



Path Integral Molecular Dynamics

Grégory GENESTE
CEA, DAM, DIF, F-91297 Arpajon, France



Coworkers:

Marc Torrent (parallelization over images)

François Bottin

Jessica Hermet (proton transport in oxides)

Hichem Dammak, labo SPMS, Ecole Centrale Paris

Marc Hayoun, LSI, Ecole Polytechnique

Introduction: why studying quantum effects associated to atomic motions ?

I - Path Integral (PI) methods

II - Technical points related to Path Integral Molecular Dynamics (PIMD)

III – Implementation of PIMD in ABINIT, keywords, etc

IV – Langevin PIMD, choice of random number generator, friction coefficient

V – Conclusion: in progress and future work

Why studying quantum effects of atomic motions ?

Quantum effects of atomic motions are important
Below the *Debye temperature*

- CRUCIAL in the case of LIGHT elements, up to very high temperatures:

H₂, Debye T ~ 6000 K (vibration)

He: liquid down to zero K (under 1 atm) because of quantum effects

- IMPORTANT for « ordinary solids » with Debye temperature ~ RT or above

One way to account for quantum effects =
Path Integral (PI) methods

Based on the discretized version of Feynman's path
Integral applied to the density operator.

Path integral for time evolution operator:

$$\langle x | e^{-iHt/\hbar} | x' \rangle = \int_x^{x'} Dx(s) e^{\frac{i}{\hbar} \int_0^t ds L(x(s), \frac{dx}{ds}(s))} = \int_x^{x'} Dx(s) e^{\frac{i}{\hbar} A(x(s))}$$

... and for the canonical density operator: $t = -i\beta\hbar$

$$\langle x | e^{-\beta H} | x' \rangle = \int_x^{x'} Dx(s) e^{-\frac{1}{\hbar} \int_0^{\beta\hbar} ds [\frac{m}{2} (\frac{dx}{ds})^2 + V(x(s))]}$$

Canonical partition function:

$$Z = \int dx \int_x^x Dx(s) e^{-\frac{1}{\hbar} \int_0^{\beta \hbar} ds \left[\frac{m}{2} \left(\frac{dx}{ds} \right)^2 + V(x(s)) \right]} = \oint Dx(s) e^{-\frac{1}{\hbar} \int_0^{\beta \hbar} ds \left[\frac{m}{2} \left(\frac{dx}{ds} \right)^2 + V(x(s)) \right]}$$

$x(0) = x(\beta \hbar) = x$

Discretized version:

$$Z = \lim_{P \rightarrow \infty} \left[\frac{2 \pi m P k_B T}{h^2} \right]^{3NP/2} \int_{\vec{R}_0} \dots \int_{\vec{R}_{P-1}} e^{-\beta V_{eff}(\vec{R}_0 \dots \vec{R}_{P-1})} d\vec{R}_0 \dots d\vec{R}_{P-1}$$

with

$$\vec{R}_s = (\vec{r}_1^{(s)} \dots \vec{r}_N^{(s)}) \quad 3N - vector$$

$$V_{eff}(\vec{R}_0 \dots \vec{R}_{P-1}) = V_{eff}(\vec{r}_1^{(0)} \dots \vec{r}_N^{(0)} \dots \vec{r}_1^{(P-1)} \dots \vec{r}_N^{(P-1)})$$

$$V_{eff}(\vec{R}_0 \dots \vec{R}_{P-1}) = \sum_{s=0}^{P-1} \left[\sum_{i=1}^N \frac{1}{2} k(P, \beta) (\vec{r}_i^{(s)} - \vec{r}_i^{(s+1)})^2 + \frac{1}{P} V(\vec{r}_1^{(s)} \dots \vec{r}_N^{(s)}) \right]$$

Spring constant $k(P, \beta) = \frac{m P}{\hbar^2 \beta^2} = \frac{m P k_B^2 T^2}{\hbar^2}$

P = « Trotter » number

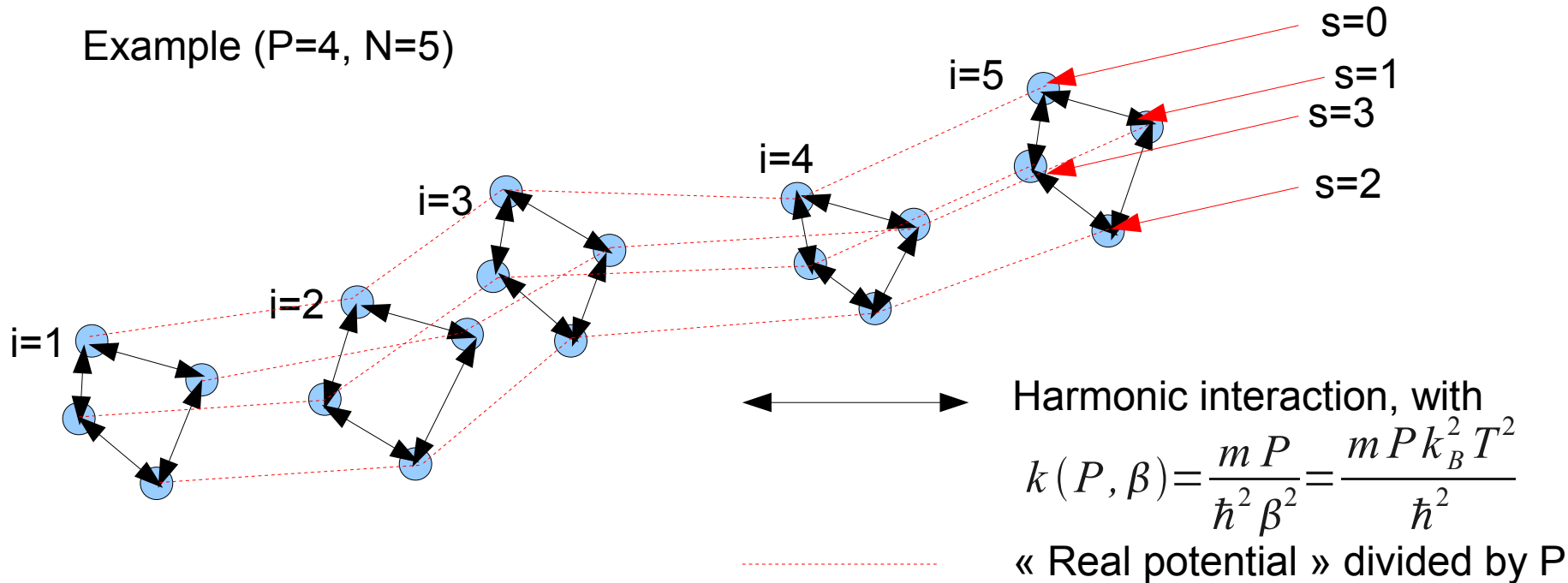
with cyclic boundary condition:

