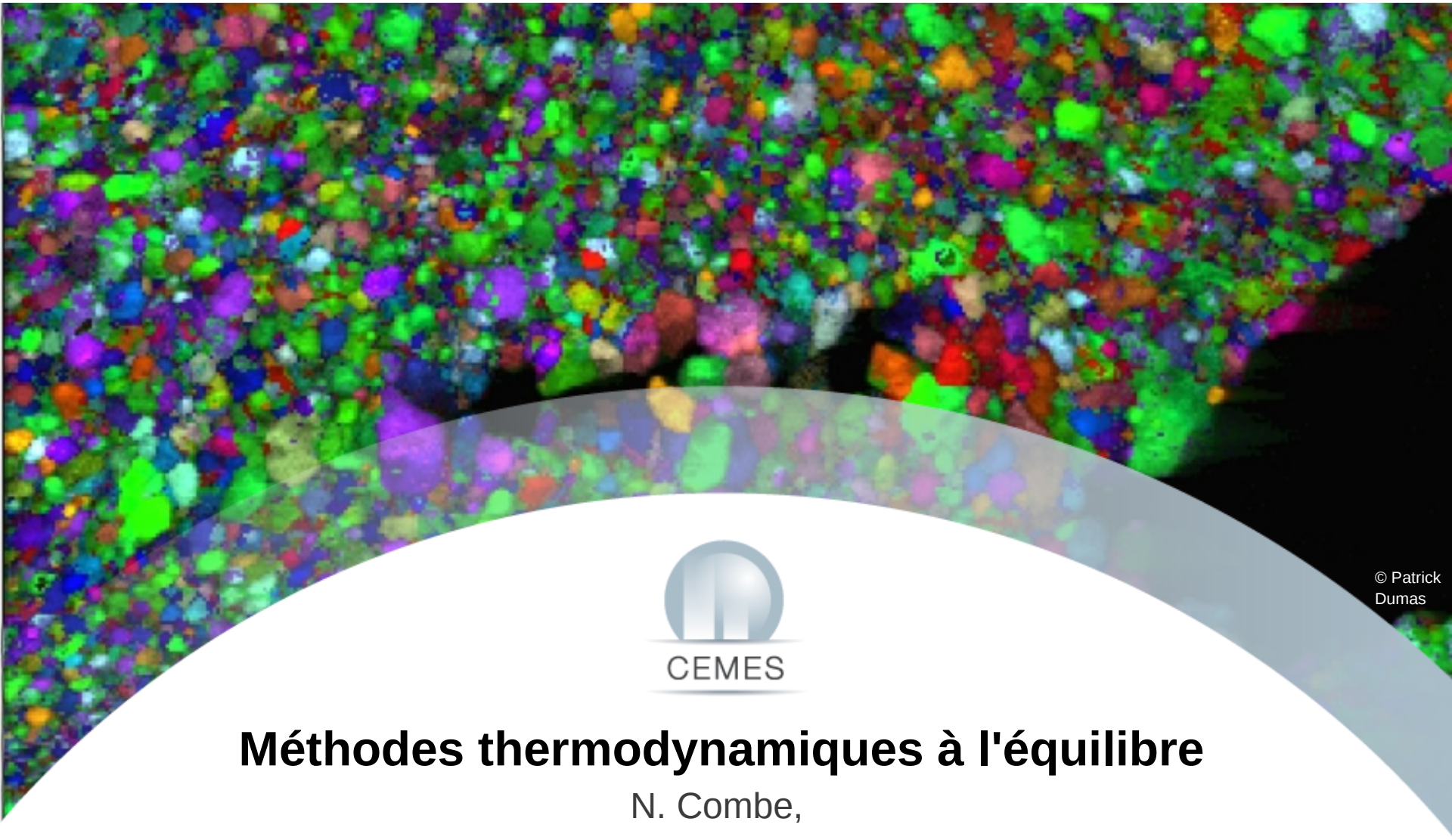

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CEMES

Méthodes thermodynamiques à l'équilibre

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cnrs

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Contents

1) Simulations and statistical mechanics
   - macroscopic and microscopic approaches
   - Ergodic principle
   - Simulation tools

2)Theoretical tools

3) Molecular dynamics

4) Monte Carlo

5) Free energy calculation

Macroscopic versus microscopic approach

Macroscopic world
Thermodynamic

1 system defined from
Few variables (macroscopic)

N, V, E
N , V, <E> or T… } Extern parameters

Transformation : modif. external parameter

Microscopic description
Statistical physics

1 set of microscopic states

Microstate $\vec{R}=\vec{r}_1\vec{r}_2..\vec{r}_N$ $\dot{\vec{R}}=\dot{\vec{r}}_1\dot{\vec{r}}_2...\dot{\vec{r}}_N$ N ~ 10^{23}

+ spin, charge...

"Average" of A
on microscopic states ⟷ Observable $A(\vec{r}_1,\vec{r}_2,....\vec{r}_N,\dot{\vec{r}}_1,...\dot{\vec{r}}_N,t)$

Exple: Ec, Ep, Force on wall...

Biblio : *Balian, From Microphysics to Macrophysics: Methods and Applications of Statistical Physics*
Reif, Fundamentals of Statistical and thermal physics
Zwanzig, non equilibrium statistical mechanics
Forster, hydrodynamic fluctuations, broken symmetry ans correlation function

Averages of observables : Ergodic principles

System of N atoms

masses $m_1 m_2 \dots m_N$

positions $\vec{R} = \vec{r}_1 \vec{r}_2 .. \vec{r}_N$

speeds $\dot{\vec{R}} = \dot{\vec{r}}_1 \dot{\vec{r}}_2 \dots \dot{\vec{r}}_N$

Newton Laws : $m_i \frac{d^2 \vec{r}_i}{dt^2} = \vec{F}_i$

Forces : $\vec{F}_i = \vec{F}_i(\vec{r}_1, \vec{r}_2 \dots \vec{r}_N, \dot{\vec{r}}_1, \dot{\vec{r}}_2 \dots \dot{\vec{r}}_N)$

Probabilistic description

$f(\vec{r}_1, \vec{r}_2, \dots . \vec{r}_N, \dot{\vec{r}}_1, \dots \dot{\vec{r}}_N, t)$

Initial microstate (t=0)

→ Evolution t>0 (ou t<0)

$\bar{A} = \lim_{\tau \to \infty} \frac{1}{\tau} \int_t^{t+\tau} A(\vec{R}(t'), \dot{\vec{R}}(t'), t') dt'$

Ergodicity

at equilibrium

$\langle A \rangle = \int A(\vec{R}, \dot{\vec{R}}) f(\vec{R}\, \dot{\vec{R}}) d^{3N} R\, d^{3N} \dot{R}$

Molecular Dynamics

To generate trajectories $\vec{R}(t)$

Phase space sampling : Monte Carlo

To generate a set $\{\vec{R}_1, \vec{R}_2 \dots \vec{R}_\Omega\}$

according $f(\vec{R}, \dot{\vec{R}})$

Simulations tools

Equilibrium properties

Monte Carlo
Molecular Dynamic
Kinetic Monte Carlo

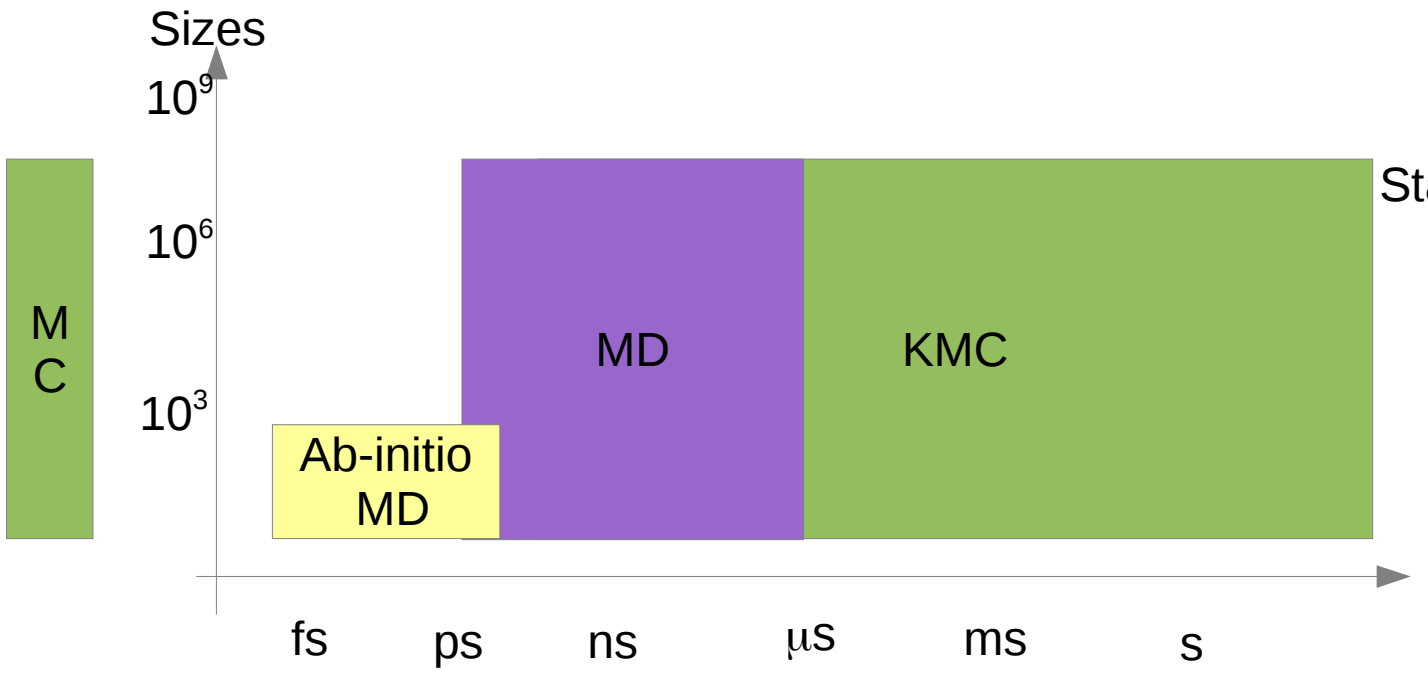
Statistical mechanics
Thermodynamics

Dynamic properties

Molecular Dynamic
Kinetic Monte Carlo

Out of equilibrium statistical mechanics (linear response theory, transport theory...)

Remark: dynamic properties can be calculated from equilibrium properties through fluctuation-dissipation theorem



Standard deviation

$N \sim 10^{23}$

$$\frac{1}{\sqrt{N}}$$

Contents

1) Simulations and statistical mechanics

2)Theoretical tools
- Lagrangian formulation
- generalized coordinates
- Noether Theorem
- Hamiltonian formulation
- Propagator formalism
- Symplectic property

3) Molecular dynamics

4) Monte Carlo

5) Free energy calculation

Lagragian formulation of classical mechanics

Important restrictions

- Classical mechanics
- The forces are described by a force field
- The forces are conservative
- Workless constraints

$$\vec{F} = -\vec{\nabla} U(\vec{r}_1 \ldots \vec{r}_N)$$

Lagragian $$L(\vec{r}_1, \ldots, \vec{r}_N, \dot{\vec{r}}_1, \ldots, \dot{\vec{r}}_N) = \sum_i \frac{1}{2} m_i \dot{\vec{r}}_i^{\,2} - U(\vec{r}_1, \ldots, \vec{r}_N)$$

Newton laws :

$$m_i \frac{d^2 \vec{r}_i}{dt^2} = \vec{F}_i$$

3N 2nd order differential equations

Lagrangian equation

$$\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{r}_{i\alpha}}\right) = \frac{\partial L}{\partial r_{i\alpha}}$$

Derived from Hamilton principle

From a scalar quantity, the Lagrangian, we can derive the motion equations.

Classical mechanics : generalized coordinates

System of N atoms $\vec{R}=\vec{r}_1\vec{r}_2..\vec{r}_N$

$\dot{\vec{R}}=\dot{\vec{r}}_1\dot{\vec{r}}_2...\dot{\vec{r}}_N$

S : degree of freedom of the system
Number of independent quantities necessary to define the state ot the system

If s $\neq$3N Constraints ⟷ forces

3N-s holonomic constraints $\Phi_j(\vec{r}_1,\vec{r}_2,...,\vec{r}_N,t)=0 \quad j=1...3N-s$

Example : a rigid bond

$\vec{R}=\vec{R}(\vec{Q})$ $\vec{Q}=q_1q_2..q_s$ $\dot{\vec{Q}}=\dot{q}_1\dot{q}_2...\dot{q}_s$

Generalized coordinates Generalized speeds

Biblio : *Landau and Lifhitz, mechanics, MIR*
Goldstein, Classical mechanics, Addison-Wesley

Lagragian and generalized coordinates

Lagrangian

$$\vec{R}=\vec{r}_1\vec{r}_2..\vec{r}_N$$
$$\dot{\vec{R}}=\dot{\vec{r}}_1\dot{\vec{r}}_2...\dot{\vec{r}}_N$$

$$L(\vec{r}_1,...,\vec{r}_N,\dot{\vec{r}}_1,...,\dot{\vec{r}}_N)=\sum_i \frac{1}{2}m_i\dot{\vec{r}}_i^{\,2}-U(\vec{r}_1,...,\vec{r}_N)$$

$$L(\vec{Q},\dot{\vec{Q}})=\sum_{kl}\frac{1}{2}G_{kl}(\vec{Q})\dot{q}_k\dot{q}_l-U(\vec{Q})$$

$$\vec{R}=\vec{R}(\vec{Q})$$

$$\vec{Q}=q_1q_2..q_s$$
$$\dot{\vec{Q}}=\dot{q}_1\dot{q}_2...\dot{q}_s$$

$$G_{kl}(\vec{Q})=\sum_i m_i\frac{\partial\vec{r}_i}{\partial q_k}\frac{\partial\vec{r}_i}{\partial q_l}$$

Mass metric matrix

Lagrangian equation

$$\frac{d}{dt}\left(\frac{\partial L}{\partial\dot{q}_k}\right)=\frac{\partial L}{\partial q_k}$$

Same formulation

Conservation law, the Noether theorem

The lagrangian does not explicitely depend on the time

→ Invariance by Time translation

$$\frac{dL}{dt} = \sum_k \frac{\partial L}{\partial q_k}\dot{q}_k + \sum_k \frac{\partial L}{\partial \dot{q}_k}\ddot{q}_k$$

$$\frac{dL}{dt} = \sum_k \frac{d}{dt}\left(\frac{\partial L}{\partial \dot{q}_k}\dot{q}_k\right)$$

$$\frac{dH}{dt} = 0$$

$$H = \sum_k \left(\frac{\partial L}{\partial \dot{q}_k}\dot{q}_k\right) - L$$

The hamiltonian is a first integral of the motion

Noether theorem : a differentiable symmetry has a corresponding conservation law

Space invariance translation : Conservation of the total generalized momentum
Rotational invariance : Conservation of the total generalized angular momentum

→ In MD, first integrals are important to check if the integration is correct.

Hamilton formulation of mechanics

$$p_k = \left(\frac{\partial L}{\partial \dot{q}_k} \right)$$

$$H = \sum_k p_k \dot{q}_k - L$$

H is function of : q_k, p_k, t

$$dH = \sum_k \dot{q}_k dp_k - \dot{p}_k d q_k - \frac{\partial L}{\partial t} dt$$

$$\left.\begin{aligned} \dot{q}_k &= \frac{\partial H}{\partial p_k} \\ \dot{p}_k &= -\frac{\partial H}{\partial q_k} \end{aligned}\right\}$$

2s first order diff. Equations for 2s independent variables q_k, p_k

$$\frac{\partial H}{\partial t} = -\frac{\partial L}{\partial t}$$

$$\frac{dH}{dt} = \sum_k \dot{q}_k \dot{p}_k - \dot{p}_k \dot{q}_k - \frac{\partial L}{\partial t} = -\frac{\partial L}{\partial t}$$

Remark: Lagrangian formulation : s 2nd order differential equations for s independent variables q_k

The propagator formalism

$$\dot{q}_k = \frac{\partial H}{\partial p_k}$$

$$\dot{p}_k = \frac{-\partial H}{\partial q_k}$$

An observable $A(q_{1,} \ldots q_s, p_1 \ldots., p_s)$

No explicit dependence on time

$$\frac{dA}{dt} = \sum_k \frac{\partial A}{\partial q_k}\dot{q}_k + \frac{\partial A}{\partial p_k}\dot{p}_k$$

$$= \sum_k \frac{\partial A}{\partial q_k}\frac{\partial H}{\partial p_k} - \frac{\partial A}{\partial p_k}\frac{\partial H}{\partial q_k}$$

$$= \{A, H\}$$

Poisson brackets

$$= iLA$$

Liouville operator

The propagator formalism

$$\frac{d\,A}{dt} = i\,LA$$

Formal solution

$$A(q_{1,}\ldots q_s, p_1\ldots., p_s)(t) = e^{iLt}\,A(q_{1,}\ldots q_s, p_1\ldots., p_s)(0)$$

Classical propagator (physics) / Resolvante (maths)

Canonical transformations

Hamilton formulation

$$x=(q_k,p_k)\rightarrow X=(Q_k,P_k)$$

$$Q_k=Q_k(q_k,p_k)$$
$$P_k=P_k(q_k,p_k)$$

Example:
cartesian → spherical

A wide class of possible transformations

Among them : the canonical transformations

$$H(q_k,p_k)=H(Q_k,P_k)$$

$$\begin{cases}\dot{q}_k=\dfrac{\partial H}{\partial p_k}\\ \dot{p}_k=-\dfrac{\partial H}{\partial q_k}\end{cases}$$

The transformation
$q_k,p_k\rightarrow Q_k,P_k$

is canonical if

$$\begin{cases}\dot{Q}_k=\dfrac{\partial H}{\partial P_k}\\ \dot{P}_k=-\dfrac{\partial H}{\partial Q_k}\end{cases}$$

$$\left|det\ J\right|=1 \qquad J_{kl}=\frac{\partial X_k}{\partial x_l}$$

Consequences: the symplectic property

Particular case :

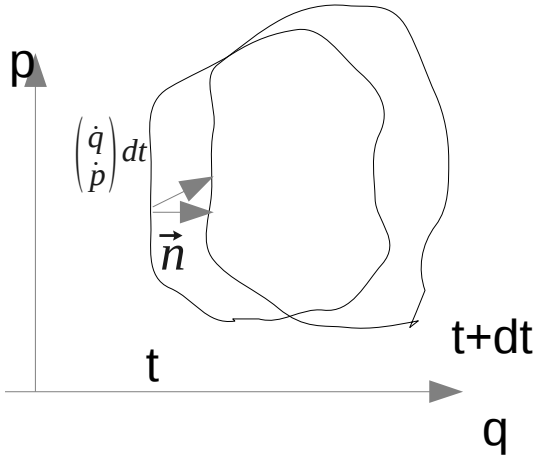
$q_k(t), p_k(t) \rightarrow q_k(t+\tau), p_k(t+\tau)$ is canonical if the system is hamiltonian

$$J_{kl} = \frac{\partial x_k(t+\tau)}{\partial x_l(t)}$$

$$\left| det\ J \right| = 1$$

$$\int_{V(t)} A(X(t))\, dX(t) = \int_{V(t+\tau)} A(X(t+\tau)) \left| det(J) \right| dX(t+\tau)$$
$$= \int_{V(t+\tau)} A(X(t+\tau))\, dX(t+\tau)$$

Conservation of the volume in the phase space



$$\iiint_{V(t)} \prod_k dp_k\, dq_k = \iiint_{V(t+dt)} \prod_k dp_k\, dq_k$$

Liouville theorem

→ MD algorithm should have the symplectic property

$$q_k(t), p_k(t) \rightarrow q_k(t+\tau), p_k(t+\tau)$$

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- Motion equation Integration
- Application: Energy conservation / Timestep / Reversibility / Lyapunov / Trajectories
- Cutoff issues
- Liouville formalism →Multiple Time step
- Numerical Performance
- Ensembles : NVT: Andersen Thermostat
  Nose-Hoover thermostat / Nose Hoover chains
  Other ensembles NPE, NPT

4) Monte Carlo

5) Free energy calculation

Molecular Dynamics

Microstate $\vec{R}=\vec{r}_1\vec{r}_2..\vec{r}_N$

$\dot{\vec{R}}=\dot{\vec{r}}_1\dot{\vec{r}}_2...\dot{\vec{r}}_N$

How to integrate Newton equation

$$m_i\frac{d^2\vec{r}_i}{dt^2}=\vec{F}_i$$

I) A model : description of the force fields
II) The numerical integration
III) Ensemble

Microstate $\vec{Q}=q_1q_2..q_s$

$\vec{P}=p_1p_2...p_s$

$$H=\sum_k p_k\dot{q}_k-L$$

$$\dot{q}_k=\frac{\partial H}{\partial p_k}$$

$$\dot{p}_k=\frac{-\partial H}{\partial q_k}$$

I) A model : description of the Hamiltonian
II) The numerical integration
III) Ensemble

$$A(q_1,...q_s,p_1....,p_s)(t)=e^{iLt}A(q_1,...q_s,p_1....,p_s)(0)$$

Remark: if some constrains → generalized coordinates
→ SHAKE algorithm

Basic principles of numerical integrators

$$A(q_{1,}\dots q_s, p_1\dots., p_s)(t) = e^{iLt}\, A(q_{1,}\dots q_s, p_1\dots., p_s)(0)$$

1) time is discretized $t, t+\Delta t, t+2\Delta t \dots etc$

$$e^{iLt} = \left[e^{iL\Delta t}\right]^n \qquad \Delta t = \frac{t}{n}$$

$$A(q_{1,}\dots q_s, p_1\dots., p_s)(t+\Delta t) = e^{iL\Delta t}\, A(q_{1,}\dots q_s, p_1\dots., p_s)(t)$$

Idea : to find an approximate analytical expression $e^{i\tilde{L}\Delta t}$ of $e^{iL\Delta t}$

$$e^{iLt} = \lim_{n\to\infty}\left[e^{i\tilde{L}\Delta t}\right]^n \qquad \Delta t = \frac{t}{n}$$

Both $e^{i\tilde{L}\Delta t}$ and $e^{iL\Delta t}$ provide the same evolution in the limit $\Delta t \to 0$

Numerical integration

What do we expect from the integration algorithm : $e^{i\tilde{L}\Delta t}$

- accuracy: same results as analytical solutions for solvable problem
- conservation of first integrals
- stability for very long simulations should not be governed by numerical artefacts.
- efficiency

- reversibility

$$A(\vec{Q},\vec{P})(\Delta t) = e^{i\tilde{L}\Delta t} A(\vec{Q},\vec{P})(0)$$
$$A(\vec{Q},\vec{P})(0) = e^{-i\tilde{L}\Delta t} A(\vec{Q},\vec{P})(\Delta t)$$

- Symplectic property $q_k(t), p_k(t) \rightarrow q_k(t+\tau), p_k(t+\tau)$ is a canonical transformation

Taylor expansion

2) Taylor expansion of motion equation

$$\vec{r}_i(t+\Delta t)=\vec{r}_i(t)+\Delta t\,\dot{\vec{r}}_i(t)+\ldots+\Delta t^n\frac{\vec{r}_i^{(n)}(t)}{n!}+O\left(\Delta t^{(n+1)}\right)$$

$$\vec{p}_i(t+\Delta t)=\vec{p}_i(t)+\Delta t\,\dot{\vec{p}}_i(t)+\ldots+\Delta t^n\frac{\vec{p}_i^{(n)}(t)}{n!}+O\left(\Delta t^{(n+1)}\right)$$

Verlet algorithm

$$\vec{r}_i(t+\Delta t)=\vec{r}_i(t)+\Delta t\,\vec{v}_i(t)+\frac{\Delta t^2}{2\mathrm{m}_i}\vec{F}_i(t)+\frac{\Delta t^3}{6}\vec{r}_i^{(3)}(t)+\frac{\Delta t^4}{24}\vec{r}_i^{(4)}(t)+o(\Delta t^4)$$

$$\vec{r}_i(t-\Delta t)=\vec{r}_i(t)-\Delta t\,\vec{v}_i(t)+\frac{\Delta t^2}{2\mathrm{m}_i}\vec{F}_i(t)-\frac{\Delta t^3}{6}\vec{r}_i^{(3)}(t)+\frac{\Delta t^4}{24}\vec{r}_i^{(4)}(t)+o(\Delta t^4)$$

$$\begin{cases}\vec{r}_i(t+\Delta t)=2\vec{r}_i(t)-\vec{r}_i(t-\Delta t)+\dfrac{\Delta t^2}{m_i}\vec{F}_i(t)+O(\Delta t^4)\\ \vec{v}_i(t)=\dfrac{\vec{r}_i(t+\Delta t)-\vec{r}_i(t-\Delta t)}{2\Delta t}+O(\Delta t^2)\end{cases}$$

Verlet algorithm: reversibility, symplectic property.
But only generates the position, velocities are derived from positions.

