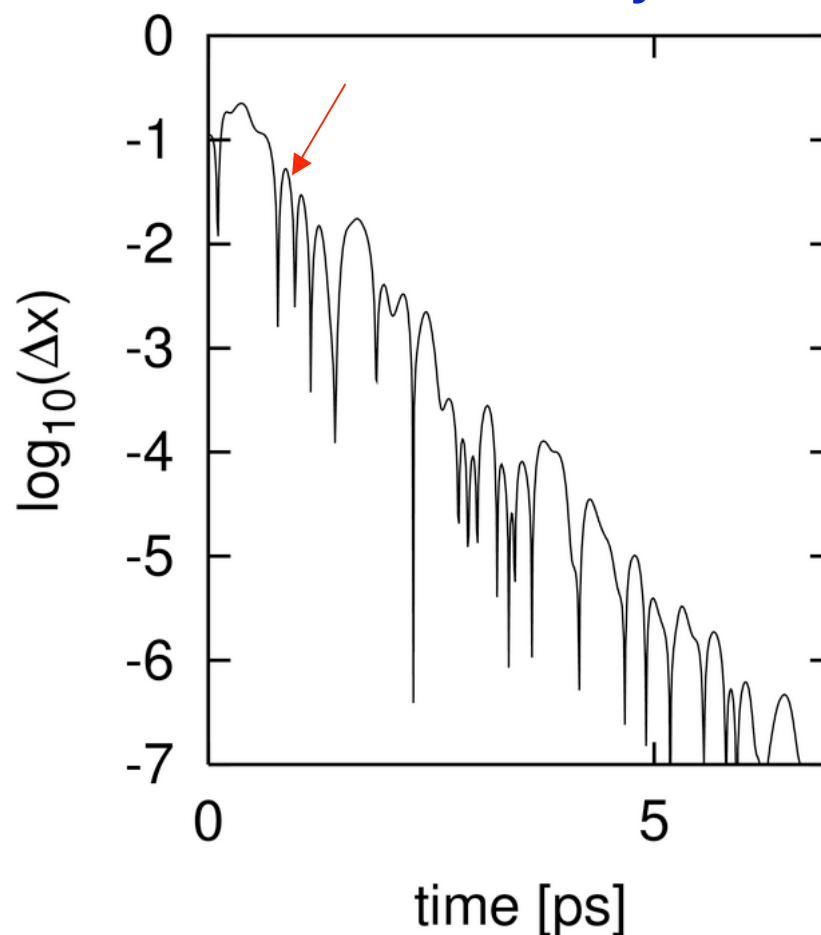
Synchronization in Stochastic Thermostats

Trajectories run under either Langevin or Andersen thermostat, with matched noise (i.e., Same random number seed), are driven to *synchronize*.

Synchronization in EAM surface system

Ag/Ag(100), EAM potential
55 moving atoms
Langevin dynamics
 $T=300\text{K}$, $\alpha=5 \times 10^{12} \text{ s}^{-1}$

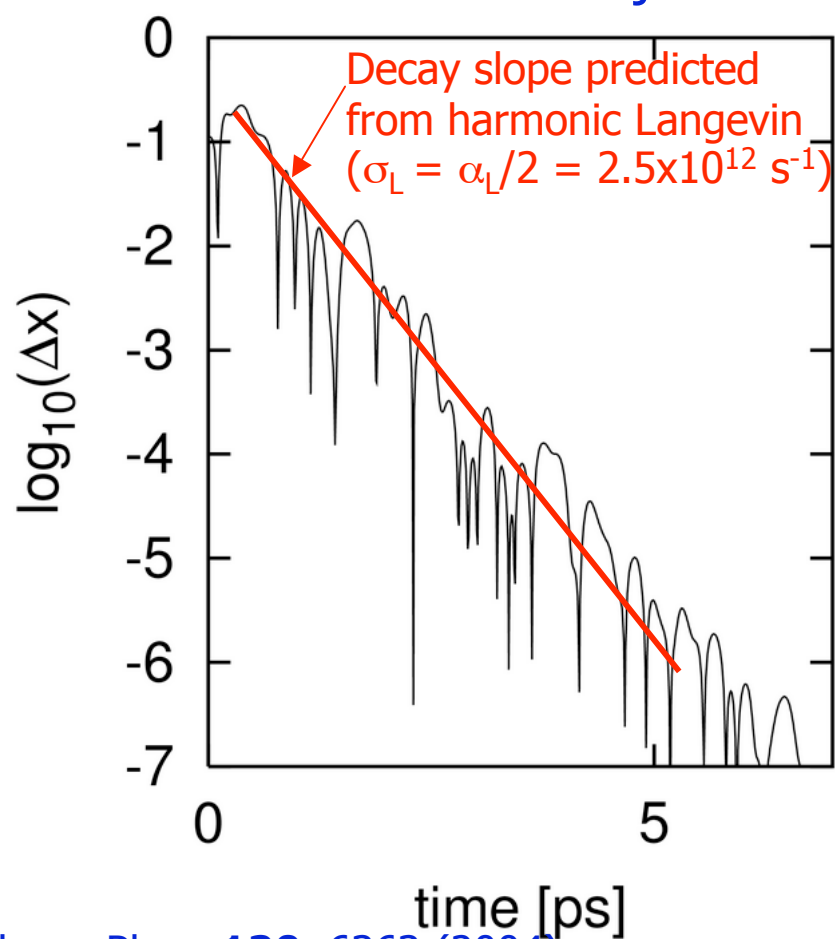
Absolute difference in adatom
x positions between two
matched-noise trajectories



