Nouvelle approche pour la simulation de la croissance de couches de matériaux réactifs : Monte Carlo cinétique à trajectoires d'atomes hyperthermiques

Anne Hémeryck

Alain Estève, Mehdi Djafari Rouhani,
Marie Brut, Georges Landa

Cloé Lanthony, Darius Djafari Rouhani

Collaboration expérimentale : Carole Rossi

Collaboration : Nicolas Richard

LAAS-CNRS

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Université Paul Sabatier (UPS), Institut National des Sciences Appliquées de Toulouse (INSA),
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Université du Mirail (UTM) and Université Toulouse 1 Capitole (UT1)

Feb. 2013 :
624 persons work in LAAS
Researchers and Faculty Members: 501
91 CNRS researchers
128 Faculty researchers
9 Associated Researchers
30 Post-doc – 243 PhD Students
Engineers, Technicians, Admin Clerks (ITA): 123

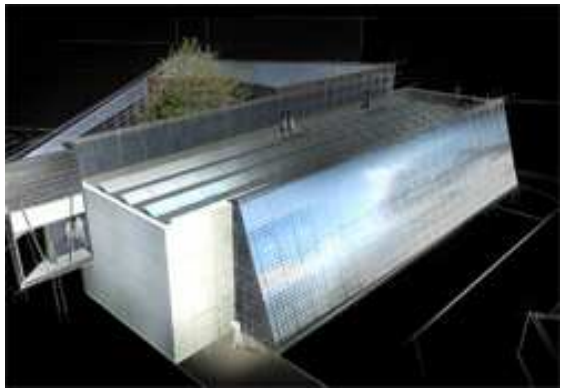
Scientific Research in 8 main research areas

Critical Infomation Processing
Networks and Communications
Robotics
Decision and Optimization
MicroNanosystems RF and Optical
Nano-Engineering and Integration
Energy Management
MicroNanoBio Technologies

ALIVE

ADREAM

2 Transversal axes



various application domains such as aeronautics and space, telecommunications, transports, production, services, security and defense, energy management, healthcare, cyber security, environment and sustainable development.

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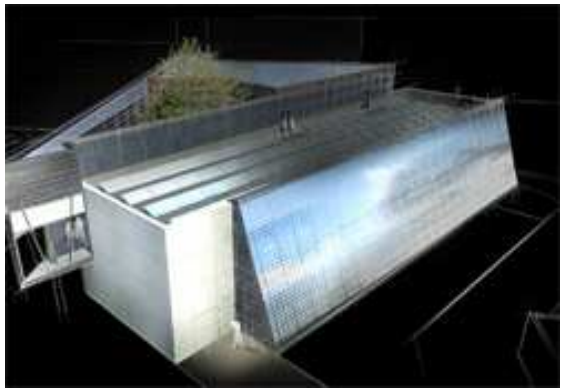

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LAAS-CNRS

Atomic Scale Modeling and Simulation for Micro, Nano and BioNano Technologies

Members:
-2CR, 1MdC, 1DR, 1 Prof
-1 doc, 1 PostDoc

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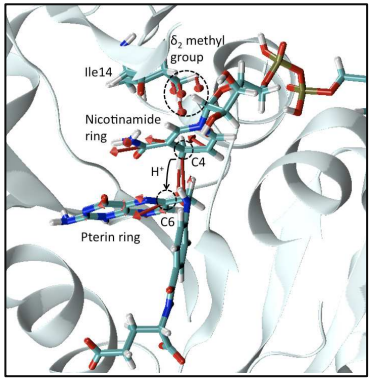
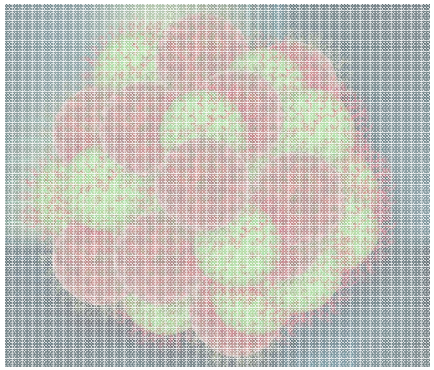


BioTechnologies

SAMs
vdW interactions
DNA Technologies
(DNA assembled
Nanoparticles, Aptamers)



Oxides *(materials)* encountered in Microelectronics

SiO2,
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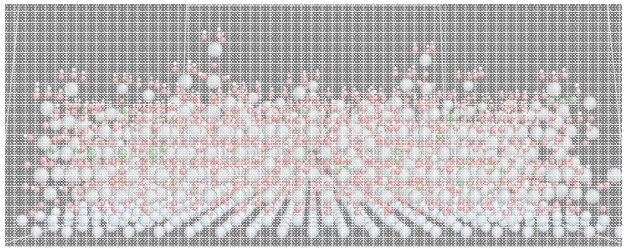


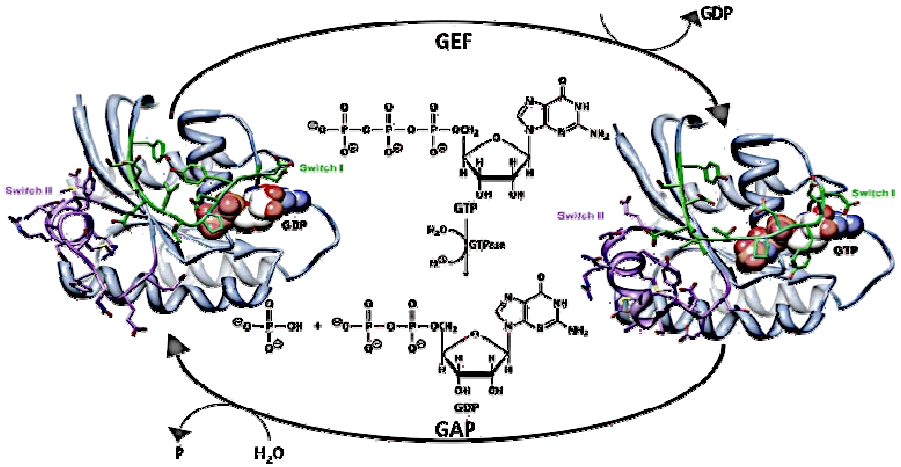
Atomic Scale Modeling and Simulation
for Micro, Nano and BioNano Technologies

Characterizing biomolecular flexibility, docking

(Collab. Stanford Univ., M. Levitt; INRIA, N. Redon)

➢**Development of original modeling approach - Static Modes** Eur. Phys. J. E **28**, 17 (2009)

➢**Structural oncology modelling and simulation platform**
(SAMO RITC Project: RAS oncoprotein - Collab. Claudius Regaud Institute, G. Favre)



Providing a new expertise and modelling facilities to achieve physico-chemical characterization of oncomolecules

Objective
• restoring Ras switching mechanism
(GTP hydrolysis / GAP interaction)
• preventing Ras from binding its effectors

Using Static Modes as a "probe" to:
• Exploring Ras biomechanical properties
• Screening of mutation impact
• Proposing custom design modifications
• Building a Static Mode databank
• Authorizing end users to custom *in silico* experiments
• Guide mutation experiments

Contact : marie.brut@laas.fr

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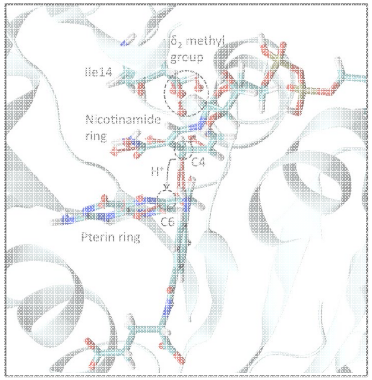

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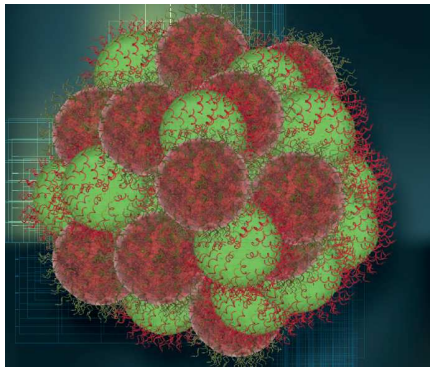

