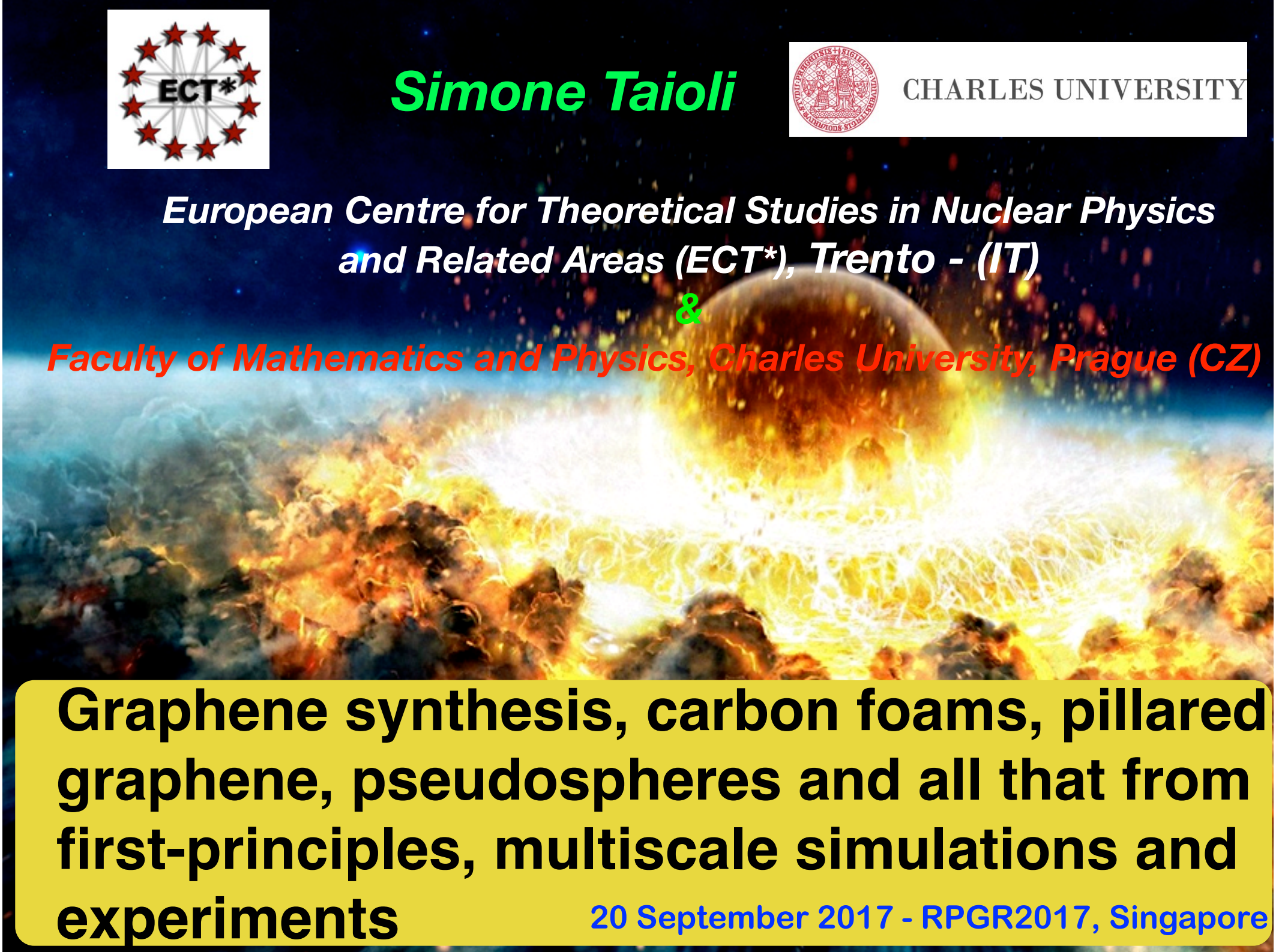

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&

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Graphene synthesis, carbon foams, pillared graphene, pseudospheres and all that from first-principles, multiscale simulations and experiments

20 September 2017 - RPGR2017, Singapore

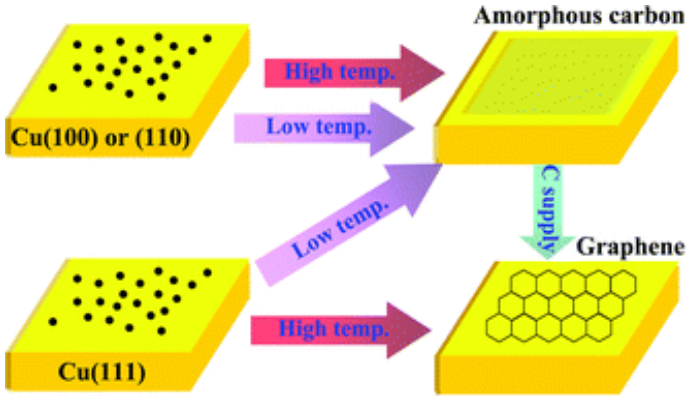
Motivation and outline of the work

Can we think a more exotic way, cheaper and lower in temperature, to produce SiC and graphene? Supersonic Molecular Beam Epitaxy (SuMBE): how to grow materials at low T in a way conceptually different from what used so far.

Due to the rarity in nature, SiC and graphene are typically synthesised using heteroepitaxy on Si or CVD on metals.

These procedures are plagued by three similar drawbacks:

- high processing temperature (T>1200 K)
- high lattice/thermal exp. coeff. mismatch
- Si diffusion through the SiC film or C segregation



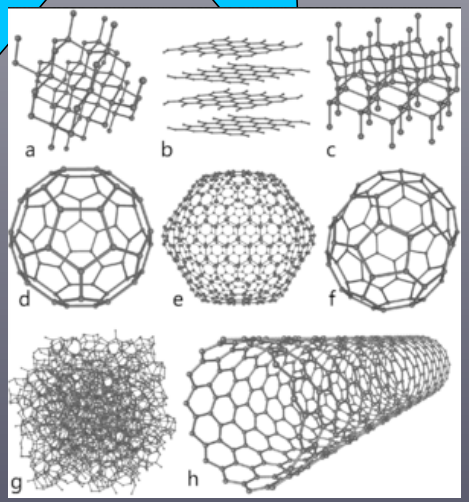
Temperature can cause defects and high cost, no scalability

Can computational modelling help our understanding (and thus controlling and designing) the growth mechanisms of materials?

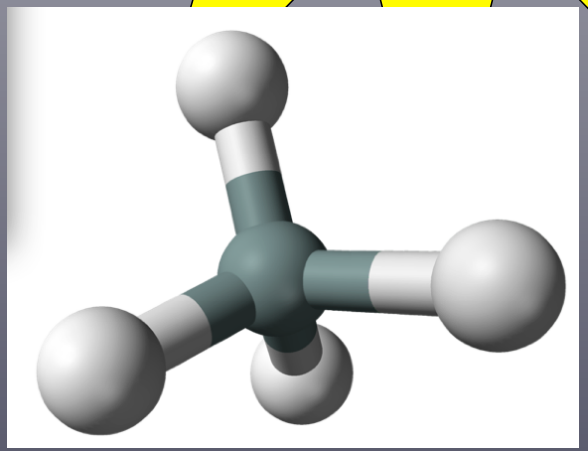
First example: SiC growth at room T

No doubt you need silicon and carbon to build SiC

Carbon exists in many shapes



Silicon comes as inorganic compounds silane family or bulk



+ = ?

Our building blocks: Si(111) and C_{60}

Si(111) reconstructed surface: cleave along 111 direction

GOOD FOR SuMBE:

19 dangling bonds make this surface very reactive

GOOD FOR SuMBE:

No hydrogen or oxygen

Mechanically and chemically stable but not totally unreactive (electronegative) as the carbon atoms are sp^2-hybridized

Cheap, sublimates below T=800 K

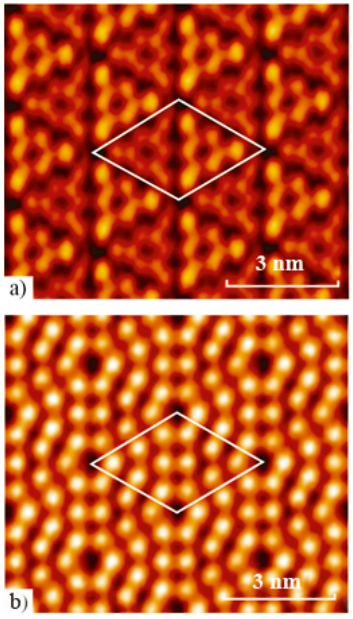
Simple to accelerate and massive

ELECTRONIC PROPERTIES of C_{60} :

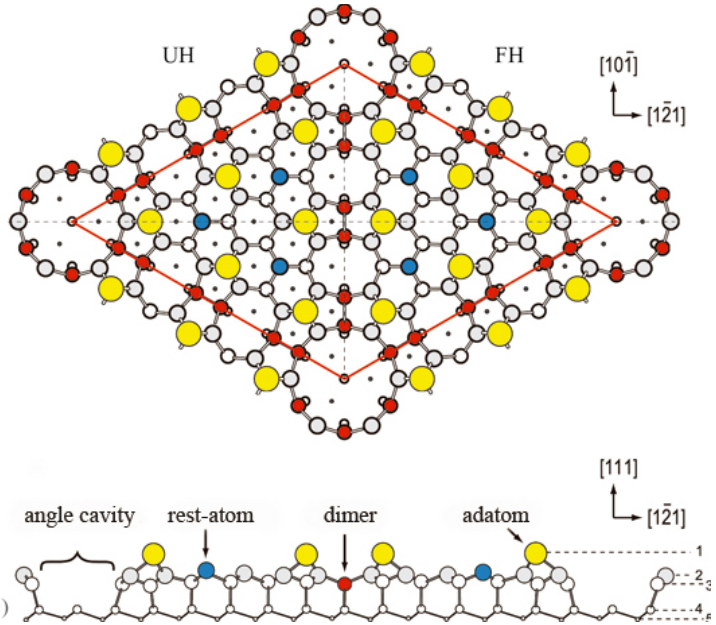
Semicond: 1.6 eV in the ground state

Aromatic but not superaromatic (K)