$$\vec{r}_i^{(P)} = \vec{r}_i^{(0)}$$

$$Z = \lim_{P \rightarrow \infty} \left[\frac{2 \pi m P k_B T}{h^2} \right]^{3NP/2} \int_{\vec{R}_0} \dots \int_{\vec{R}_{P-1}} e^{-\beta V_{\text{eff}}(\vec{R}_0 \dots \vec{R}_{P-1})} d\vec{R}_0 \dots d\vec{R}_{P-1}$$

The right member is the CLASSICAL partition function (for fixed Trotter number P) of the following CLASSICAL system (of NxP particles):
(up to a multiplicative constant)

Example (P=4, N=5)



s = « imaginary time »

Ensemble of « quasi-particles » for fixed s = « imaginary time slice »

Each quantum system has, for fixed P , a classical equivalent
= « CLASSICAL ISOMORPHISM »

In the limit of **infinite Trotter numbers**, the physical EQUILIBRIUM properties of the quantum system are the same as those of the classical equivalent.

One gets directly the observables in the CANONICAL ensemble.

Can be extended easily to the isothermal-isobaric (NPT) ensemble.

Ex: Barrat, Loubeyre, Klein, J. Chem. Phys. 90, 5644 (1989)

Thus, the EQUILIBRIUM properties of the classical equivalent system can be reached by any CLASSICAL simulation technique

Monte Carlo Method
= PIMC

Molecular Dynamics Method
= PIMD

Path Integral is an elegant way to do Quantum Mechanics ...

... without wave function !!!

NB: at low temperature, the Trotter number should be chosen very high

=> one recovers the complexity of QM !

Limitations

$$Z = \lim_{P \rightarrow \infty} \left[\frac{2 \pi m P k_B T}{h^2} \right]^{3NP/2} \int_{\vec{R}_0} \dots \int_{\vec{R}_{P-1}} e^{-\beta V_{eff}(\vec{R}_0 \dots \vec{R}_{P-1})} d\vec{R}_0 \dots d\vec{R}_{P-1}$$

Is obtained from

$$Z = \int_{\vec{R}} \rho(\vec{R}, \vec{R}; \beta) d\vec{R}$$

where $\rho(\vec{R}, \vec{R}'; \beta)$ is the density matrix in the position representation:

$$\rho(\vec{R}, \vec{R}'; \beta) = \langle \vec{R} | e^{-\beta H} | \vec{R}' \rangle$$

Such a formulation implicitly assumes DISCERNABLE particles.

In the case of INDISTINGUISHABLE particles, Z writes:

1) for BOSONS:

$$Z^B = \frac{1}{N!} \sum_{p \in S(n)} \int_{\vec{R}} \rho(\vec{R}, p \vec{R}; \beta) d\vec{R}$$

2) for FERMIONS:

$$Z^F = \frac{1}{N!} \sum_{p \in S(n)} \epsilon(p) \int_{\vec{R}} \rho(\vec{R}, p \vec{R}; \beta) d\vec{R}$$

Permutation signature

IN PRACTISE: Primitive Approximation (PA)

For fixed P:

$$Z \approx \left[\frac{2 \pi m P k_B T}{h^2} \right]^{3NP/2} \int_{\vec{R}_0} \dots \int_{\vec{R}_{P-1}} e^{-\beta V_{eff}(\vec{R}_0 \dots \vec{R}_{P-1})} d\vec{R}_0 \dots d\vec{R}_{P-1}$$

$$Z = \lim_{P \rightarrow \infty} Z_P$$

$$Z_P = \left[\frac{2 \pi m P k_B T}{h^2} \right]^{3NP/2} \int_{\vec{R}_0} \dots \int_{\vec{R}_{P-1}} e^{-\beta V_{eff}(\vec{R}_0 \dots \vec{R}_{P-1})} d\vec{R}_0 \dots d\vec{R}_{P-1}$$

Calculations are performed for fixed P

Observables are computed using Z_P , i.e. in the PA.

Quantities must be CONVERGED with P

$\langle A \rangle$ computed from $Z_P =$ **Primitive Estimator of A**

Example: Energy Primitive Estimator: $\langle E \rangle_P = -\frac{\partial \ln Z_P}{\partial \beta}$

Using

$$Z_P = \left[\frac{2\pi m P k_B T}{h^2} \right]^{3NP/2} \int_{\vec{R}_0} \dots \int_{\vec{R}_{P-1}} e^{-\beta V_{\text{eff}}(\vec{R}_0 \dots \vec{R}_{P-1})} d\vec{R}_0 \dots d\vec{R}_{P-1}$$

one gets:

$$\langle E \rangle_P = \frac{3}{2} NP k_B T - \left\langle \sum_{s=0}^{P-1} \sum_{i=1}^N \frac{1}{2} k(P, \beta) (\vec{r}_i^{(s)} - \vec{r}_i^{(s+1)})^2 \right\rangle + \frac{1}{P} \left\langle \sum_{s=0}^{P-1} V(\vec{r}_1^{(s)} \dots \vec{r}_N^{(s)}) \right\rangle$$