Remark: The algorithm is related to the propagator $e^{i\tilde{L}\Delta t}$ and thus to $\tilde{L}$

Velocity Verlet algorithm

$$\vec{r}_i(t+\Delta t)=\vec{r}_i(t)+\Delta t\,\vec{v}_i(t)+\frac{\Delta t^2}{2\mathrm{m}_i}\vec{F}_i(t)+\frac{\Delta t^3}{6}\vec{r}_i^{(3)}(t)+O(\Delta t^4)$$

$$\vec{r}_i(t)=\vec{r}_i(t+\Delta t)-\Delta t\,\vec{v}_i(t+\Delta t)+\frac{\Delta t^2}{2\mathrm{m}_i}\vec{F}_i(t+\Delta t)-\frac{\Delta t^3}{6}\vec{r}_i^{(3)}(t+\Delta t)+O(\Delta t^4)$$

$$\vec{r}_i(t+\Delta t)=2\vec{r}_i(t)-\vec{r}_i(t-\Delta t)+\frac{\Delta t^2}{m_i}\vec{F}_i(t)+O(\Delta t^4)$$

$$\vec{v}_i(t+\Delta t)=\vec{v}_i(t)+\frac{\Delta t(\vec{F}_i(t)+\vec{F}_i(t+\Delta t))}{2m_i}+O(\Delta t^3)$$

Time reversible / symplectic property

Comparison of algorithms

Based on Taylor development at 2 order

Verlet	Error on position order 4 Time reversible Symplectic property	Error on velocity order 2 Need of the position at t+dt and t-dt to evaluate velocity at time t All First integrals are not conserved Energy approximately conserved
Velocity Verlet	Error on position order 4 Error on velocity order 3 Time reversible Symplectic property	All First integrals are not conserved Energy approximately conserved

Increasing the order - increases the accuracy
- decreases the efficiency
More memory and/or force evaluation

Many high order schemes (noticeably predictor-corrector methods) are not time reversible or simplectic
(4^{th} order Runge Kutta is not simplectic)

Verlet or Velocity Verlet is a good compromise

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Application

Collision of two 2D aggregates
(31 pseudo-atoms each)
Velocity Verlet

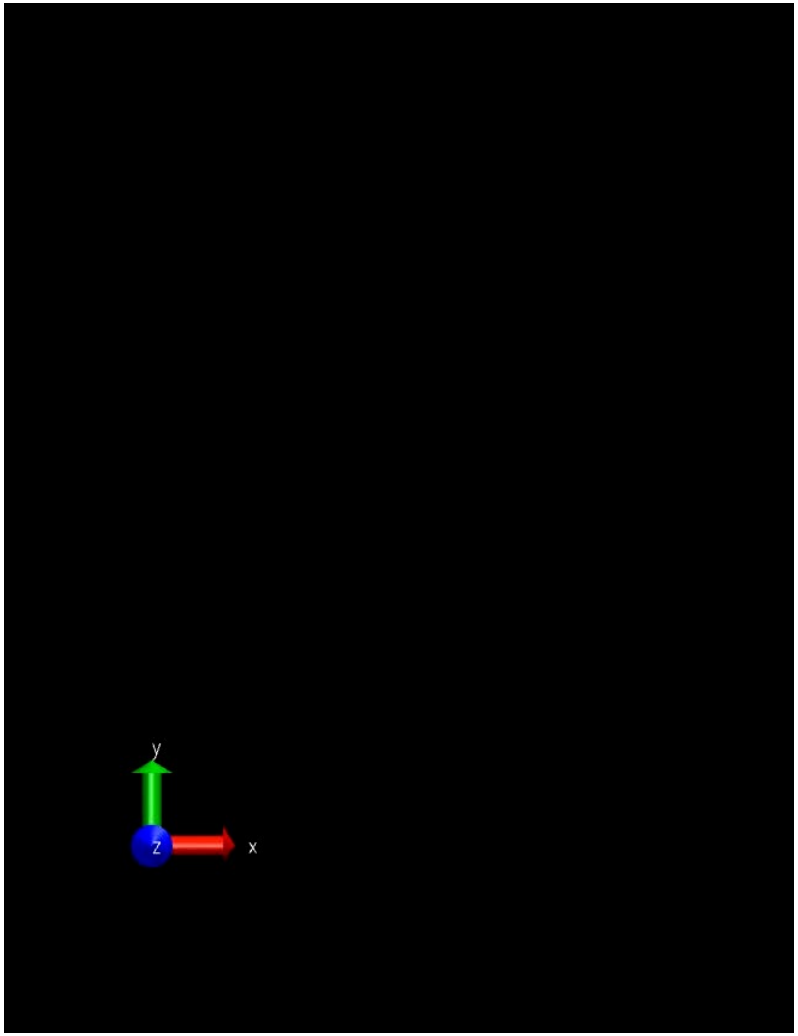
Lennard Jones potential $\epsilon = 1$ $\sigma = 1$

No cutoff

$$V(r) = 4\epsilon\left(\left[\frac{\sigma}{r}\right]^{12} - \left[\frac{\sigma}{r}\right]^{6}\right)$$

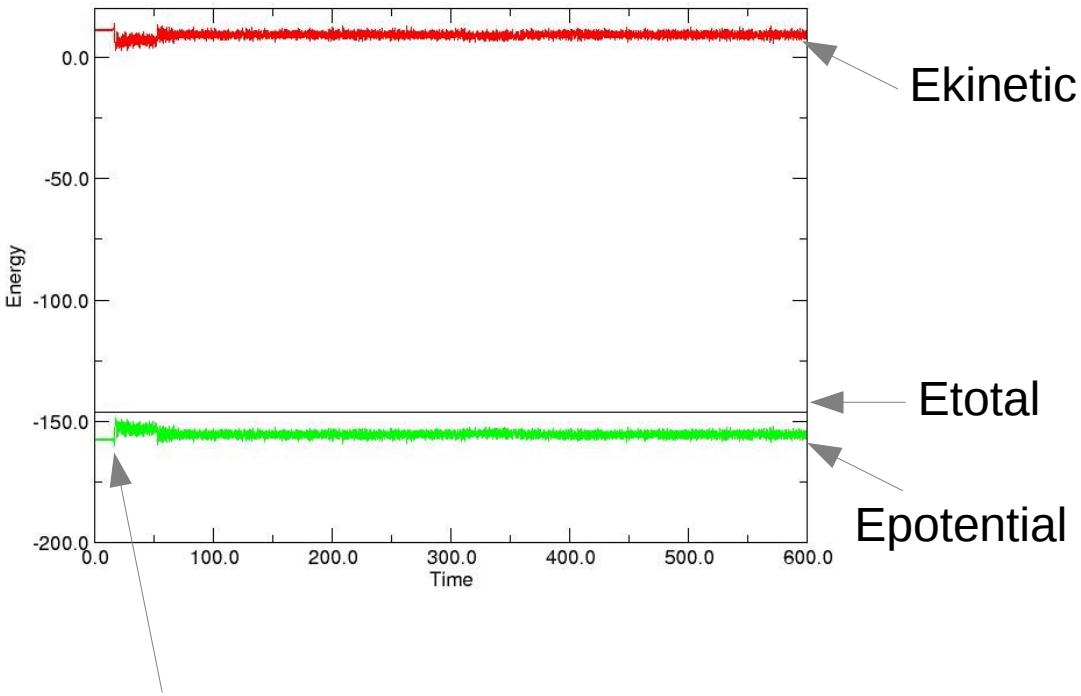
m=1.

Total time = 600 Lj units
Δt = 0.0001 Lj units
Initial speeds= 0.6



t<200

Application : Energy conservation

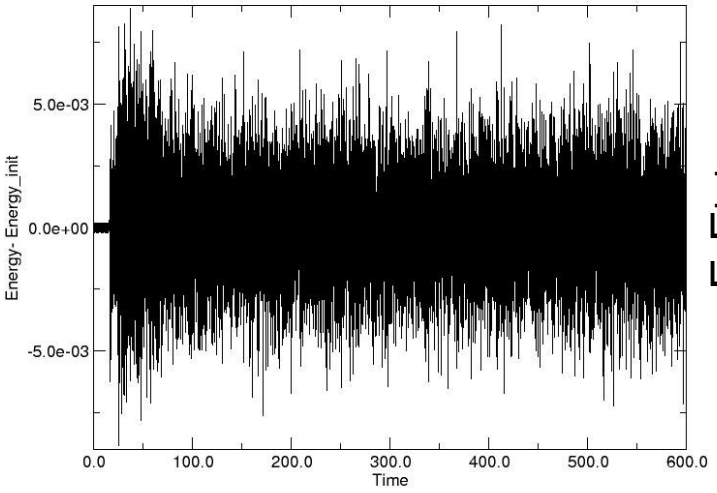


Ekinetic

Etotal

Epotential

Collision



E-Einit

Energy Conservation

The energy is not exactly conserved!

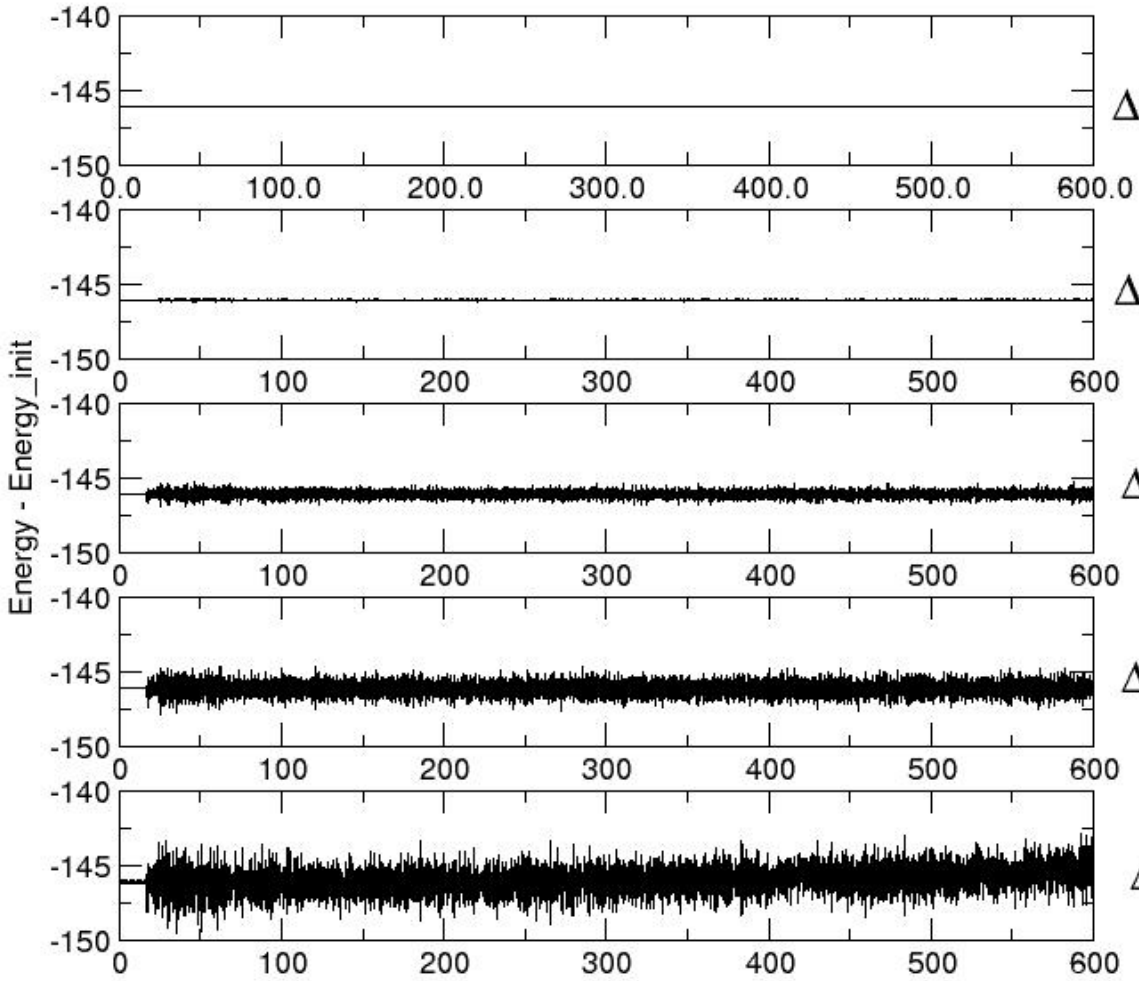
The operator $\tilde{L}$ does not conserve the Hamiltonian H.

There exists a shadow hamiltonian $\tilde{H}(\Delta t)$ that is exactly conserved

$$H = \lim_{\Delta t \to 0} \tilde{H}(\Delta t)$$

Energy Conservation and Time step

Effect of the change of the timestep Δt on the energy conservation



<E> = -146.10102
<ΔE>= 1.5e-6

<E>=-146,10114
<ΔE>= 1.17e-4

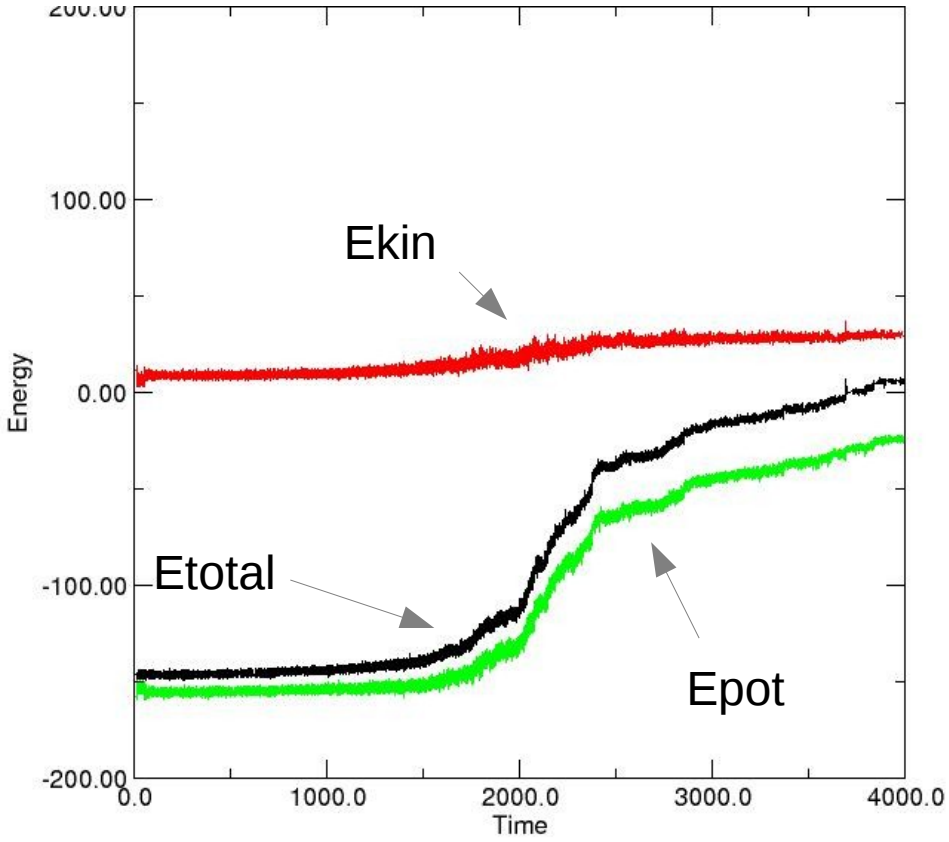
<E> = -146.11232
<ΔE>= 1.12e-2

<E> = -146.14713
<ΔE>= 4.6e-2

<E> = -146.0025
<ΔE>= 0.1

Drift in the energy

Drift in energy



$\Delta t = 4e\text{-}2$

The example that you should not follow

Energy Conservation and Timestep

Lenard Jones $V(r)=4\epsilon\left(\left[\frac{\sigma}{r}\right]^{12}-\left[\frac{\sigma}{r}\right]^{6}\right)$

Verlet algorithm $\vec{r}_i(t+\Delta t)=2\vec{r}_i(t)-\vec{r}_i(t-\Delta t)+\frac{\Delta t^2}{m_i}\vec{F}_i(t)$

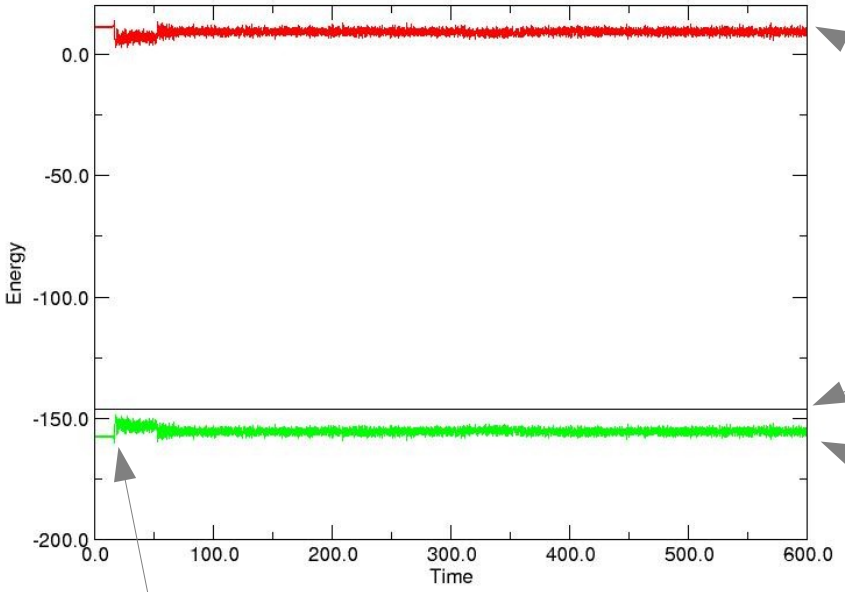
For LJ potential, the forces are proportional to ε

To keep the same precision, if ε increases, Δt should decrease

Δt should be adapted to forces : stiff forces, tiny Δt
Soft forces, small Δt

Time Reversibility

Evolution of energies



Ekinetic

Etotal

Epotential

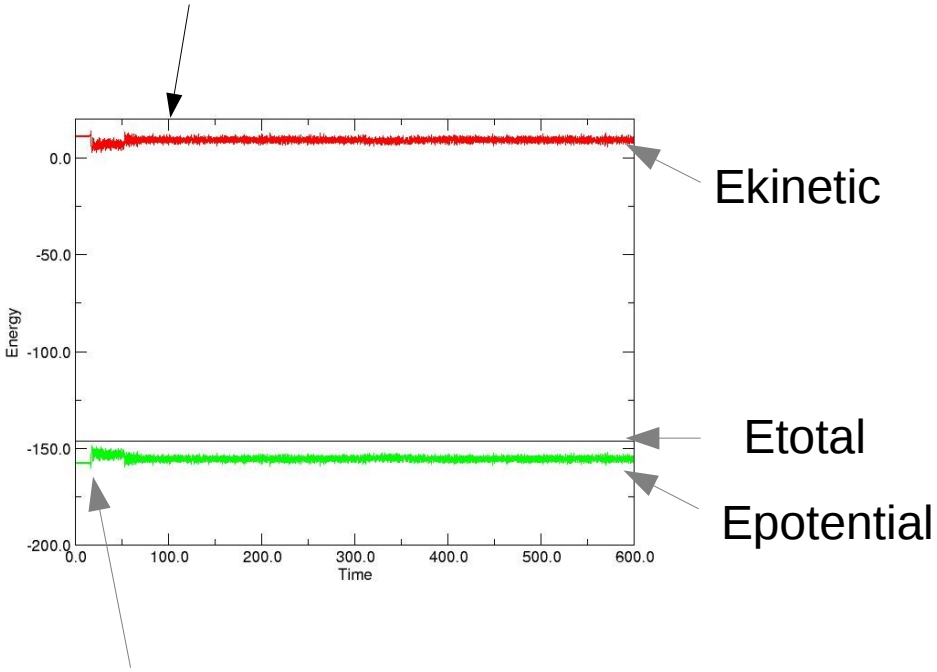
Total time = 600 Lj units
Δt = 0.0001 Lj units
Inital speeds= 0.6

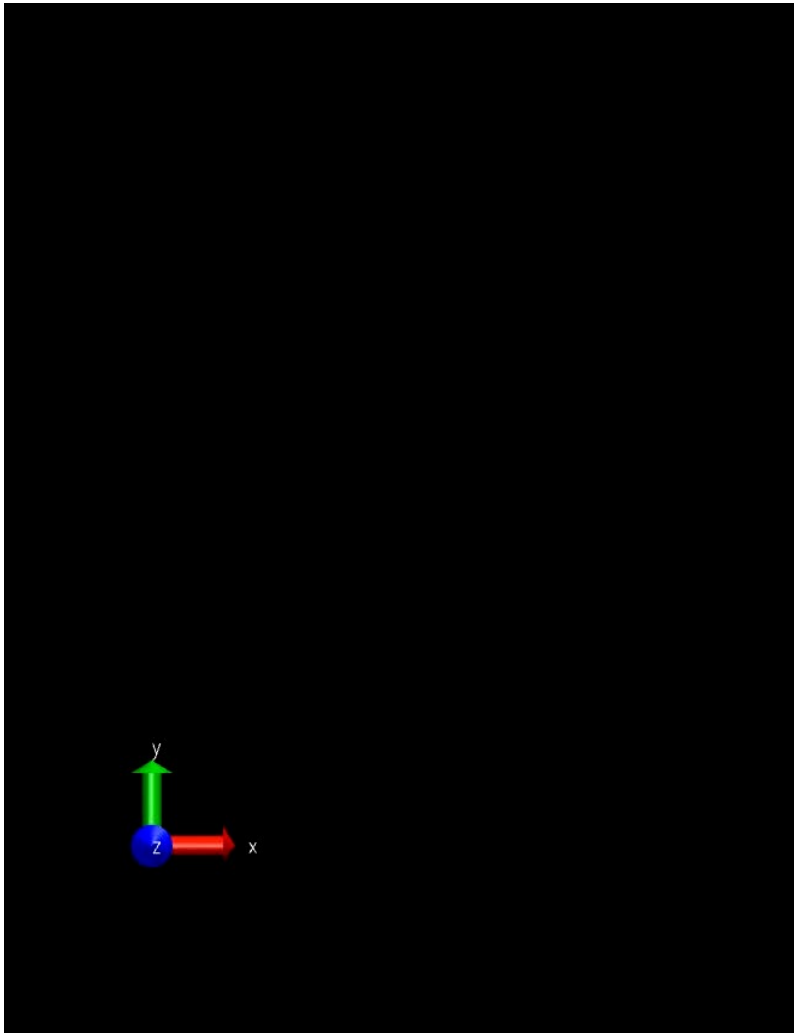
Collision

What happen, if at t=100, we reverse the speeds ?