STM image

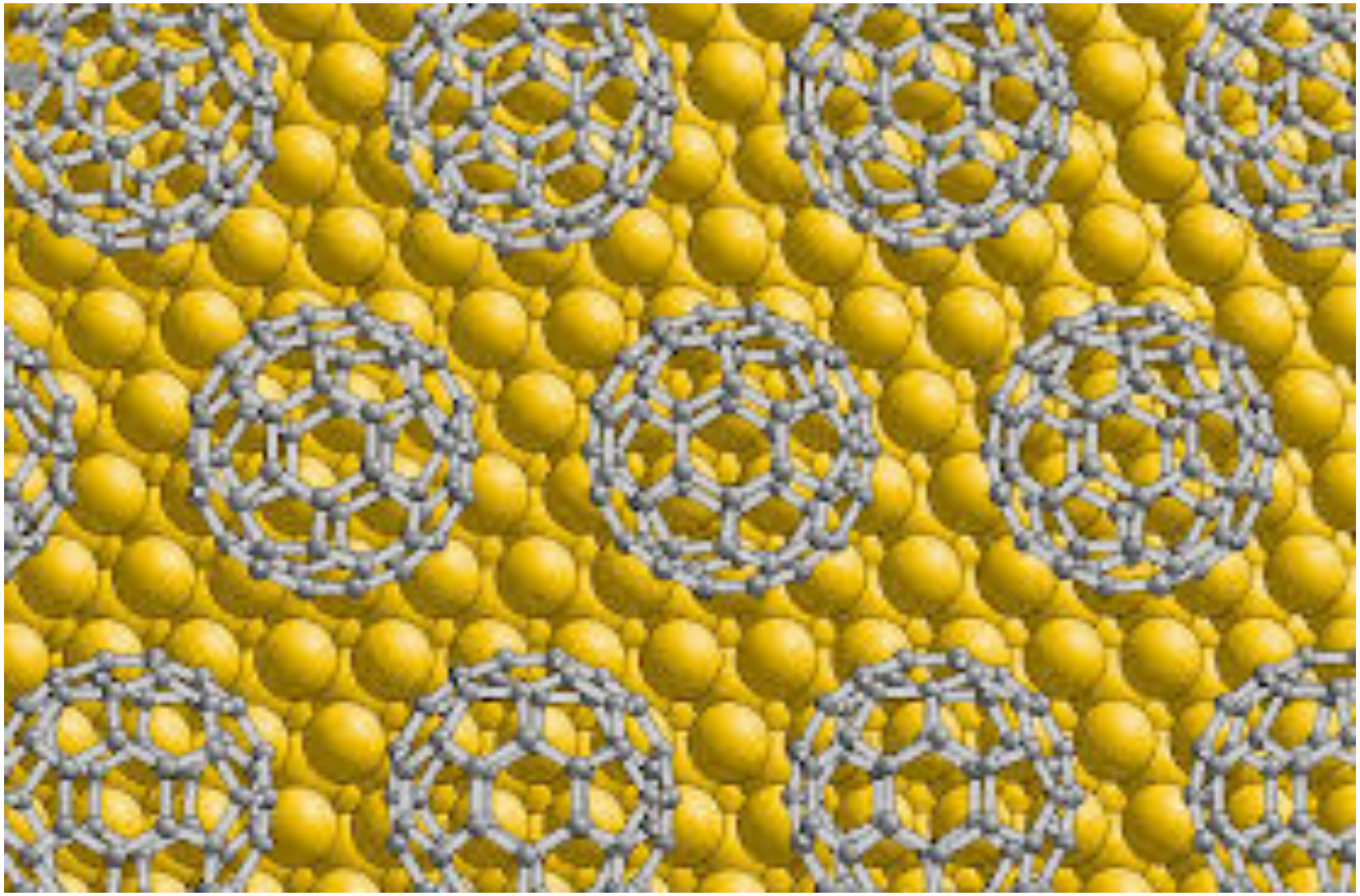


A success story of DFT



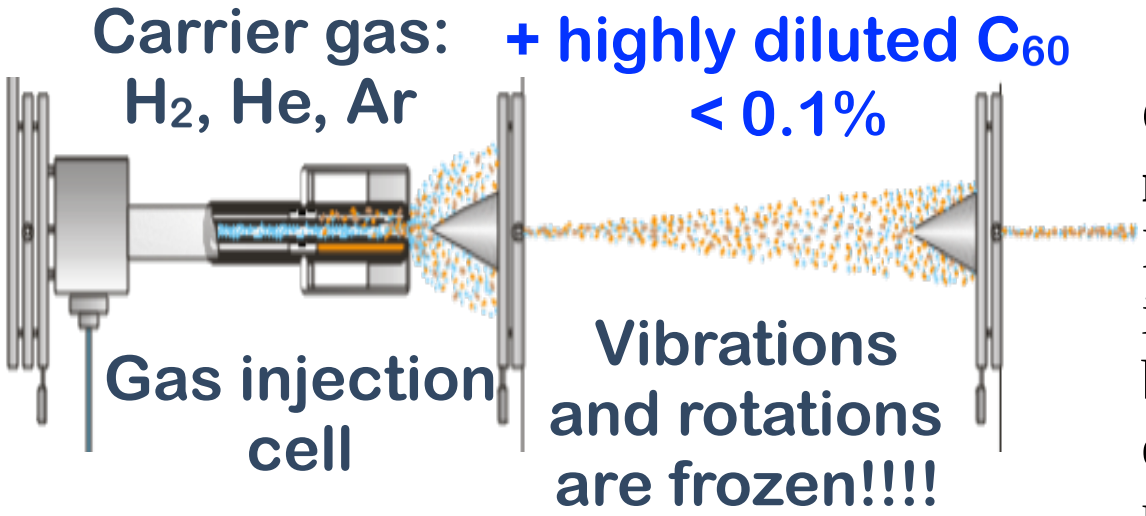
Luca Pacioli "De Divina proportione" 1509

NO WAY!!!



The SuMBE approach

Highly diluted supersonic beams are appealing for both organic thin films and cluster-assembled nanomaterials depositions.



- A first experiment of deposition (carrier gas: He) gave evidence of SiC islands formation at 800 K for a C_{60} kinetic energy of 20 eV (not below though).

- A second experiment (carrier gas: H_2) at higher C_{60} kinetic energy (30 to 35 eV) formed SiC islands at room T.

Continuous supersonic molecular beam source

In a quartz tube an inert carrier gas is seeded with species sublimated by Joule heating. The mixture then expands into vacuum through a nozzle. Kinetic energy can be tuned by changing the carrier gas and the seeding parameters (source temperature, gas inlet pressure).

TRANSLATIONAL KINETIC ENERGY

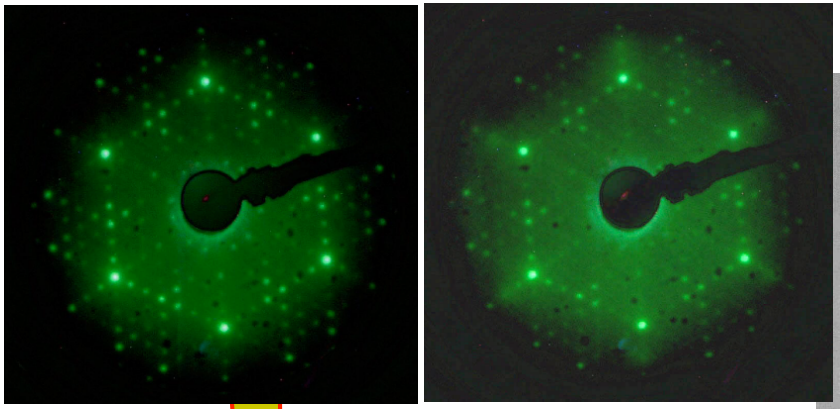
Aerodynamic acceleration up to tens of eV!!
For MBE, KE~0.05eV

$$E^i_K \approx (m_i/\langle m\rangle)T_0$$

$$\langle m\rangle = \Sigma_i X_i m_i$$

C_{60} /Si(111)7x7 @ RT: structural properties

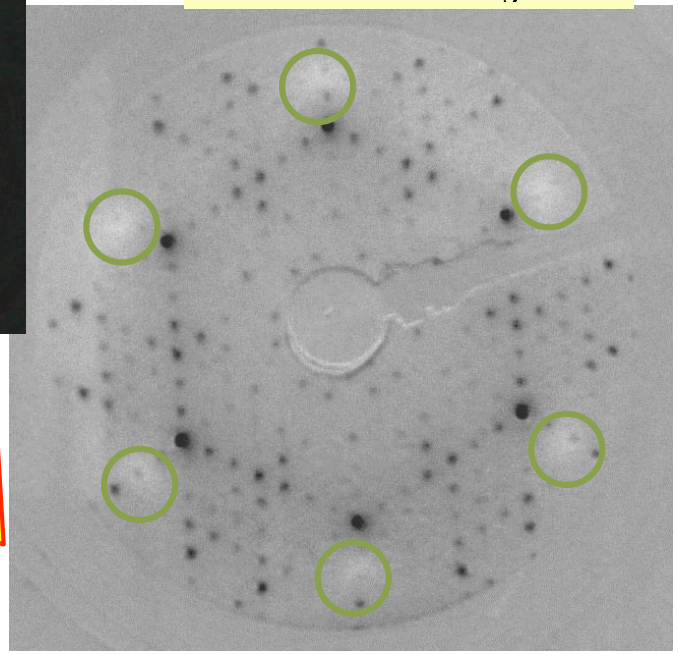
0.70 ML C_{60}/Si(111)7 × 7 film formed @ 35 eV KE

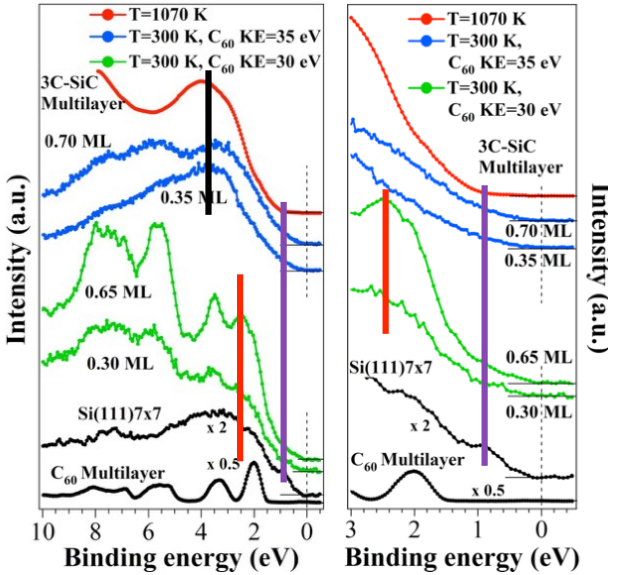


-20% lattice parameter vs. Si, typical of **3C-SiC!**

Nanoislands >20nm

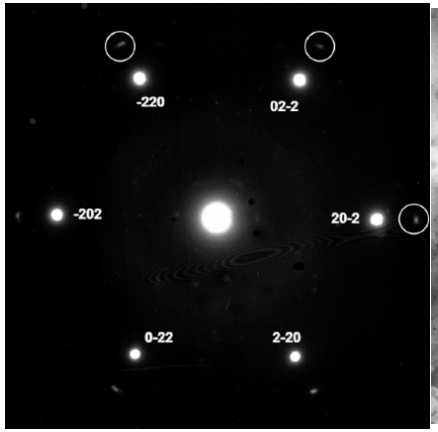
LEED analysis

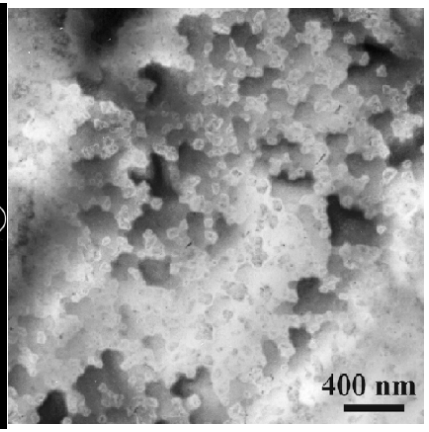




Si(111) bright spots and weak reflections from the 3C-SiC phase (circled spots)

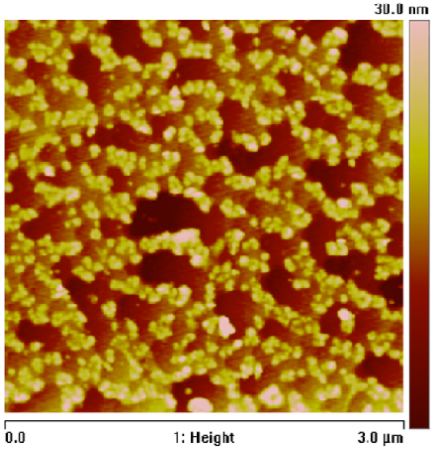
TEM analysis



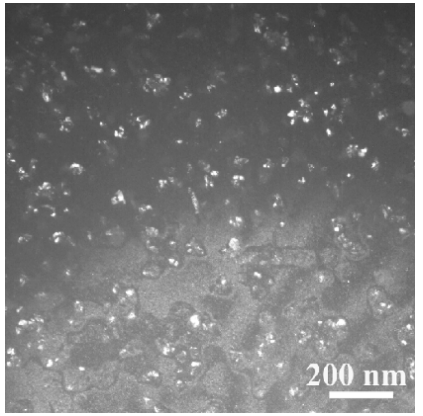


JACS 134 (42), 17400 (2013)

AFM analysis



3C-SiC nanocrystalline islands, <10nm, with a completely relaxed lattice!



