DE LA RECHERCHE À L'INDUSTRIE

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IMPLEMENTATION OF THE « BLUE-MOON » ENSEMBLE METHOD IN ABINIT

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CONTENT

1- CONTEXT : SIMULATION OF « RARE » EVENTS

- Many problems in physics involve **RARE** events, i.e
events occuring rarely w/r typical atomic vibrations

- Yet, these events may control some **MACROSCOPIC** properties

Ex 1 : diffusion of an ionic impurity/defect in a solid
=> diffusion coefficient / ionic conductivityin an **IONIC CONDUCTOR**

Ex 2 : reorientation of a dipolar impurity / cluster
=> dielectric relaxation phenomena in the RF in a **RELAXOR**

- Events thermally activated => controlled by an activation energy E_a

Occurrence rate :

$$r = r_0 e^{-E_a/k_B T}$$

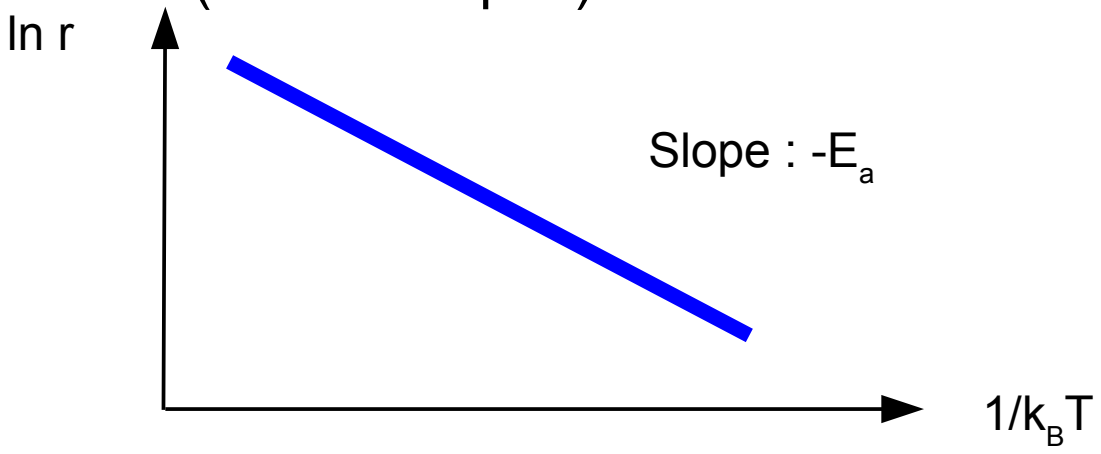
1- CONTEXT : SIMULATION OF « RARE » EVENTS

$$r = r_0 e^{-E_a / k_B T}$$

How to obtain E_a (at finite T) ?

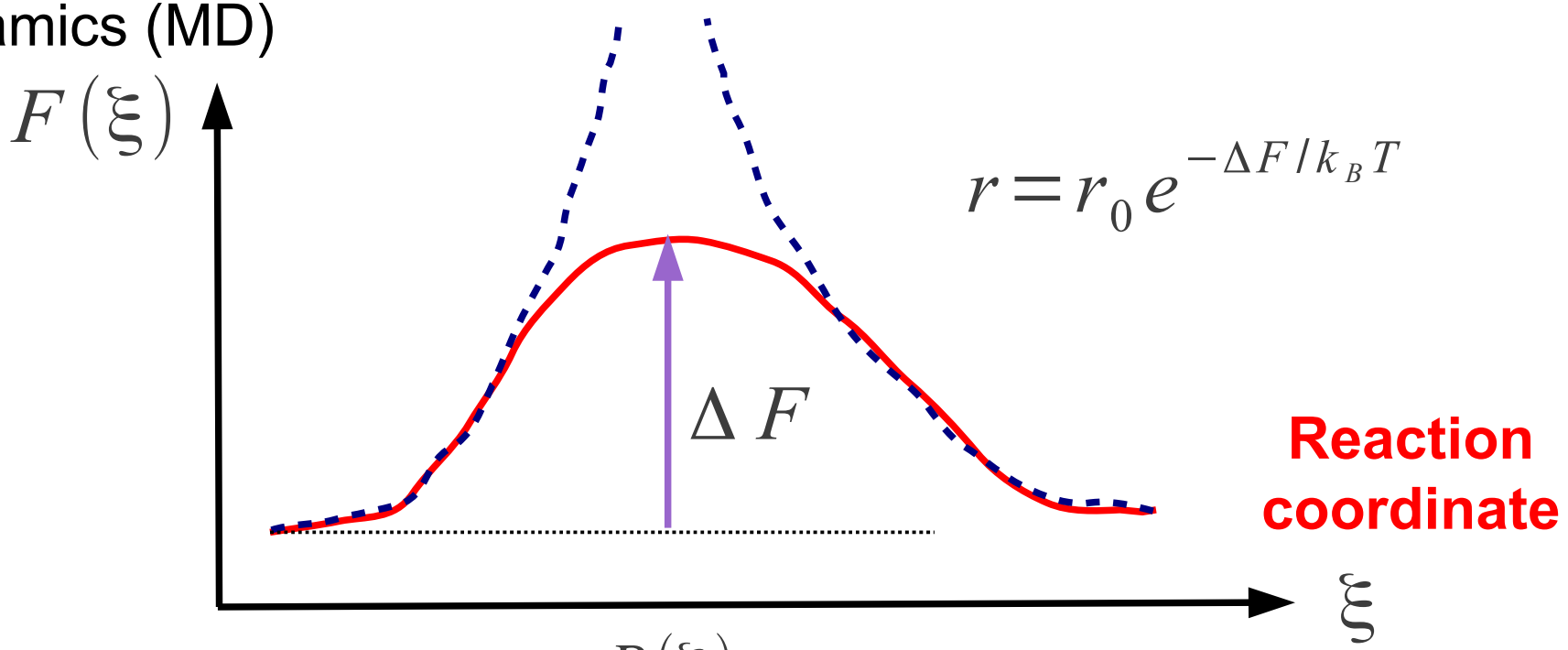
1st possibility : **simulating the dynamics of the system (MD),**
… and **counting** the occurrences of the events