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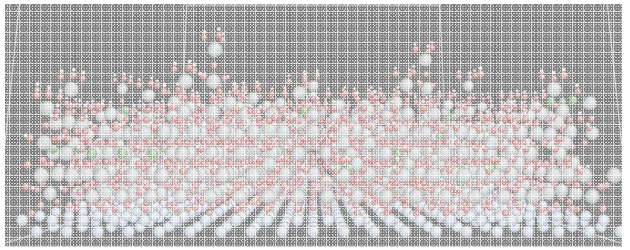
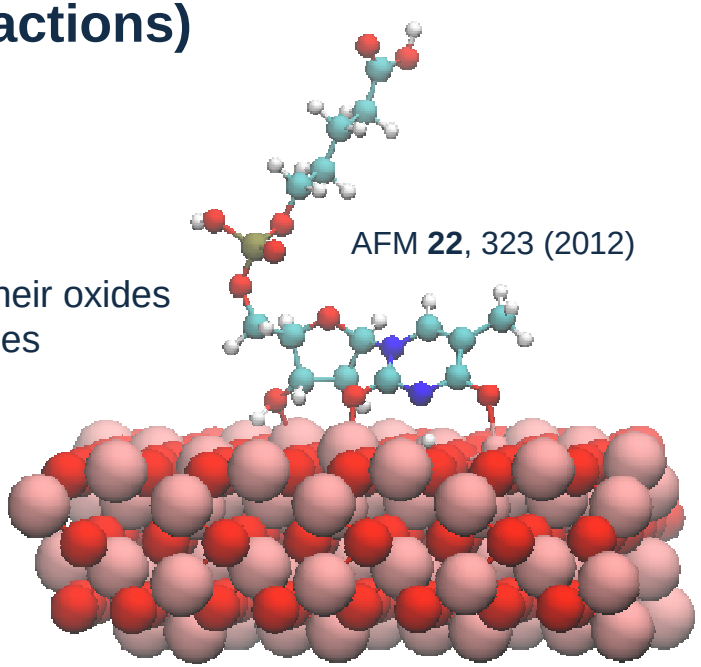


Atomic Scale Modeling and Simulation
for Micro, Nano and BioNano Technologies

DNA Nanotechnologies (bio/non bio interactions)

➢**Self-assembly and chemistry of DNA/surface and nanoparticles interactions**

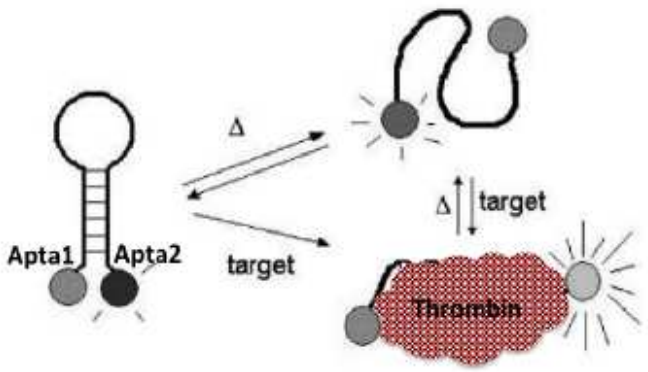
- Thiol or COOH DNA terminations on Au, Al, Cu surfaces and their oxides
- Intrinsic DNA interactions on Au, Al, Cu surfaces and their oxides
- Role of London interactions on DNA/Surface interactions

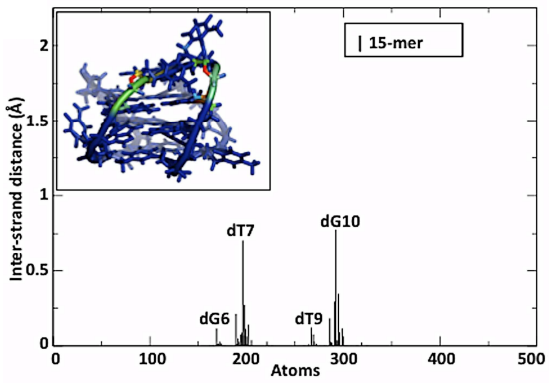


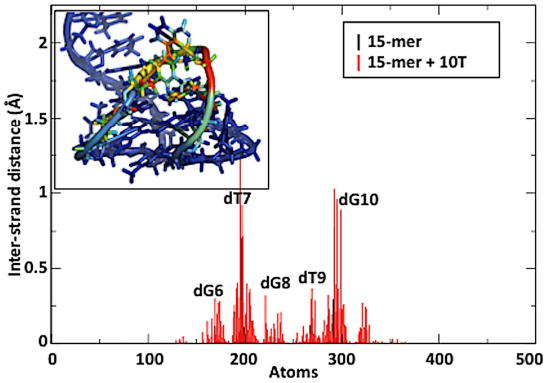
AFM **22**, 323 (2012)

➢**Aptamer sensors** (ANR VIBBnano)

- Impact of aptamer spacer termination on aptamer stability
- Design of aptamer tweezers







APL **100**, 163702 (2012)

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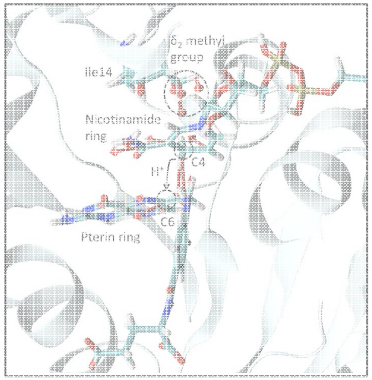

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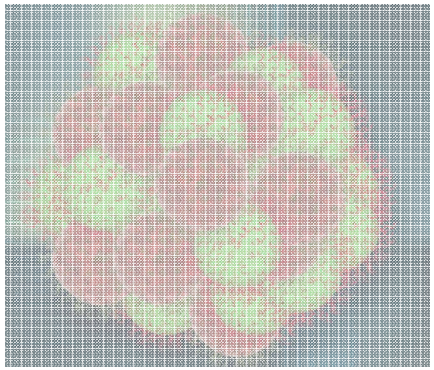

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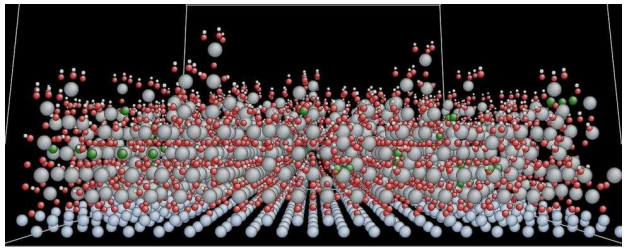
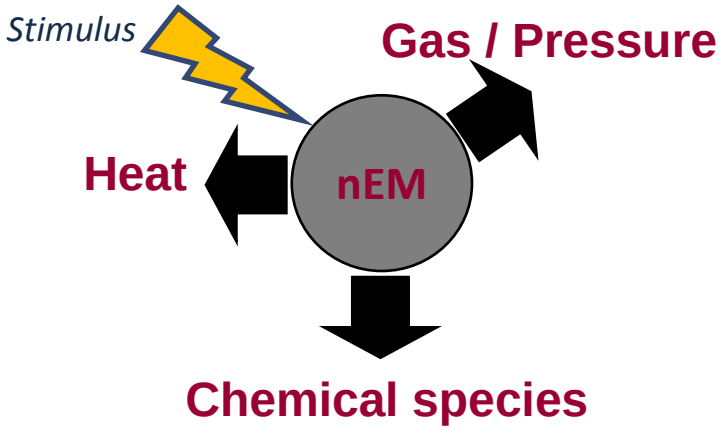


Growth of **reactive materials**
Kinetic Monte Carlo with Hot Atoms Trajectories

Growth of reactive materials
Kinetic Monte Carlo with Hot Atoms Trajectories

Context

➢**NanoEnergetic Materials**



Bimetallics: Al/Ni
Thermites: Al / CuO

$$2\ Al + 3\ CuO \rightarrow Al_2O_3 + 3\ Cu + \Delta H$$

With $\Delta H = 21\ kJ/cm^3$

Compatible with technologies
Integration towards “on a chip” nanoenergetics)

Growth of reactive materials
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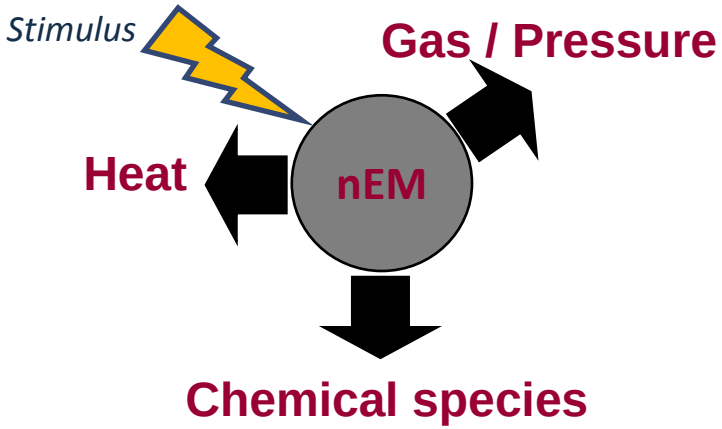