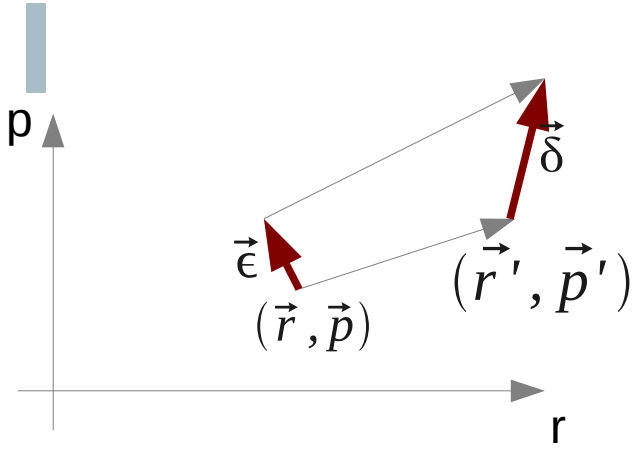
Time Reversibility

After t= 100 We reverse the speeds





Lyapunov instability



Time t

$(\vec{r}_k, \vec{p}_k)$

$(\vec{r}_k(t)+\vec{\epsilon}_r, \vec{p}_k(t)+\vec{\epsilon}_p)$

Time t+Δt

$(\vec{r}'_k, \vec{p}'_k)$

$(\vec{r}'_k+\vec{\delta}_r, \vec{p}'_k+\vec{\delta}_p)$

$$\left\|\vec{\delta}\right\| \simeq \left\|\vec{\epsilon}\right\| e^{\lambda \Delta t}$$

(Largest) Lyapunov exponent = Average value of λ along a trajectory

Generally, the largest Lyapunov exponent is positive, trajectories are chaotic.

Trajectories are highly sensitive to initial conditions.

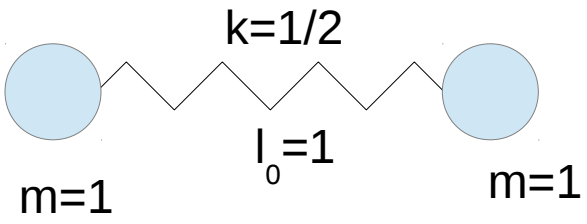
Computers have a finite precision.

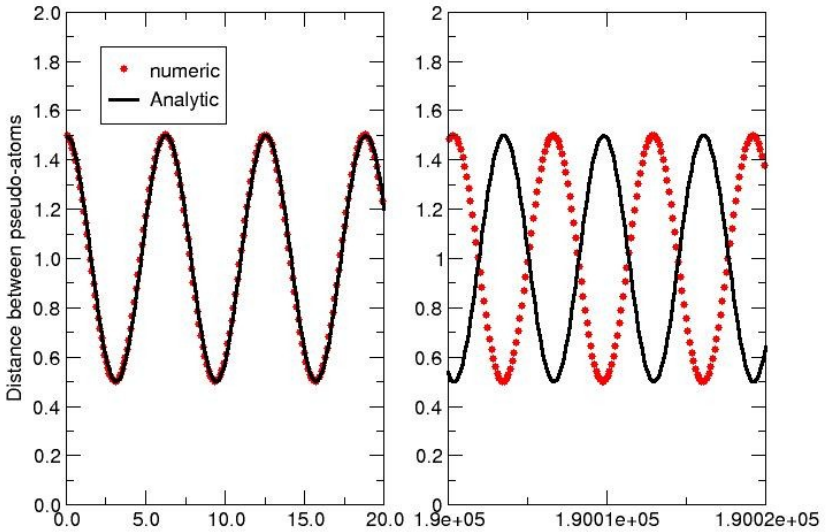
} Time-reversibility can not be satisfied due to numerical issues.

Trajectories

2 pseudo-atoms linked by a spring

Comparison between the theoretical results
The numerical results





Δt=0,02

$$\omega_{theo} = \sqrt{\frac{k}{\mu}} = \sqrt{2\frac{k}{m}} = 1$$

$$\omega_{num} = \omega_{theo}\left[1 + O(\Delta t^2)\right]$$

The shadow hamiltonian $\tilde{H}(\Delta t)$

The accuracy of the trajectories depends on the timestep Δt

In the end

Conservation of Energy
Accuracy of trajectories } depends on the timestep Δt

Time-reversibility — Lyapunov instability

Symplectic property (not check)

However, in MD, we perform some averages (on time, on particles...) of observables.

The trajectories we generate closely follow the true trajectories for a time small compared to the inverse of the largest Lyapunov coefficient.
We have evidences that these averages are good enough.

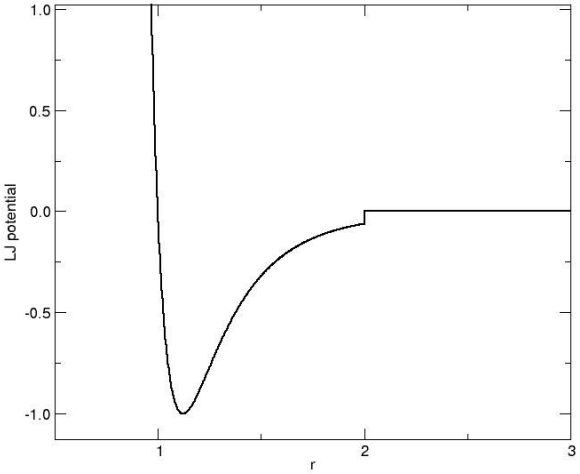
« Our trust on MD simulations as a tool to study the time evolution of many-body systems is based largely on belief » Frenkel and Smith

Some technical issues : Cutoff

Collision of two 2D aggregates
(31 pseudo-atoms each)

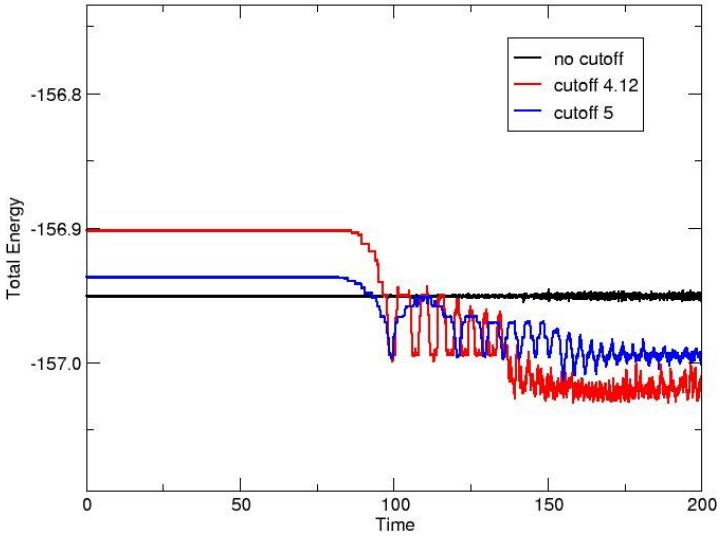
Lennard Jones potential $\epsilon = 1$ $\sigma = 1$

$$V(r) = 4\epsilon\left(\left[\frac{\sigma}{r}\right]^{12} - \left[\frac{\sigma}{r}\right]^{6}\right)$$



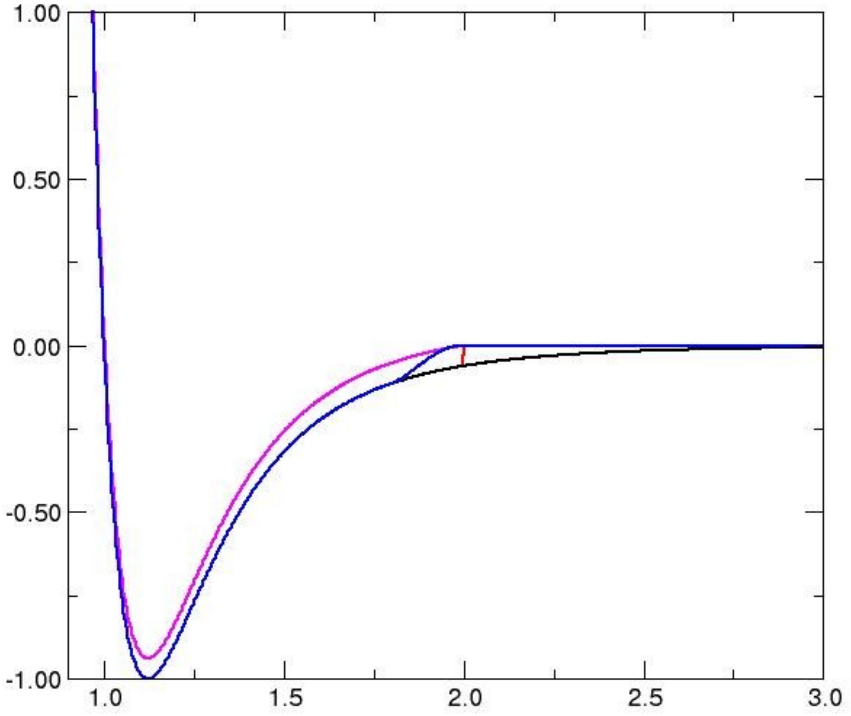
M=1.
Total time = 200 Lj units
Δt = 0,0001 Lj units
Initial speeds =0.1

Direct truncation
Of the potential



Some technical issues : Cutoff

Solutions : - shifted potential
- switching function



Some technical issues : Cutoff

Collision of two 2D agregates (31 pseudo-atoms each)

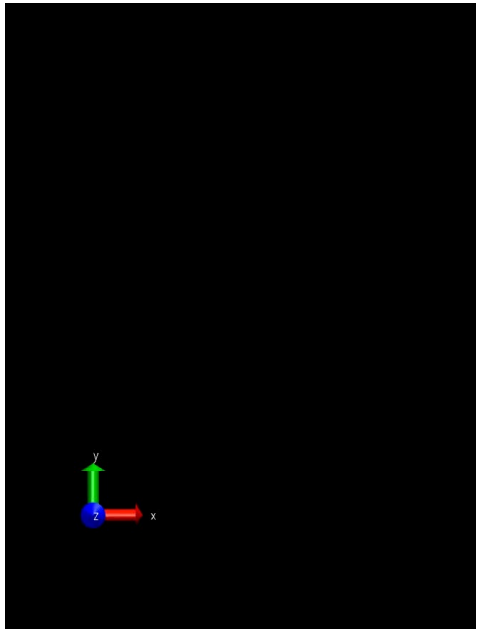
$\epsilon = 1$

$\sigma = 1$

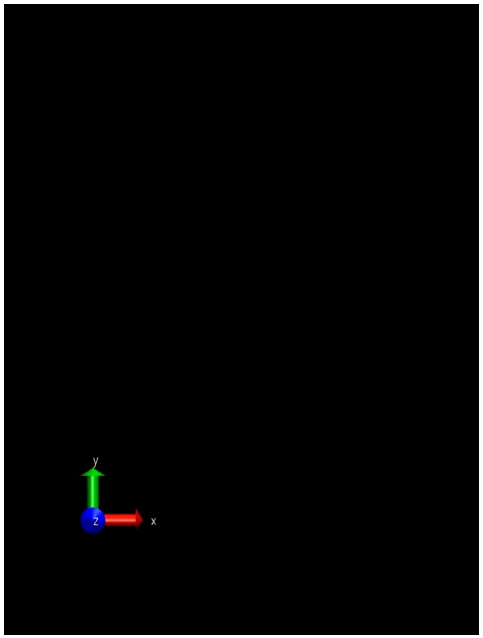
M=1.

Total time = 200 Lj units
Δt = 0,0001 Lj units
Initial speeds =0.6

Lenard Jones potential, no cutoff



Lenard Jones shifted potential
Cutoff 3,16



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  Nose-Hoover thermostat / Nose Hoover chains
  Other ensembles NPE, NPT

4) Monte Carlo

5) Free energy calculation

Liouville formalism of Velocity Verlet

$$iL = \sum_k \dot{q}_k \frac{\partial}{\partial q_k} + \dot{p}_k \frac{\partial}{\partial p_k} = iL_q + iL_p$$

$$e^{iLt} = \left[e^{iL_q \Delta t + iL_p \Delta t} \right]^n$$

B A

Trotter identity $\left[e^{A+B}\right] = \lim_{n\to\infty} \left[e^{\frac{A}{2n}} e^{\frac{B}{n}} e^{\frac{A}{2n}} \right]^n$

$$e^{i\tilde{L}\Delta t} = e^{iL_p \frac{\Delta t}{2}} e^{iL_q \Delta t} e^{iL_p \frac{\Delta t}{2}}$$

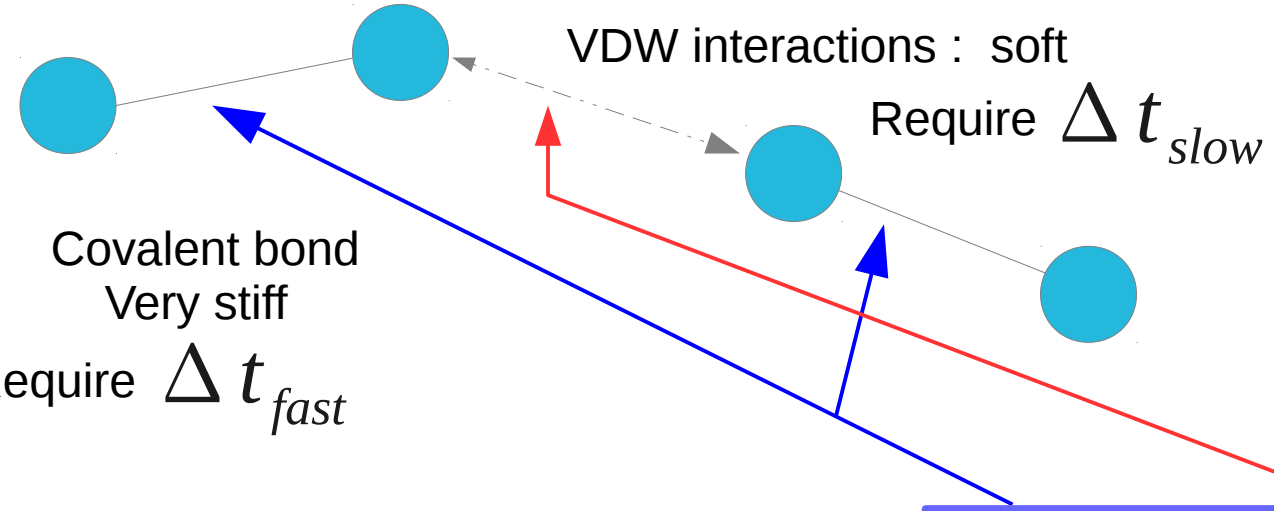
Equivalent to Velocity Verlet algorithm

$$\vec{v}_i\left(t + \frac{\Delta t}{2}\right) = \vec{v}_i(t) + \frac{\Delta t}{2} \frac{\vec{F}_i(t)}{m_i}$$

$$\vec{r}_i(t + \Delta t) = \vec{r}_i(t) + \Delta t\, \vec{v}_i\left(t + \frac{\Delta t}{2}\right)$$

$$\vec{v}_i(t + \Delta t) = \vec{v}_i\left(t + \frac{\Delta t}{2}\right) + \frac{\Delta t}{2} \frac{\vec{F}_i(t + \Delta t)}{m_i}$$

Multiple time step method



$$iL = \sum_k \dot{q}_k \frac{\partial}{\partial q_k} + \dot{p}_k \frac{\partial}{\partial p_k} = \sum_k \dot{q}_k \frac{\partial}{\partial q_k} + \sum_{k\,fast} \dot{p}_k \frac{\partial}{\partial p_k} + \sum_{k\,slow} \dot{p}_k \frac{\partial}{\partial p_k}$$

$$= iL_q + iL_p^{fast} + iL_p^{slow}$$

$$e^{iLt} = \left[e^{iL_q \Delta t + iL_p^{fast} \Delta t + iL_p^{slow} \Delta t} \right]^n$$

B A

Multiple time step method

$$e^{iL\,t} = \left[e^{iL_q \Delta t + iL_p^{fast} \Delta t + iL_p^{slow} \Delta t} \right]^n$$

$$= \lim_{n \to \infty} \left[e^{iL_p^{slow} \frac{\Delta t}{2}} e^{iL_q \Delta t + iL_p^{fast} \Delta t} e^{iL_p^{slow} \frac{\Delta t}{2}} \right]^n$$

$$= \lim_{n \to \infty} \left[e^{iL_p^{slow} \frac{\Delta t}{2}} \left[\lim_{m \to \infty} e^{iL_p^{fast} \frac{\Delta t}{2m}} e^{iL_q \frac{\Delta t}{m}} e^{iL_p^{fast} \frac{\Delta t}{2m}} \right]^m e^{iL_p^{slow} \frac{\Delta t}{2}} \right]^n$$

$$\Delta t = \frac{t}{n}$$

$$dt = \frac{\Delta t}{m}$$

$$e^{i\tilde{L}\Delta t} = e^{iL_p^{slow} \frac{\Delta t}{2}} \left[e^{iL_p^{fast} \frac{dt}{2}} e^{iL_q dt} e^{iL_p^{fast} \frac{dt}{2}} \right]^m e^{iL_p^{slow} \frac{\Delta t}{2}}$$

Fast forces calculated every dt
Slow Forces calculated every Δt

} The computer works less...

We can create an arbitrary number of intermediate levels of integration time.
This integrator is symplectic/time reversible.

Tuckerman, Berne and Martyna, J. Chem. Phys., 97 1990 (1992)

Performance

$$e^{i\tilde{L}\Delta t} = \left[e^{iL_p \frac{\Delta t}{2}} e^{iL_q \Delta t} e^{iL_p \frac{\Delta t}{2}} \right]$$

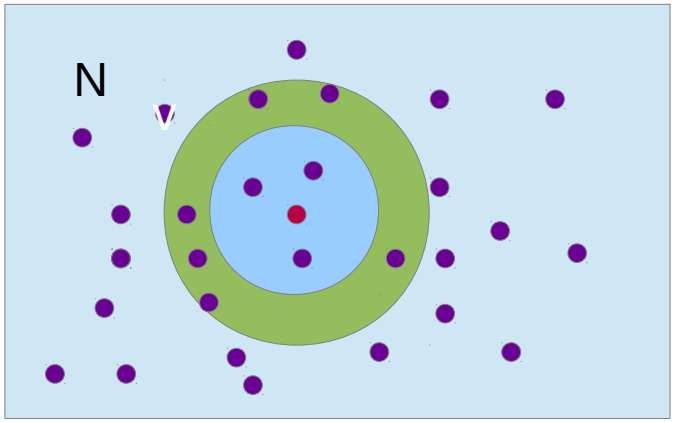
$$iL_q = \sum_k \dot{q}_k \frac{\partial}{\partial q_k}$$

$$iL_p = \sum_k \dot{p}_k \frac{\partial}{\partial p_k}$$

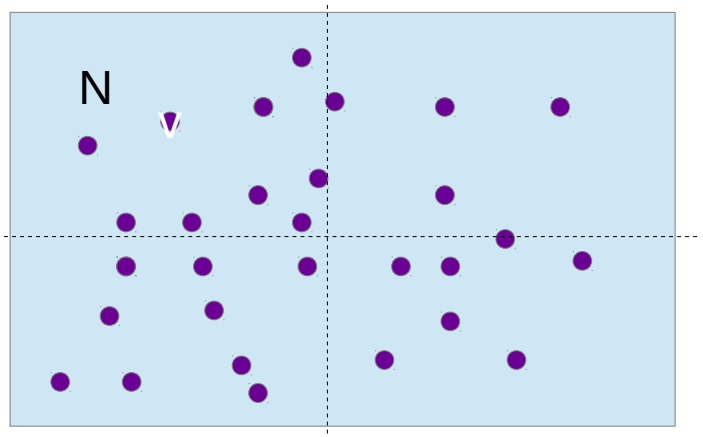
→ Imply forces calculation

Most time-consumming part : forces calculation

List of neighbors of an atom update periodically



Parallel computing (diff. Strategies)



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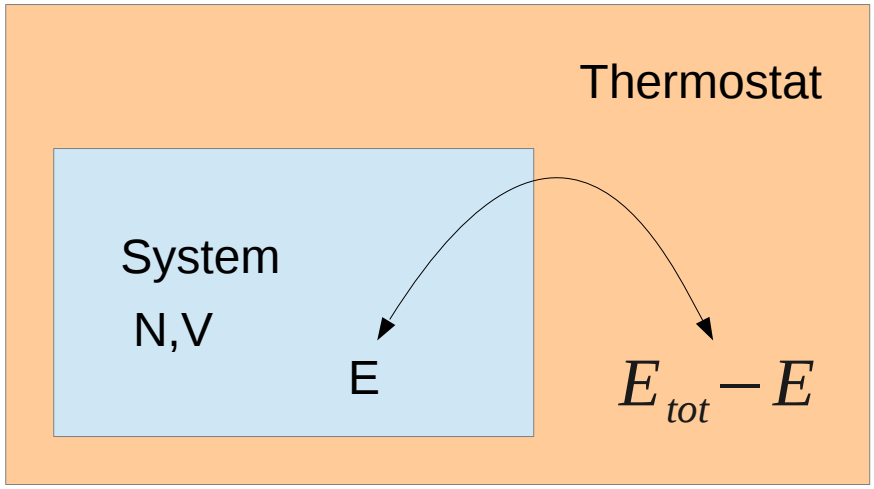
The canonical ensemble (NVT)

(Thermostat+ system) isolated at equilibrium $E_{thermostat} + E_{system} = E_{tot} - E + E = E_{tot}$

$$E \ll E_{tot}$$



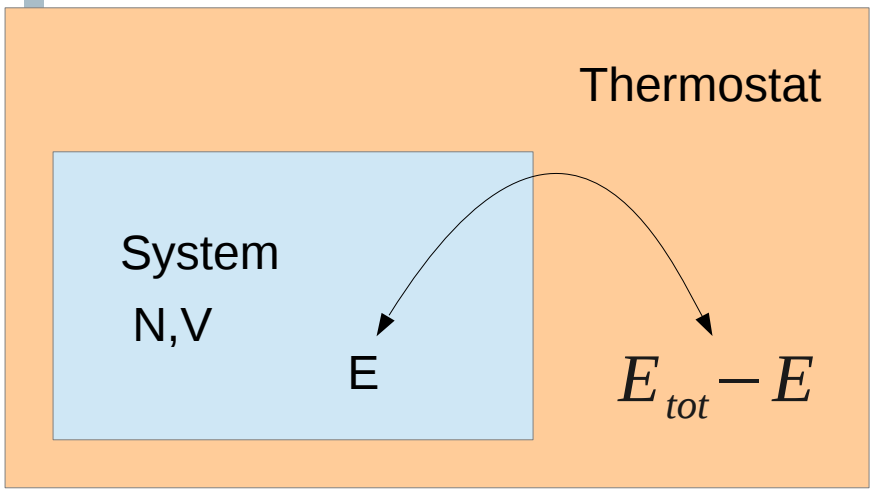
T: the microcanonical temperature of the thermostat

$$P(\alpha) = \frac{\Omega_{therm}(E_{tot} - E)}{\Omega_{tot}(E_{tot}, V_{tot})} = \frac{e^{\frac{S_{therm}(E_{tot}-E)}{k}}}{\Omega_{tot}(E_{tot}, V_{tot})} = \frac{e^{\frac{-E}{kT}}}{Z}$$

$$P(\alpha) = \frac{1}{Z} e^{\frac{-E}{kT}}$$

- the equipartition theorem $\langle E_{kin} \rangle^{NVT} = s \frac{kT}{2}$

Nose-Hoover Hamiltonian



Extended space method (general method) :

To describe the energy exchange with the thermostat, we need
-Some generalized coordinates for the thermostat.
-to specify the coupling between our system and the thermostat

Thermostat : (s, p_s)

Nose has proposed:

$$H_{Nose} = \sum_{k=1}^{N} \frac{\vec{p}_k^{\,2}}{2 m_k s^2} + U(\vec{r}_1, \ldots, \vec{r}_N) + \frac{p_s^2}{2Q} + g k T \ln s$$

6N + 2 coordinates.