Kinetic Energy Estimator

Potential Energy Estimator

$$Z = \lim_{P \rightarrow \infty} \left[\frac{2 \pi m P k_B T}{h^2} \right]^{3NP/2} \int_{\vec{R}_0} \dots \int_{\vec{R}_{P-1}} e^{-\beta V_{eff}(\vec{R}_0 \dots \vec{R}_{P-1})} d\vec{R}_0 \dots d\vec{R}_{P-1}$$

$$V_{eff}(\vec{R}_0 \dots \vec{R}_{P-1}) = \sum_{s=0}^{P-1} \left[\sum_{i=1}^N \frac{1}{2} k(P, \beta) (\vec{r}_i^{(s)} - \vec{r}_i^{(s+1)})^2 + \frac{1}{P} V(\vec{r}_1^{(s)} \dots \vec{r}_N^{(s)}) \right]$$

$$k(P, \beta) = \frac{m P}{\hbar^2 \beta^2} = \frac{m P k_B^2 T^2}{\hbar^2}$$

This term grows to infinity
as P tends to infinity

tends to ZERO as
P tends to infinity!

In the limit of large P, the classical system is mainly
HARMONIC

Standard MD algorithms such as Nose-Hoover thermostat
fail to correctly sample the phase space => non ergodic trajectory

How to recover ergodicity in PIMD ?

Marx, Parrinello, J. Chem. Phys. 104, 4080 (1996)

Tuckerman, Marx, Klein, Parrinello, J. Chem. Phys. 104, 5579 (1996)

1) Thermostat chains (*Martyna, Tobias, Klein, J. Chem. Phys. 101, 4177 (1994)*)
 + coordinate transformations
 (staging or normal mode)

=> the corresponding scheme has been extended to the NPT ensemble

Equations of PIMD in the NPT ensemble:

Martyna, Hugges, Tuckerman, J. Chem. Phys. 110, 3275 (1999)

2) Alternative way: Langevin dynamics

Uses random numbers

LANGEVIN DYNAMICS

NVT: « Langevin thermostat »
$$m \frac{d^2 \vec{r}_i^{(s)}}{dt^2} = \vec{f}_i^{(s)} - \gamma m \frac{d \vec{r}_i^{(s)}}{dt} + \vec{R}_i^{(s)}$$

with
$$\vec{f}_i^{(s)} = -\frac{1}{P} \vec{\nabla}_{\vec{r}_i} V_{\vec{r}_i}(\vec{r}_1^{(s)} \dots \vec{r}_N^{(s)}) - k(P, \beta) (2 \vec{r}_i^{(s)} - \vec{r}_i^{(s+1)} - \vec{r}_i^{(s-1)})$$

$$-\gamma m \frac{d \vec{r}_i^{(s)}}{dt} = \text{friction force}$$

$$+ \vec{R}_i^{(s)} = \text{random « Langevin » force (white noise)}$$

Langevin force: *Quigley, Probert, Comput. Phys. Comm. 169, 322 (2005)*

Gaussian with variance

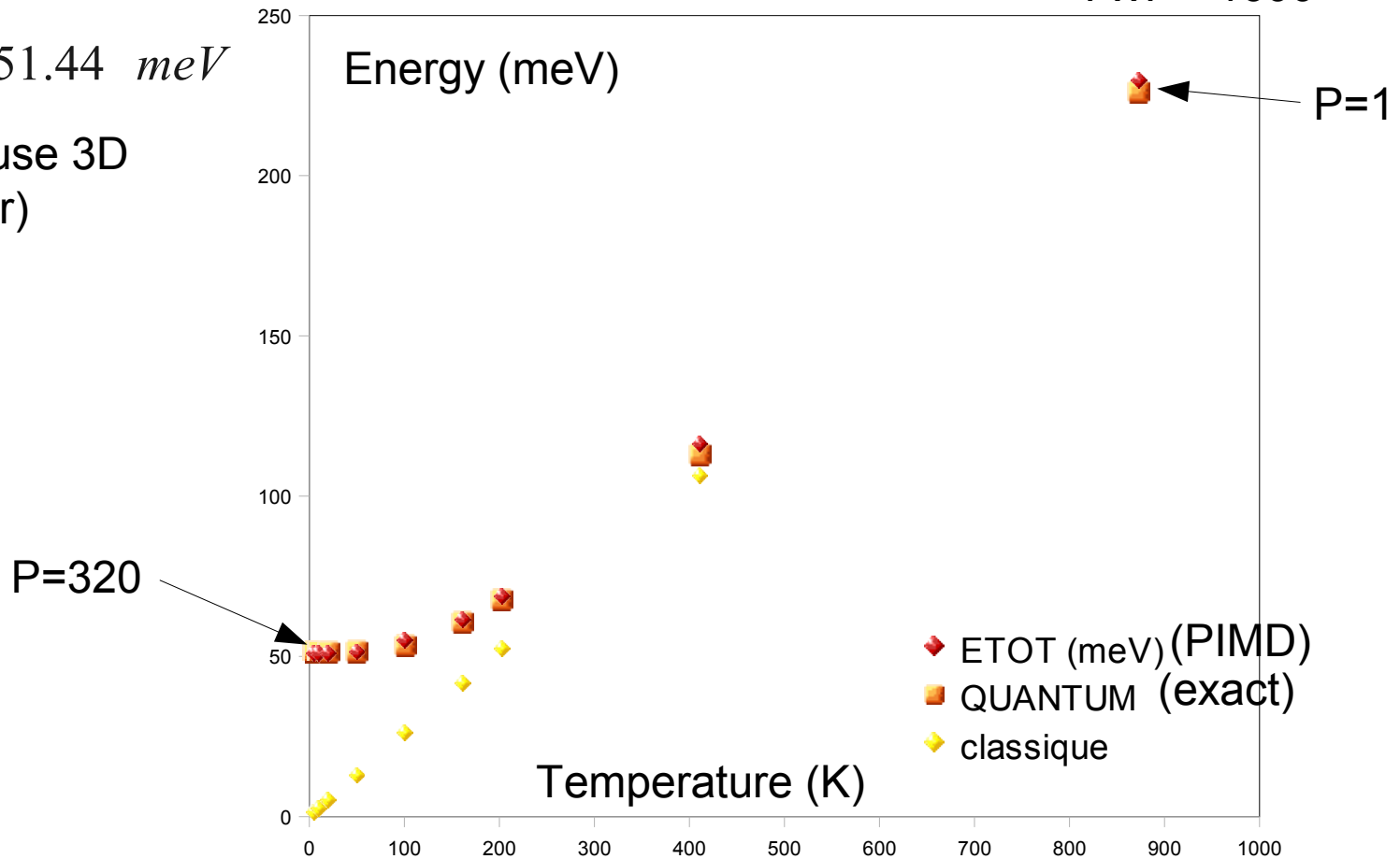
$$\sqrt{\frac{2 \gamma m k_B T}{\delta t}}$$