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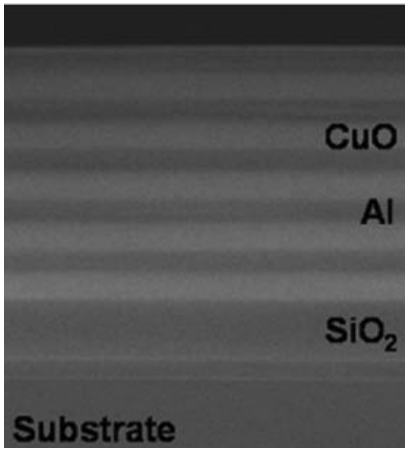
Al/CuO NLs
~ 50-100 nm/layer



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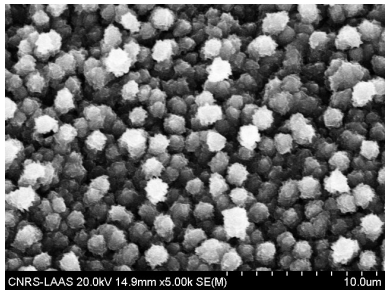
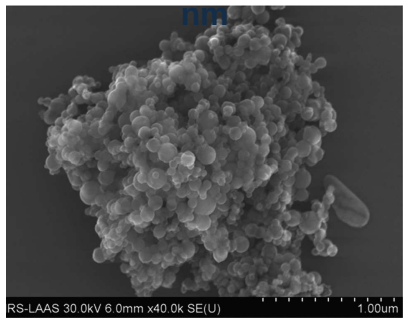
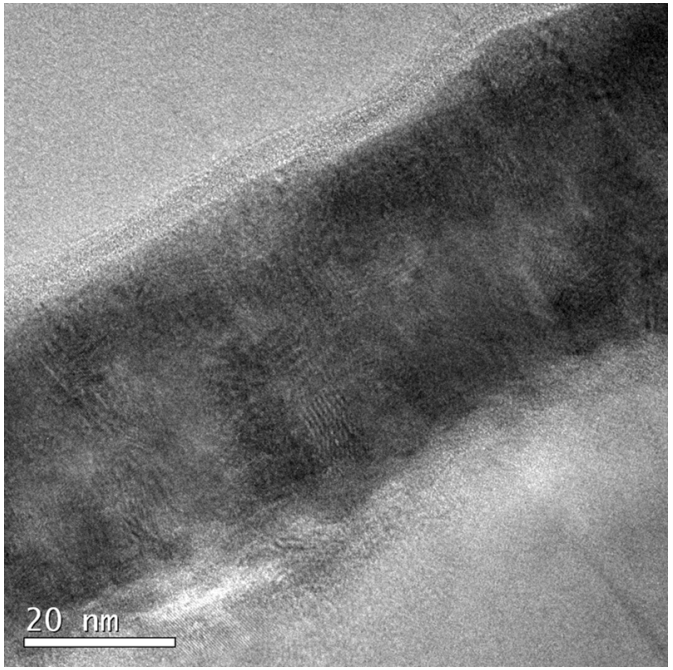


Al/CuO NPs
Ø ~ 50-120 nm



Growth of reactive materials
Kinetic Monte Carlo with Hot Atoms Trajectories

Technological & scientific Issue: interfacial premixing



- Called Barrier layers
- Define final properties (stability, reactivity, sensitivity, released Energy)

- **Formation still not controlled during deposition process (and asymmetric)**

→ Final properties neither not mastered nor guaranteed

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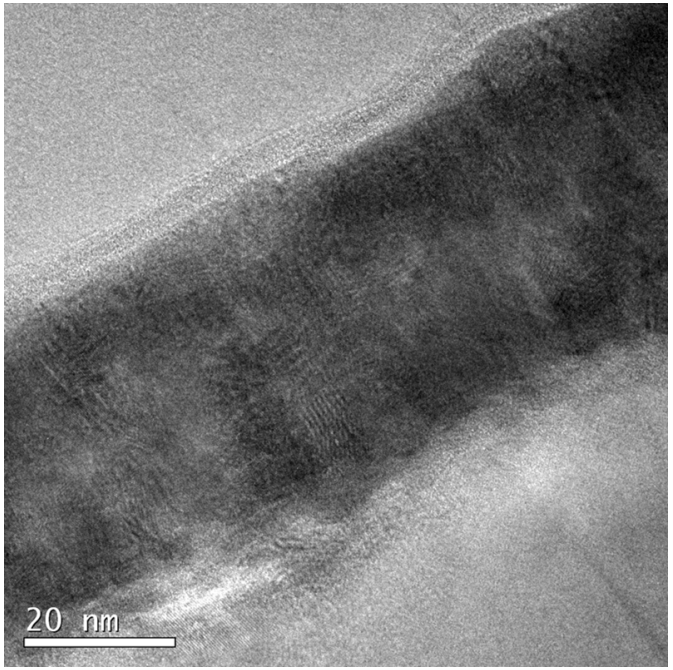

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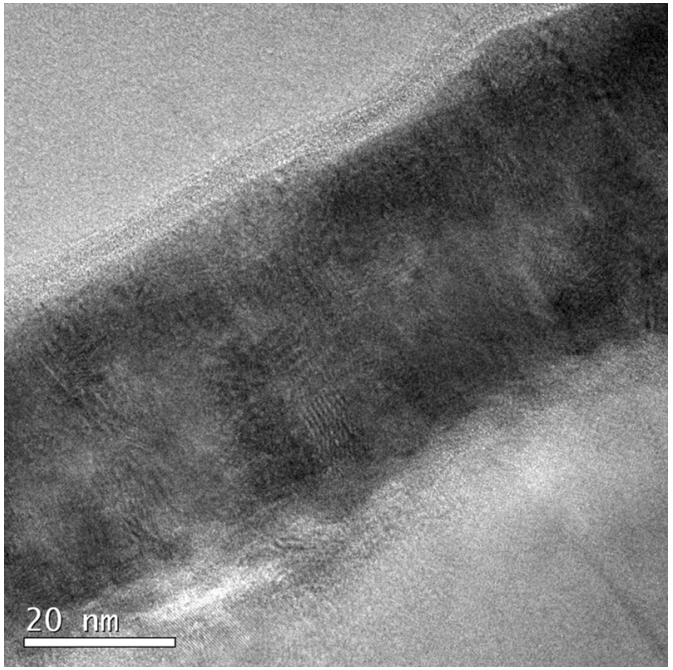

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⇩

Process requires **MODELING**

NanoLayers requires **ATOMIC SCALE**

Growth of reactive materials
Kinetic Monte Carlo with Hot Atoms Trajectories

Preliminary studies on bimetallics Al/Ni

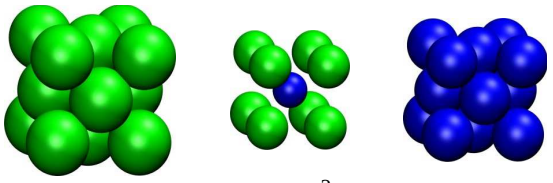
- Basics from DFT:
  SAl, SNi, V, INi, ~~IAl~~

$S_{Ni,i} \rightleftarrows V_i + I_{Ni,j}$

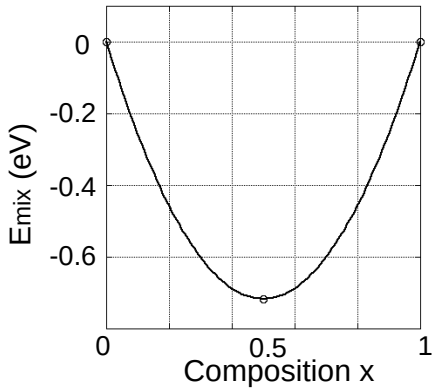
$S_{Ni,i+1} + V_i \; S_{Ni,i} \rightleftarrows + V_{i+1}$

$S_{Al,i+1} + V_i \; S_{Al,i} \rightleftarrows + V_{i+1}$

$I_{Ni,i} \rightleftarrows I_{ni,i+1}$



$E_{Mix}(x)=2.865\,x^2 - 2.865\,x$



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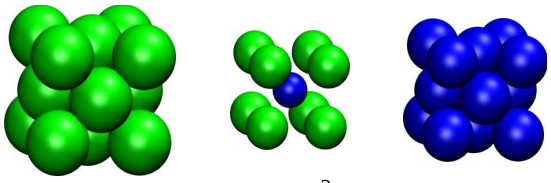

