

Towards the modelling of the self-assembly of metal clusters on graphene epitaxied on metals

G. D. Förster, Y. Magnin, F. Calvo, F. Rabilloud

electronic mail: georg.forster@univ-lyon1.fr, yann.magnin@univ-lyon1.fr

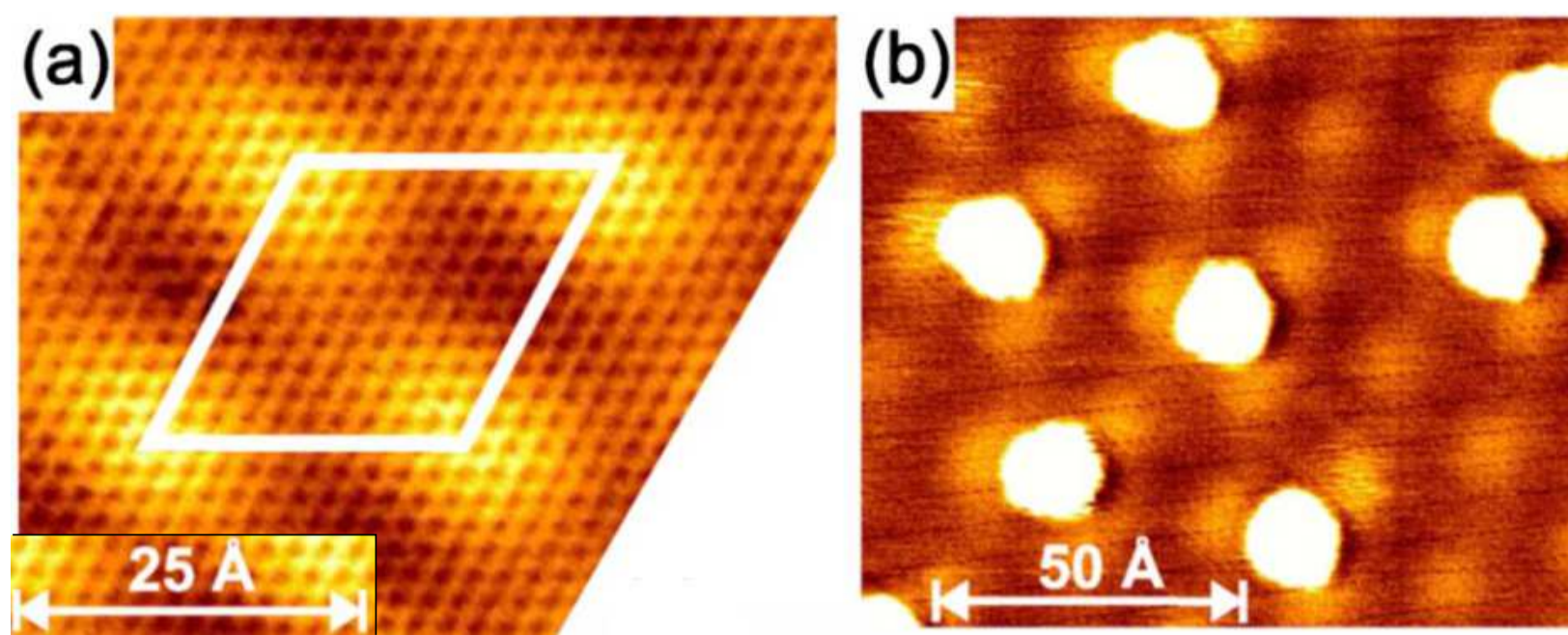
Institut Lumière Matière, UMR 5306 Université Claude Bernard Lyon 1 - CNRS, Université de Lyon, 10 rue Ada Byron, F 69622 Villeurbanne Cedex, France



Introduction and background

In epitaxial **graphene on metal (GOM)**, the lattice mismatch between the two materials gives rise to periodic **moiré superstructures**. The resulting corrugation may act as a **template for well-ordered arrays of magnetic nanoclusters** with promising applications in high-density storage devices. The use of atomistic simulations enables us to study **large systems** that are currently **inaccessible to DFT**. Here we focus on the archetypal case of **ruthenium** for which a **wealth of experimental and DFT data** are available.^[1,2]

Experimental STM measurements^[1]



(a) Graphene on Ir(111): moiré superstructure. (b) Ir clusters deposited on GOM

Goals

- Investigate the **stability** of deposited clusters
- Study of dynamical effects at **finite temperature**

Methods

- Assess different **Bond-order Potentials (BOPs)** by NPT Monte Carlo simulations for pristine graphene
- Adjust **Brenner BOP parameters** for metal-metal and carbon-metal interactions to experimental and DFT data, respectively
- Study **moiré geometry** for various inplane angles between graphene and metal substrate