Time step

Example: (3D) harmonic oscillator

$\frac{3}{2} \hbar \omega = 51.44 \text{ meV}$
 (3 because 3D oscillator)

$P \times T = 1600$



How to implement the Langevin method in the NPT ensemble ?
 This has been formulated by Quigley and Probert

J. Chem. Phys. 120, 11432 (2004); *Comput. Phys. Comm.* 169, 322 (2005)

$$\frac{d\vec{p}_i^{(s)}}{dt} = \vec{f}_i^{(s)} - \gamma \frac{d\vec{p}_i^{(s)}}{dt} + \vec{R}_i^{(s)} - \frac{p_G}{W_g} \vec{p}_i^{(s)} - \left(\frac{1}{N_f}\right) \frac{\text{Tr}[p_G]}{W_g} \vec{p}_i^{(s)}$$

$$\frac{d\vec{r}_i^{(s)}}{dt} = \frac{\vec{p}_i^{(s)}}{m} + \frac{p_G}{W_g} \vec{r}_i^{(s)}$$

$$\frac{dh}{dt} = \frac{p_G h}{W_g} \quad \frac{dp_G}{dt} = V(X - P_{\text{exp}} \text{Id}) + \frac{1}{N_f} \sum_{i,s} \frac{p_i^{(s)2}}{m} \text{Id} - \gamma_G p_G + R_p$$

in which X is an « internal pressure » defined by

$$V X_{\alpha\beta} = \sum_{i,s} p_{i,\alpha}^{(s)} \frac{p_{i,\beta}^{(s)}}{m} + r_{i,\alpha}^{(s)} f_{i,\beta}^{(s)} - (\phi' h^T)_{\alpha\beta}$$

$$(\phi')_{\alpha\beta} = \frac{\partial \phi}{\partial h_{\alpha\beta}}$$

Combines Langevin dynamics and
 Martyna *et al* barostat

- ABINIT already contains a structure adapted to PIMD
- this structure is devoted to algorithms using different IMAGES of the system
- these images are propagated at the same time, according to the chosen algorithm
- well adapted to NEB, string method, etc
- the two subroutines contained in ABINIT that control these algorithms:
 - gstateimg.F90
 - predictimg.F90

First, let us have a look at these two existing routines:

Subroutine `gstateimg.F90`, general structure :

Loop on `itimimage` (propagation of images)

```
do itimimage=1,ntimimage
```

```
    1) loop on the images (that evolve) to compute energy,  
    forces...
```

```
    do idynimage=1,ndynimage
```

```
        Call gstate : computed total energy, forces, stress  
        for each image
```

```
    end do
```

```
    2) Evolution of images
```

```
        Call predictimg
```

```
end do
```

Subroutine predicting

=> chooses the algorithm to propagate the images
(according to the value of imgmov)

Other
Algorithms
(string, etc)

```
select case(imgmov)
```

```
case(0)
```

```
call predict_copy(acell_timimage,itimimage,list_dynimage,natom,ndynimage,nimage,ntimimage,&  
& rprim_timimage,vel_timimage,xred_timimage)
```

```
case(1)
```

```
call predict_steepest(acell_timimage,fxcartfactor,itimimage,list_dynimage,natom,ndynimage,nimage,ntimimage,&  
& results_gs_timimage,rprim_timimage,vel_timimage,xred_timimage)
```

```
case(2)
```

```
call predict_string(acell_timimage,fxcartfactor,iatfix,itimimage,list_dynimage,natom,ndynimage,nimage,ntimimage,&  
& results_gs_timimage,rprim_timimage,vel_timimage,xred_timimage)
```

```
case(9, 13)
```

```
! Path Integral Molecular Dynamics
```

```
call predict_pimd(acell_timimage,fxcartfactor,itimimage,list_dynimage,natom,ndynimage,nimage,ntimimage,&  
& results_gs_timimage,rprim_timimage,vel_timimage,xred_timimage,mdparam)
```

```
case default
```

```
end select
```

Here comes
PIMD !

PIMD implemented in: SUBROUTINE predict_pimd.F90

Two algorithms:

- Langevin dynamics
- Nose Hoover chains + coordinate transformation

In two ensembles:

- NVT
- NPT

Rq: Langevin NPT uses Quigley-Probert algorithm

Associated keywords:

Choice of algorithm:

`imgmov`=9 (Langevin) or 13 (Nose-Hoover chains)

Choice of statistical ensemble:

`optcell` = 0 if NVT, 2 if NPT

`nimage` = TROTTER number

`ntimimage` = number of time steps

`mdtemp` = initial temperature

`mdftemp` = thermostat temperature

`dtion` = time step

Langevin thermostat:

`vis`= friction coeff in the case of Langevin dynamics

Langevin dynamics is a powerful way to recover ergodicity, ...

... but special care should be paid to:

1) Choice of random number generator

2) Choice of friction coefficient

1) Random number generator:

Langevin dynamics requires random numbers

The quality of the random number generator is crucial !