CAKE WITHOUT COOKING IN 3 MOVES

Kinetically driven synthesis of SiC (obtained by supersonic beams implanted with C_{60}) is a promising technique able to reduce drastically the growth temperature and increase structural order…for the first time SiC ordered domains have been observed at such a low temperature.

Open questions for theory

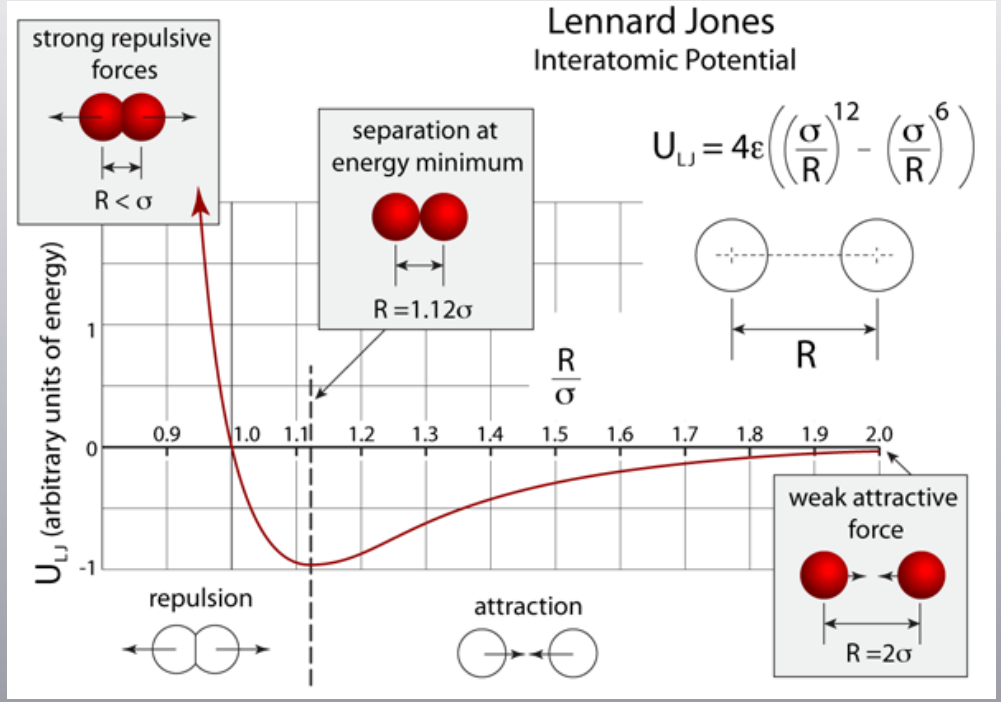
What is the nature of the chemical-physical processes at the film/Si interface?

Can we model the SiC synthesis by using classical, quantum mechanics and multiscale approaches?

What is the C_{60} beam KE threshold for the Si-C covalent bond formation?

First approach: Molecular Mechanics

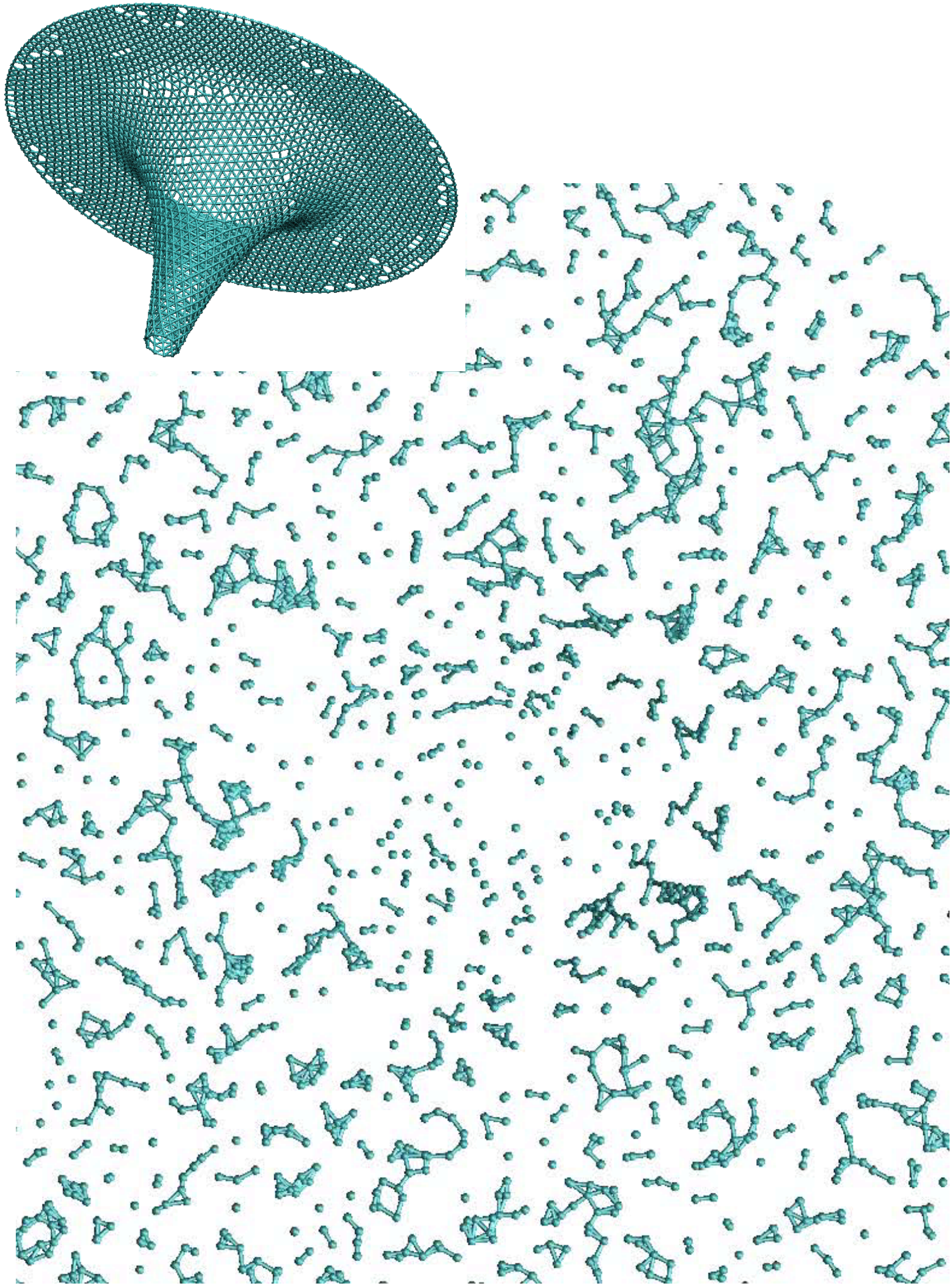
Hard spheres interacting through empirical pair-wise potential (LJ)



Computer simulation can find the equilibrium structure or dynamical properties of many carbon-based materials and work particularly well on rare-gas elements, such as helium and argon, due to their closed shell electronic structure.

We can do better and use 3-body interaction terms (Stillinger-Weber, Tersoff-Brenner, ReaxFF)

$$\Phi(1,..,N) = \sum_i v_1(i) + \sum_{\substack{i \\ i<j}} v_2(i,j) + \sum_i v_1(i) + \sum_{\substack{i,j,k \\ i<j<k}} v_3(i,j,k) + ...$$

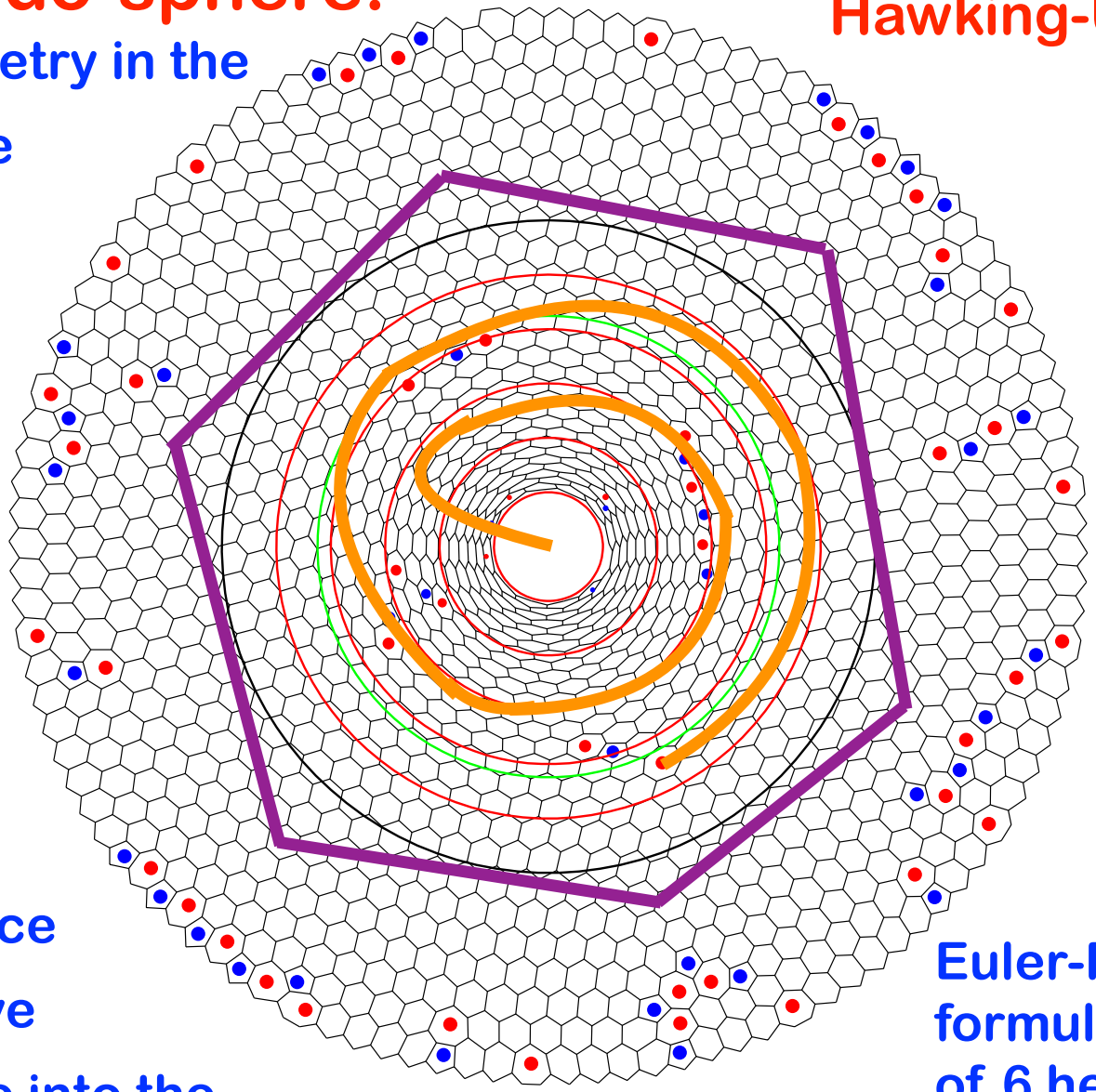


Intermezzo : Graphene trumpets

Beltrami pseudo-sphere:

Lobachevsky geometry in the Euclidean 3D space

Find a signature of the Hawking-Unruh effect



Embedding a surface of constant negative Gaussian curvature into the real Euclidean 3D-space to mimic a black-hole

Euler-Poincare formula: an excess of 6 heptagons with respect to pentagons

J. Phys.: Cond. Mat. 28 (13), 13LT01 (2016)

Area = 2.4 × 3.8 = 9.12

amorphous glycine-rich
(CHARMM27)

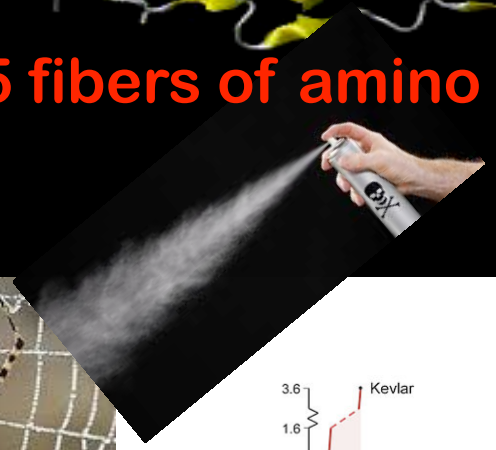
graphene
(DREIDING)

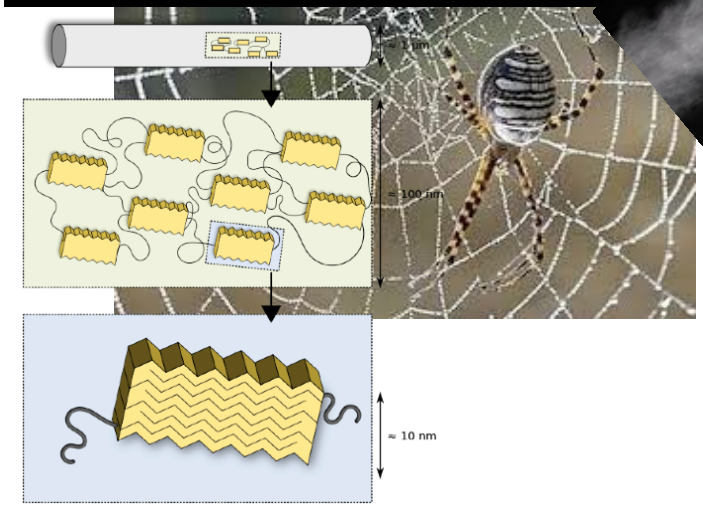
quasi-crystalline poly-alanine central region
(CHARMM27)

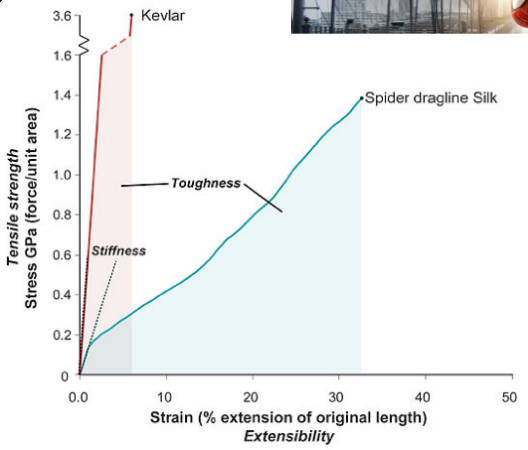
F equally distributed

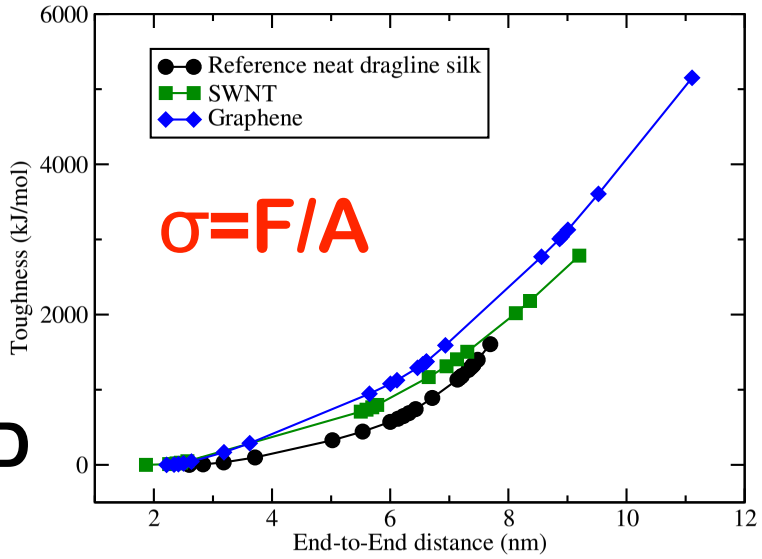
F equally distributed

15 fibers of amino acids MASP1







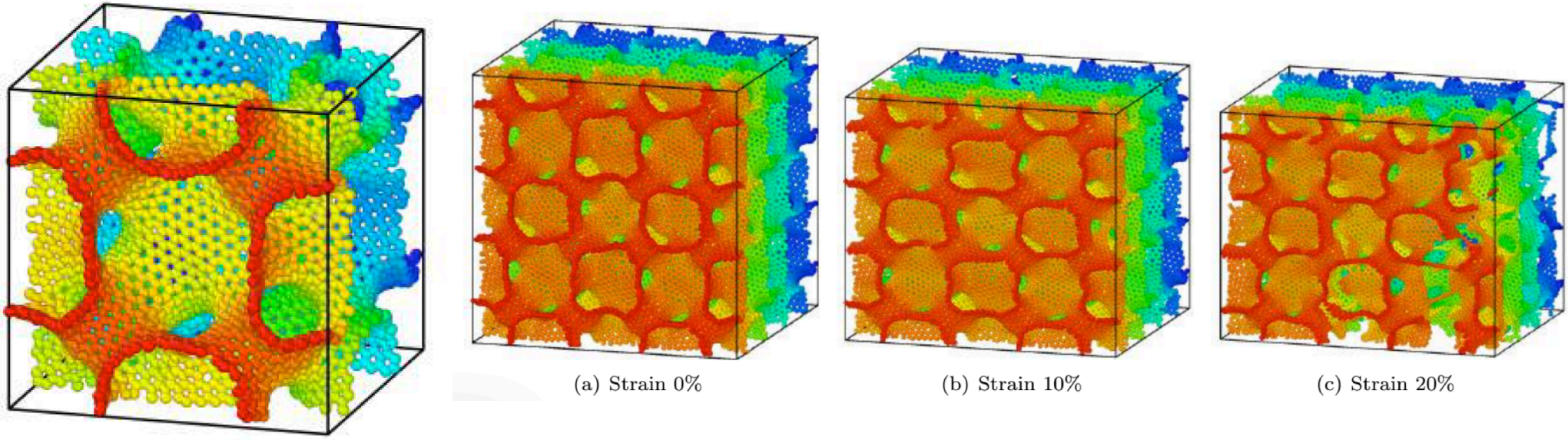


After CG minimization, we perform 150 ps MD runs at T=10K, followed by 500 ps at T=300K

ε=distance between COM of head and tail/original length

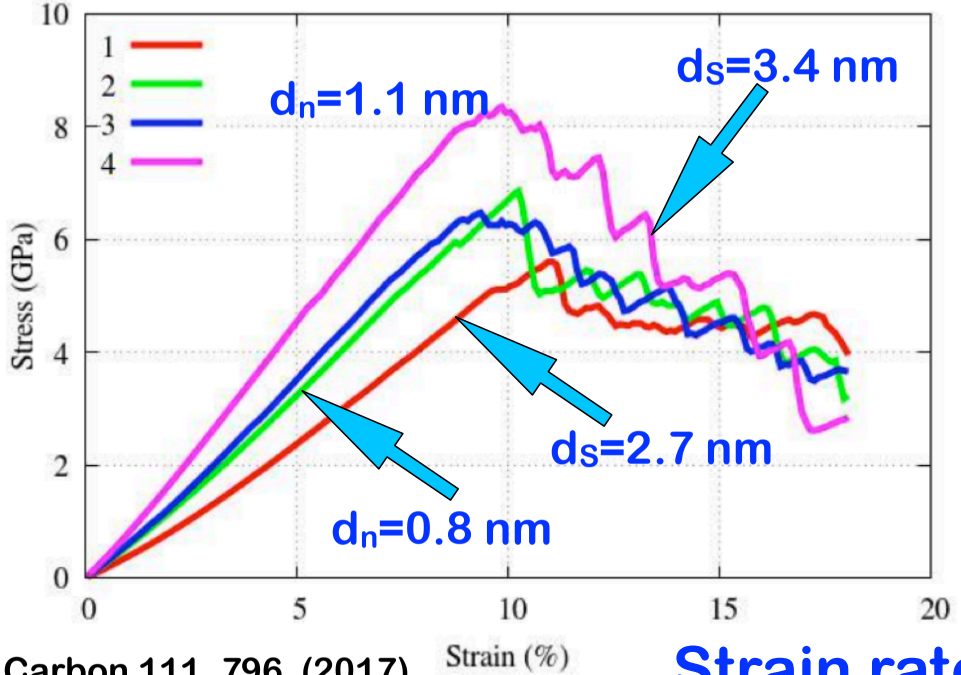
2D MATERIALS 4 (3), 031013/1-9 (2017)