Each particle is coupled to the thermostat, Independently on their positions.

Q: not a mass (unit energy x time^2)
fix the inertia of the thermostat

Nose, J. Chem. Phys., 81,511 (1984)
Nose, Mol. Phys. 52, 255 (1984)
Hoover, PRA, 31,1695 (1985)
Hoover, PRA, 34,2499 (1986)

Nose Hoover Thermostat

H_{Nose} in the microcanonical ensemble
6N+2 independent variables

$$s, p_s, \vec{r}_k, \vec{p}_k$$

$$H_{Nose} = \sum_{k=1}^{N} \frac{p_k^2}{2 m_k s^2} + U(\vec{r}_{1,\ldots}, \vec{r}_N) + \frac{p_s^2}{2Q} + g\,k\,T \ln s$$

Si g = 3N+1

$$\dot{\vec{r}}_k = \vec{\nabla}_{\vec{p}_k} H_{Nose} = \frac{\vec{p}_k}{m_k s^2}$$

$$\dot{\vec{p}}_k = -\vec{\nabla}_{\vec{r}_k} H_{Nose} = -\vec{\nabla}_{\vec{r}_k} U$$

$$\dot{s} = \vec{\nabla}_{p_s} H_{Nose} = \frac{p_s}{Q}$$

$$\dot{p}_s = -\vec{\nabla}_s H_{Nose} = \frac{1}{s}\left[\sum_{k=1}^{N} \frac{\vec{p}_k^2}{m_k s^2} - g\,kT\right]$$

For any observable, if the system is ergodic

For system + thermostat

For system alone

$$\lim_{T\to\infty} \frac{1}{T}\int_0^T dt\, A\left(\frac{\vec{p}(t)}{s}, \vec{r}(t)\right) = \left\langle A\left(\frac{\vec{p}(t)}{s}, \vec{r}(t)\right)\right\rangle_{NOSE}^{NVE} = \left\langle A\left(\frac{\vec{p}(t)}{s}, \vec{r}(t)\right)\right\rangle_{H}^{NVT}$$

$$H = \sum_{k=1}^{N} \frac{\vec{p}_k^2}{2 m_k} + U(\vec{r}_{1,\ldots}, \vec{r}_N)$$

Nose Hoover thermostat

$$H_{Nose} = \sum_{k=1}^{N} \frac{\vec{p}_k^{\,2}}{2 m_k s^2} + U(\vec{r}_1, \ldots, \vec{r}_N) + \frac{p_s^2}{2Q} + g\,k\,T \ln s$$

$$\dot{\vec{r}}_k = \vec{\nabla}_{\vec{p}_k} H_{Nose} = \frac{\vec{p}_k}{m_k s^2}$$

$$\dot{\vec{p}}_k = -\vec{\nabla}_{\vec{r}_k} H_{Nose} = -\vec{\nabla}_{\vec{r}_k} U$$

$$\dot{s} = \vec{\nabla}_{p_s} H_{Nose} = \frac{p_s}{Q}$$

$$\dot{p}_s = -\vec{\nabla}_s H_{Nose} = \frac{1}{s}\left[\sum_{k=1}^{N} \frac{\vec{p}_k^{\,2}}{m_k s^2} - g\,kT\right]$$

Particles : virtual variables $(\vec{r}_k, \vec{p}_k)$ ⟷ Real variable $\left(\vec{r}_k, \frac{\vec{p}_k}{s}\right)$

Virtual time t ⟷ Real time $t' = \int \frac{dt}{s}$

Thermostat : (s, p_s)

Nose, J. Chem. Phys., 81,511 (1984)
Nose, Mol. Phys. 52, 255 (1984)
Hoover, PRA, 31,1695 (1985)
Hoover, PRA, 34,2499 (1986)

Nose Hoover thermostat

$$T' = \int_0^T dt \frac{1}{s(t)}$$ An observable

$$\lim_{T' \to \infty} \frac{1}{T'} \int_0^{T'} dt' A\left(\vec{p}'(t'), \vec{r}(t')\right) = \frac{\lim_{T \to \infty} \frac{1}{T} \int_0^T dt \frac{A\left(\frac{\vec{p}(t)}{s(t)}, \vec{r}(t)\right)}{s(t)}}{\lim_{T \to \infty} \frac{1}{T} \int_0^T dt \frac{1}{s(t)}}$$

$$= \frac{\left\langle A\left(\frac{\vec{P}}{s}, \vec{r}\right)/s \right\rangle_{NOSE}}{\left\langle \frac{1}{s} \right\rangle_{NOSE}} = \left\langle A\left(\frac{\vec{P}}{s}, \vec{r}\right) \right\rangle_{NVT}$$

Equality if g=3N !!!!

$$H_{Nose} = \sum_{k=1}^{N} \frac{\vec{p}_k^{\,2}}{2 m_k s^2} + U(\vec{r}_1, \ldots, \vec{r}_N) + \frac{p_s^2}{2Q} + g k T \ln s$$

If a sampling scheme in real time, not the same value of g

Nose Hoover: thermostat inertia?

Choice of the thermostat mass $Q = 3\,NkT\,\tau^2$

Any mass Q gives
the same Boltzman distribution.

Q fixes the inertia of the thermostat:
controls the fluctuation of temperature.

Large Q. inefficient sampling
of phase space
Equilibration in a very large time

Small Q : degree of freedom s
tends to decouple from
the physical system. Temperature
fluctuates widely.

In practice, a reasonable choice : $\tau \approx 20 - 100\,\Delta t$

Nose, J. chem. Phys. 81, 511 (1984)
Martyna et al. J. Chem. Phys., 97,2635 (1992)

Ergodicity

$$Z_{Nose}^{NVE} = \int dp_s\, ds \prod_k d^3 r_k\, d^3 p_k\, \delta\left(E_{tot} - H_{Nose}\right)$$

$$\lim_{T\to\infty} \frac{1}{T}\int_0^T dt\, A\left(\frac{\vec{p}(t)}{s}, \vec{r}(t)\right) \overset{?}{=} \left\langle A\left(\frac{\vec{p}(t)}{s}, \vec{r}(t)\right)\right\rangle_{NOSE}^{NVE} = \left\langle A\left(\frac{\vec{p}(t)}{s}, \vec{r}(t)\right)\right\rangle_{H}^{NVT}$$

True if the system is ergodic

$$\frac{d\vec{r}_k}{dt'} = \frac{\vec{p'}_k}{m_k}$$

$$\frac{d\vec{p'}_k}{dt'} = -\vec{\nabla}_{\vec{r}_k} U - \frac{p_s}{Q}\vec{p'}_k$$

$$\frac{d\xi}{dt'} = \frac{p_s}{Q}$$

$$\frac{dp_s}{dt'} = \left[\sum_{k=1}^{N} \frac{\vec{p'}_k^{\,2}}{m_k} - g\,kT\right]$$

Are these dynamical equations ergodic?
(in the virtual or real world?)

Example of non ergodicity

A simple harmonic oscillator coupled to Nose-Hoover thermostat

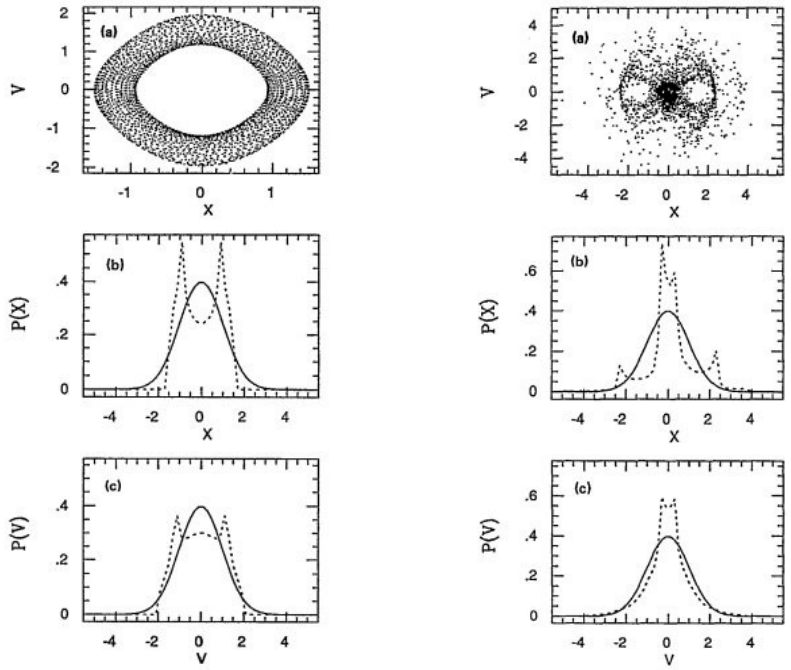


FIG. 1. (a) Density plot of the Nosé–Hoover dynamics of a harmonic oscillator [$q(0) = 1, p(0) = 1, p_\eta(0) = 1, Q = 1$]. (b) Position distribution function obtained from Nosé–Hoover dynamics of a harmonic oscillator (dotted line). The solid line is the exact result. (c) Velocity distribution function obtained from Nosé–Hoover dynamics of a harmonic oscillator (dotted line). The solid line is the exact result.

FIG. 2.(a) Density plot of the Nosé–Hoover dynamics of a harmonic oscillator [$q(0) = 1, p(0) = 1, p_\eta(0) = 10, Q = 1$]. (b) Position distribution function obtained from Nosé–Hoover dynamics of a harmonic oscillator (dotted line). The solid line is the exact result. (c) Velocity distribution function obtained from Nosé–Hoover dynamics of a harmonic oscillator (dotted line). The solid line is the exact result.

Explained for non hamiltonian system

$$Z = \int dx_t \sqrt{g(x_t, t)} \prod_k \delta\left(\Lambda_k(x) - C_k\right)$$

For the harmonic oscillator : there is a hidden conservative law

If more than one conserved quantity :
the Nose Hoover equations fail to generate the correct distribution

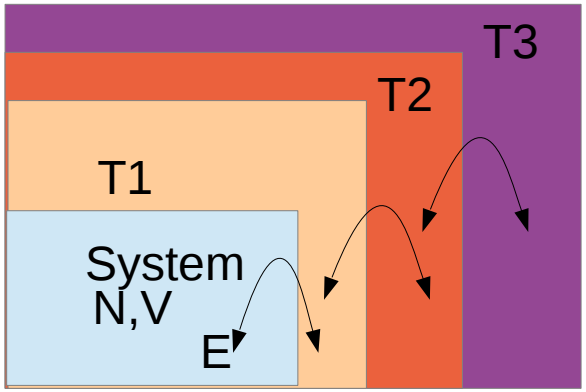
Martyna et al. J. Chem. Phys., 97,2635 (1992)

Tuckerman et al, J. Chem. Phys, 115,1678 (2001)

Solution: Nose Hoover chains

More variables are needed to describe the thermostat.

Introduction of additional variables to thermostat



$\vec{r}_k, \vec{p}\,'_k$ $\quad \xi_{1,} p_{\xi_1}, \xi_{2,} p_{\xi_2}, \xi_{3,} p_{\xi_3}$

M thermostat, variables $\left(\xi_{1,} p_{\xi_1}, \ldots, \xi_M, p_{\xi_M}\right)$

$$H_{Nose} = \sum_{k=1}^{N} \frac{\vec{p}\,'^2_k}{2m_k} + U(\vec{r}_{1,}, \ldots, \vec{r}_N) + \sum_{j=1}^{M} \frac{p^2_{\xi_j}}{2Q_j} + 3\mathrm{N}\,k\,T\,\xi_1 + \sum_{j=2}^{M} k\,T\,\xi_j$$

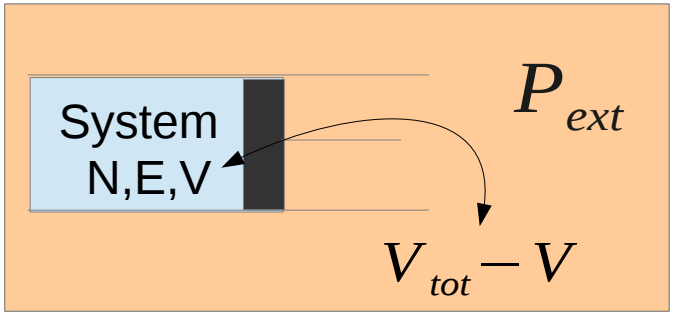
With the thermostat chain, we recover

$$Z^{NVE}_{Nose} \propto Z^{NVT}_{H}$$

Martyna et al. J. Chem. Phys., 97,2635 (1992)

Other ensembles

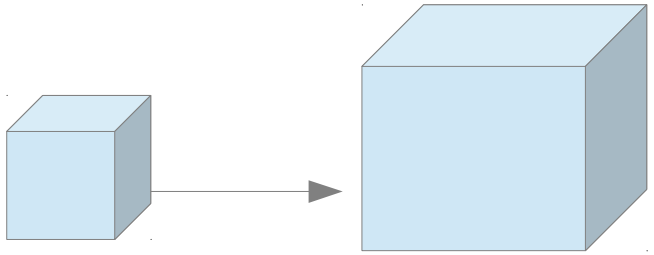
Idea : Extended space method (general method) :
- additional variables to describe the barostat….



$$dE = -P_{ext}\, dV$$
$$d(E + P_{ext} V) = 0$$

isoenthalpic-isobaric

$$H_{Andersen} = \sum_{k=1}^{N} V^{-2/3} \frac{\vec{\pi}_k^2}{2 m_k} + U(V^{1/3} \vec{s}_1, \ldots, V^{1/3} \vec{s}_N) + \frac{p_V^2}{2W} + P_{ext} V$$

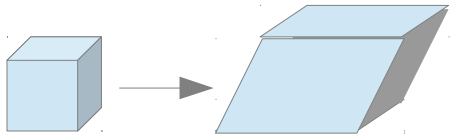


Andersen, J. Chem. Phys, 72,2384 (1980)

Extension to

→ isothermal-isobaric (rather subtle) *Martyna, Tobias, Klein, J. Chem. Phys. 101,4177 (1994)*

→ Parrinello-Rahman



Parrinello, Rahman PRL, 45, 1196 (1980)
J. Appl. Phys, 52, 7182 (1981)

Conclusion on MD

Molecular dynamics : - integration of Newton law for
a reduced number of particles ($N_{max} = 10^{6-8}$)
- time average ↔ ensemble average

Integrator → time-reversible
Symplectic properties
} Liouville formulation to generate algorithms

Ensemble → Nose Hoover thermostat virtual/real time – Nose Hoover chains
→ isobaric/isenthalpic or isobaric/isothermal ensemble

Lots of MD available code with many implemented methods (lammps…)

Remember that a code always gives an answer
→ your work: to be sure the answer is correct
- methods: check the conservation of 1st integral (energy or hamiltonian)
check distribution kinetic energy (if thermostat)….

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- Application
- Ensemble NPT, μVT
- Parallel Tempering

5) Free energy calculation

Monte Carlo method

How to calculate $\langle A \rangle = \int A(\vec{R}, \dot{\vec{R}}) f(\vec{R}\,\dot{\vec{R}})\, d^{3N}R\, d^{3N}\dot{R}$

How to calculate an integral in 6N dimensions?

How to sample a distribution?

Monte Carlo method

A class of algorithm that relies on repeated random sampling.

Possible applications :

- to calculate some integrals
- to locate absolute minima of a function
- to find « a reaction path »

Mathematics

Physics → Statistical physics, Equilibrium properties

Physics → Quantum Monte Carlo

Biology → Protein

Engineering

Finance

Games

Security (encryptation keys)...

How to calculate an integral

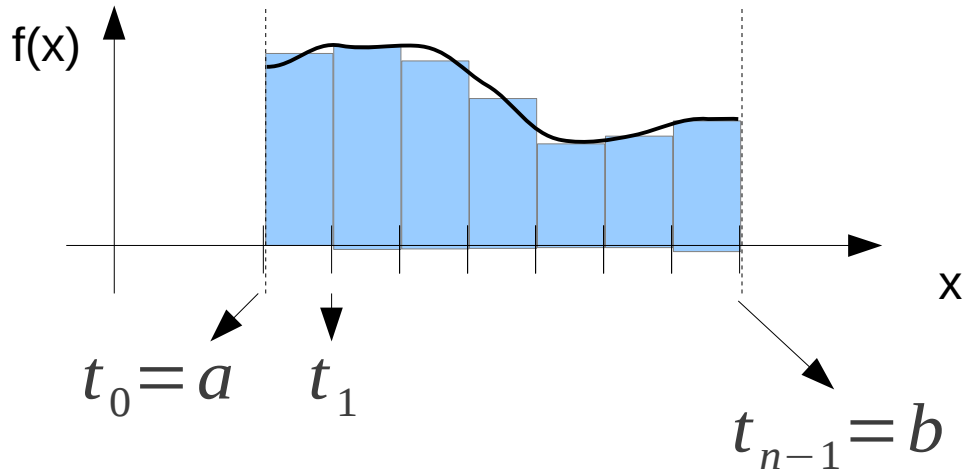
Rieman definition of integral

$$I = \frac{1}{b-a}\int_a^b f(x)\,dx = \lim_{n\to\infty,\delta\to 0}\sum_{i=0}^{n-1} f(x_i)\frac{(t_{i+1}-t_i)}{b-a}$$

$$t_0 = a < t_1 < .... < t_{n-1} = b$$

$$t_i < x_i < t_{i+1}$$

$$\delta = max\,(t_{i+1}-t_i)$$



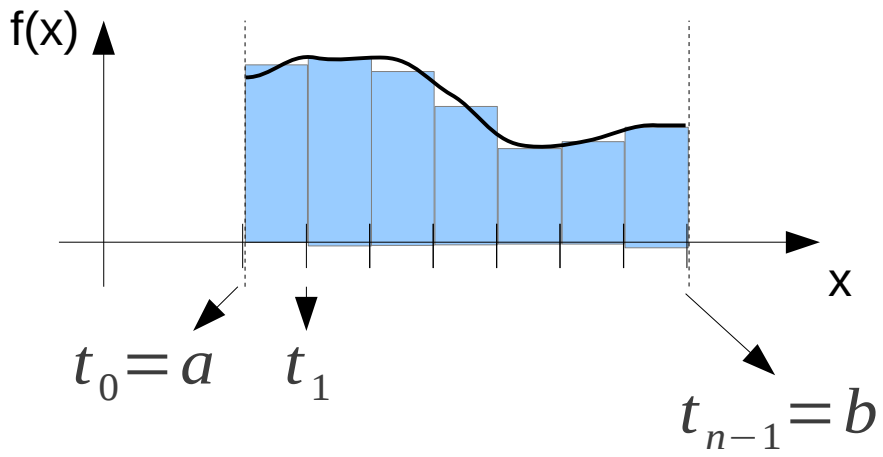
- Direct sampling of the phase space

- Number of points : n^D

How to calculate an integral with a Monte Carlo method

Rieman definition of integral

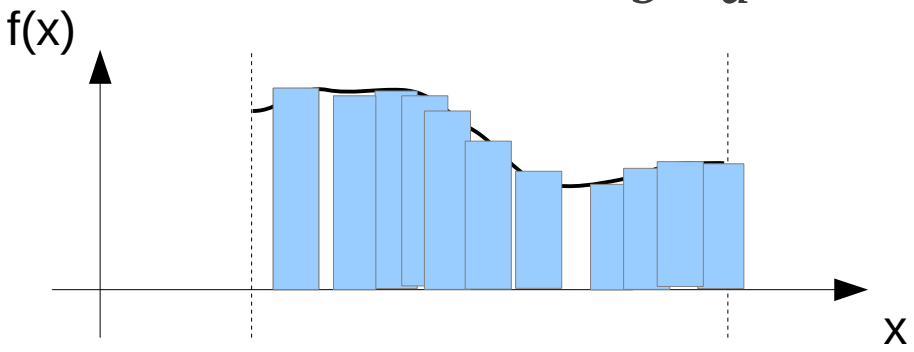
$$I=\frac{1}{b-a}\int_a^b f(x)\,dx=\lim_{n\to\infty,\delta\to 0}\frac{1}{b-a}\sum_{i=0}^{n-1} f(x_i)(t_{i+1}-t_i)$$



Probabilist approach

$$I=\frac{1}{b-a}\int_a^b f(x)\,dx=\lim_{n\to\infty}\frac{1}{n}\sum_{i=0}^{n-1} f(x_i)$$

With $$P(x)\,dx=\frac{dx}{b-a}$$



Monte Carlo method
Simple and important sampling

Simple sampling

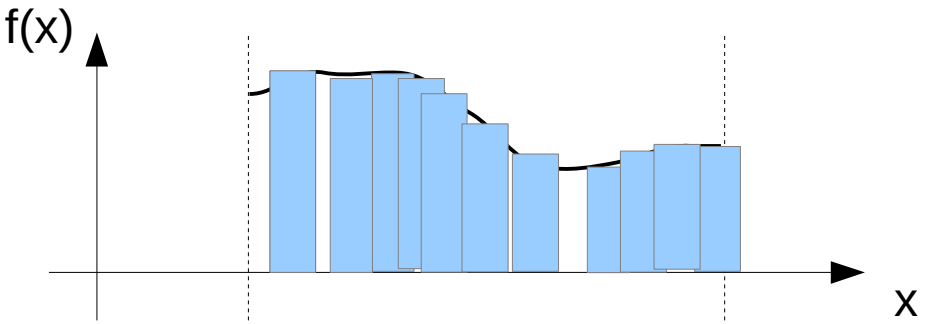
$$I_n = \frac{1}{n}\sum_{i=0}^{n-1} f(x_i)$$

probability $\dfrac{dx}{b-a}$

$$I = \frac{1}{b-a}\int_a^b f(x)\,dx = \lim_{n\to\infty} I_n$$

Important sampling

$$I_n = \frac{1}{n}\sum_{i=0}^{n-1} g(x_i) \qquad P(x)\,dx$$



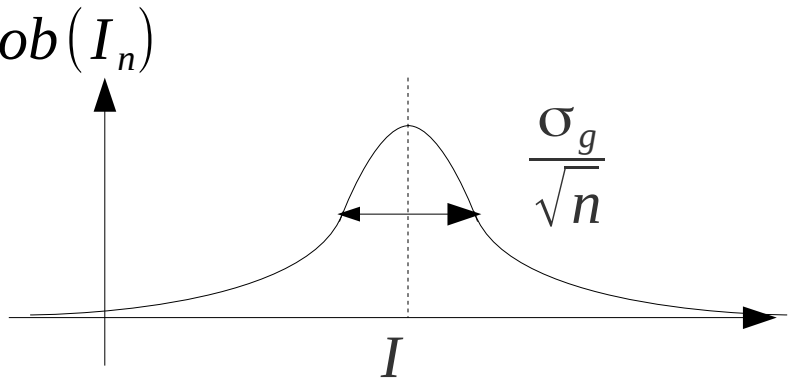
$$I = \frac{1}{b-a}\int_a^b \frac{f(x)}{P(x)} P(x)\,dx = \int_a^b g(x)P(x)\,dx = \lim_{n\to\infty} I_n$$

Monte Carlo method
Central limit theorem

$$I_n = \frac{1}{n}\sum_{i=0}^{n-1} g(x_i) \qquad I = \frac{1}{b-a}\int_a^b \frac{f(x)}{P(x)} P(x)\,dx = \int_a^b g(x)P(x)\,dx = \lim_{n\to\infty} I_n$$

In the limit n → ∞

$$Prob(I_n) = \sqrt{\frac{n}{2\pi\sigma_g^2}}\, e^{\frac{-n(I_n - I)^2}{2\sigma_g^2}}$$



Choose P(x) to minimize σ_g to ensure a fast convergence

Tuckerman, Statistical mechanics : theory and molecular simulation.2010

Application to statistical physics

For the canonical ensemble

Generate a serie $X_1 \ldots X_n$ following P(α)

$$P(\vec{r}_{1,\ldots},\vec{r}_N,\vec{p}_{1,\ldots},\vec{p}_N)=\frac{e^{-\beta H}}{\int\prod d\vec{r}_k\, d\vec{p}_k\, e^{-\beta H}}$$

$$x_i \in \{\alpha_{1,}\alpha_{2,}\ldots,\alpha_\Omega\}$$

Microstate

$$A_n=\frac{1}{n}\sum_i^n A(x_i) \xrightarrow[n\to\infty]{} \langle A\rangle_{NVT}=\int\prod d\vec{r}_k\, d\vec{p}_k\, A(\vec{r}_1\ldots.\vec{r}_N,\vec{p}_1\ldots\vec{p}_N)P(\vec{r}_1\ldots.\vec{r}_N,\vec{p}_1\ldots\vec{p}_N)$$

$$I_n=\frac{1}{n}\sum_{i=0}^{n-1} g(x_i) \xrightarrow[n\to\infty]{} I=\int_a^b g(x)P(x)dx$$

Simple acceptance/rejection algorithm

How to generate a serie $X_1 .... X_n$ following P(α) $X_i \in \{\alpha_1, \alpha_2, \ldots, \alpha_\Omega\}$

Microstate

Simple algorithm

- pick up randomly a configuration α in the phase space
- calculate P(α)
- pick up a randum number r in [0,1].
  * If r <P(α), keep the configuration in the serie $X_{i+1} = \alpha$
  * else reject (do nothing...).