Plot the log of the rate as a function 1/T :
(Arrhenius plot)



Unfortunately,
this is NOT always
POSSIBLE
because the statistics may
be too bad:
Ex : low T, high E_a ...

- **2nd possibility** : **« Blue-Moon » ensemble :** Method to simulate the **occurrence of RARE events** within Molecular Dynamics (MD)



$$r = r_0 e^{-\Delta F / k_B T}$$

$$F(\xi) - F(\xi_0) = -k_B T \ln \frac{P(\xi)}{P(\xi_0)}$$

$$P(\xi) \propto C \int \dots \int_{\{x_{i\alpha}\}} \delta(\xi(\{x_{i\alpha}\}) - \xi) e^{-V(\{x_{i\alpha}\})/k_B T} dX$$

2 – THE « BLUE-MOON » ENSEMBLE METHOD

Blue-Moon Ensemble method in practise :

- simulate each step of the event by **« forcing » ξ to take a chosen value :**

=> MD under (holonomic) constraint of FIXED ξ

Method of Lagrange multipliers

- Obtain for each value of ξ the derivative of the free energy

« mean force » on the constraint : $-\frac{dF}{d\xi}$

- recover the (free) energy profile by (thermodynamic) integration :

$$\Delta F = F(\xi) - F(\xi_0) = \int_{\xi_0}^{\xi} \frac{dF}{d\xi}(\xi')\, d\xi'$$

Sprik, Cicotti, J. Chem. Phys. ***109****, 7737, (1998)*

2 – THE « BLUE-MOON » ENSEMBLE METHOD

General case :

$$\xi\left(\{x_{i\alpha}\}\right)$$

$$\frac{dF}{d\xi}=\frac{\langle Z^{-1/2}\left(-\lambda+k_B T\, G\right)\rangle_\xi}{\langle Z^{-1/2}\rangle_\xi}$$

with :

$$Z=\sum_{i=1}^{N}\frac{1}{m_i}\left(\frac{\partial\xi}{\partial\vec{r}_i}\right)^2$$

$$G=\frac{1}{Z^2}\sum_{i=1}^{N}\sum_{j=1}^{N}\frac{1}{m_i m_j}\frac{\partial\xi}{\partial\vec{r}_i}\frac{\partial^2\xi}{\partial\vec{r}_i\partial\vec{r}_j}\frac{\partial\xi}{\partial\vec{r}_j}$$

Time average under fixed ξ (constrained MD)
= « blue-moon » ensemble average

$$F\left(\xi_2\right)-F\left(\xi_1\right)=\int_{\xi_1}^{\xi_2}\frac{dF}{d\xi}\left(\xi'\right)d\xi'$$