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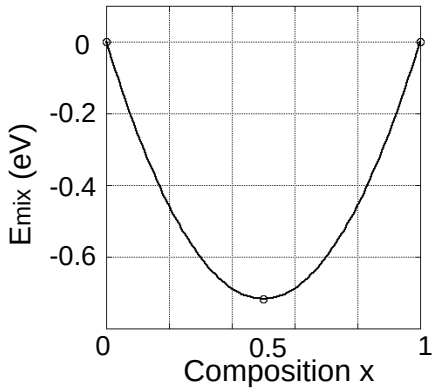

◆ Macroscopic 1D model of atomic mix according to chemical kinetics

◆ Environment dependent rate equation formulation

◆ Mixing releases energy that translate into a temperature increase

◆ **Kinetic part**: *Time evolution*
4 differential equations with RK4-5 scheme and a dynamic time step

$$k_i = \frac{k_B T}{h} \times \exp\left(\frac{-\Delta E_i}{k_B T}\right)$$

◆ **Energetic part**:
Link between composition and energetic parameters (activation energies, rate constants & released energy using DFT calcul.)

$$E_{system} = \sum E_{layer}$$

$$E_{layer} = \left[L(Al)\right] \times E_{Al} + \left[L(Ni)\right] \times E_{Ni}$$

$$+ \left(\left[L(Al)\right] + \left[L(Ni)\right]\right) \times E_{Mix}(x) + \left[I(Ni)\right] \times E_{INi}(x) + \left[V\right] \times E_V(x)$$

◆ **Thermal part**:
Translate energy changes into temperature changes

$$\Delta T = \frac{-\Delta E - dt \times (P_{rad} + P_{conv})}{3k_b \times \sum_i \left(n_i(L_{Al}) + n_i(L_{Ni}) + n_i(I_{Ni})\right)}$$

Growth of reactive materials
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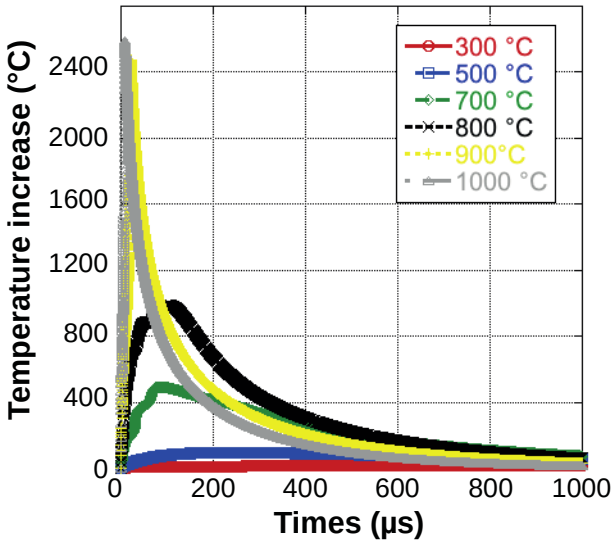
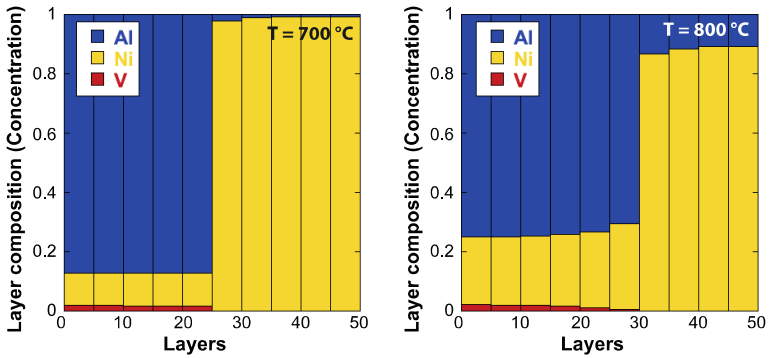
Preliminary studies on bimetallics Al/Ni

- Ignition Temperature



- Layers composition



JVST A **28**, L15 (2010)
JPCS **71**, 130 (2010)
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En review à JAP

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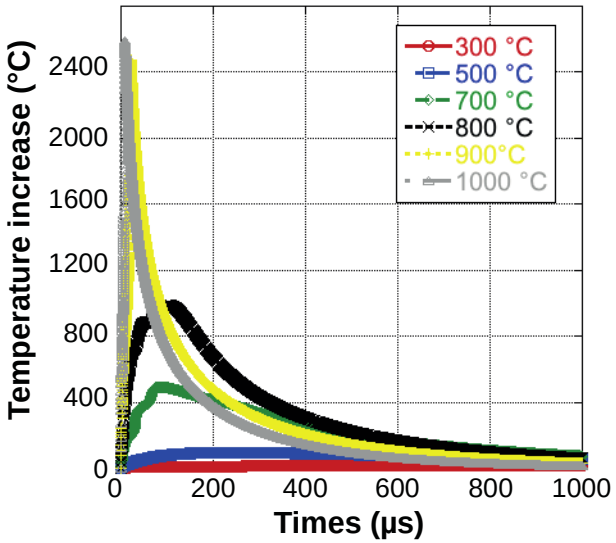
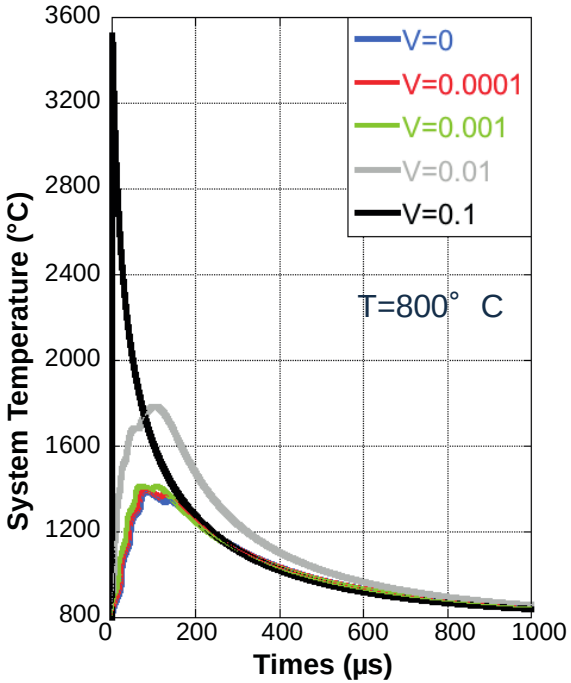
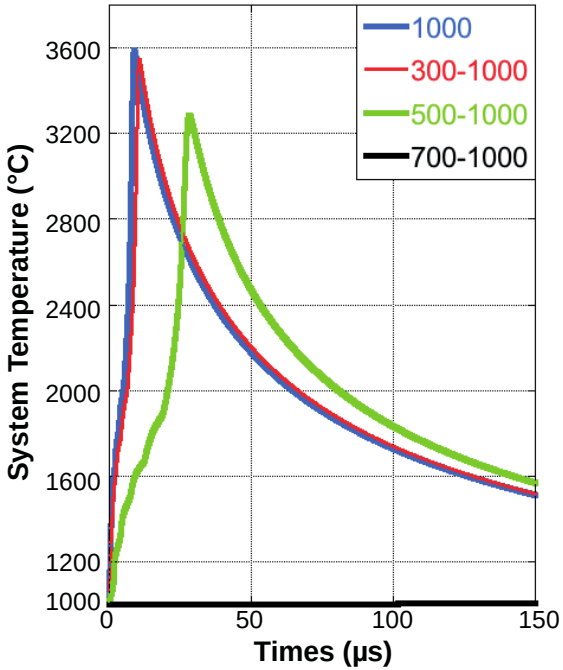


◆ Influence [Vacancies]



◆ Premixing layer Influence



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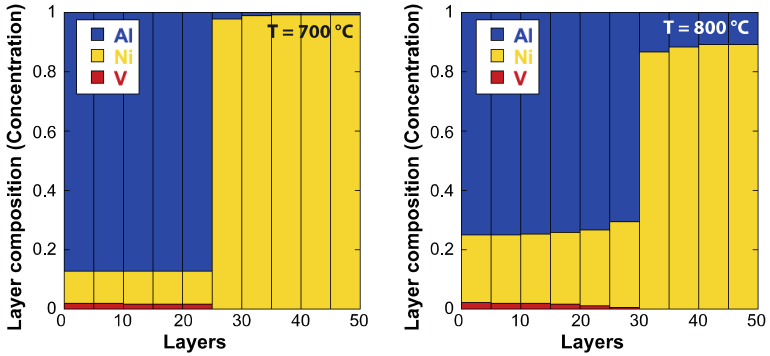