Points are chosen independently from each other

Let's try to apply this algorithm to statistical mechanics.

Sampling distribution and statistical mechanics

N particles
In the NVT ensemble

$$\langle A \rangle_{NVT} = \int \prod d\vec{r}_k \, d\vec{p}_k \, A(\vec{r}_1 .... \vec{r}_N, \vec{p}_1 ... \vec{p}_N) P(\vec{r}_1 .... \vec{r}_N, \vec{p}_1 ... \vec{p}_N)$$

$$P(\vec{r}_{1,} ..., \vec{r}_N, \vec{p}_{1,} ..., \vec{p}_N) = \frac{e^{-\beta H}}{\int \prod d\vec{r}_k \, d\vec{p}_k \, e^{-\beta H}}$$

Simple algorithm

- pick up randomly a configuration α in phase space
- calculate P(α)
- pick up a randum number r in [0,1]
  * If r <P(α), keep the configuration in the serie
  * else reject. $X_{i+1} = \alpha$

$$x_i \in \{\alpha_{1,} \alpha_{2,} ..., \alpha_\Omega\}$$

Choose randomly the position and momentum **OK**

Calculate
- $e^{-\beta H}$ **OK**
- $\int \prod d\vec{r}_k \, d\vec{p}_k \, e^{-\beta H}$ **Not OK**

In statistical mechanics, we a priori only know a quantity proportional to the probability of a configuration

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5) Free energy calculation

Markov chain

In the simple acceptance/rejection sampling algorithm, configurations are chosen Independently from each other

$$X_1 \ldots X_i X_{i+1} X_n \qquad P\left(x_{i+1} | x_i, x_{i-1}, x_{i-2} \ldots\right) = P\left(x_{i+1}\right)$$

independents on $x_i, x_{i-1}, x_{i-2} \ldots$

In a Markov chain, points are not chosen independently from each other

$$X_1 \ldots X_i X_{i+1} X_n$$

$$P\left(x_{i+1} | x_i, x_{i-1}, x_{i-2} \ldots\right) = P\left(x_{i+1} | x_i\right)$$

only depends on x_{i+1}, x_i

The stochastic transition matrix

A formal derivation

$x_1 .... x_i x_{i+1} x_n \qquad P(x_{i+1}|x_i) \longleftrightarrow T(\alpha_k|\alpha_l) = P(x_{i+1}=\alpha_k | x_i=\alpha_l)$

Supposed indep. on i

$x_i \in \{\alpha_1, \alpha_2, \ldots, \alpha_\Omega\}$

$$P(x_{i+1}=\alpha_k) = P_{i+1}(\alpha_k) = \sum_{\alpha_l} T(\alpha_k|\alpha_l)\, P_i(\alpha_l)$$

$$\begin{bmatrix} P_{i+1}(\alpha_1) \\ P_{i+1}(\alpha_2) \\ \ldots \\ P_{i+1}(\alpha_\Omega) \end{bmatrix} = \begin{bmatrix} \\ T \\ \\ \end{bmatrix} \begin{bmatrix} P_i(\alpha_1) \\ P_i(\alpha_2) \\ \ldots \\ P_i(\alpha_\Omega) \end{bmatrix} \qquad \text{OR} \qquad \vec{P}_{i+1} = T\,\vec{P}_i$$

The stochastic matrix : the Perron-Frobenius theorem

Hypothesis : - T is a stochastic matrix $\sum_{\alpha_l} T(\alpha_l|\alpha_k)=1$

- T is irreducible $\forall(\alpha_l,\alpha_k),\exists m/T^m(\alpha_l|\alpha_k)\neq 0$

Perron-Frobenius theorem :

- T has a non degenerate eigen value 1 for vector $\vec{\pi}$ $T\vec{\pi}=\vec{\pi}$
- all other eigen values $0<\lambda_l<1$

Whatever $\vec{P}_0$ $\lim_{n\to\infty} T^n \vec{P}_0=\vec{\pi}$

Monte Carlo

$\lim_{n \to \infty} T^n \vec{P}_0 = \vec{\pi}$ We choose T so that $\vec{\pi}$ is the desired probability distribution (the Boltzman distribution NVT...)

Implementation :

$y_0 \in \{\alpha_1, \alpha_2, \dots, \alpha_\Omega\}$

- start from an initial configuration. $y_0 = \alpha_k$ → $\vec{P}_0 = \begin{bmatrix} \frac{1}{\Omega} \\ \frac{1}{\Omega} \\ .. \\ \frac{1}{\Omega} \\ \frac{1}{\Omega} \end{bmatrix}$

- randomly choose y_{i+1} following the probability T

m times

- generate the sequence $x_1 \dots . x_n$
  By randomly choosing x_{i+1} following the probability T
  With $x_1 = y_m$

$T^m \vec{P}_0 \approx \vec{\pi}$

Generating the stochastic matrix the detailed balance condition

The master equation

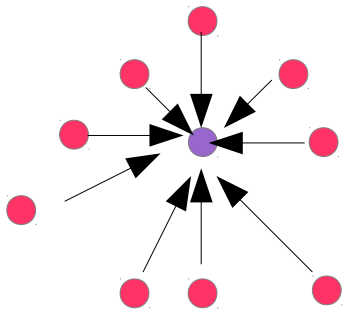
$$P_{i+1}(\alpha_k) - P_i(\alpha_k) = \sum_l T(\alpha_k|\alpha_l) P_i(\alpha_l) - P_i(\alpha_k)$$

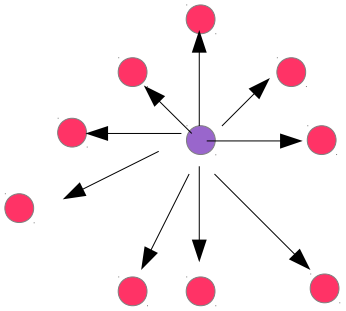
$$= \sum_l T(\alpha_k|\alpha_l) P_i(\alpha_l) - \sum_l T(\alpha_l|\alpha_k) P_i(\alpha_k)$$

$$= \sum_{l \neq k} T(\alpha_k|\alpha_l) P_i(\alpha_l) - \sum_{l \neq k} T(\alpha_l|\alpha_k) P_i(\alpha_k)$$

Probability flux to arrive in state k

Probability flux to leave state k





Generating the stochastic matrix the detailed balance condition

The master equation

$$P_{i+1}(\alpha_k) - P_i(\alpha_k) = \sum_{l \neq k} T(\alpha_k|\alpha_l) P_i(\alpha_l) - \sum_{l \neq k} T(\alpha_l|\alpha_k) P_i(\alpha_k)$$

$$\lim_{n \to \infty} T^n \vec{P}_0 = \vec{\pi} \qquad \vec{P}_{i+1} = \vec{P}_i = \vec{\pi}$$

the desired probability distribution (Boltzman distribution...)

$$T\vec{\pi} = \vec{\pi}$$

Necessary condition

$$\sum_{l \neq k} T(\alpha_k|\alpha_l) \pi(\alpha_l) = \sum_{l \neq k} T(\alpha_l|\alpha_k) \pi(\alpha_k)$$

A sufficient condition is to impose

sufficient condition

$$T(\alpha_k|\alpha_l) \pi(\alpha_l) = T(\alpha_l|\alpha_k) \pi(\alpha_k)$$

Detailed balance condition

« In practice, most algorithms that do not statisfy the detailed balance condition are simply wrong. » *Frenkel and Smit. Understanding molecular simulations*

See also Manousiouthakis and Deem, J. Chem. Phys., 110, 2753 (1999)

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Monte Carlo Metropolis

$$T(\alpha_k|\alpha_l)\pi(\alpha_l) = T(\alpha_l|\alpha_k)\pi(\alpha_k)$$

Detailed balance condition

We will use an acceptance/rejection algoritm

$$T(\alpha_k|\alpha_l) = P_{gen}(\alpha_k|\alpha_l)\, P_{accept}(\alpha_k|\alpha_l)$$

Metropolis proposes :

$$P_{accept}(\alpha_k|\alpha_l) = min\left(1, \frac{P_{gen}(\alpha_l|\alpha_k)\pi(\alpha_k)}{P_{gen}(\alpha_k|\alpha_l)\pi(\alpha_l)}\right) \qquad k \neq l$$

Advantages : - satisfy the detailed balance
- only need to know a quantity proportional to the probability of a configuration

$$T(\alpha_k|\alpha_k) = 1 - \sum_{l \neq k} T(\alpha_l|\alpha_k) \longrightarrow$$

T is a stochastic matrix

T is irreducible } Depends on the generation

Metropolis et al., J. chem. Phys. 21,1087 (1953)

Monte Carlo Metropolis algorithm

$$x_i = \alpha_l \qquad x_i \in \{\alpha_1, \alpha_2, \ldots, \alpha_\Omega\}$$

- generate a new trial configuration α_k following $P_{gen}(\alpha_k|\alpha_l)$
- calculate

$$P_{accept}(\alpha_k|\alpha_l) = min\left(1, \frac{P_{gen}(\alpha_l|\alpha_k)\pi(\alpha_k)}{P_{gen}(\alpha_k|\alpha_l)\pi(\alpha_l)}\right)$$

- pick up a random number r in [0,1]

$$r < P_{accept}(\alpha_k|\alpha_l) \rightarrow x_{i+1} = \alpha_k$$

$$r > P_{accept}(\alpha_k|\alpha_l) \rightarrow x_{i+1} = \alpha_l$$

Metropolis and Biased Monte Carlo

Original Metropolis Monte Carlo

$$\begin{cases} P_{gen}(\alpha_k|\alpha_l) = P_{gen}(\alpha_l|\alpha_k) \\ P_{accept}(\alpha_k|\alpha_l) = min\left(1, \dfrac{\pi(\alpha_k)}{\pi(\alpha_l)}\right) \end{cases}$$

Metropolis et al., J. chem. Phys. 21,1087 (1953)

Biased Monte Carlo :

Choice of P_{gen} to propose moves that are more likely to be accepted.
Biased Monte Carlo methods have been shown to improve sampling in many cases

Frenkel, Mooij, Smit, J. Phys. : Condens. Matter, 3, 3053 (1992)
Falcioni and Deem, J. chem. Phys. 110,1754 (1999)
Frenkel and Smith, Understanding Molecular Simuation.

Random number generator

Generation of a random sequence of real

From atomic or subatomic physical phenomenon : radiative decay, thermal noise...Etc

From an algorithm that generates a sequence of quasi-random numbers.

Hardware random number generator

Pseudo-random number generator

Can generate truly random number sequence

Generate a sequence that have approximately the properties of a random sequence

Pseudo -random generator

- Algorithms that generate a sequence in a deterministic way

- needs a first number : the seed → - Good point for the reproducibility in simulation (rare events in KMC, debugging)
- not good for security, games applications

- because the precision of computers is finite, the sequence generated by the algorithm is necessarily periodic

Most of the time, not an issue for the simulation (period very long)

-uniformly random distribution
-correlation of successive values
-Shorter than expected periods for some seeds

There exists algorithm without problem
(Mersenne Twister, Berlekamp-Massey, Redd-Sloane, …)

Before using a pseudo random generator, check it or read the bibliography.

Pseudo-random generators are well adapted to Monte Carlo simulations

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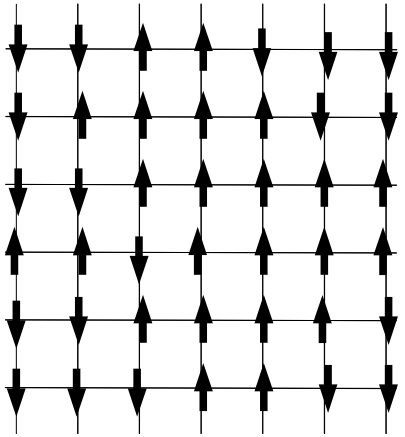
Application : the Ising model

Ensemble of N spins (up or down) on a square lattice in the NVT ensemble

$$H = -\sum_{i,\,j\ neighbors} J\,S_i S_j - \sum_i h\,S_i$$

Exchange energy (Pauli principle)
Ferromagnetic coupling
$J > 0$

External magnetic field
(here h=0)



$S = +1$

$S = -1$

Periodic boundary conditions

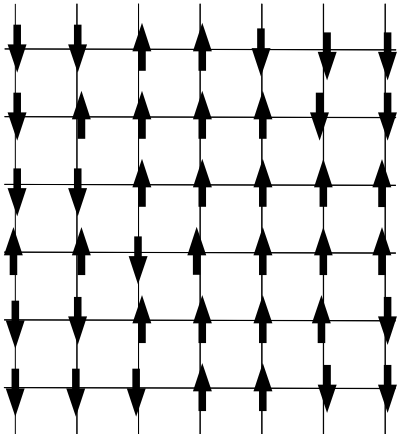
A microstate is defined from $S_1, \ldots, S_N$

Simulation in the NVT ensemble :

$$\pi(S_1, \ldots, S_N) = \frac{e^{-\beta H}}{\sum_{microstates} e^{-\beta H}}$$

Application : the Ising model

- Initialisation : choose randomly the direction of the spin on the lattice



- Metropolis algoritm:

  Markov chain step i in microstate : α_l

$$x_i = \alpha_l$$

  - choose randomly a spin
  - flip this spin to create a new microstate α_k

$$P_{gen}(\alpha_k|\alpha_l) = \frac{1}{N}$$

$\uparrow \quad S = +1$

$\downarrow \quad S = -1$

  - calculate

$$P_{accept}(\alpha_k|\alpha_l) = min\left(1, \frac{P_{gen}(\alpha_l|\alpha_k)\pi(\alpha_k)}{P_{gen}(\alpha_k|\alpha_l)\pi(\alpha_l)}\right) = min\left(1, e^{-\beta[H(\alpha_k)-H(\alpha_l)]}\right)$$

  - pick up a randum number r in [0,1]

If $r < P_{accept}(\alpha_k|\alpha_l) \longrightarrow x_{i+1} = \alpha_k$

Else $r > P_{accept}(\alpha_k|\alpha_l) \longrightarrow x_{i+1} = \alpha_l$

Application : the Ising model

- Averages :

$$A_n = \frac{1}{n}\sum_{i=1}^{n} A(x_i) \xrightarrow[n\to\infty]{} \langle A\rangle_{NVT} = \int \prod d\vec{r}_k\, d\vec{p}_k\, A(\vec{r}_1 \ldots \vec{r}_N, \vec{p}_1 \ldots \vec{p}_N) P(\vec{r}_1 \ldots \vec{r}_N, \vec{p}_1 \ldots \vec{p}_N)$$

Properties of T

« Ergodicity »

$$\vec{P}_{i+1} = T\,\vec{P}_i$$

T is stochastic **OK**

T is irreducible

- the generation process ensures that any microstate can be generated from any other one in a finite number of step.

$$\forall (\alpha_l|\alpha_k), \exists m / T^m(\alpha_l|\alpha_k) \neq 0 \quad \textbf{OK}$$

Perron- Frobenius theorem $\lim_{n\to\infty} T^n \vec{P}_0 = \vec{\pi}$

Detailed balance condition **OK**
With Boltzmann weight

$\vec{\pi}$ is the Boltzman probability

Application : the Ising model

- Remember : need to equilibrate the system : for the convergence of $T^m \vec{P}_0 \approx \vec{\pi}$

Number m of step ? Depends on the stochastic matrix T
and so on your choice of $P_{gen}(\alpha_k|\alpha_l)$

Depends on $\vec{P}_0$

For the Ising model : need at least to be able to change several times each spin :
So that m scales as N...

Fine tuning

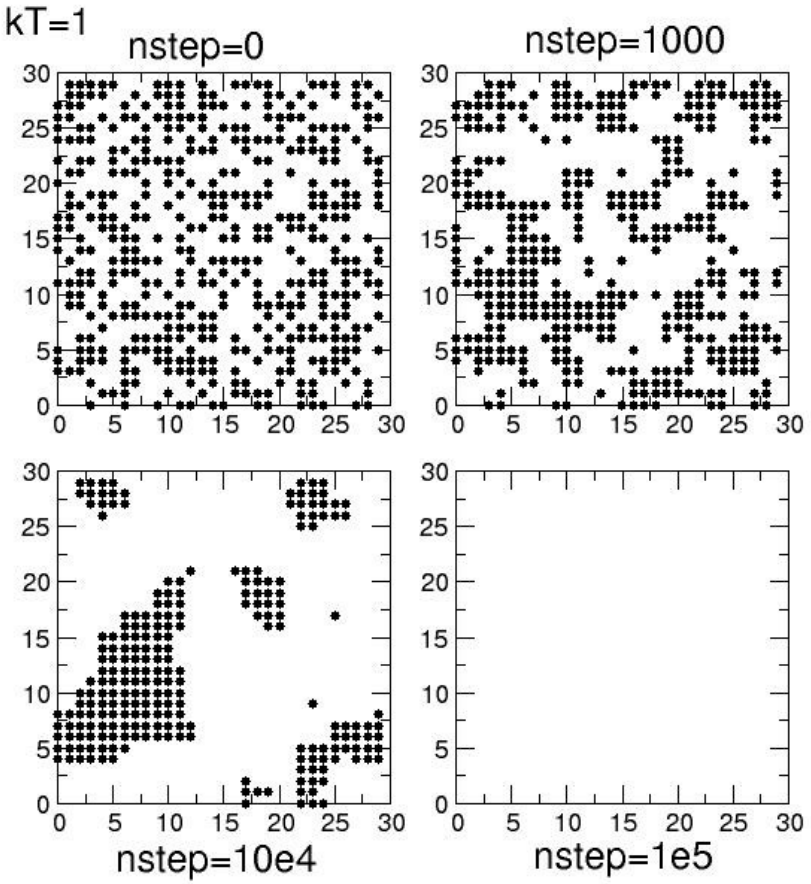
- the rejection rate → Rejected configurations are useless
If too much rejection : MC is inefficient

If too much acceptance, the phase space is not sufficiently sampled

Choose $P_{gen}\left(\alpha_k \middle| \alpha_l\right)$ so that the rejection rate is about 50 %

Example of implementation

The Ising Model : J = 1. 30x30 lattice



Convergence of the system to the Ferromagnetic phase

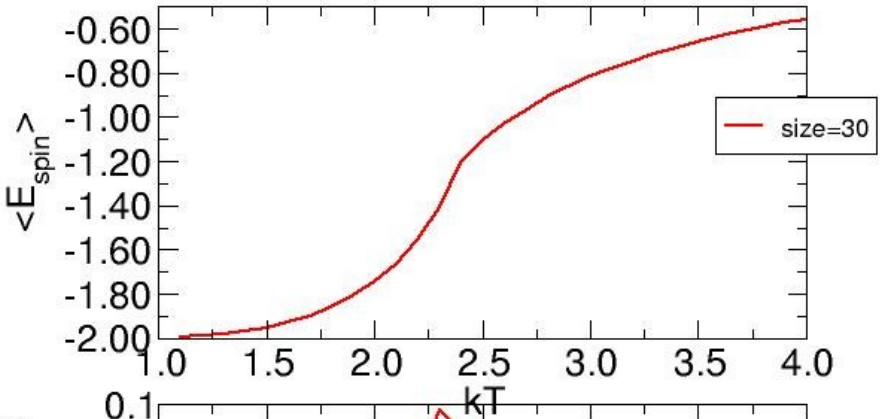
Necessary number of steps to converge depends :

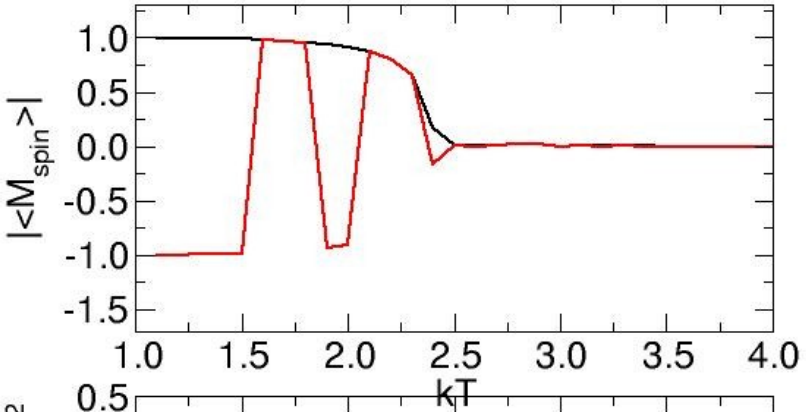
- initial configuration
- the size of the lattice
- the temperature : especially closed to the transition ferro-paramagnetic