Possible choices:

(1) in ABINIT: subroutine `uniformrandom.f90`

(2) intrinsic function of fortran = `random_number`

(3) random number generator: ZBQ

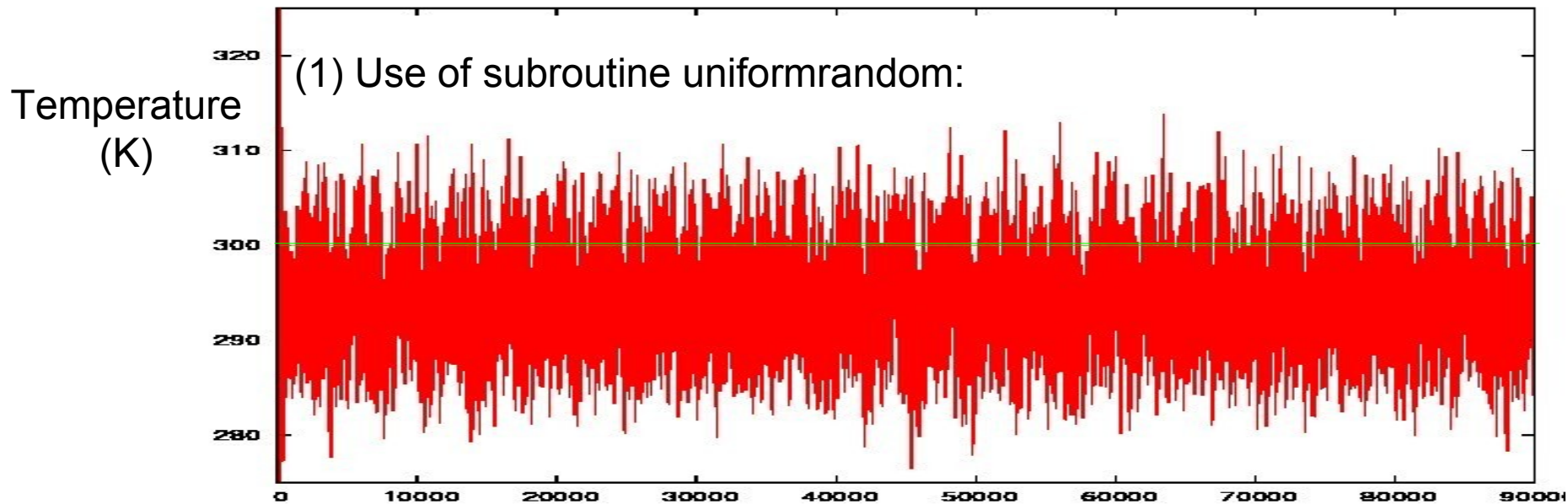
*(R.Chandler, generator from G. Marsaglia and A. Zaman,
Annals of Appl. Probability 1 (1991), 462-480)*

Test of algorithm on a long trajectory => (2) and (3)
give better result than (1)

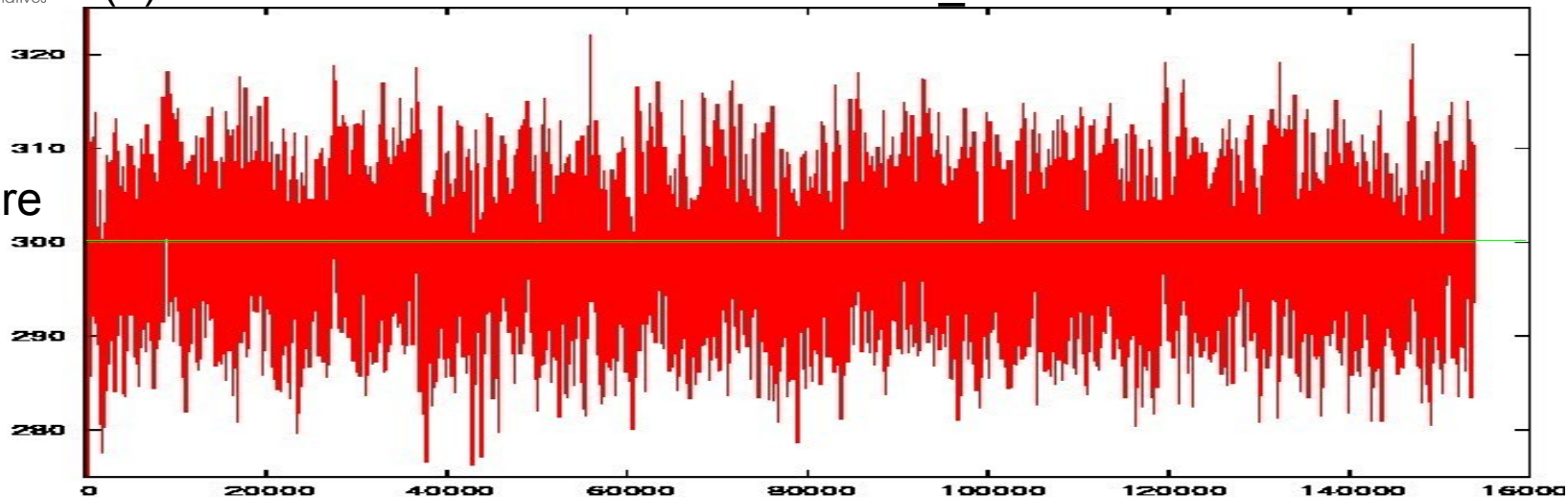
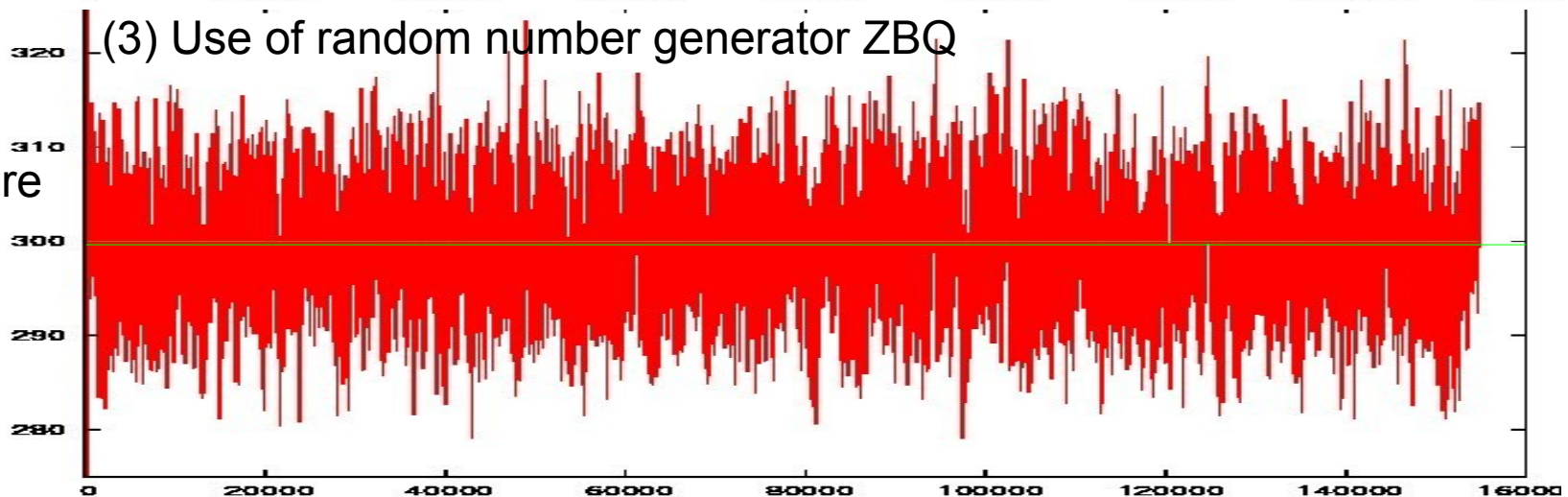
Best way to test MD algorithm is to perform
A LONG trajectory on a BIG system, but