Sprik, Cicotti, J. Chem. Phys. ***109****, 7737, (1998)*

3 – IMPLEMENTATION OF THE LINEAR CONSTRAINT

Implementation **in ABINIT of the LINEAR constraint**
i.e. linear combination between atomic positions

$$\xi\left(\{x_{i\alpha}\}\right)=\sum_{i\alpha} a_{i\alpha}x_{i\alpha}$$

Real coefficients

1) *Lagrangian* with *constraints*

$$L=[T\left(\{\dot{x}_{i\alpha}\}\right)-V\left(\{x_{i\alpha}\}\right)]-\lambda[\sum_{i\alpha} a_{i\alpha}x_{i\alpha}-\xi]$$

2) Apply *Euler-Lagrange equations* :

$$m_i\frac{d^2x_{i\alpha}}{dt^2}=f_{i\alpha}-\lambda a_{i\alpha}$$

Lagrange multiplier computed at each step as $\lambda(t)=\dfrac{\sum_{i\alpha} a_{i\alpha}\dfrac{f_{i\alpha}(t)}{m_i}}{\sum_{i\alpha}\dfrac{a_{i\alpha}^2}{m_i}}$

3) *Derivative of the free energy* :

$$\frac{dF}{d\xi}=-\langle\lambda\rangle_\xi=-\frac{\sum_{i\alpha}\dfrac{a_{i\alpha}}{m_i}\langle f_{i\alpha}\rangle_\xi}{\sum_{i\alpha}\dfrac{a_{i\alpha}^2}{m_i}}$$

3 – IMPLEMENTATION OF THE LINEAR CONSTRAINT

- **Physically acceptable** linear constraints satisfy : $\sum_{i\alpha} a_{i\alpha} = 0$

- However, even if $\sum_{i\alpha} a_{i\alpha} \neq 0$, a supplemental constraint

has been added to ensure that center of mass does not move.

- Value of the constraint ξ : **FIXED** by **INITIAL** set of positions.

- Initialization of the velocities :

The initial velocities must be modified to ensure that the constraint is obeyed, i.e.

$$\sum_{i\alpha} a_{i\alpha} \frac{d\,x_{i\alpha}}{dt} = 0$$

- Implemented in the routine **pimd_apply_constraint** (m_pimd.F90).

- PIMD : the constraint is applied on the centroid.

3 – IMPLEMENTATION OF THE LINEAR CONSTRAINT

- The constraint is STRICTLY obeyed all along the MD trajectory (at EACH step, NOT on average)

Ex :

- *Reaction coordinate = -36.5852098477*
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- the Center of mass is also strictly FIXED

Center of mass:
4.6876358799 6.5991695708 4.6808066009
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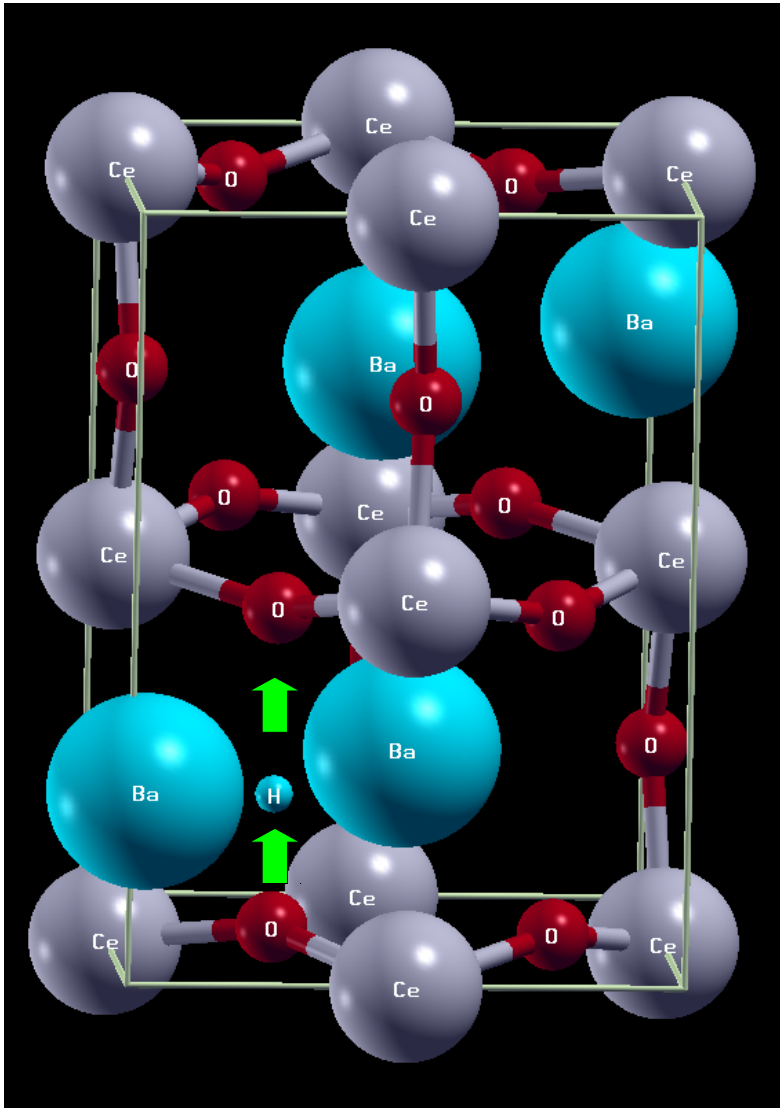
4 - EXAMPLE