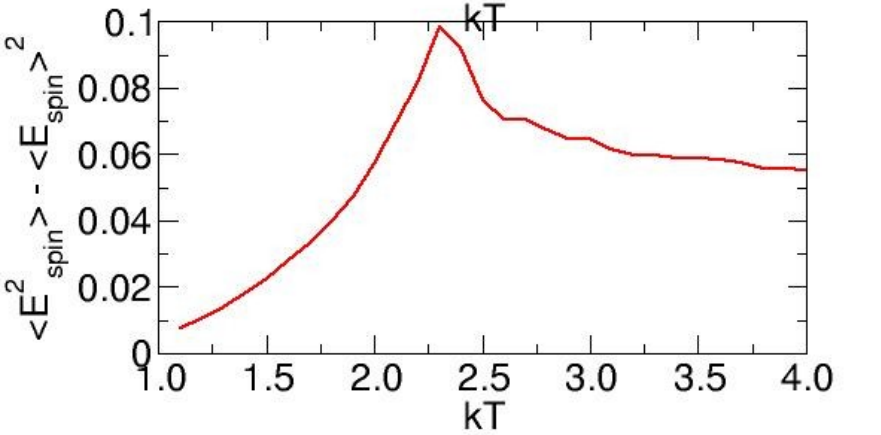
No prior equilibration

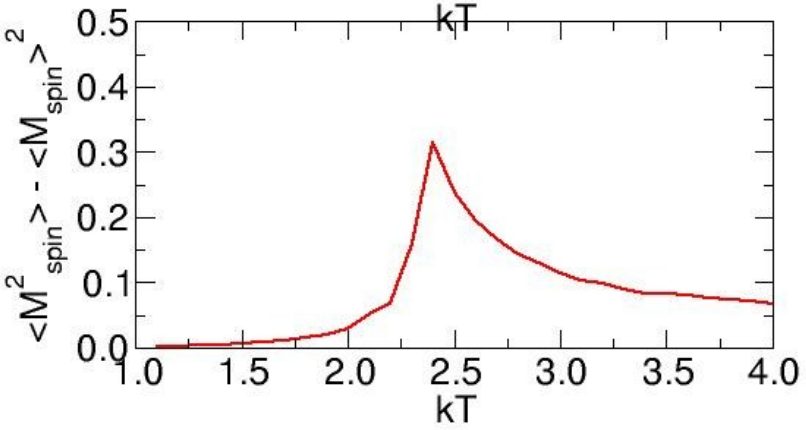
The ferro-paramagnetic transition

Nequil: 1e8
Nstep: 1e8
Size 30





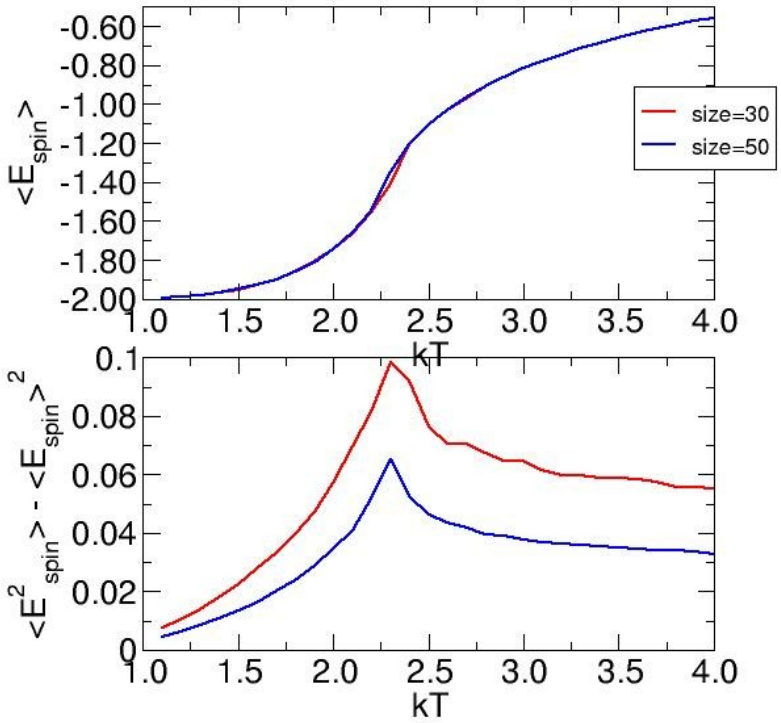


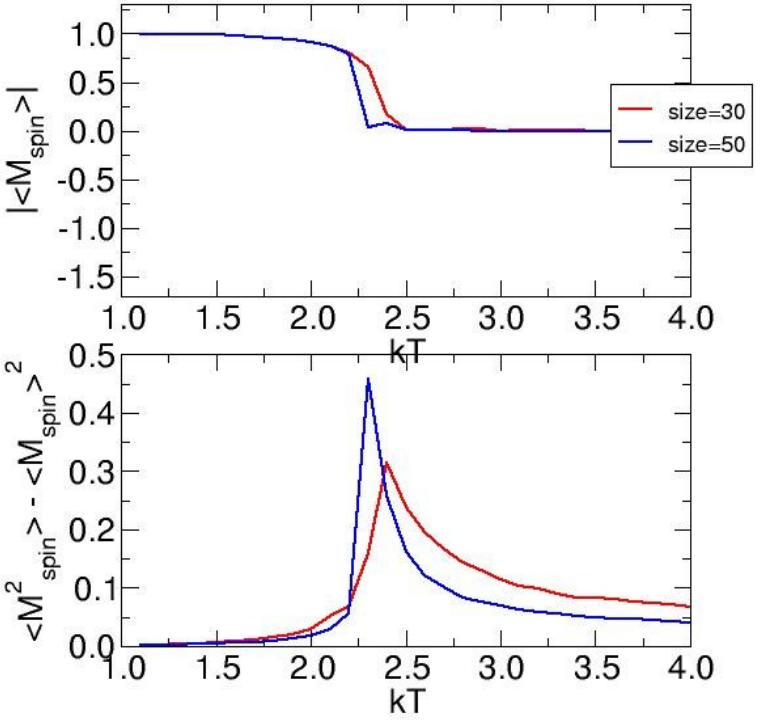


Phase transition point is smeared out for systems of finite size

Finite size effects

Nequil=1e8
Nstep = 1e8





Binder and Heerman, Monte Carlo Simulation in Statistical physics, solid -state science 80, Springer Verlag . 1992

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5) Free energy calculation

Ensemble : the Canonical ensemble - NVT

The Canonical ensemble :

$$\langle A \rangle_{NVT} = \frac{\int \prod d\vec{r}_k d\vec{p}_k A(\vec{r}_1 .... \vec{r}_N, \vec{p}_1 ... \vec{p}_N) e^{-\beta H}}{\int \prod d\vec{r}_k d\vec{p}_k e^{-\beta H}}$$

common situations: $H = \sum_i \frac{\vec{p}_i^2}{2m_i} + U(\vec{r}_{1,}, ..., \vec{r}_N)$

The observable A does not depend on momenta.

$$\langle A \rangle_{NVT} = \frac{\int \prod d\vec{r}_k d\vec{p}_k A(\vec{r}_1 .... \vec{r}_N) e^{-\beta H}}{\int \prod d\vec{r}_k d\vec{p}_k e^{-\beta H}} = \frac{\int \prod d\vec{r}_k A(\vec{r}_1 .... \vec{r}_N) e^{-\beta U}}{N! \Lambda^{3N} Q}$$

A has a polynomial dependence on the momenta (example Kinetic energy).

indiscernability

Thermal De Broglie wavelength

Analytic integration on the moment

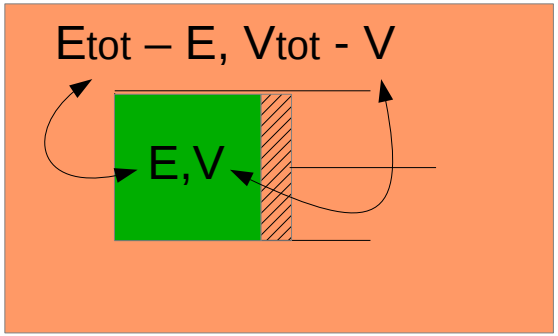
Sampling only on the position.

Ensemble : the isobaric-isothermal ensemble - NPT

The ensemble : $H=\sum_i \frac{\vec{p}_i^{\,2}}{2\,m_i}+U(\vec{r}_{1,}...,\vec{r}_N)$

$$P(\alpha)=\frac{\Omega_0(E_{tot}-E,V_{tot}-V)}{\Omega_{tot}(E_{tot},V_{tot})}$$

$$=\frac{e^{\frac{S(E_{tot}-E,V_{tot}-V)}{k}}}{\Omega_{tot}(E_{tot},V_{tot})}=\frac{e^{\frac{-E}{kT}-\frac{pV}{kT}}}{Z}$$



$$\vec{r}=\sqrt[3]{V}\,\vec{s}$$

$$Z=\frac{1}{N!\,\Lambda^{3N}}\int_0^{V_{tot}} dV \int \prod_k d\vec{r}_k e^{\frac{-U(\vec{r})}{kT}-\frac{pV}{kT}}=\frac{1}{N!\,\Lambda^{3N}}\int_0^{V_{tot}} dV\, V^N \int \prod_k d\vec{s}_k e^{\frac{-U(\vec{s},V)}{kT}-\frac{pV}{kT}}$$

$$\langle A\rangle=\int_0^{V_{tot}} dV \int \prod_k d\vec{s}_k A(\vec{s},V)\left[\frac{V^N e^{\frac{-U(\vec{s},V)}{kT}-\frac{pV}{kT}}}{N!\,\Lambda^{3N} Z}\right]$$

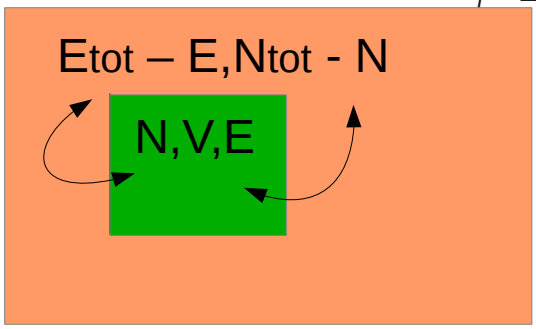
For a Metropolis sampling on the reduced variable s and the volume V.

- trial move to change coordinate s
- trial move to change the coordinate V : V → V'

$$P_{accept}(\alpha_k|\alpha_l)=min\left(1,\frac{P_{gen}(\alpha_l|\alpha_k)\,e^{-\beta[U(s,V')-U(s,V)]-\beta P[V'-V]-N\ln(\frac{V'}{V})}}{P_{gen}(\alpha_k|\alpha_l)}\right)$$

Ensemble : the grand canonical ensemble - μVT

The ensemble : $H=\sum_i \frac{\vec{p}_i^{\,2}}{2\,m_i}+U(\vec{r}_{1,\ldots},\vec{r}_N)$



$$P(\alpha)=\frac{\Omega_0(E_{tot}-U,N_{tot}-N)}{\Omega_{tot}(E_{tot},V_{tot})}$$

$$=\frac{e^{\frac{-U}{kT}+\frac{\mu N}{kT}}}{\Xi}$$

$$\Xi=\sum_N \frac{1}{N!\Lambda^{3N}} V^N \int \prod_k d\vec{s}_k\, e^{\frac{-U(\vec{s},V)-\mu N}{kT}}$$

$$\langle A\rangle=\sum_N \int \prod_k d\vec{s}_k\, A(\vec{s},V)\left[\frac{V^N e^{\frac{-U(\vec{s},V)-\mu N}{kT}}}{N!\Lambda^{3N}\Xi}\right]$$

For a Metropolis sampling on the reduced variable s, and the number of particles N
-Trial move to change coordinate s
-Trial move to change the number of particle N → N+1

$$P_{accept}(N\rightarrow N+1)=min\left(1,\frac{P_{gen}(N+1\rightarrow N)\frac{V}{(N+1)\Lambda^3}e^{-\beta[U(s,V,N+1)-U(s,V,N)]+\beta\mu}}{P_{gen}(N\rightarrow N+1)}\right)$$

- Trial move to change the number of particle N → N-1

$$P_{accept}(N\rightarrow N-1)=min\left(1,\frac{P_{gen}(N-1\rightarrow N)\frac{(N)\Lambda^3}{V}e^{-\beta[U(s,V,N-1)-U(s,V,N)]-\beta\mu}}{P_{gen}(N\rightarrow N-1)}\right)$$

Contents

1) Simulations and statistical mechanics

2)Theoretical tools :

3) Molecular dynamics

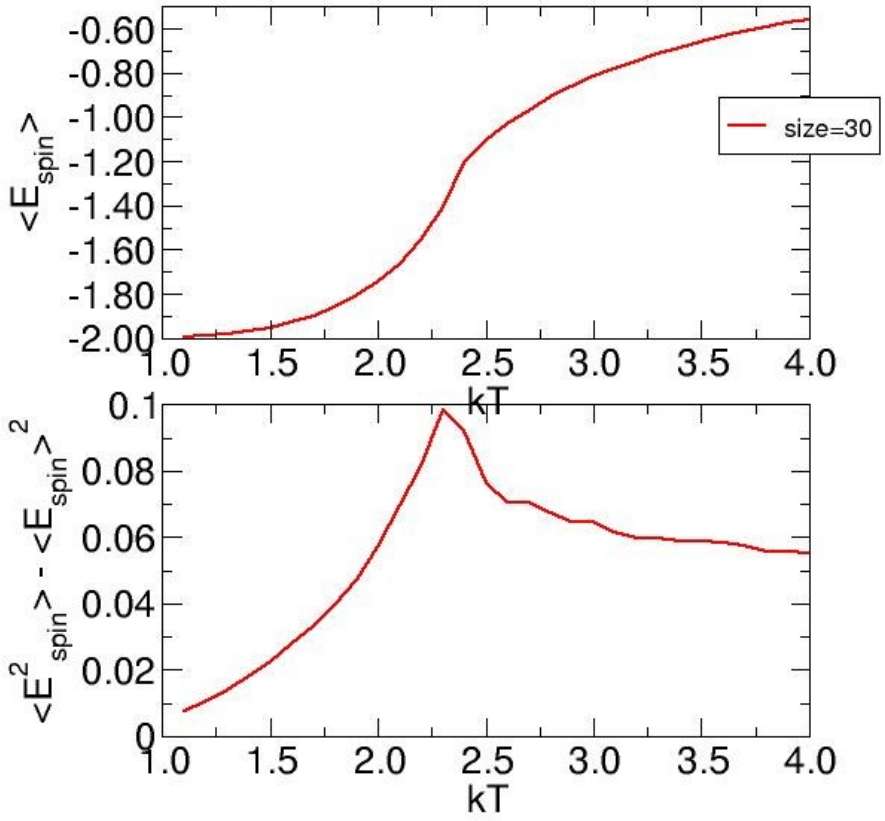
4) Monte Carlo
- Integral calculations
- Markov Chains
- Perron Frobenius theorem
- Detailed balance
- Metropolis MC
- Random number generator
- Application
- Ensemble NPT, μVT
- Parallel Tempering

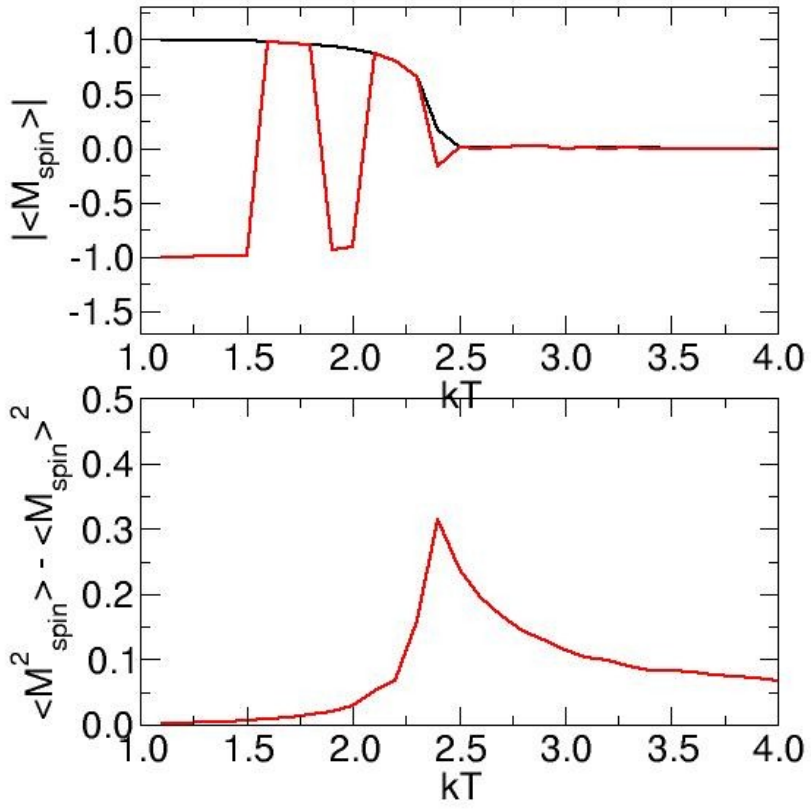
5) Free energy calculation

The Ising model

Nequil: 1e8
Nstep: 1e8

Obviously wrong $\langle M \rangle = \sum_{microstates} \left(\sum_i S_i \right) \frac{e^{-\beta H}}{Z} = 0$

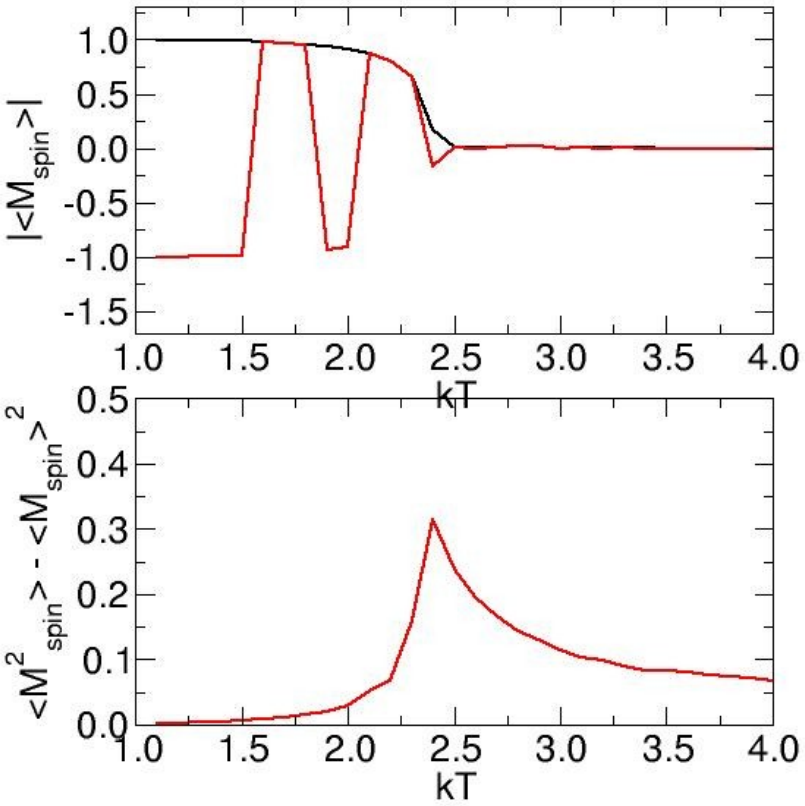


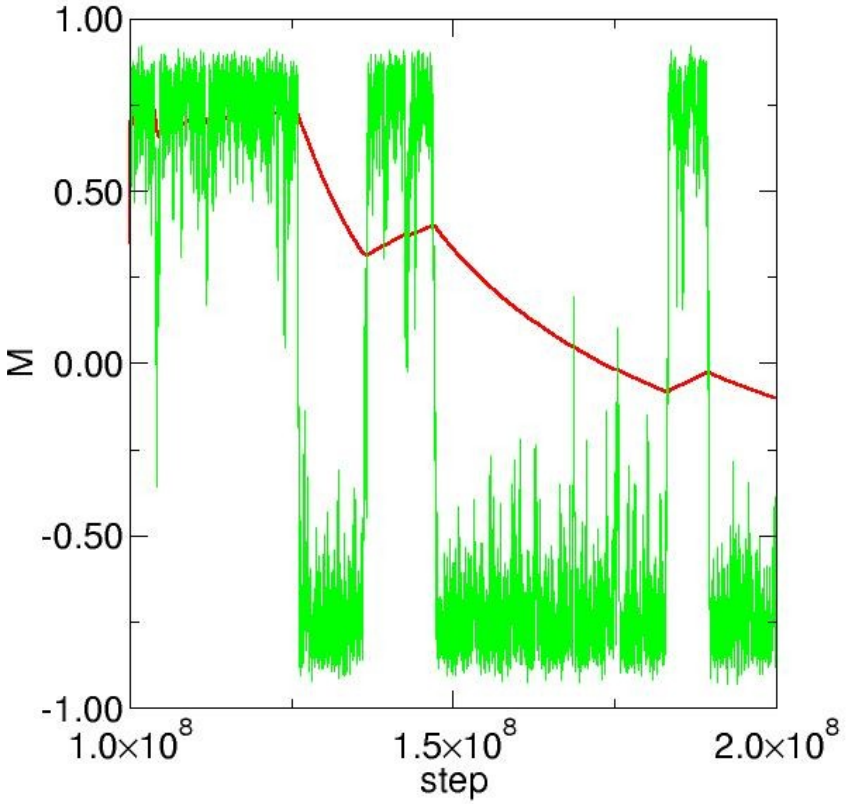


kTtheo = 2.269 ?

The ferro-paramagnetic transition

In the ferro-magnetic phase,
transtition from M to -M → a simple average does not yield the correct value.