- Defects: incoming from deposition process
- Premixing layer

➢ Impact on final properties
➢ Process Simulation

JVST A **28**, L15 (2010)
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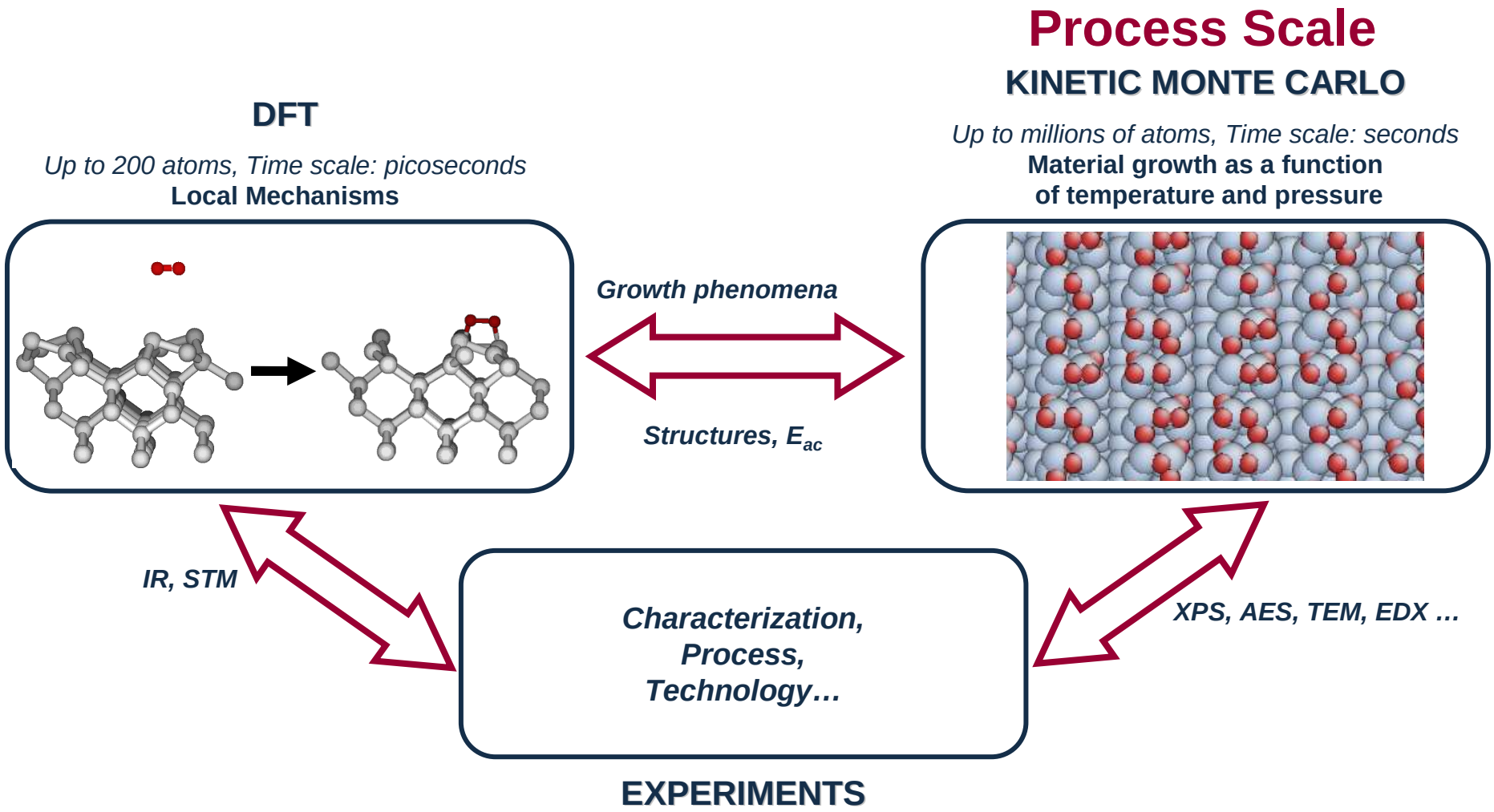
Kinetic Monte Carlo with Hot Atoms Trajectories

→ **Multiscale Modeling of technological process** (oxidation, vapor deposition)



Growth of reactive materials
Kinetic Monte Carlo with Hot Atoms Trajectories

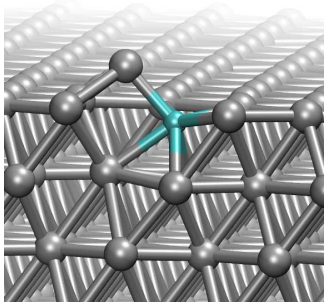
Technology and modeling of reactive composite materials and systems

➢**Al-CuO nanolaminates: basic mechanisms of CuO/Al PVD growth through first principles calculations** (DGA-REI funding)

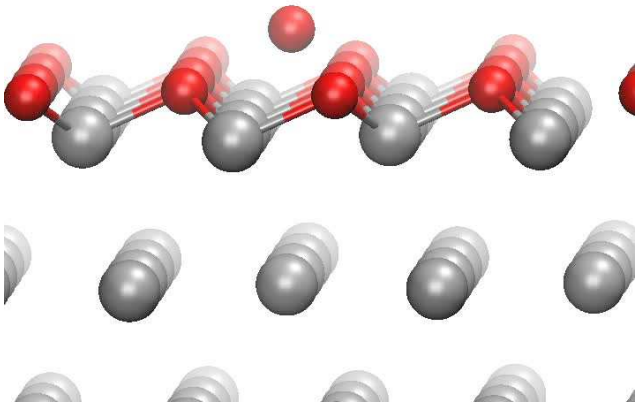
•Mechanisms and energetics using DFT calculations of:

- Al adsorption and penetration path on CuO
- Dissociative chemisorption of CuO on Al (+ O, Cu separation)
- Cu aggregation and penetration
- Al extraction through oxygen exposure → Al oxidation
- Partial order and orientation of grown alumina ultrathin layer

Cu on Al



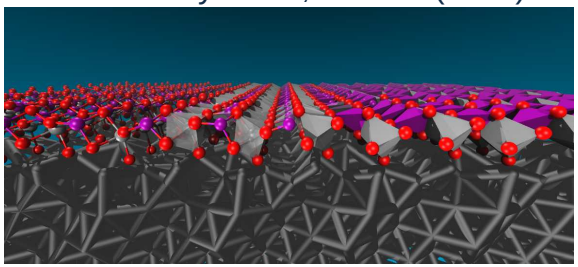
Thin Solid Films **520**, 4768 (2012)

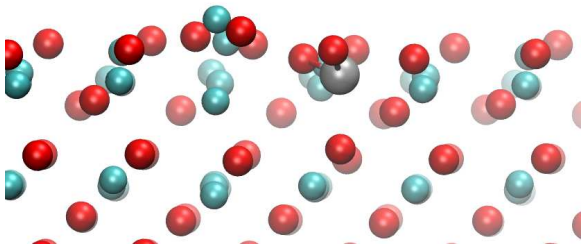


O on Al

Al oxide after 2 ML of Oxygen atom deposition

J. Chem. Phys. **137**, 094707 (2012)





Al on CuO

Growth of reactive materials
Kinetic Monte Carlo with Hot Atoms Trajectories

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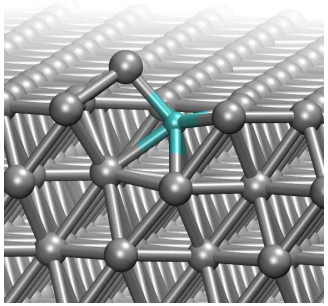
•Mechanisms and energetics using DFT calculations of:

- Al adsorption and penetration path on CuO **5.1 + 2.3 eV**
- Dissociative chemisorption of CuO on Al (+ O, Cu separation) **6.6 eV**
- Cu aggregation and penetration **3.15 + 0.55 eV**
- Al extraction through oxygen exposure → Al oxidation **5-8 eV**
- Partial order and orientation of grown alumina ultrathin layer