... difficult in ab initio !

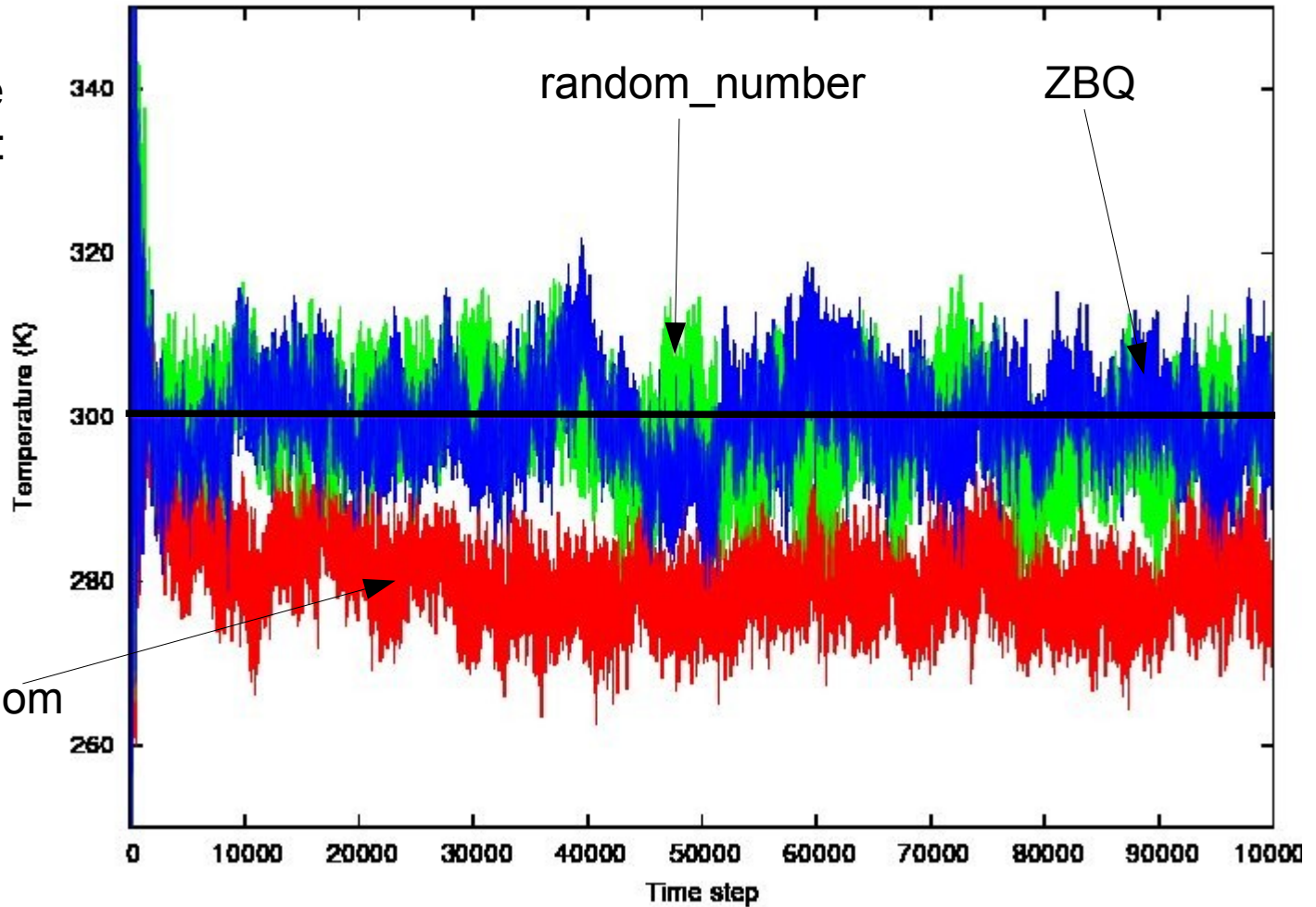
=> **remove (temporary) the ab initio part of ABINIT !!!!!**
and replace it by a phenomenological potential
=> 100 000 time steps on 1728 particles, T=300 K