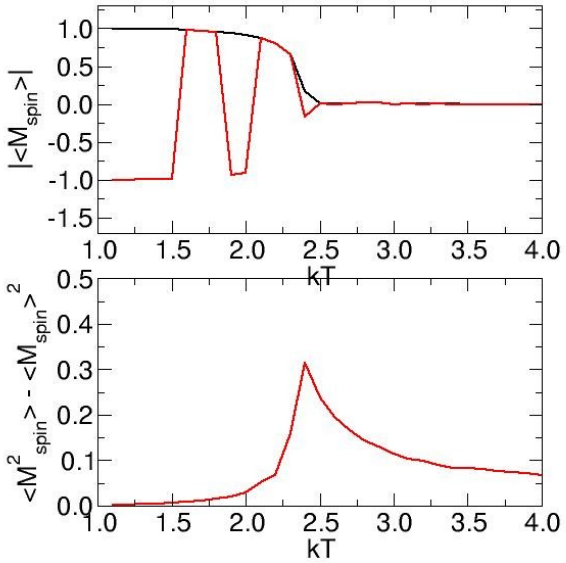


Size= 30 , N=1e8

KT = 2.25

Histogram of the magnetization
Free-energy

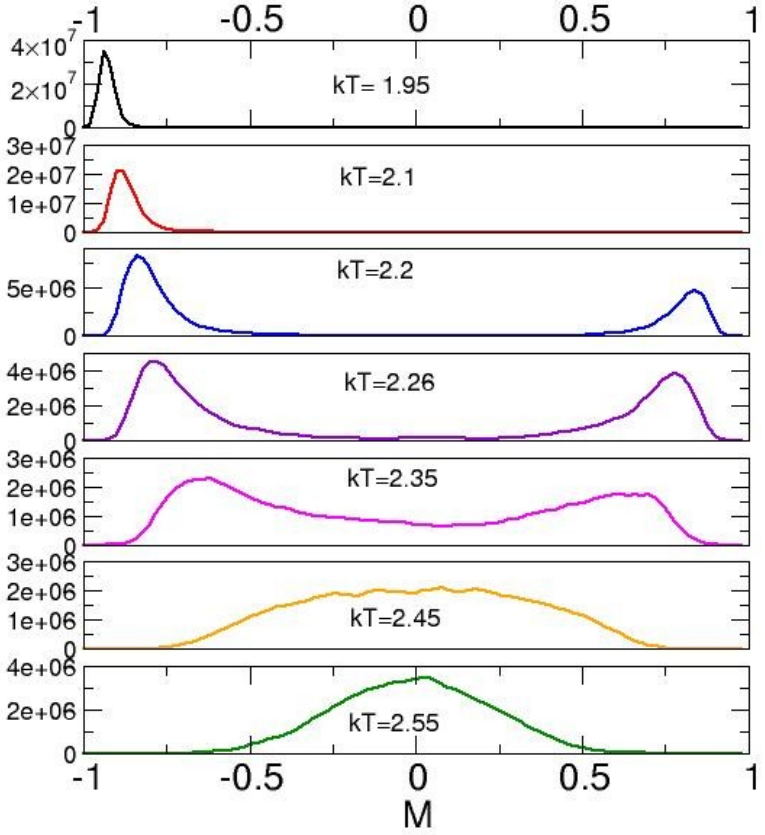
Nstep=1e8, size=30



M: is an order parameter

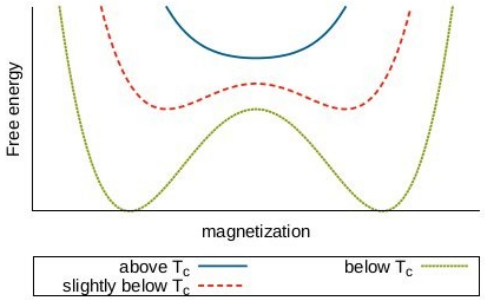
$$P(M)=\frac{e^{-\beta F(M)}}{Z}$$

Histogram of Magnetization

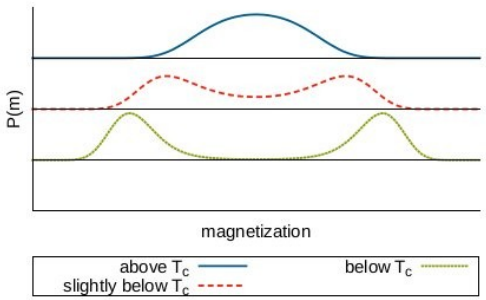


Problem of ergodicity

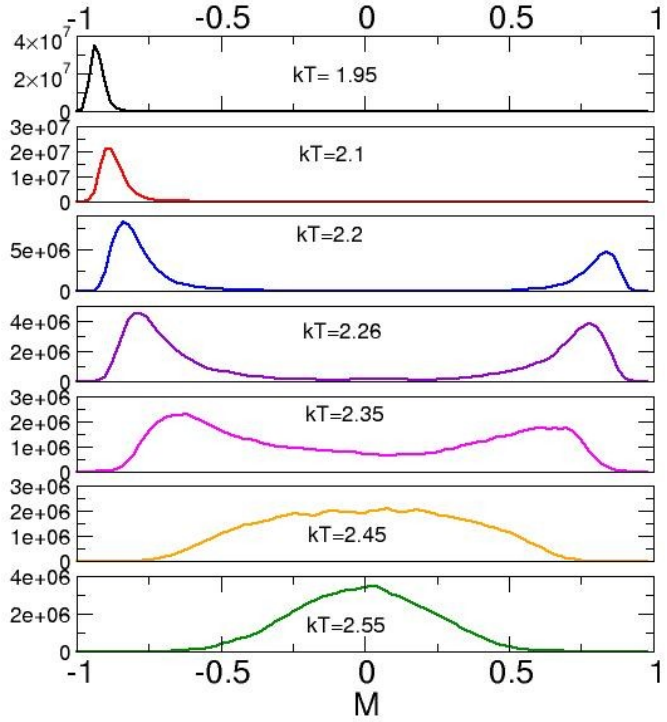
Our simulation does not correctly sample the phase space:
histograms are not the expected ones.
Related to P_{gen}



(a) Free energy at magnetization



(b) Probability of magnetization



The same problem occurs for 1st order phase transitions:
- 2 phases, one stable, one meta-stable and we observe only one
- a critical problem in very rough free-energy landscape (many local minima)

Same analysis for Molecular dynamic simulation!

Correctly sampling the phase space

Different methods to overcome this problem of ergodicity:
to found the true histogram and true phases transition temperature

Specific techniques
for phases coexistence
(1st order phase transition)

The Gibbs ensemble : two boxes containing each one phase. Exchange of particles between phases.
Panagiotopoulos, mol. Phys. 61, 813 (1987)

For 2 phases

Accelerating Monte Carlo Sampling

the parallel tempering technique.

For rough free-energy landscape

Biasing the potential

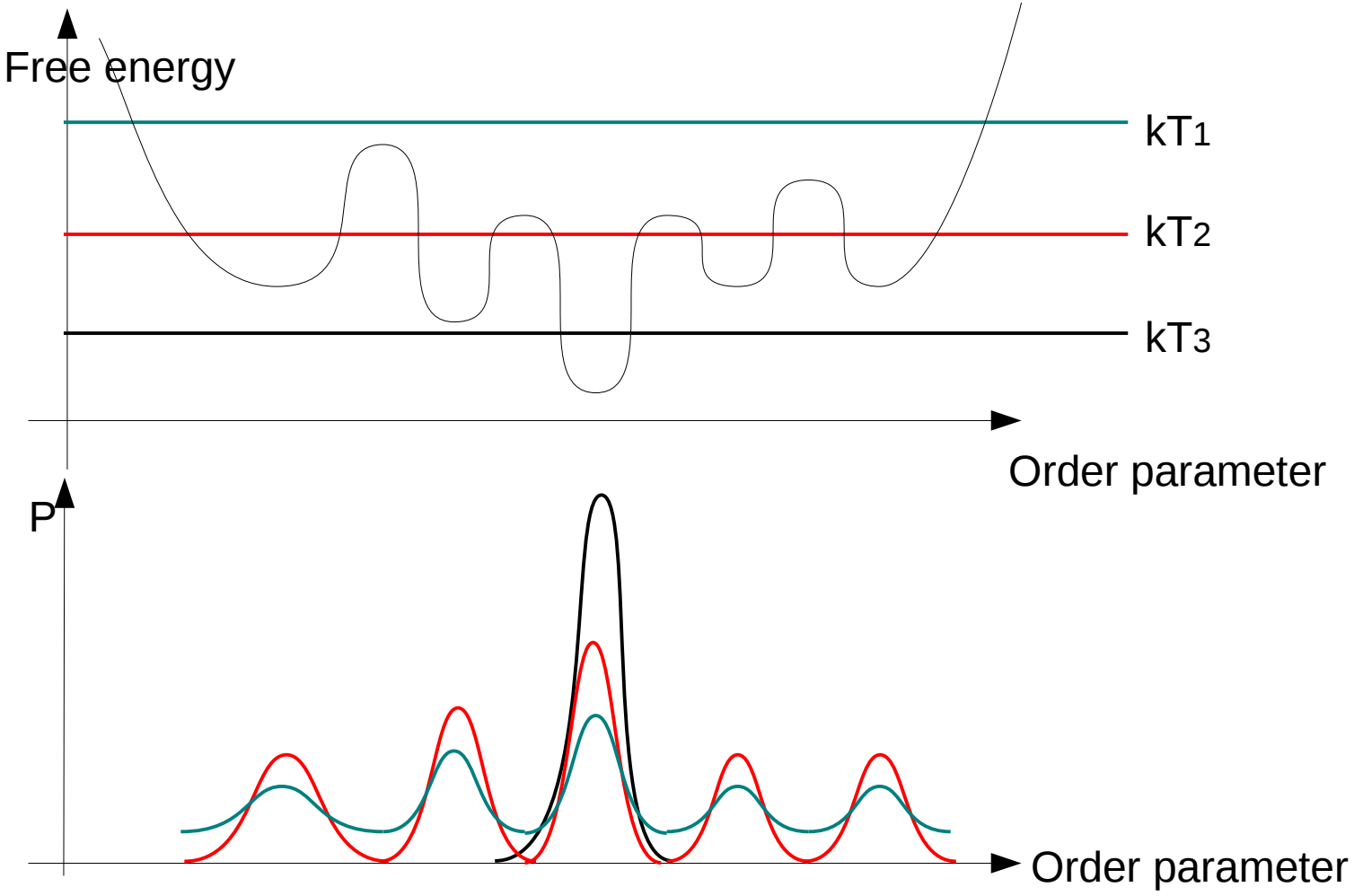
Umbrella Sampling
Metadynamics
ABF

→ Free energy calculations

Parallel tempering technique

- Basic principles

  1) the probability to cross an energy barrier depends on T



Parallel Tempering technique

2) an extented system

M replica
MN particles

$$H_1 = \sum_i \frac{\vec{p}_{1i}^{\,2}}{2m_i} + U(\vec{r}_{11,\dots},\vec{r}_{1N}) \quad \text{At} \quad kT_1$$

$$H_2 = \sum_i \frac{\vec{p}_{2i}^{\,2}}{2m_i} + U(\vec{r}_{21,\dots},\vec{r}_{2N}) \qquad kT_2$$

...

$$H_k = \sum_i \frac{\vec{p}_{ki}^{\,2}}{2m_i} + U(\vec{r}_{k1,\dots},\vec{r}_{kN}) \qquad kT_k$$

...

$$H_M = \sum_i \frac{\vec{p}_{Mi}^{\,2}}{2m_i} + U(\vec{r}_{M1,\dots},\vec{r}_{MN}) \qquad kT_M$$

Extended system : M*N particles.

Microstate : $\vec{R} = (\vec{r}_{11,\dots},\vec{r}_{1N})(\vec{r}_{21,\dots},\vec{r}_{2N})\dots(\vec{r}_{M1,\dots},\vec{r}_{MN})$ $P(\vec{R}) = \prod_{k=1}^{M} \frac{e^{\frac{-H_k}{kT_k}}}{N!\,\Lambda_k^{3N} Q}$

Lyurbatsev at al. J. Chem. Phys, 96, 1776 (1992)
Marinari and Parisi, Europhyslett. 19, 451 (1992)
Geyer and Thompson, J. Am. Stat. Assoc. 90,909 (1995)

Parallel tempering

Equilibration of the system is obtained by :

$$P(\vec{R}) = \prod_{k=1}^{M} \frac{e^{\frac{-H_k}{kT_k}}}{N!\,\Lambda_k^{3N} Q}$$

-Trial move to change particle positions within each replica
- trial move to exchange configuration/temperature between replica.

Microstate : $\vec{R} = (\vec{r}_{11,}\ldots,\vec{r}_{1N})(\vec{r}_{21,}\ldots,\vec{r}_{2N})\ldots(\vec{r}_{M1,}\ldots,\vec{r}_{MN})$
$= \vec{R}_1 \vec{R}_2 \ldots \vec{R}_M$

Old configuration

$\vec{R}_{1,} T_1$
$\vec{R}_{2,} T_2$
...
$\vec{R}_k, T_k$
...
$\vec{R}_l, T_l$
...
$\vec{R}_M, T_M$

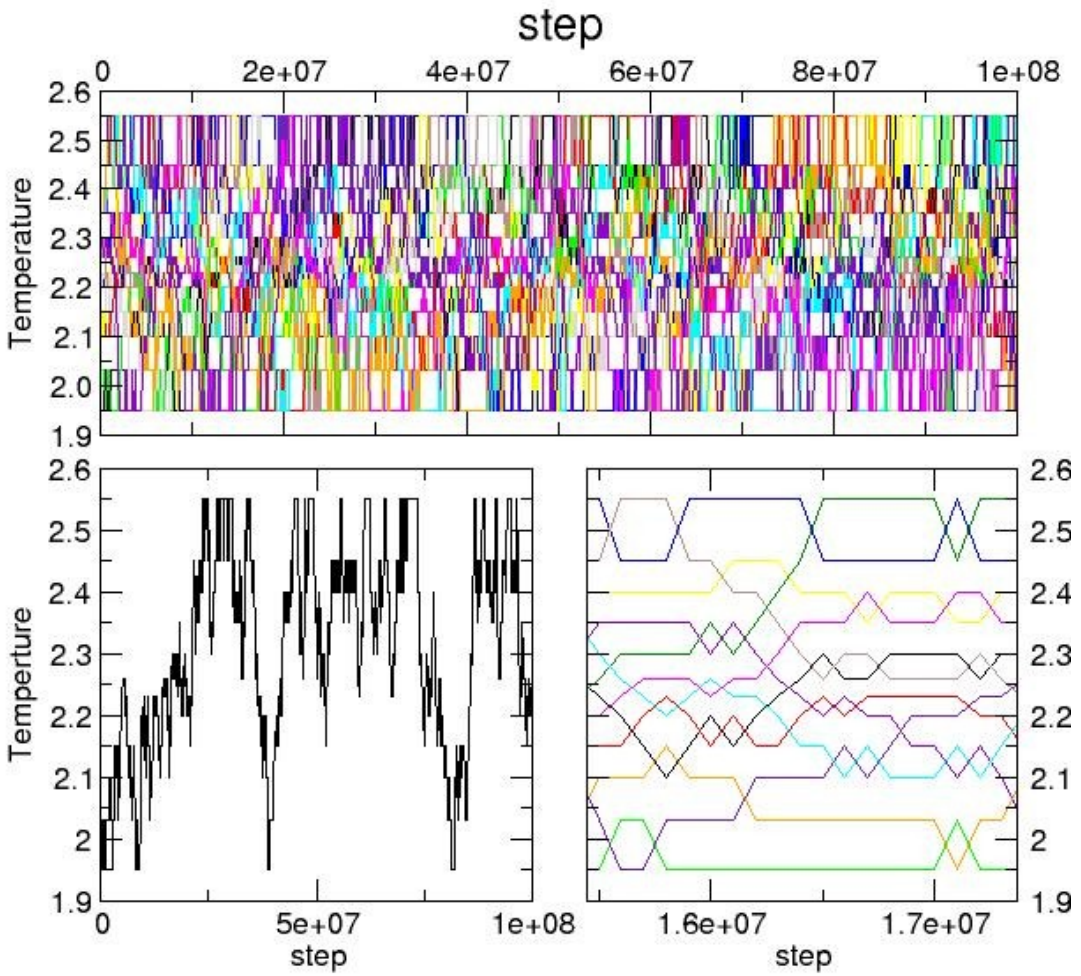
New(trial) configuration

$\vec{R}_{1,} T_1$
$\vec{R}_{2,} T_2$
...
$\vec{R}_k, T_l$
...
$\vec{R}_l, T_k$
...
$\vec{R}_M, T_M$

Application to the Ising model

Ising model :

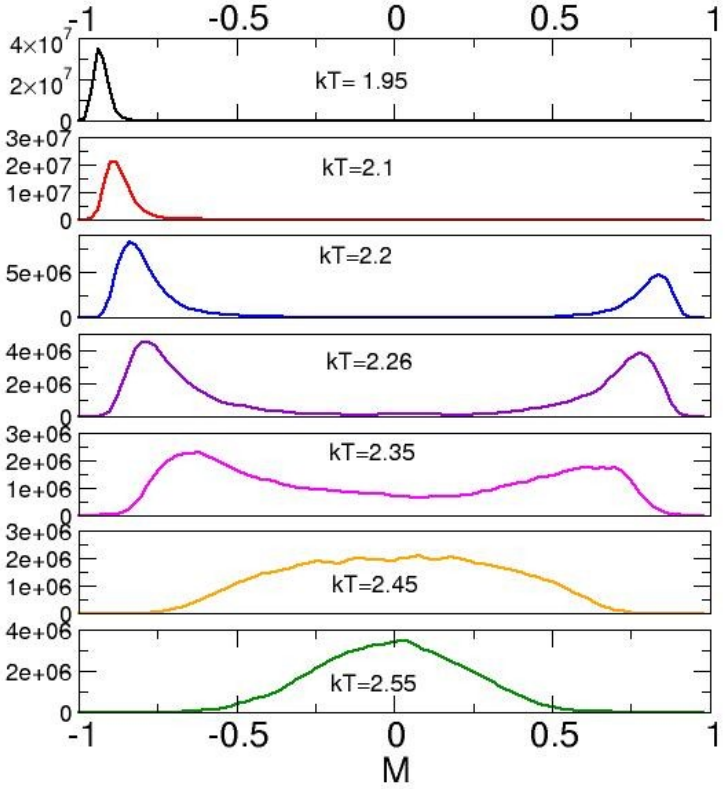
Size=30
Nstep=1e8
12 temperatures between
1.95 and 2.55
Trial swap : every 1e5



1 curve : temperature of a given replica.

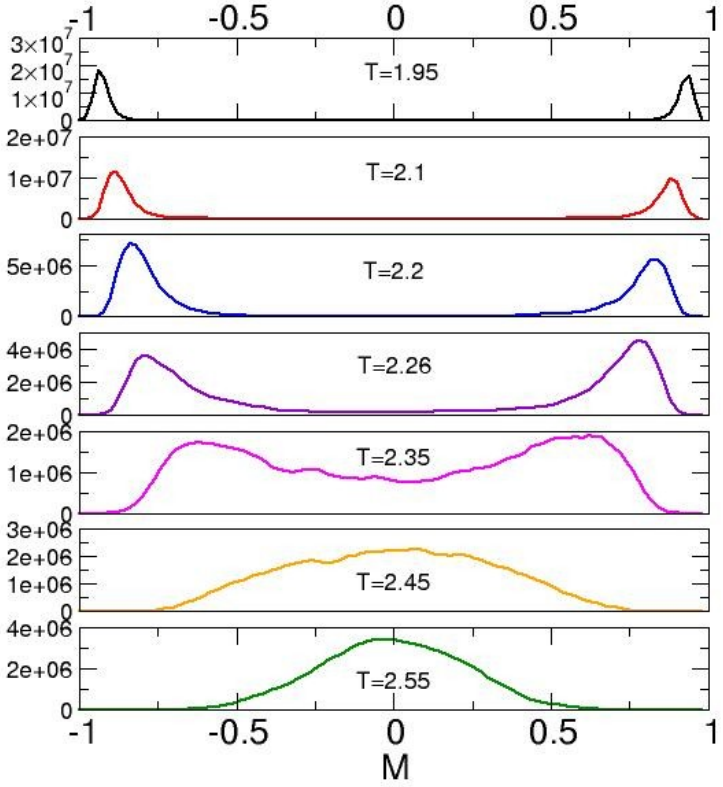
Histogram of magnetization

Individual runs.



Parallel Tempering

Nstep=1e8, size=30



Example : Lennard-Jones Fluid-Gaz coexistence

Yan and de Pablo, J. Chem. Phys. 111, 9509 (1999)

Hyperparallel tempering method (μVT)

B. Simulation details

In this work, the hyper-parallel tempering method is implemented in the grand canonical ensemble. By substituting Eq. (2) into Eq. (7), we arrive at the following acceptance criteria for swapping two replicas:

$$p_{\mathrm{acc}}(x_i \leftrightarrow x_{i+1}) = \min[1, \exp(\Delta\beta\Delta U - \Delta(\beta\mu)\Delta N)] \quad (10)$$

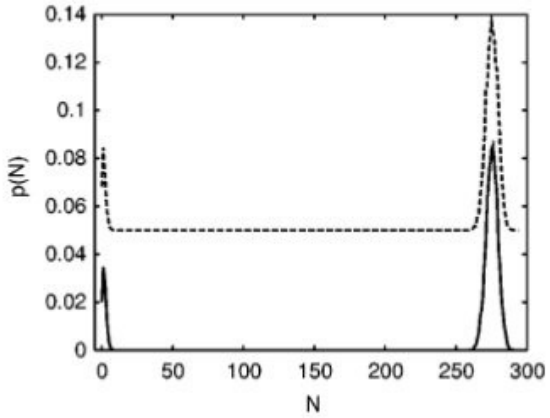


FIG. 2. Probability density of the marginal distribution of number of particles for $T^*=0.73$, $\beta\mu=-5.30$. The solid line represents the original histogram for the system at these conditions. The dashed line depicts the combined histogram that results from a full histogram reweighting analysis of all results at all conditions studied here (i.e., it is the ''true'' histogram).

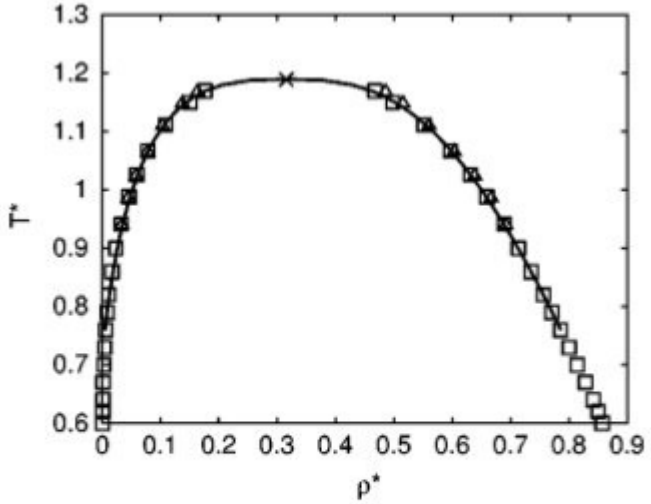


FIG. 3. Phase diagram (vapor–liquid equilibria) for a truncated Lennard-Jones fluid. The squares correspond the results of this work, and the triangles show results reported by Wilding (Ref. 18). Statistical errors are smaller than the symbol size. The solid line is an Ising form fit to the simulation data.

Determination of phase coexistence :
Peaks of gas and liquid with equal area

Use of the histogram reweighting technique to avoid many calculation

Conclusion MC

Monte Carlo

- use of random number to calculate some integrals.
- to generate an ensemble of configuration following a probality distribution (boltzman..)
- necessity of Markov Chain for Statistical physics

→ Perron-Frobenius theorem and Detailed Balance condition

- application to extended system
- Paralle tempering for ergodicity

To go further

Conditioning for variance reduction
Biased Monte Carlo method
Transition Path Sampling (in path phase space)
Kinetic Monte Carlo Simulation

Contents

1) Simulations and statistical mechanics

2)Theoretical tools :

3) Molecular dynamics

4) Monte Carlo

5) Free energy calculation
- Order Parameter/ Collective Variables
- Umbrella Sampling
- Metadynamics
-ABF

Towards free energy calculations

Macroscopic world
Thermodynamic

1 system defined from
Few variables (macroscopic)

N, V, E
N , V, <E> or T… } Extern parameters

+ a collective variable Φ_0
an order parameter
Reaction coordinate

Microscopic description
Statistical physics

1 set of microscopic states $\kappa(N, V, T, \Phi_0)$

Microstate $\vec{R} = \vec{r}_1 \vec{r}_2 .. \vec{r}_N$
$\dot{\vec{R}} = \dot{\vec{r}}_1 \dot{\vec{r}}_2 ... \dot{\vec{r}}_N$
N ~ 10^{23}

+ spin, charge...

$$\Phi(\vec{r}_1, \vec{r}_2 ... \vec{r}_N) = \Phi_0$$

Example of collective variables:
- number of atoms in a phase (nucleation)
- distance between two atoms (aggregation of two proteins, folding of proteins...)