Cu on Al



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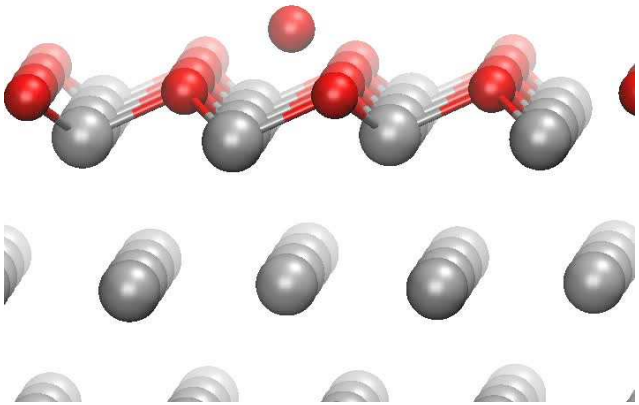

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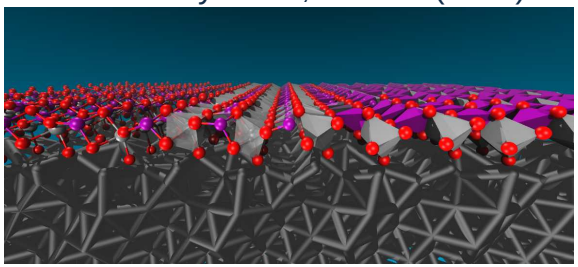
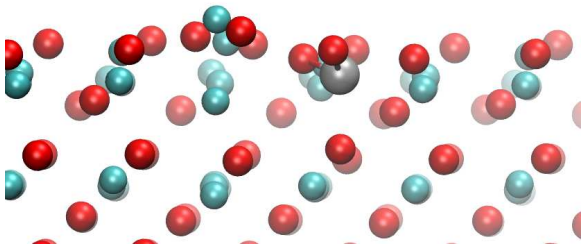


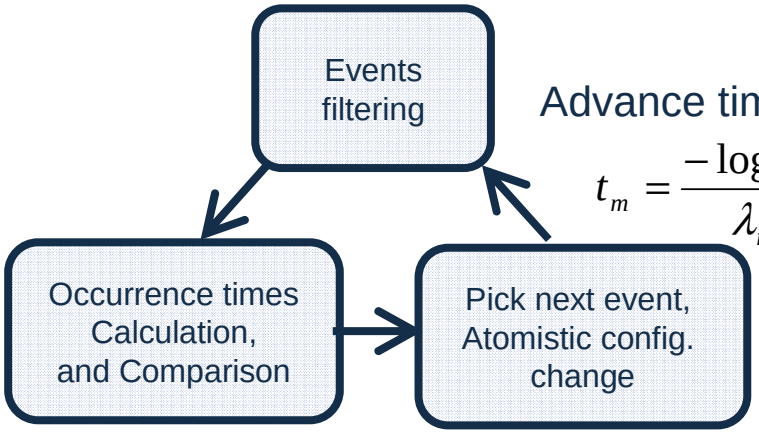


Al on CuO

Growth of reactive materials
Kinetic Monte Carlo with Hot Atoms Trajectories

Limitation of conventional kMC

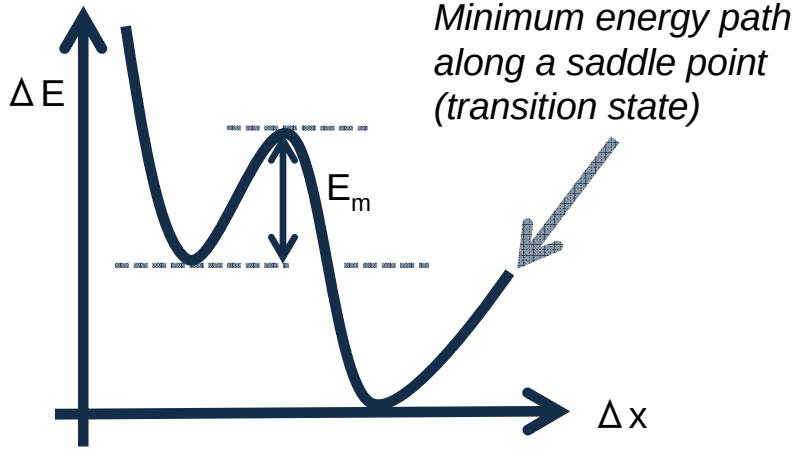
➢**No more valid when 'reactive' materials → why?**



Arrhenius law derived acceptance

$$\lambda_m = \nu . \exp\left(-\frac{E_m^{\neq}}{k_B T}\right)$$

Transition state theory



Minimum energy path along a saddle point (transition state)

Growth of reactive materials
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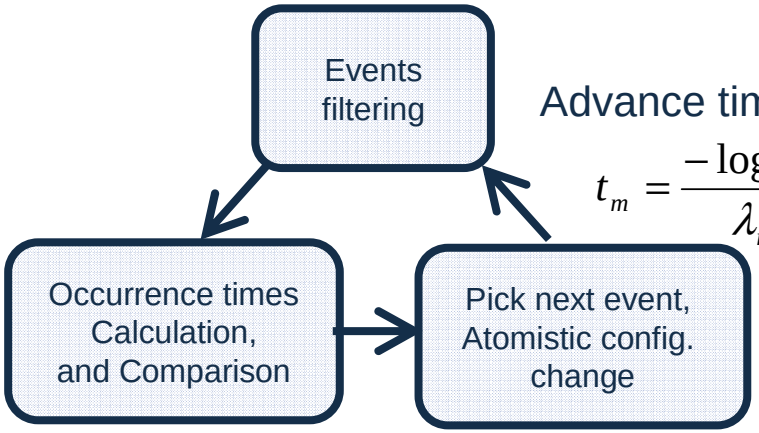

Advance time by

$$t_m = \frac{-\log(Z)}{\lambda_m}$$

Arrhenius law derived acceptance

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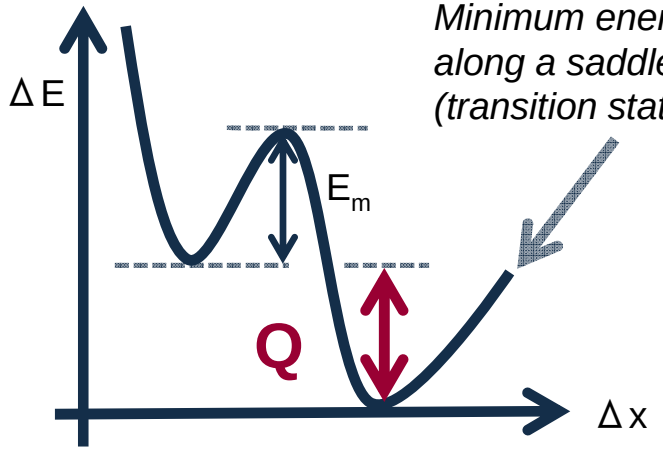
Transition state theory



Minimum energy path along a saddle point (transition state)

Local reactions involving atoms carrying extra energy

Growth of reactive materials
Kinetic Monte Carlo with Hot Atoms Trajectories

Limitation of conventional kMC

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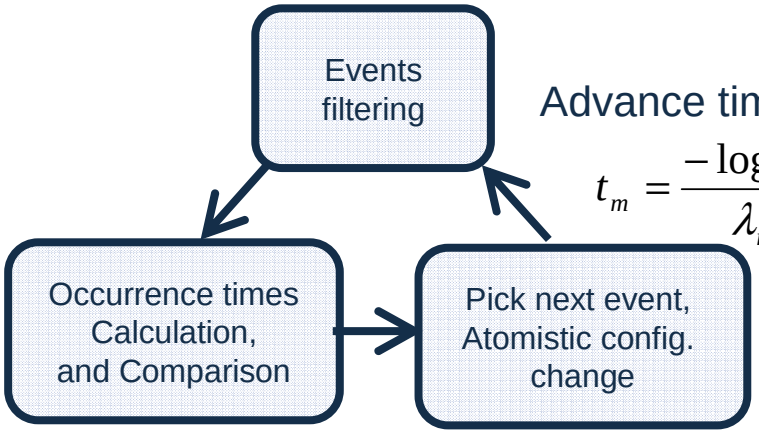