In progress :

$BaCeO_3$: orthorhombic perovskite
Pnma space group

Excellent protonic conductor

Inter-octahedral transfer of H^+

Cell = 20 atoms
Reaction coordinate : $(O_1H)_y$ - $(O_2H)_y$
$= y(H)-y(O_1) – [y(O_2) – y(H)]$

PIMD, T=200 K
P=32 beads

4 - EXAMPLE

Input file for BaCeO3:

```
nline 6
npulayit 15

# PARALLELIZATION # => 864 procs
paral_kgb 1
npkpt 9
npband 3
npfft 1
npimage 32

# PIMD/MD
optcell 0
irandom 3
restartxf -1
imgmov 9   # langevin PIMD
ntimimage 10000
nimage 32
mdtemp 400 200
vis 5d-05
dynimage 32*1
nsym 1
pitransform 0
amu      140 16 138 1 # ce o ba h
pimass  140 16 138 1
dtion 10
```

```
# CONSTRAINTS
pimd_constraint 1
nconeq 1
natcon 3
iatcon 5 20 1 #ox1 ox2 hydrogen
wtatcon
0.0 -1.0 0.0 0.0 -1.0 0.0 0.0 2.0 0.0

# DFT
nband 111
occopt 3
tsmear 0.001
pawovlp -1
ixc 11
ecut 18.0
pawecutdg 25.0
kptopt 1
ngkpt 3 2 3
nstep 100
toldff 1.0d-05
prtden 0
prtwf 0

charge 1.0
```

```
# ATOMS
znucl  58 8 56 1
ntypat 4
natom 21
typat
4 3 1 2 2 3 2 2 3 3 1 1 1 2 2 2 2 2 2 2 2

# GEOMETRY
acell 11.941471  16.813056  11.913748

xred
  0.279                 0.216                 0.723  #yH to be varied
  2.5108646807E-02  2.5000000000E-01 -8.0469316958E-03
 -1.3877787808E-17 -9.7144514655E-17  5.0000000000E-01
  4.8011508619E-01  2.5000000000E-01  7.9658009587E-02
  2.7974388262E-01  4.3160947462E-02  7.2102708776E-01 #ox1
  9.7489135319E-01  7.5000000000E-01  1.0080469317E+00
  5.1988491381E-01  7.5000000000E-01  9.2034199041E-01
  7.2025611738E-01  9.5683905254E-01  2.7897291224E-01
  5.2510864681E-01  2.5000000000E-01  5.0804693170E-01
  4.7489135319E-01  7.5000000000E-01  4.9195306830E-01
  5.0000000000E-01  5.0000000000E-01 -6.9388939039E-17
 -1.3877787808E-17  5.0000000000E-01  5.0000000000E-01
  5.0000000000E-01 -9.7144514655E-17 -6.9388939039E-17
  9.8011508619E-01  2.5000000000E-01  4.2034199041E-01
  1.9884913809E-02  7.5000000000E-01  5.7965800959E-01
  7.7974388262E-01  4.5683905254E-01  7.7897291224E-01
  7.2025611738E-01  5.4316094746E-01  2.7897291224E-01
  2.2025611738E-01  9.5683905254E-01  2.2102708776E-01
  2.2025611738E-01  5.4316094746E-01  2.2102708776E-01
  2.7974388262E-01  4.5683905254E-01  7.2102708776E-01 #ox2
  7.7974388262E-01  4.3160947462E-02  7.7897291224E-01
```

5 – CONCLUSION : FUTURE IMPLEMENTATIONS

1) Future developments : other constraints, i.e.
- distance between 2 atoms
- difference of distance
- angle between directions defined by atoms

2) Extension to the NPT ensemble :
=> study of *Structural Phase Transitions*

3) Multiple constraints