Free energy calculations

For macroscopic system defined by N,V,T → 1 set of microscopic states $\mathrm{K}(N,V,T)$

$$Z(N,V,T)=\sum_{microstate\in \mathrm{K}(N,V,T)} e^{-\beta E}$$
$$=e^{-\beta F(N,V,T)}$$

← Free energy

For macroscopic system defined by N,V,T,Φ_0 → $\kappa(N,V,T,\Phi_0)\subset \mathrm{K}(N,V,T)$

$$P(\Phi_0)=\sum_{microstate\in \mathrm{K}(N,V,T)} \delta\left(\Phi(\vec{r}_1,\vec{r}_{2,}..\vec{r}_N)-\Phi_0\right)\frac{e^{-\beta E}}{Z}$$

← On microstates defined by extern parameters

$$=\frac{\sum_{microstate\in \kappa(N,V,T,\Phi_0)} e^{-\beta E}}{Z}$$

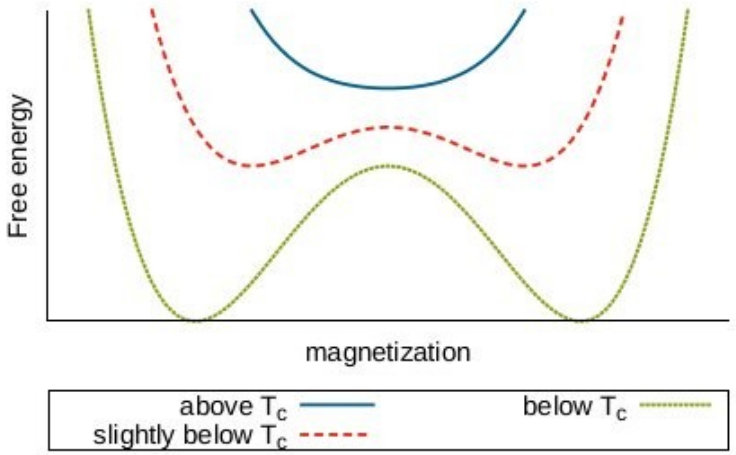
← On microstates defined by extern parameters and the collective variable

$$=\frac{e^{-\beta F(N,V,T,\Phi_0)}}{Z}$$

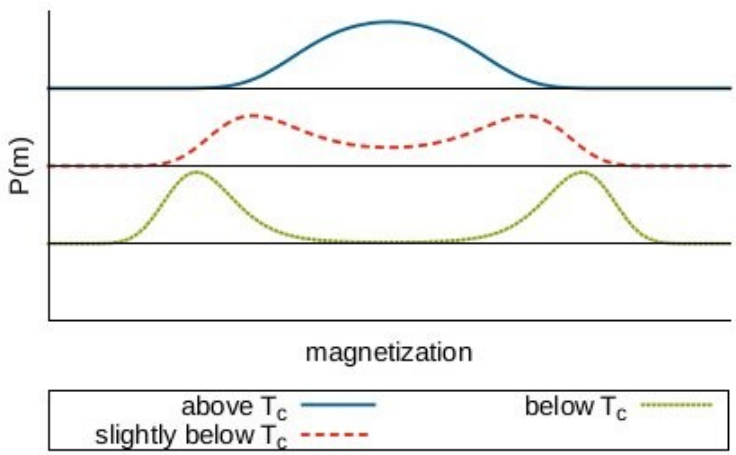
$$Z(N,V,T,\Phi_0)=\sum_{microstate\in \kappa(N,V,T,\Phi_0)} e^{-\beta E}$$
$$=e^{-\beta F(N,V,T,\Phi_0)}$$

Free energy calculations

Ising model
Collective Variable = magnetization



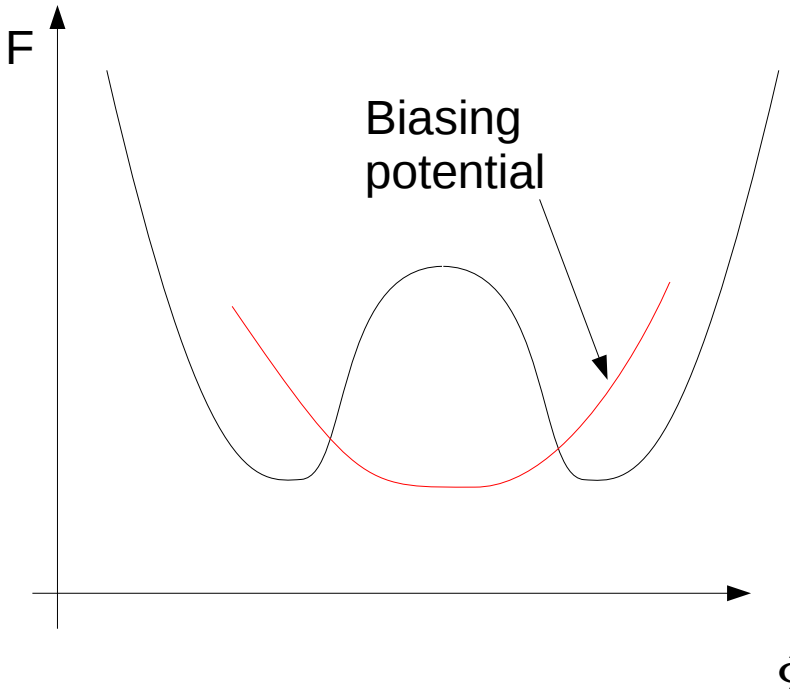
(a) Free energy at magnetization



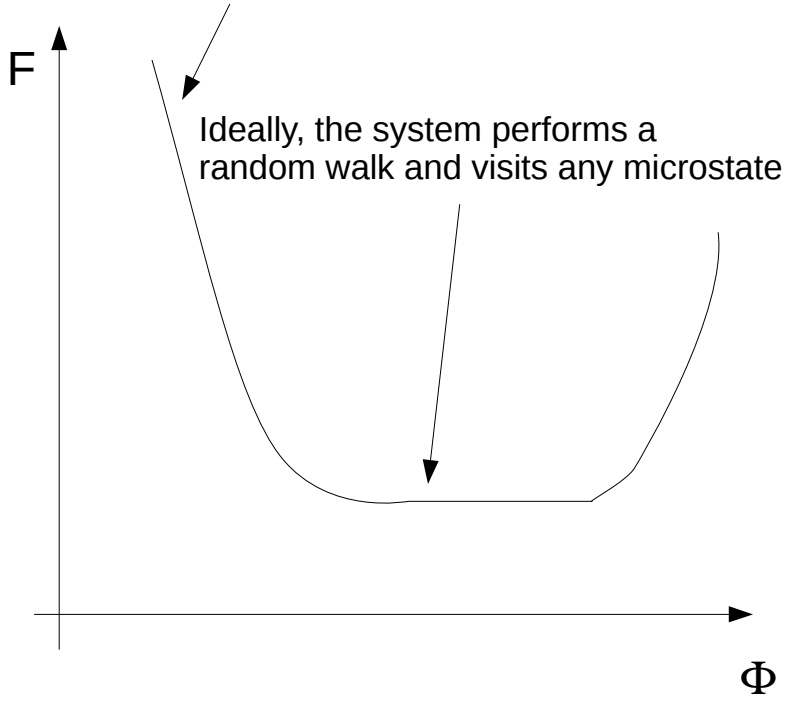
(b) Probability of magnetization

→ Provide free energy barriers (if a correct collective variable)

Main idea: Biasing the free energy



Free energy with the Bias potential



Provide free energy barriers (if a correct collective variable)

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Umbrella Sampling

MD or MC

Biasing the hamiltonian

Original hamiltonian: H_0

New hamiltonian : $H(\Phi_0) = H_0 + W(\Phi, \Phi_0) = H_0 + \frac{1}{2} k \left(\Phi(\vec{r}_{1..} \vec{r}_N) - \Phi_0\right)^2$

$$\left\langle \delta(\Phi - \Phi_1) \right\rangle_{H(\Phi_0)} = \frac{1}{Z_{H(\Phi_0)}} \sum_{microstate \in \mathrm{K}(N,V,T)} \delta(\Phi - \Phi_1) e^{-\beta H(\Phi_0)}$$

$$= \frac{1}{Z_{H(\Phi_0)}} \sum_{microstate \in \mathrm{K}(N,V,T)} \delta(\Phi - \Phi_1) e^{-\beta H_0} e^{-\beta W(\Phi, \Phi_0)}$$

$$= \frac{1}{Z_{H(\Phi_0)}} \sum_{microstate \in \kappa(N,V,T,\Phi_1)} e^{-\beta H_0} e^{-\beta W(\Phi_1, \Phi_0)}$$

$$= \frac{e^{-\beta W(\Phi_1, \Phi_0)}}{Z_{H(\Phi_0)}} \sum_{microstate \in \kappa(N,V,T,\Phi_1)} e^{-\beta H_0}$$

$$= \frac{e^{-\beta W(\Phi_1, \Phi_0)}}{Z_{H(\Phi_0)}} e^{-\beta F(N,V,T,\Phi_1)}$$

The system visit states with Φ around Φ_0

$$F(N,V,T,\Phi_1) = -W(\Phi_1, \Phi_0) - \frac{1}{\beta} \ln\left(\left\langle \delta(\Phi - \Phi_1) \right\rangle_{H(\Phi_0)}\right) - \frac{1}{\beta} \ln\left(Z_{H(\Phi_0)}\right)$$

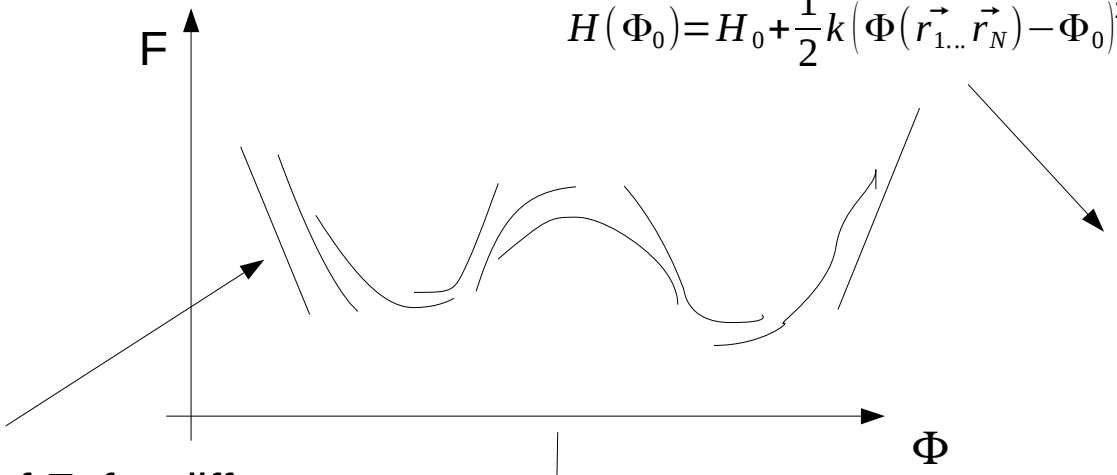
Should be independent on Φ_0

Unknown!

Chandler, Introduction to modern statistical mechanics

Umbrella sampling in practice

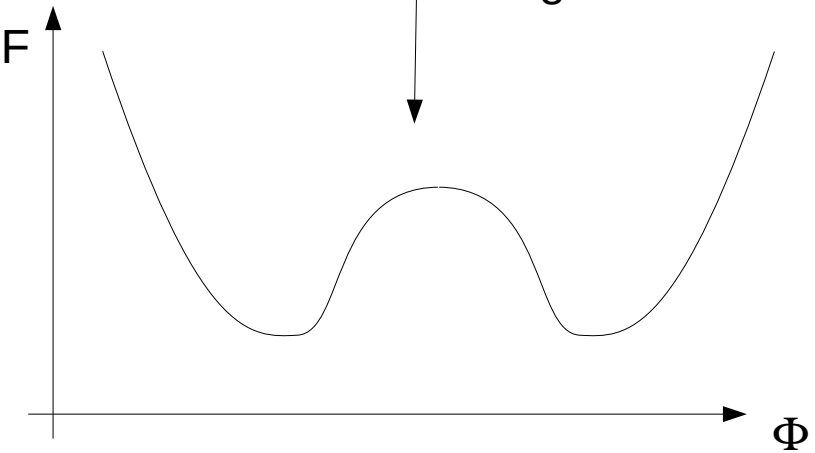
$$H(\Phi_0) = H_0 + \frac{1}{2} k \left(\Phi(\vec{r}_{1\ldots} \vec{r}_N) - \Phi_0 \right)^2$$



The system visit states with Φ around Φ_0

Curves of F for different Values of Φ_0

We can reconstruct the energy curves using the continuity F



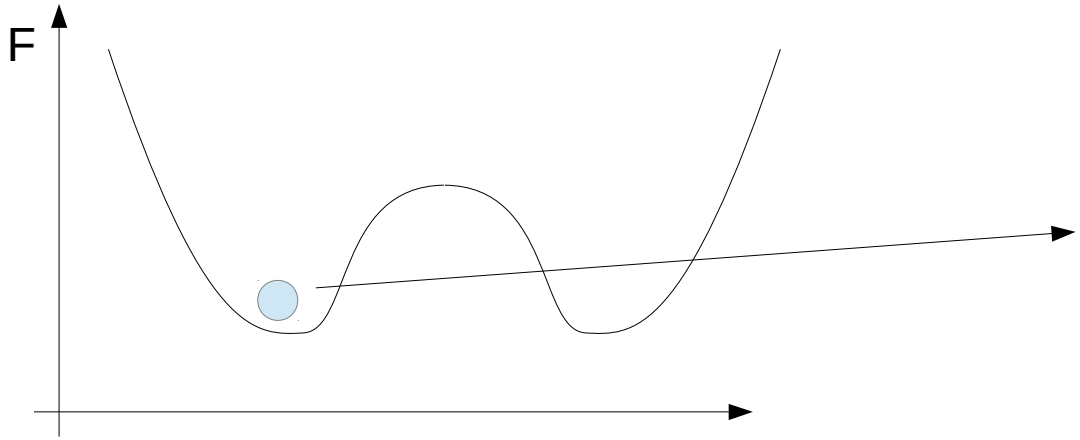
Umbrella sampling is a robust method

Remark: possible for multiple CV

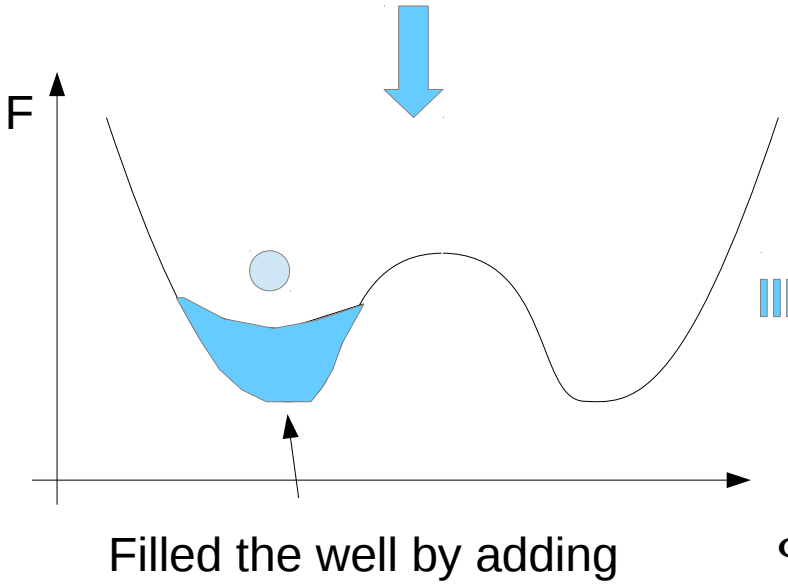
Chandler, Introduction to modern statistical mechanics

Metadynamics

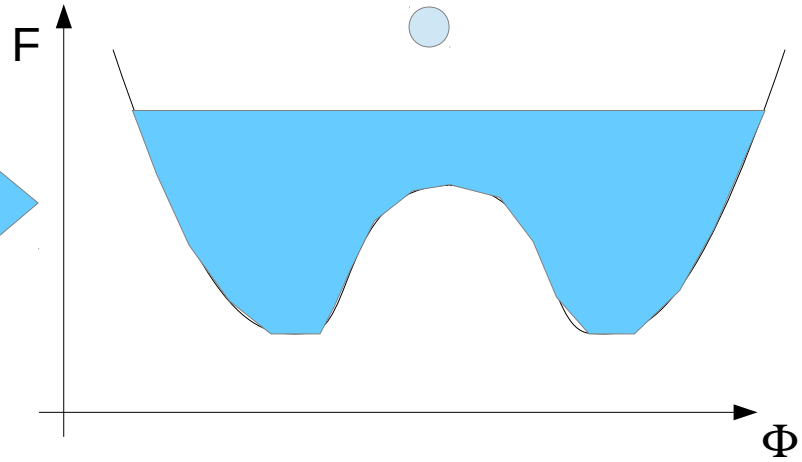
Usually used with MD



The system spends most of its time in Free energy wells



Filled the well by adding a Biasing potential



Laio, Parrinello, PNAS, 99,12562 (2002)
PRL, 100,020603 (2008)

Metadynamics (Well-tempered)

$$H = H_0 + V_{bias}(\Phi, t)$$

$$V_{bias}(\Phi, t) = \sum_k W(k\tau) e^{\frac{-(\Phi - \Phi(k\tau))^2}{2\sigma^2}}$$

We periodically add a Gaussian .

$$V_{bias}(\Phi, t \to \infty) = -F(N, V, T, \Phi) + C$$

Original metadynamic

Heigh of gaussian are fixed

W(kτ) = cte

Laio, Parrinello, PNAS, 99,12562 (2002)

Parameters to optimize : τ, σ, W

Well tempered metadynamic

Heigh of gaussian evoluate

$$W(k\tau) = W_0 e^{\frac{-V_{bias}(\Phi(k\tau), k\tau)}{k_B \Delta T}}$$

Barducci, Bucci, Parrinello, PRL, 100,020603 (2008)

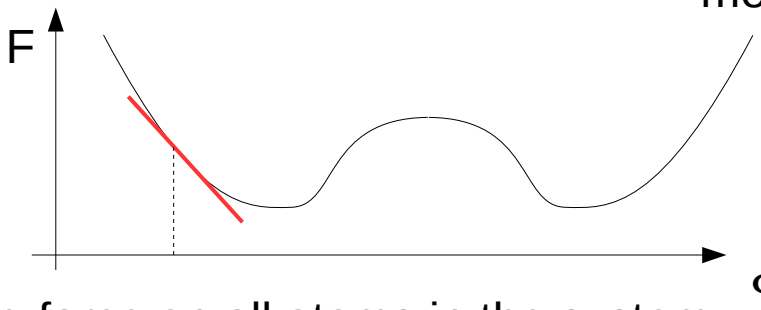
Parameters to optimize : τ, σ, W_0, ΔT

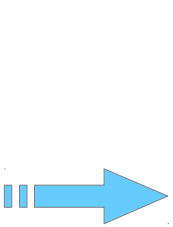
Adaptative Biasing Force

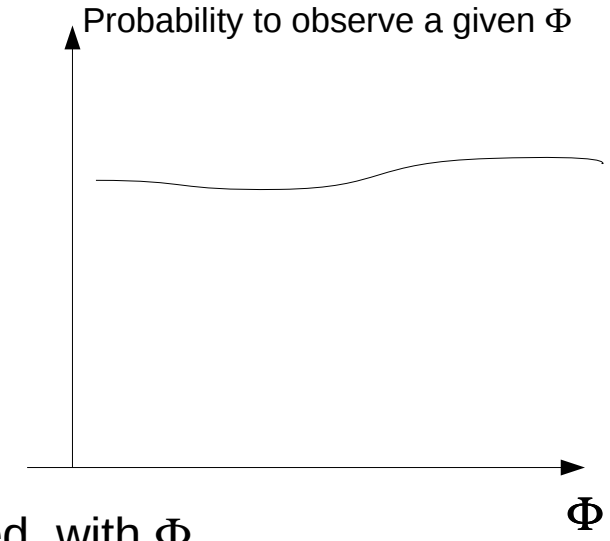
Idea: instead of biasing the potential, we can bias the force

$$\vec{F}_\Phi = -\nabla_\Phi F(N,V,T,\Phi)$$
$$= \beta \vec{\nabla}_\Phi \ln(Z_\Phi)$$
$$= \frac{\beta}{Z_\Phi} \vec{\nabla}_\Phi \left(\sum_{\kappa(N,V,T,\Phi)} e^{(-\beta H)} \right)$$
$$= -\langle \vec{\nabla}_\Phi H \rangle_{\kappa(N,V,T,\Phi)}$$

An estimate $\langle \vec{F}_\Phi \rangle_t$ of this force can be measured on the fly







Add a biasing force on all atoms in the system

$$\vec{F}^{ABF} = -\alpha(n_t(\Phi))\langle \vec{F}_\Phi \rangle_t$$

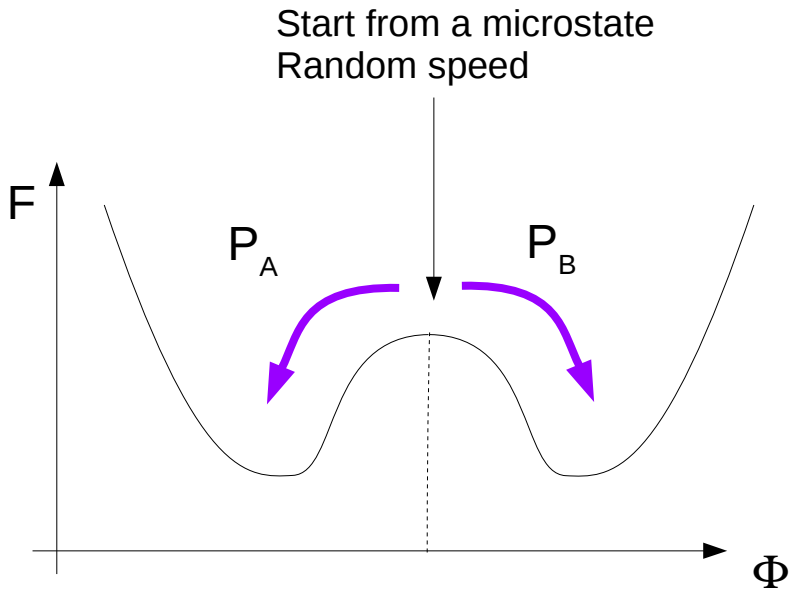
Function that goes from 0 to 1 as n(Φ) increases

Number of microstates visited with Φ

→ F(N,V,T,Φ) is calculated by integrating the force F^{ABF}

What is a good collective variable?

Good for what? → to describe a transition between two (meta)stable states



If $P_A = P_B$ (=1/2), Φ is a good order parameter to describe the transition.

Measures of P_A and P_B are called the commitor.

Conclusion

Molecular dynamics
- when using a code
  → check a maximum of conservation laws…

Monte Carlo
- usually, you have to do your own code
- detailed balance

Free energy
- finding good collective variables is often an issue

To investigate
equilibrium properties

To investigate
Non-equilibrium properties