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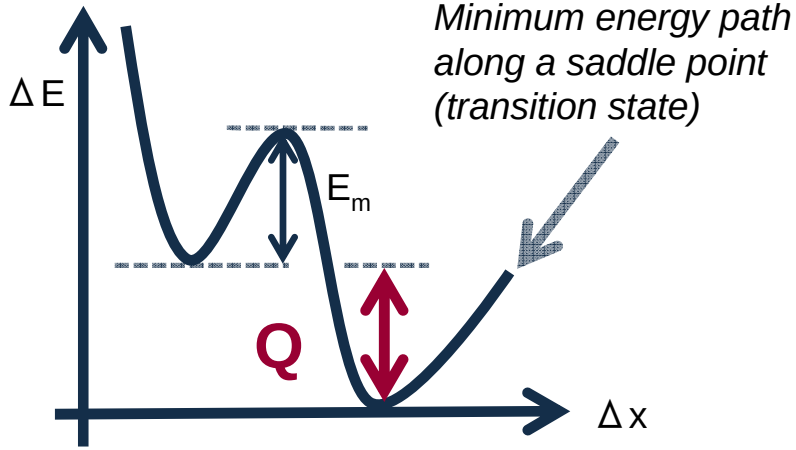

Minimum energy path along a saddle point (transition state)

Local reactions involving atoms carrying extra energy

KMC procedure no more valid when energetic particles are introduced

Energy release can not be neglected

→ New KMC approach
Coupling motion of the energetic atom to the vibrational state of the system

Growth of reactive materials
Kinetic Monte Carlo with Hot Atoms Trajectories

Limitation of conventional kMC

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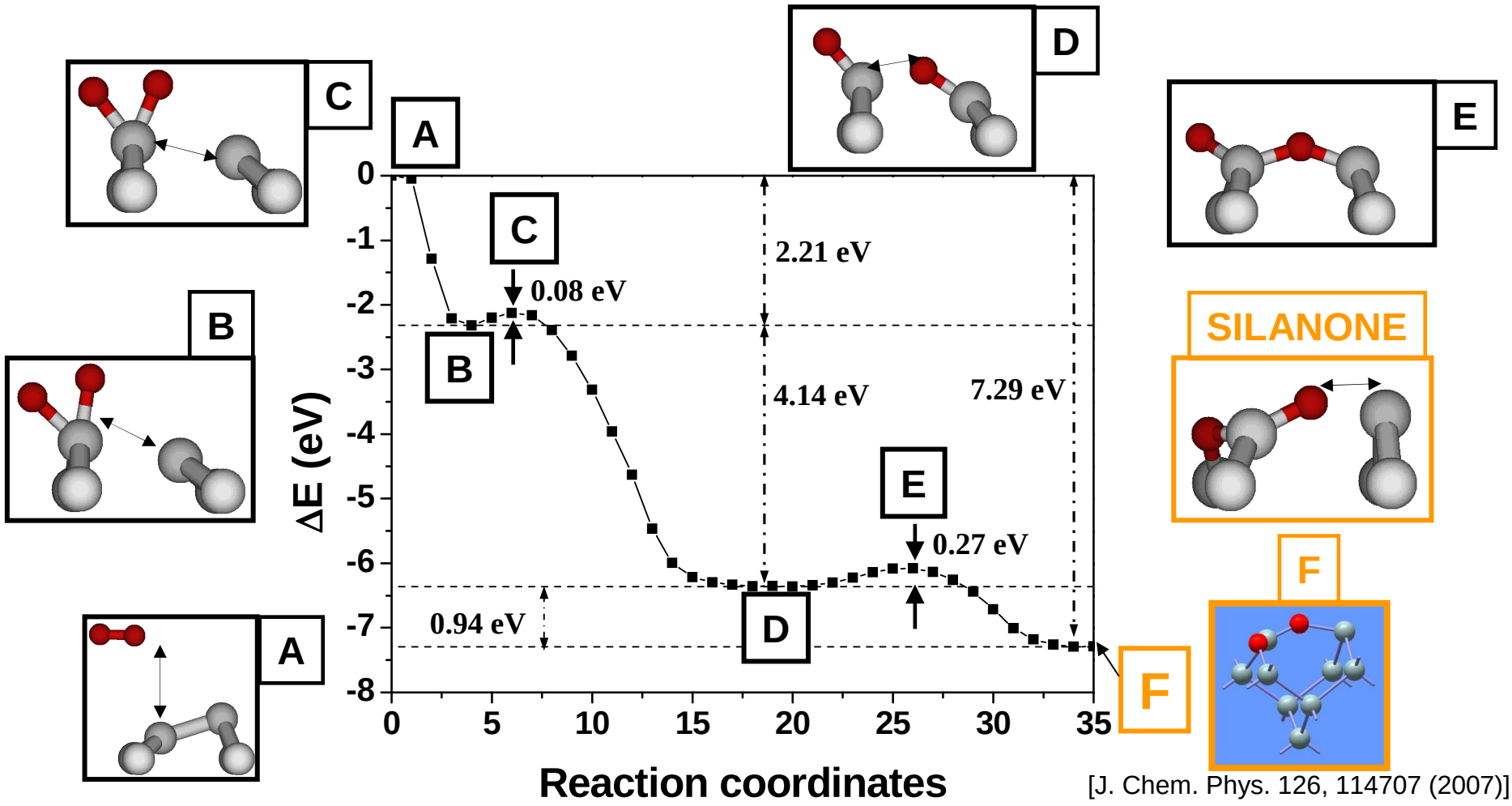
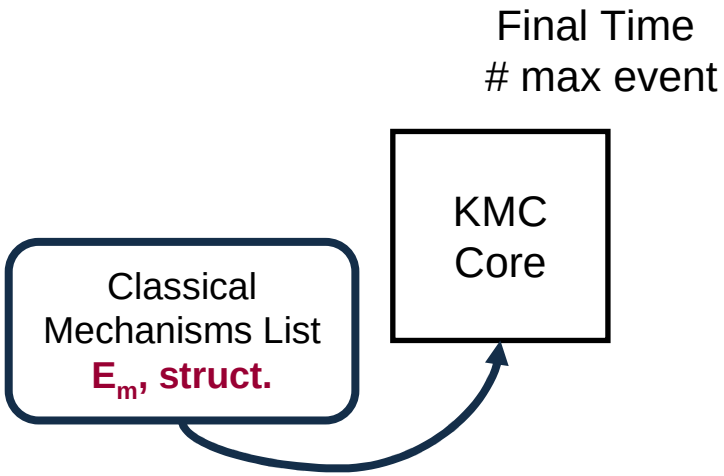


[J. Chem. Phys. 126, 114707 (2007)]

Growth of reactive materials
Kinetic Monte Carlo with Hot Atoms Trajectories

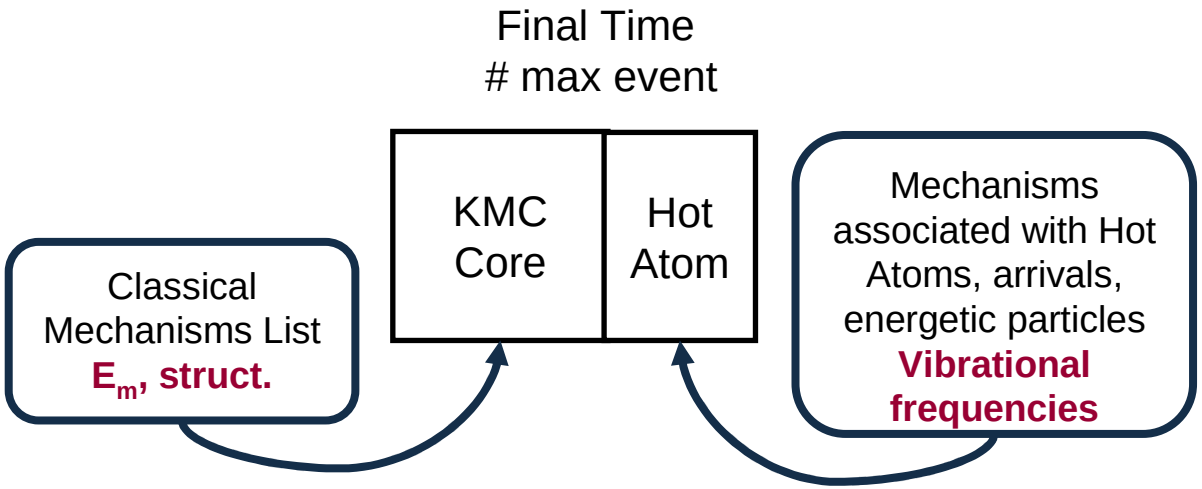
➢**Hyperthermal module for the treatment of atomistic motions and mechanisms related to exothermic reactions**



- Jump driven by activation barrier

Growth of reactive materials
Kinetic Monte Carlo with Hot Atoms Trajectories

➢**Hyperthermal module for the treatment of atomistic motions and mechanisms related to exothermic reactions**



- Jump driven by activation barrier
- Coupling motion of the hyperthermal atom to the vibrational state of the system (phonons) → trajectories