(2) Use of intrinsic fortran routine random_number

Temperature
(K)Temperature
(K)

Changing the
Friction coeff:



2) Friction coefficient

- Langevin thermostat requires special attention to the choice of the friction coefficient

$$m \frac{d^2 \vec{r}_i^{(s)}}{dt^2} = \vec{f}_i^{(s)} - \gamma m \frac{d \vec{r}_i^{(s)}}{dt} + \vec{R}_i^{(s)}$$

Random (Langevin) force randomly chosen at each step according to a normal law with variance

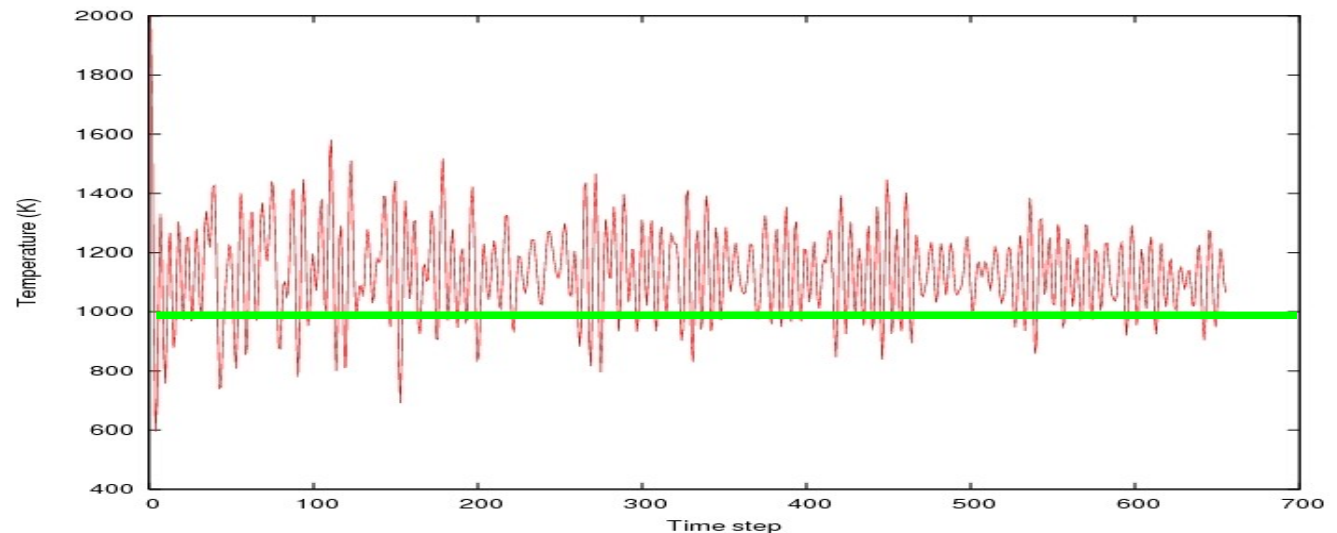
$$\sqrt{\frac{2 \gamma m k_B T}{\delta t}}$$

- $1/\gamma$ roughly corresponds to the time needed to equilibrate the system
The higher γ , the faster your system is equilibrated...
but

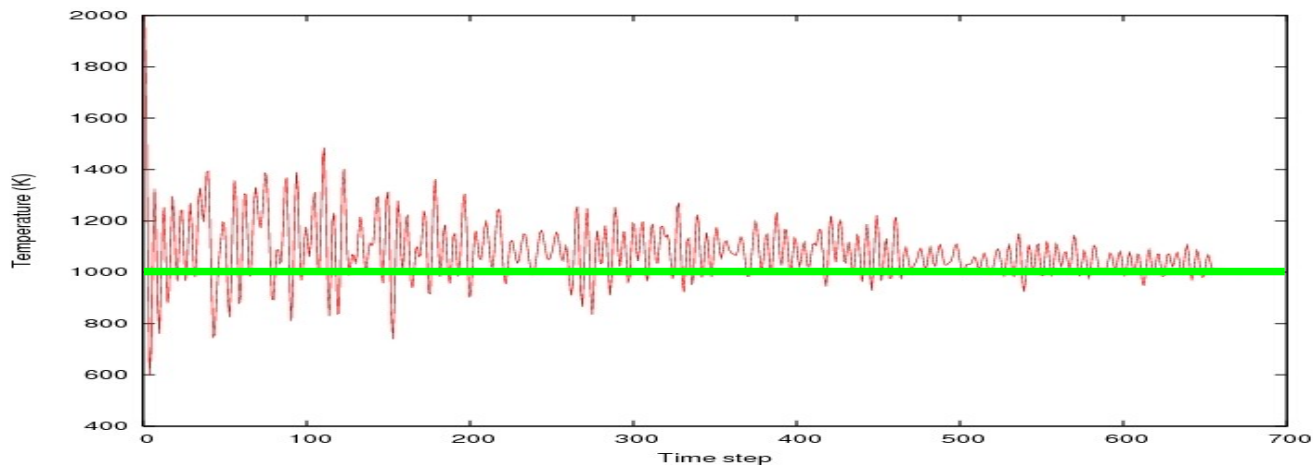
- γ (homogeneous to a frequency) should be chosen smaller than the characteristic phonon frequencies of the system
=> a compromise must be found !