Graphene foams

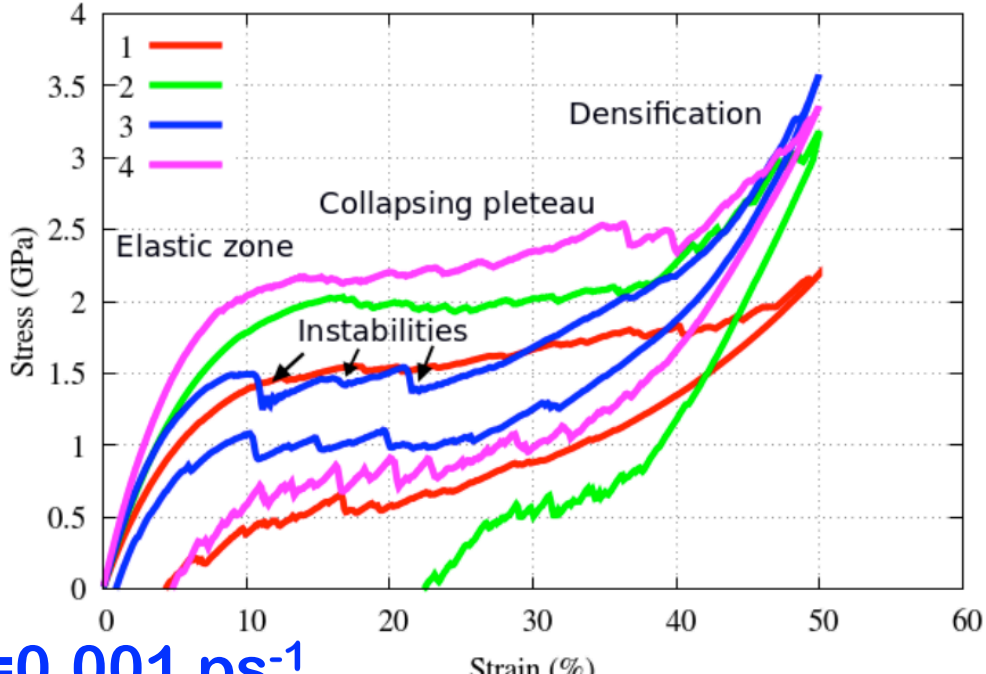


(a) Strain 0% (b) Strain 10% (c) Strain 20%

Tension [100]



Compression [111]

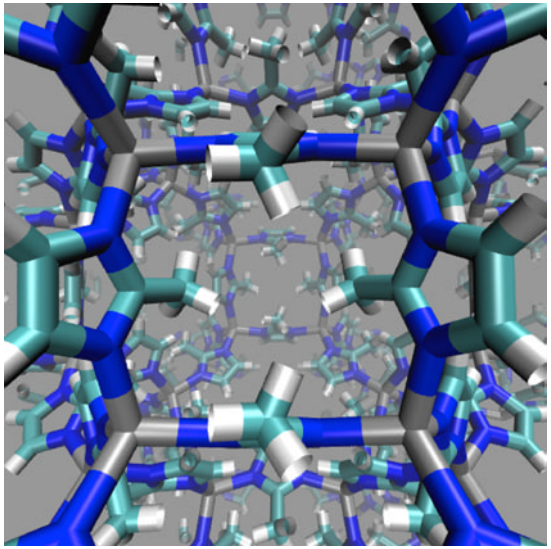


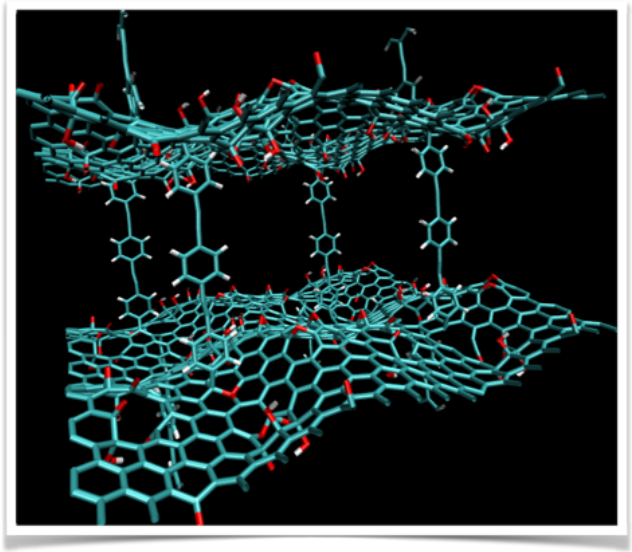
Carbon 111, 796 (2017)