Each normal mode is defined by a vibration angular frequency ω and a reduced displacement vector

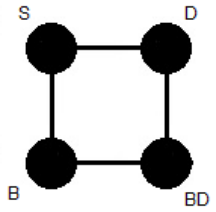
$$|u(t)\rangle = \sum_{k,p} A_{(k,p)} e^{i(k.u-wt)} |k,p\rangle e^{-t/\tau} + c.c.$$

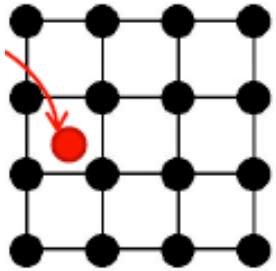
$$A_{(k,p)} = f(u(o), v(o))$$

Growth of reactive materials
Kinetic Monte Carlo with Hot Atoms Trajectories

➢**Hyperthermal module for the treatment of atomistic motions and mechanisms related to exothermic reactions**

- **Validation** on a 2D scheme coupled with analytical phonon description





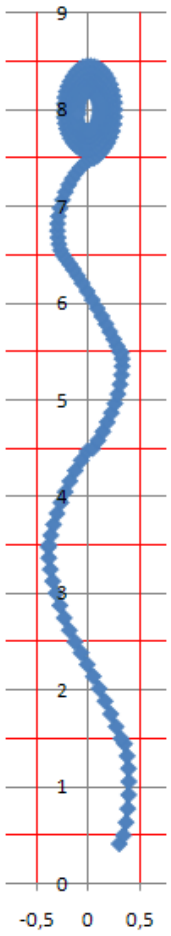
KMC includes:

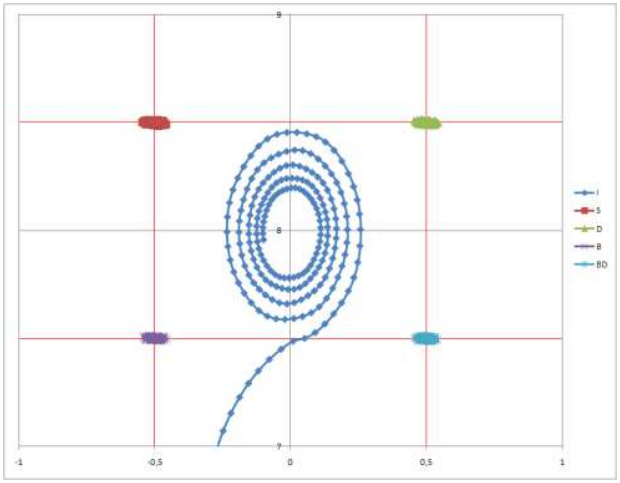
Migrations

Defect generation

One vacancy can be created

Only on the 4 nearest neighbour sites

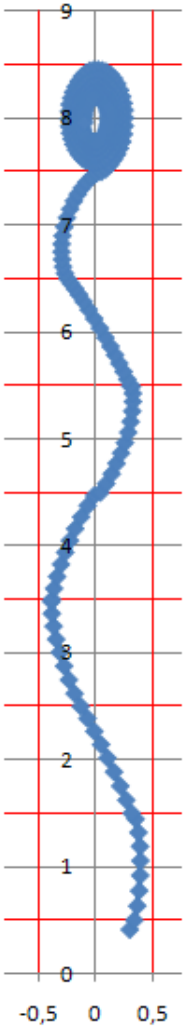


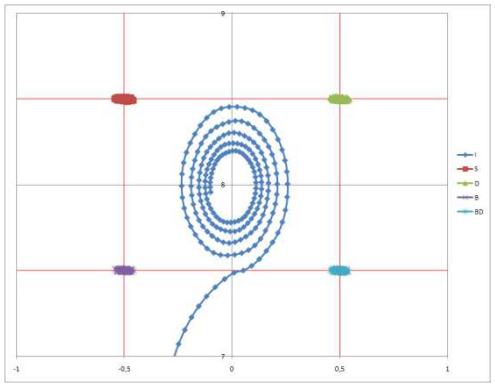


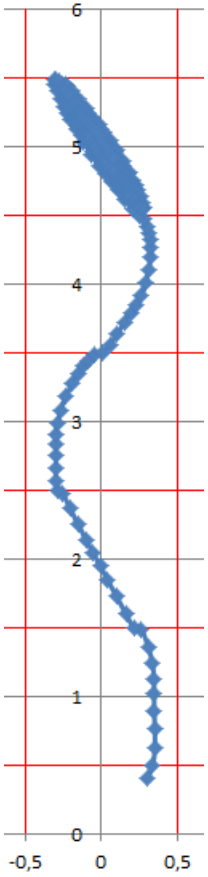
Hyperthermal migration and trapping of an Interstitial atom

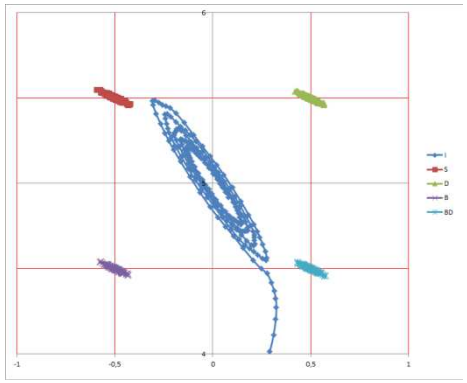
Growth of reactive materials
Kinetic Monte Carlo with Hot Atoms Trajectories

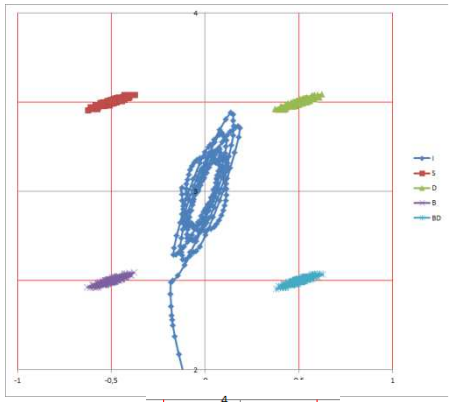
➢**Hyperthermal module for the treatment of atomistic motions and mechanisms related to exothermic reactions**

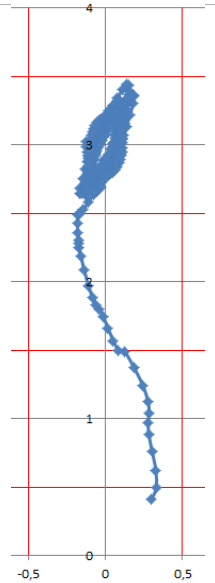








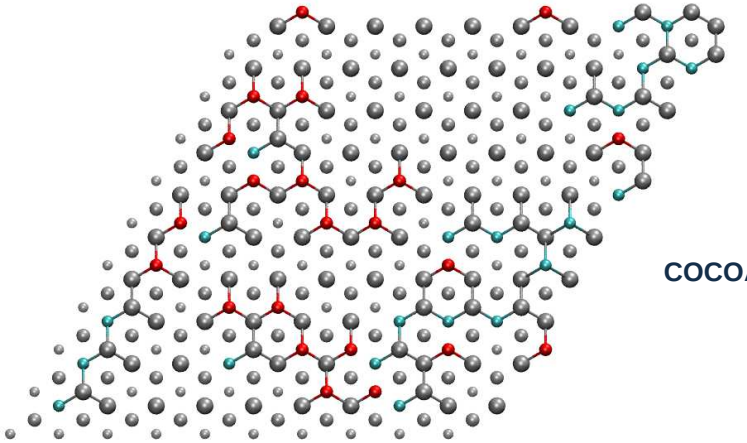




Growth of reactive materials
Kinetic Monte Carlo with Hot Atoms Trajectories

Conclusions

- **New methodology to deal with exothermic reactions in kMC procedure**



COCOA KMC

- **Applications**

  - Mechanisms occurring in material oxidation (Si, Al)

  - Deposition and ignition of nanostructured energetic materials, such as bimetallic (Ni/Al) or metal-oxide (CuO/Al) layers

  - Creation of defects under energetic radiations effects (NIEL: Non Ionizing Energy Loss) as in electronic devices in harsh environments, particularly in spatial applications or subject to solar wind.

Growth of reactive materials
Kinetic Monte Carlo with Hot Atoms Trajectories

Thank you

Sujet de thèse proposé au LAAS-CNRS

- **“ Vers une intégration optimisée des matériaux énergétiques : Modélisation multi-échelles et multi-physiques de la croissance de multicouches Al/CuO “**

- A diffuser largement … Merci