Example: PIMD with ABINIT, NVT Langevin
Box of 20 H₂ molecules, P=20, 100 processors (// band-FFT)
Several tests with $Vis = 2 \cdot 10^{-5}$, $1 \cdot 10^{-4}$, $2 \cdot 10^{-4}$, $5 \cdot 10^{-4}$
(given in inverse atomic time units)
mdtemp= 2000 K; mdftemp = 1000 K, dtion=20

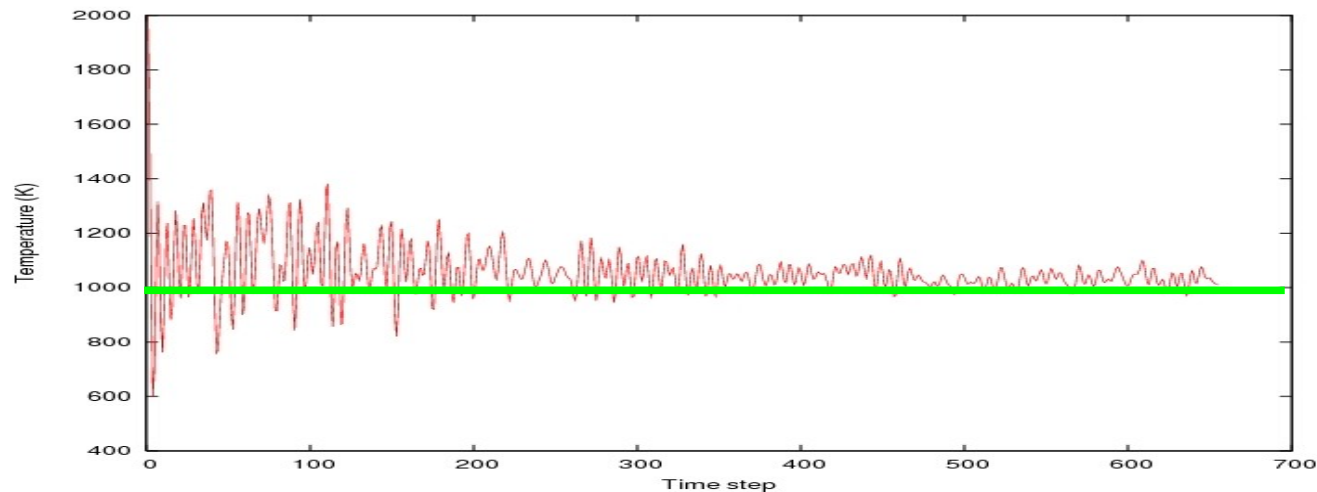
1) $vis = 2 \cdot 10^{-5} = 0.9$ THz



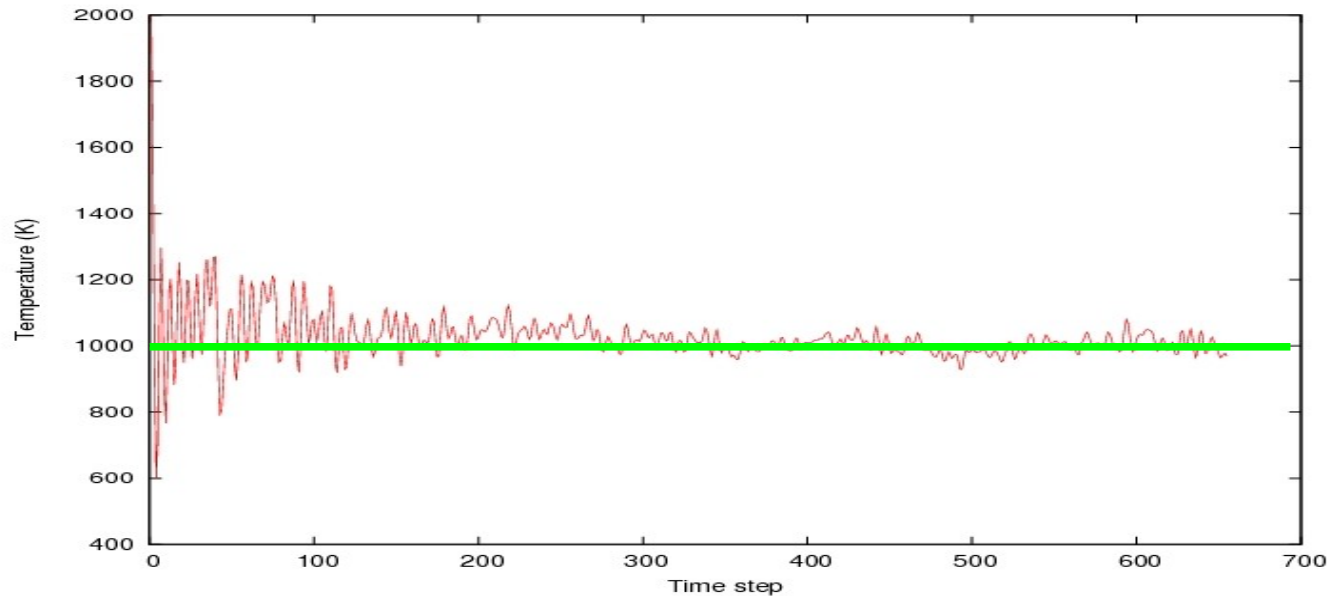
2) $\nu_{\text{vis}} = 1 \cdot 10^{-4} = 4.6 \text{ THz}$



3) $\nu_{\text{vis}} = 2 \cdot 10^{-4} = 9.3 \text{ THz}$



4) $\nu_{\text{vis}} = 5 \cdot 10^{-4} = 23.3 \text{ THz}$



Rq: stretching vibration of H_2 molecule = $4160 \text{ cm}^{-1} = 125 \text{ THz}$

Be careful to the TIME STEP !

- usually, systems interesting for PIMD contain LIGHT atoms (H, He, etc) => high phonon frequencies
- The DEFAULT value of DTION is TOO high in such cases
Default value: dtion=100 ($\sim 2 \cdot 10^{-15}$ s)

- PIMD works in NVT and NPT in the case of Langevin Dynamics, in // (k-point, band, fft)
- Nose-Hoover chains implementation in progress (NVT and NPT)
- with $P=1$, one recovers classical dynamics => PIMD also involves classical MD (=> new algorithms in ABINIT)
- systems of interest:
 - H_2 , LiH
 - proton transport in oxides

PARALLELIZATION:

- Loop over images : highly parallelizable !
 - currently IMPLEMENTED by M. TORRENT
(for all image algorithms)
- => will provide a 4th level of // in ABINIT