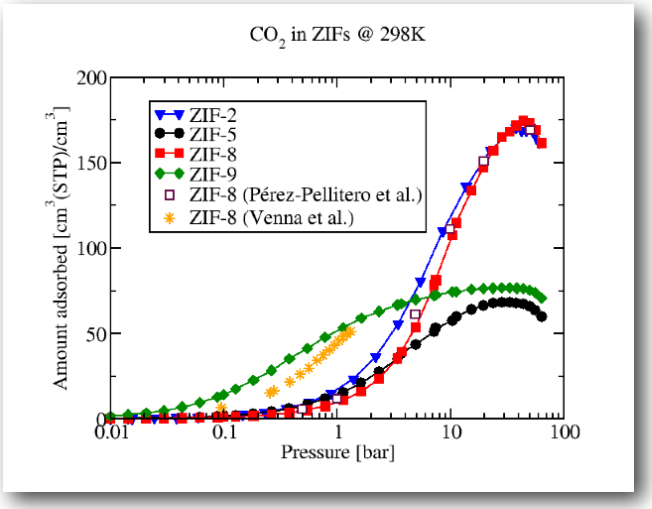
Strain rate=0.001 ps^{-1}

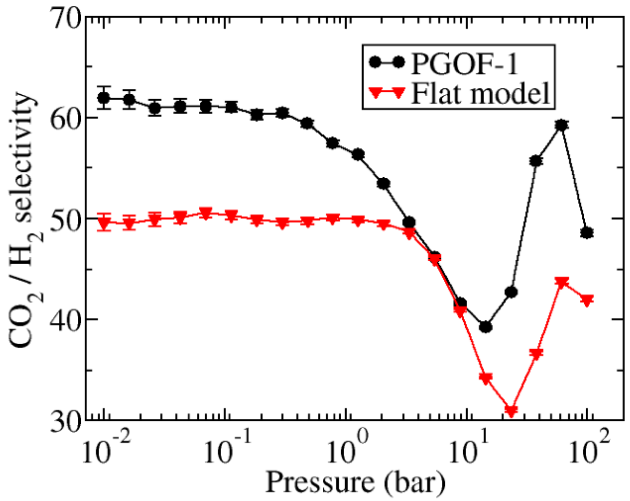
Pillared GO

ZIF, MOF and PGO for gas separation and storage



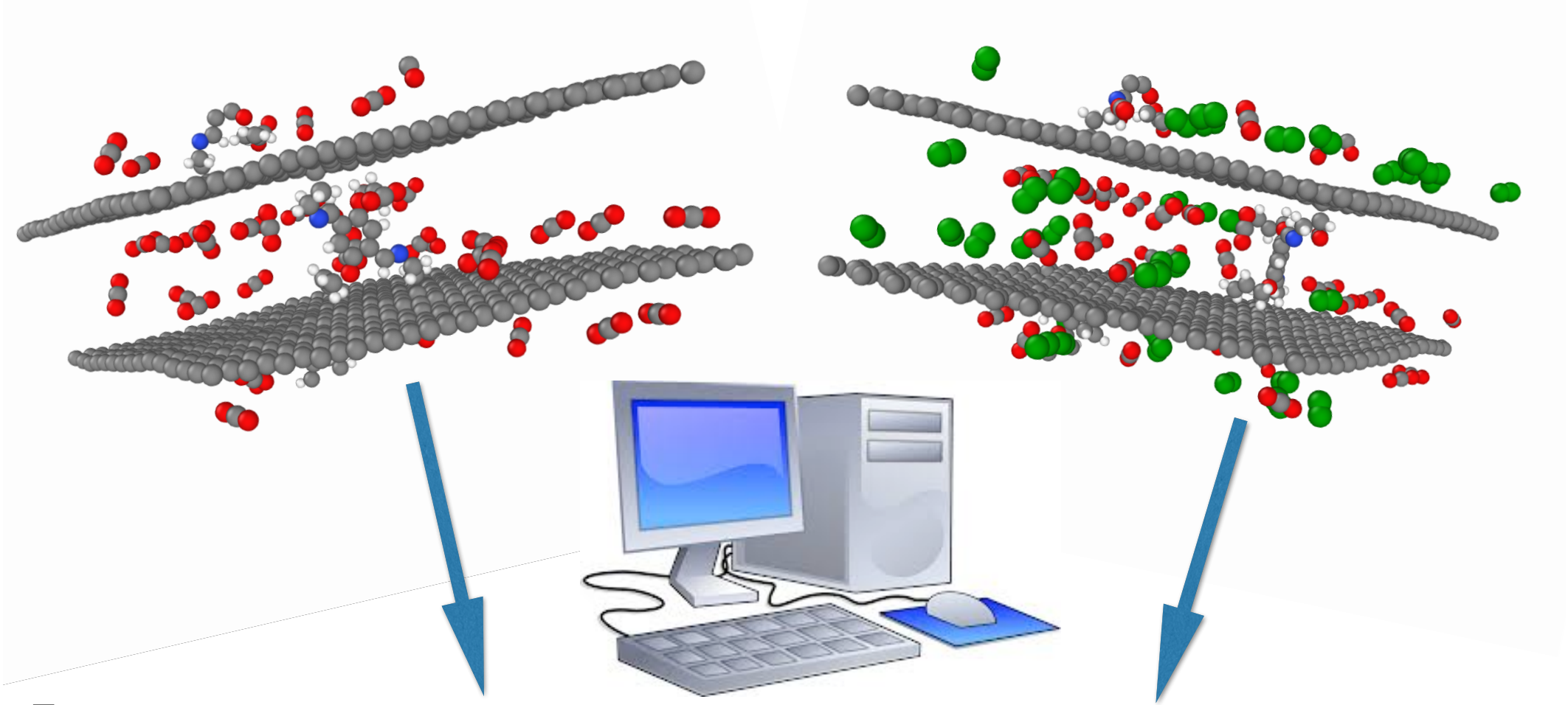


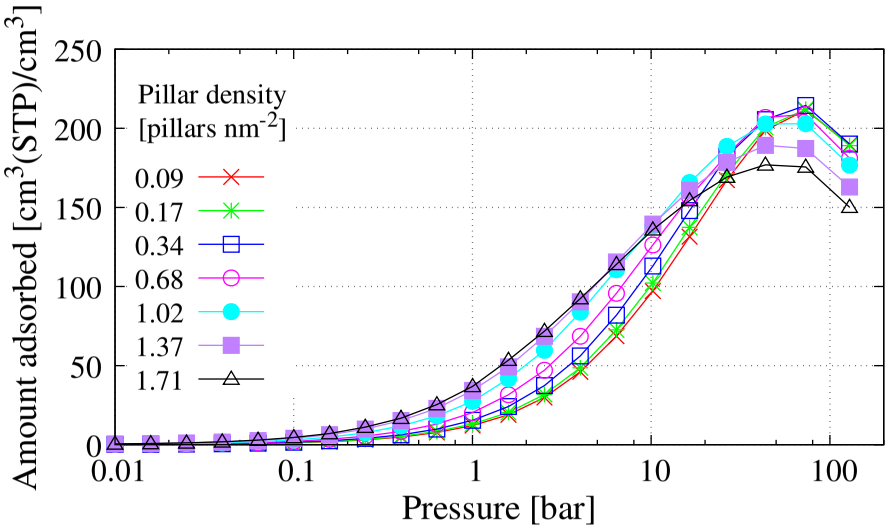


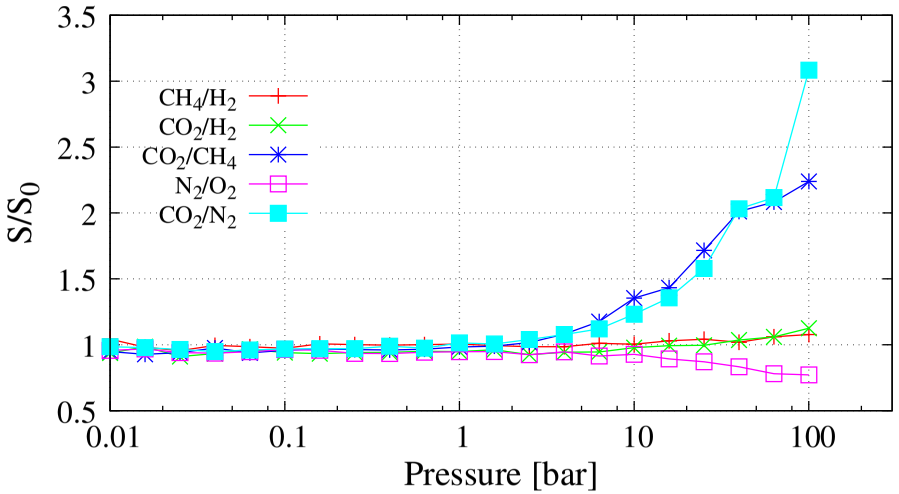


GC Monte Carlo techniques

- Dispersion (LJ)
- Interaction (DREIDING or Universal Force Field) + charges (from DFTB simulations)
- Grand canonical ensemble (fixed **temperature**, cell **volume** and **chemical potential** = external pressure)
- Usual insertion/deletion + translation/rotation moves
  - Metropolis leads to equilibration





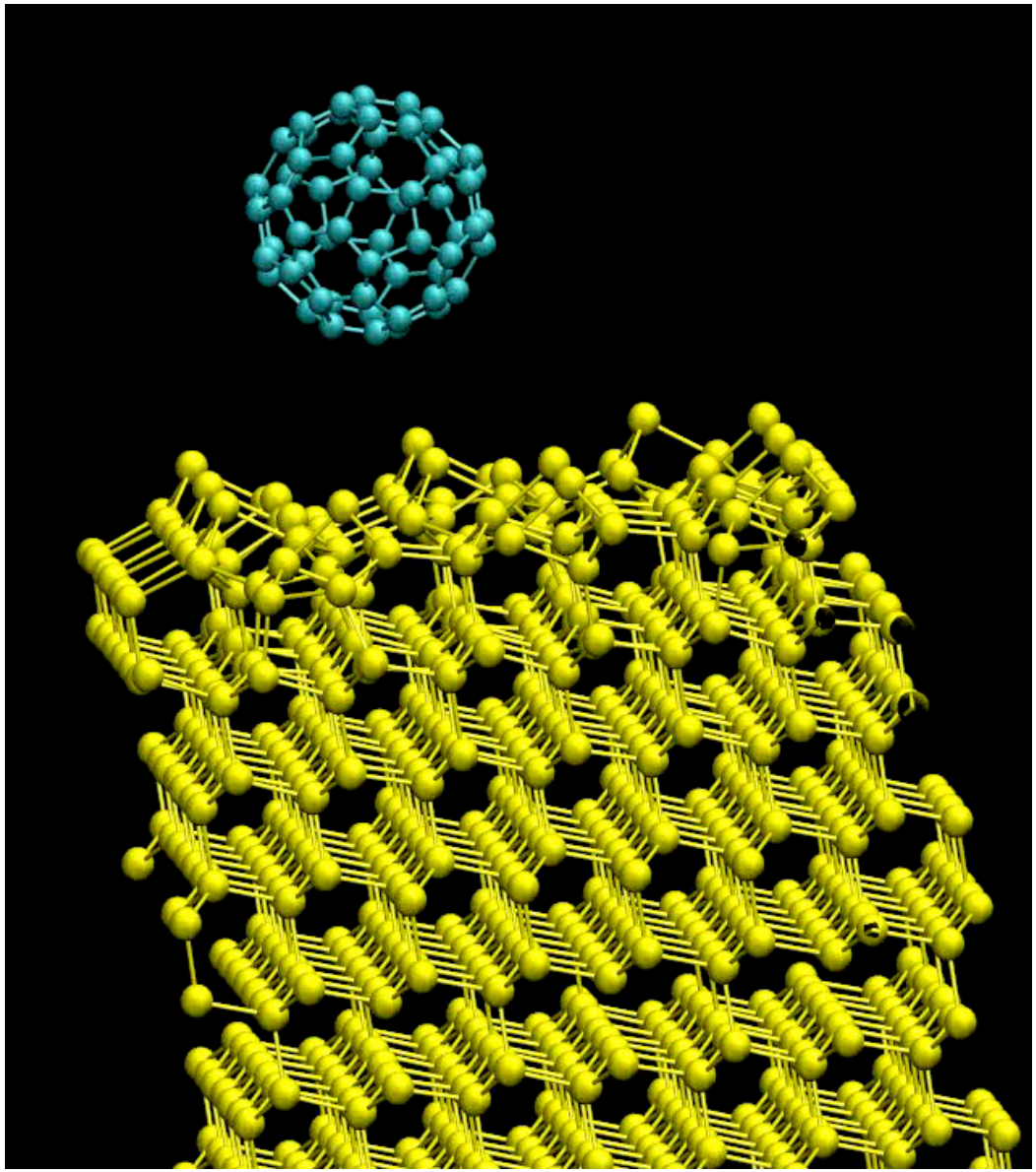


J. Phys. Chem. C 119, 1980 (2017), Mic. Mes. Mat. (2017) - arXiv preprint arXiv:1707.00571

Application of classical RT MD (450 eV)

REGIMES AT ROOM T

1. < 30 eV: CLUSTER DEPOSITION AND CHEMISORPTION OF THE CLUSTER AS A WHOLE
2. 30-100 eV: SURFACE PENETRATION
3. 100-300 eV: PARTIAL FRAGMENTATION
4. 300-500 eV: SURFACE SPREADING AND CAGE DISRUPTION
5. 500-1000 eV: CRATER FORMATION
6. > 1 KeV: SPUTTERING



- Computer simulations are in complete disagreement with experiments.
- Si structural order is kept. No evidence of C_{60} cage breaking, with superficial permeation up to an energy per atom 10 times the experimental one.

C_{60} impact on Si seems totally out of reach of classical molecular dynamics. This model has frozen electronic structure and potential is simple pair (no chemistry or description of out-of-equilibrium)

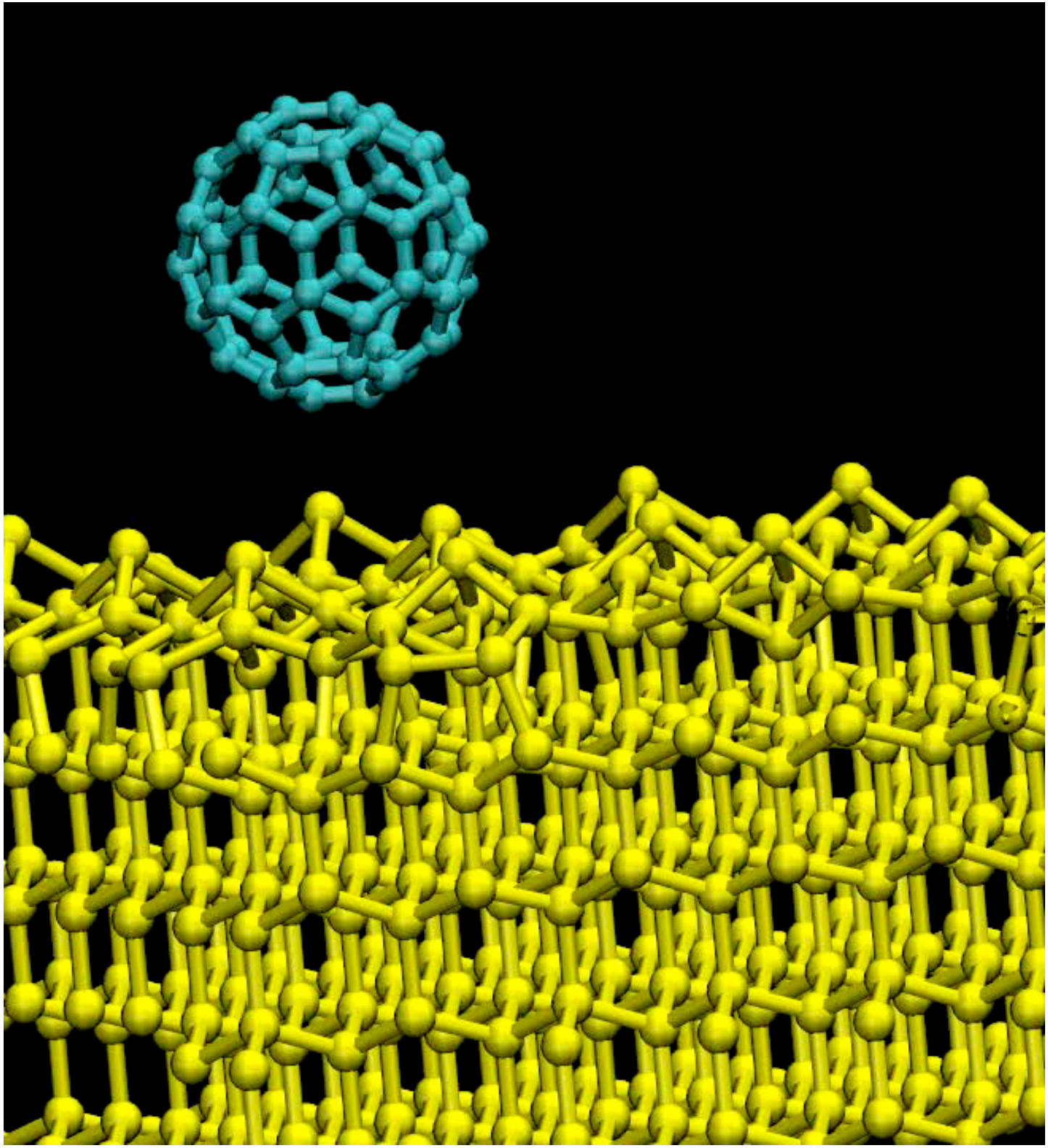
Bach: Sonata n 2

BO-DFT
AT 50 eV

Ex-corr:
LDA

PP:
LDA/GGA
PAW 500 eV
cut-off

Sampling:
Γ point



Can DFT be so much in error? What is missing?

Is the BO one-electron state model reliable for SiC?