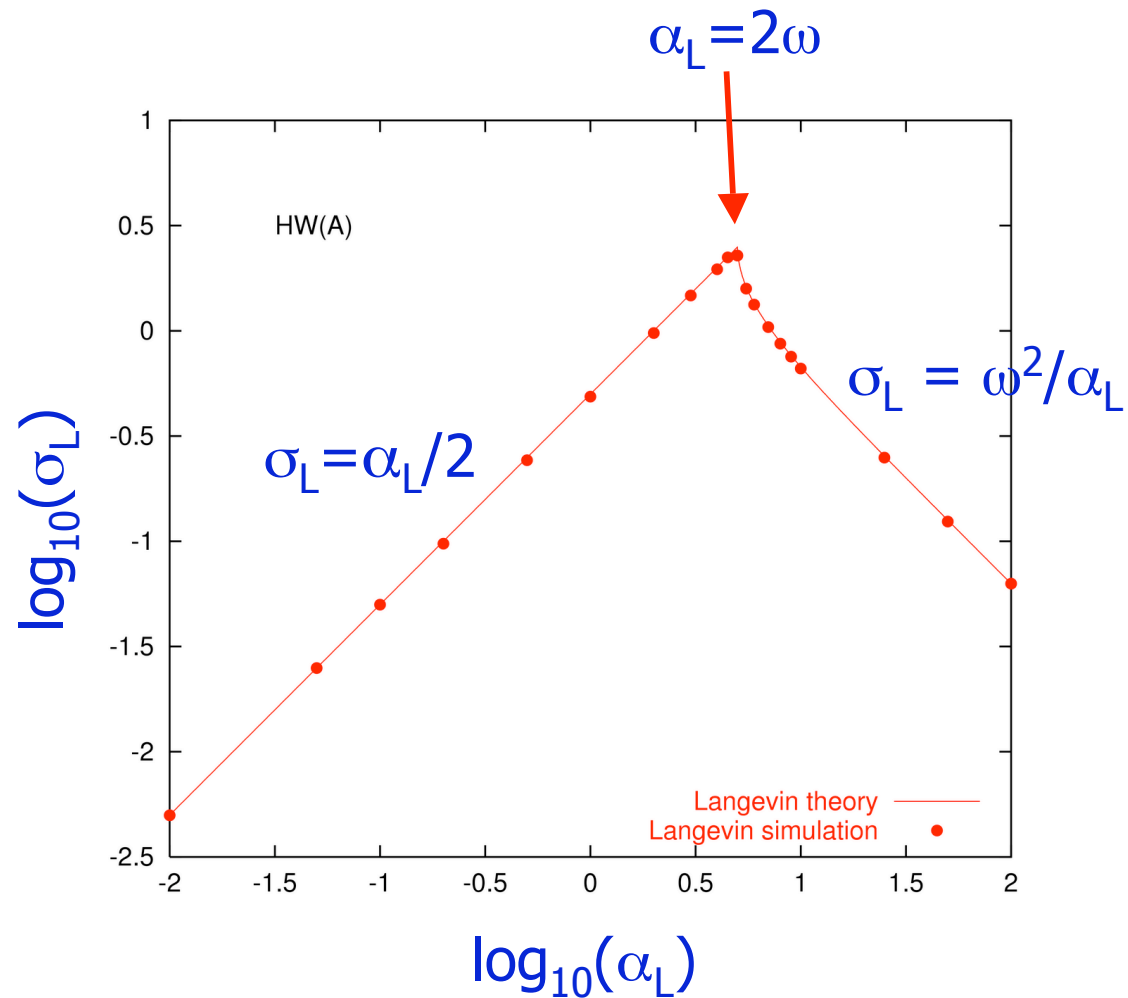
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Langevin dynamics
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Absolute difference in adatom
x positions between two
matched-noise trajectories



Synchronization rate - Harmonic well



Synchronization in Langevin

100 Langevin trajectories

cos potential

$T=0.1, \alpha_L=1.5$

Unmatched noise

Matched noise

Synchronization; higher T , α_L

Higher temperature and higher friction.

100 Langevin trajectories with matching noise.
 $T=0.3$, $\alpha_L=10$ (peak in sigma vs. alpha curve)