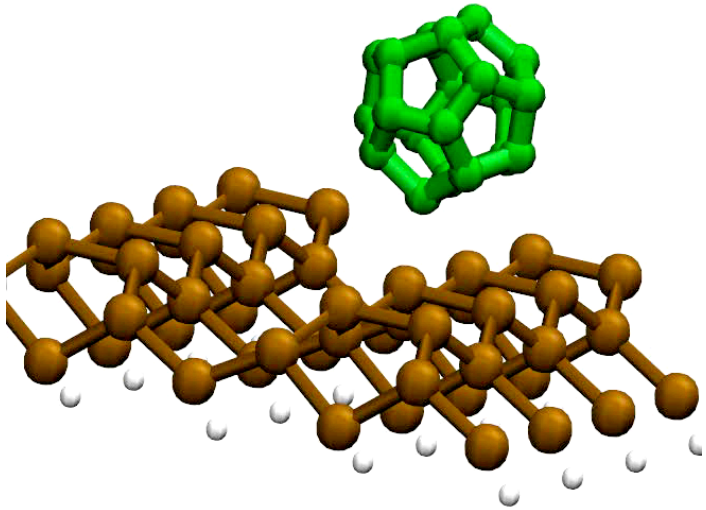
Ionic vibration period: 10^{12} Hz **Electronic transitions freq.: 10^{17} Hz**

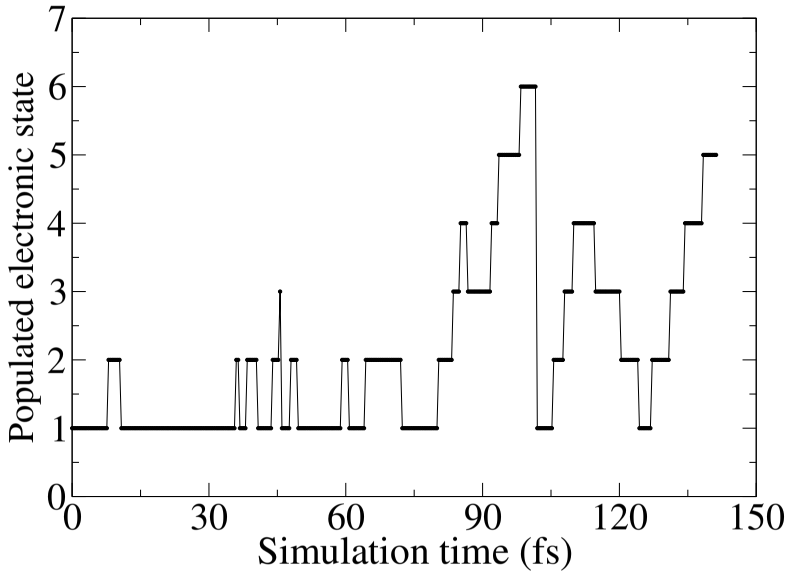
$$\chi = \tau_p/\tau_e = 10^5$$

1.6 eV band-gap corresponds to emission in the region of 10^{15} Hz, collision time scales are of the order of few femto-seconds:

$$\chi \simeq 1$$

Timescales are comparable!!! Electrons cannot relax fast enough to the ground state relative to the instantaneous configuration of the nuclei.





Beethoven: Ode to joy

Forces used in the MD simulation are calculated on the pure adiabatic PES populated at the present MD step.

The electrons "lag behind" the nuclei during the collision. PES on which nuclei move changes significantly, possibly allowing for cage breaking at lower kinetic energy.

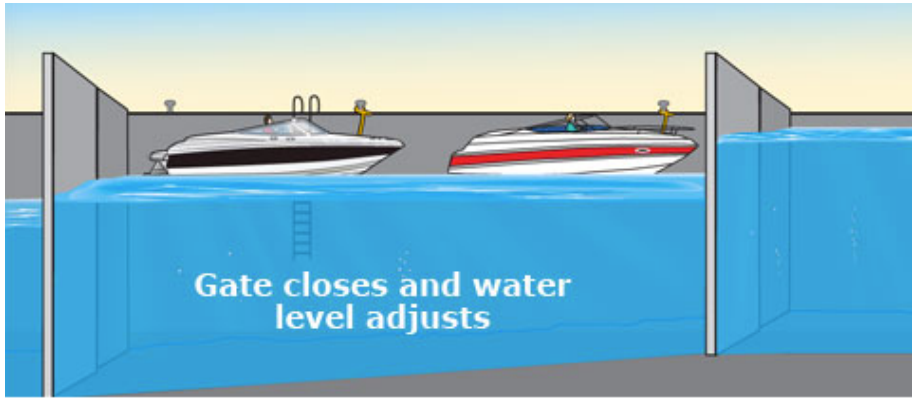
J. Chem. Phys. 138 (4), 044701 (2017)

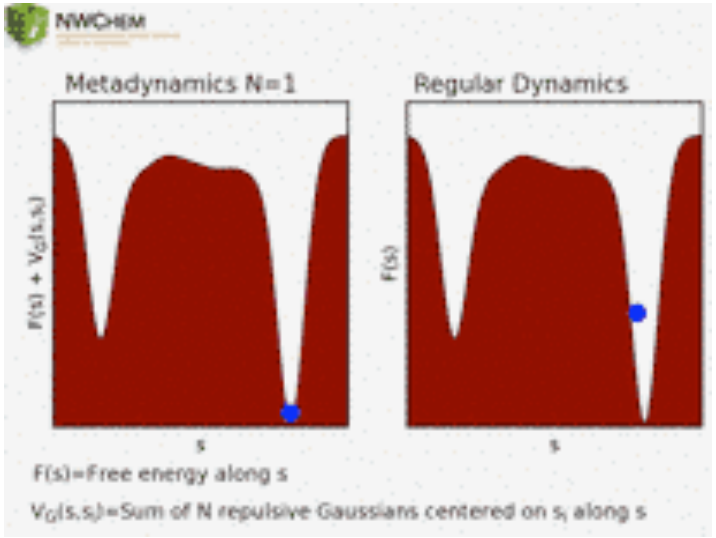
First multiscale: metadynamics

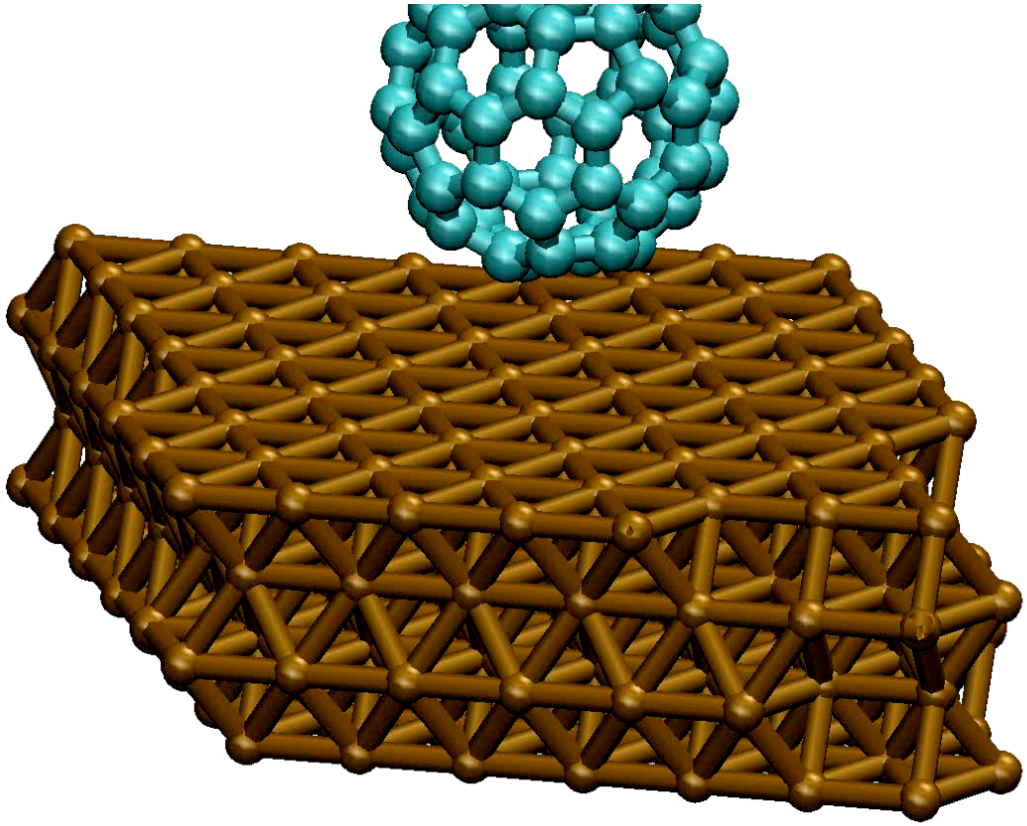
Large potential barriers (long waiting times) make it difficult to explore configurational space (typically > 1 microsec)

Metadynamics has been developed as a tool to increase sampling efficiency.

Drop repulsive Gaussians in the places already visited until the basins are filled and the system jumps to another place in the configuration space (same trick used for ships with gates)



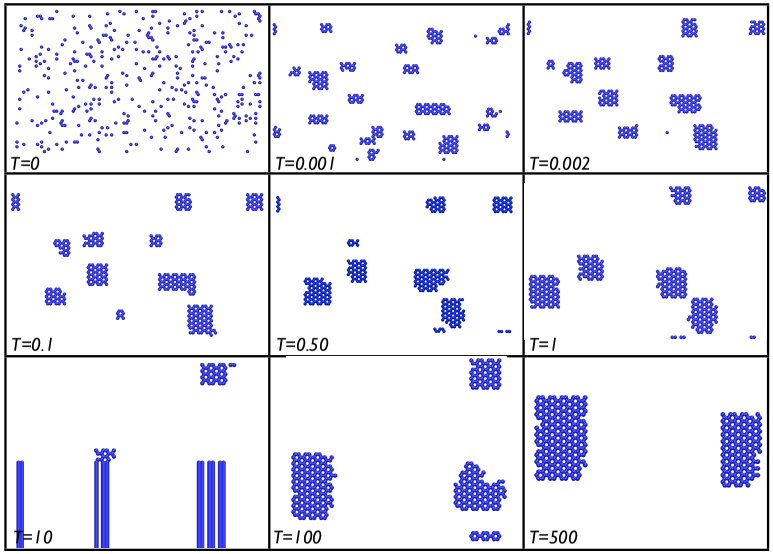


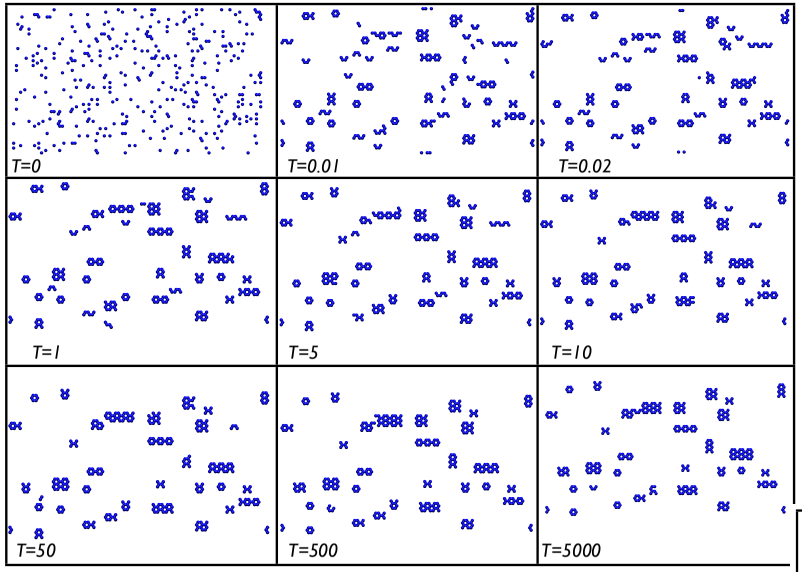


RSC Advances 6 (44), 37982 (2017)

Second multiscale: KMC + NEB

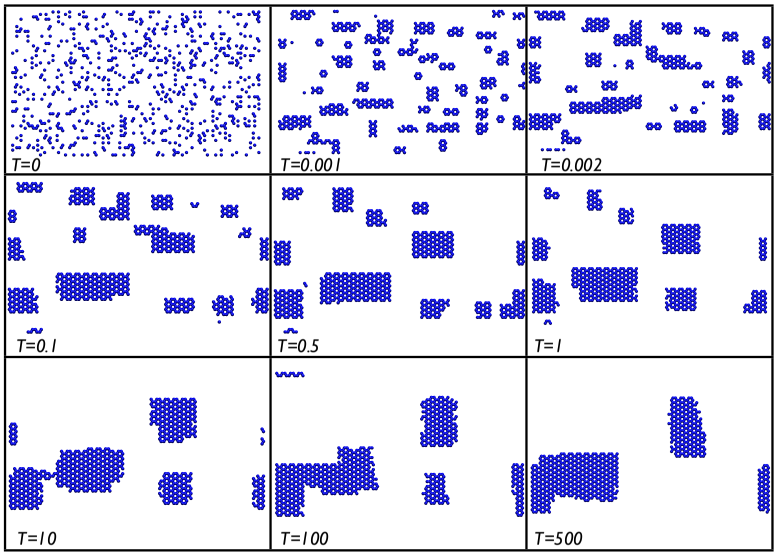
T= 900 K, coverage = 10%

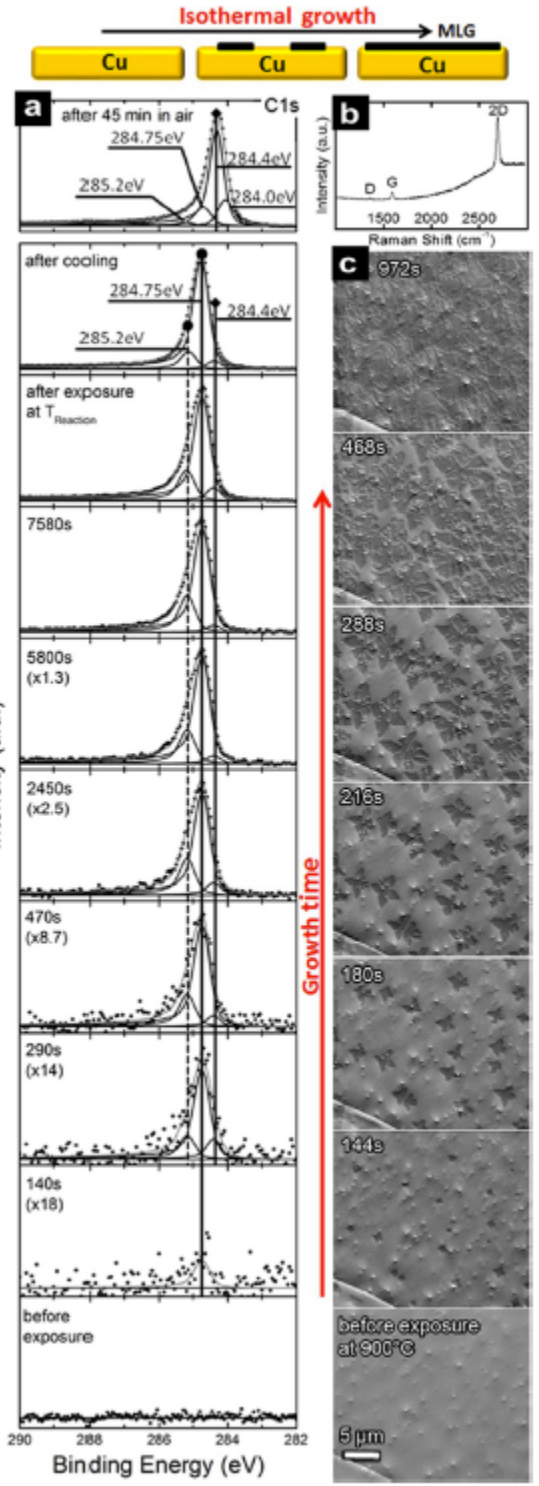




T= 600 K, coverage = 10%

T= 900 K, coverage = 20%



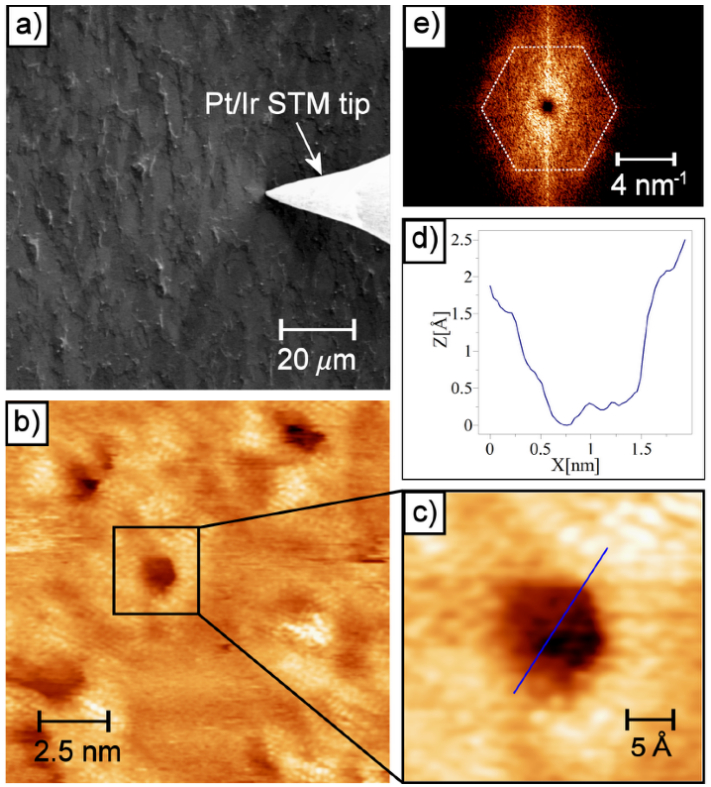


J. Mol. Mod.20 (7), 2260 (2014)

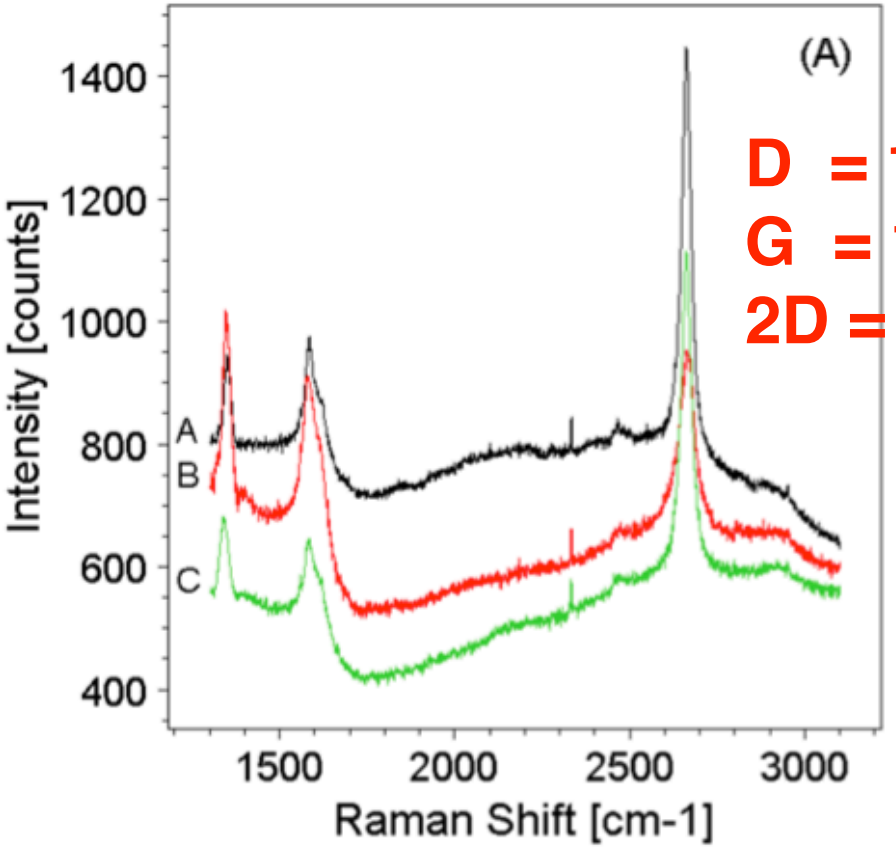
Kidanby at al. Nano Lett. 2013, 13, 4769–4778

C_{60} deposited by SuMBE, after a surface reconstruction inducing a tighter interaction with Cu, creates favorable conditions for cage unzipping via thermally activated processes at 645 °C (<< CVD).

C_{60} 1ML on Cu(111) after annealing at 645 °C.



SEM (a) and STM (b-e) analysis. c) details of a dark region, with line profile (d), compatible with fault lines on the top of the metal ; e) FFT analysis of the image in b) showing few nm extended graphene-like domains.



D = 1349 cm^{-1}
G = 1589 cm^{-1}
2D = 2665 cm^{-1}

I(D)/I(G) intensity ratio (0.71, 1.07 and 0.84) assesses the defect density = certain degree of defected G with d-d = 20 nm

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I must thank....

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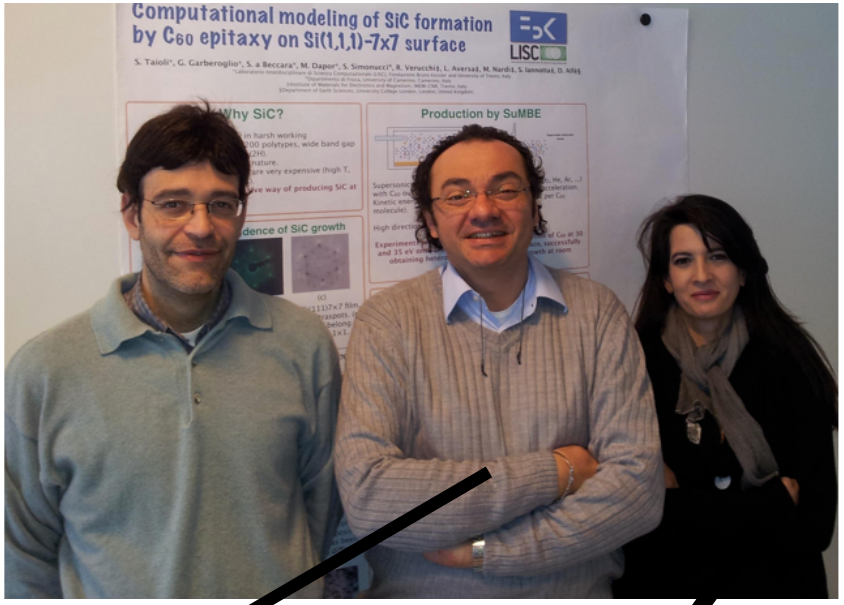

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