Bond-order potentials

Suitable to highly coordinated material, BOPs contains a built-in correlation between coordination and bond strength:

$$E = \sum_i \sum_{j>i} V_R(r_{ij}) - \sum_{ij} \bar{B}_{ij} V_A(r_{ij})$$

$$\bar{B}_{ij} = b_{ij}^{\sigma-\pi} + b_{ij}^{\pi-\pi} + b_{ij}^{\pi-\sigma}$$

$V_R(r_{ij})$, $V_A(r_{ij})$: Interatomic repulsive and attractive pair functions, respectively

\bar{B}_{ij} : Bond-order, depends on the local coordination and bond angles

The performances of three different BOPs are assessed for pristine graphene:

Brenner's BOP^[3]: Interactions only between first neighbours

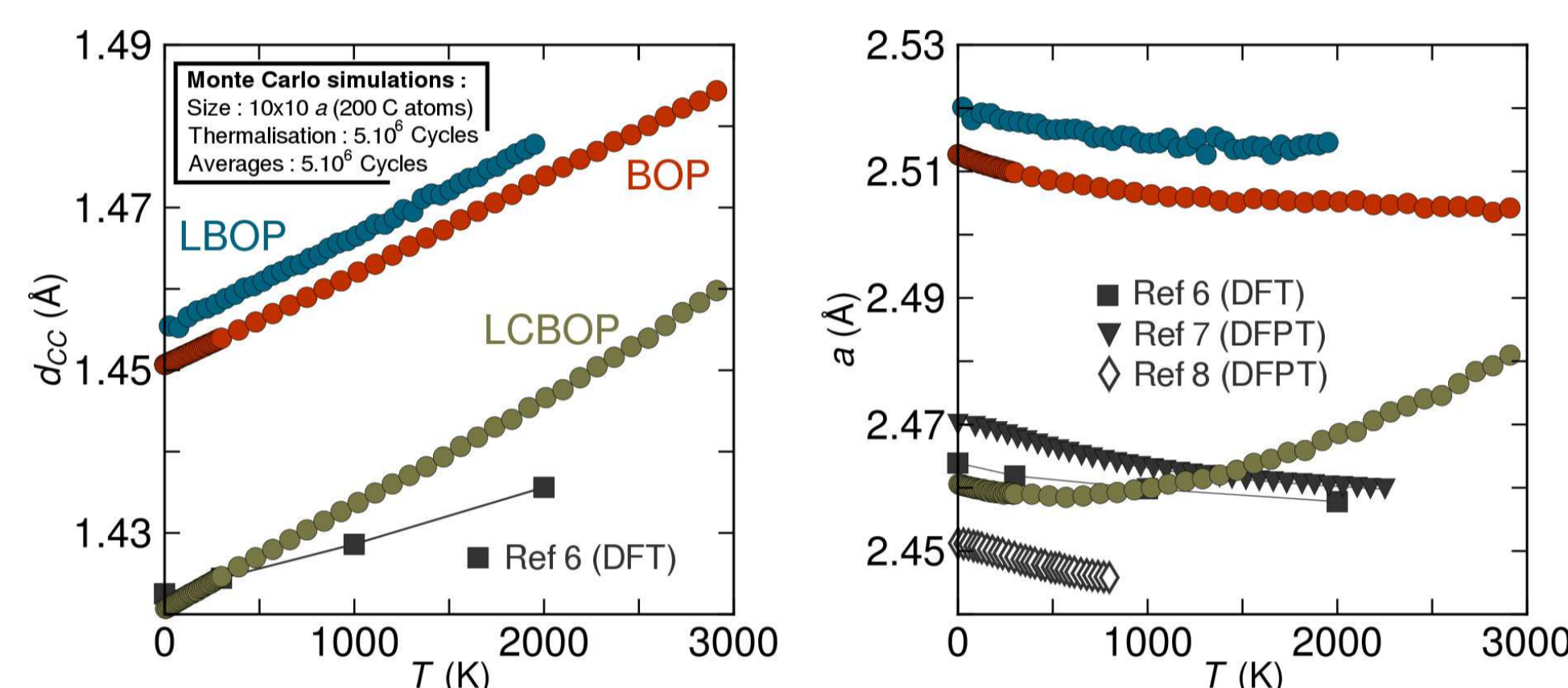
LBOP^[4]: Brenner's BOP including long-range interactions

LCBOP^[5]: BOP including long-range interactions, with a bond-order expression especially designed for carbon

Graphene

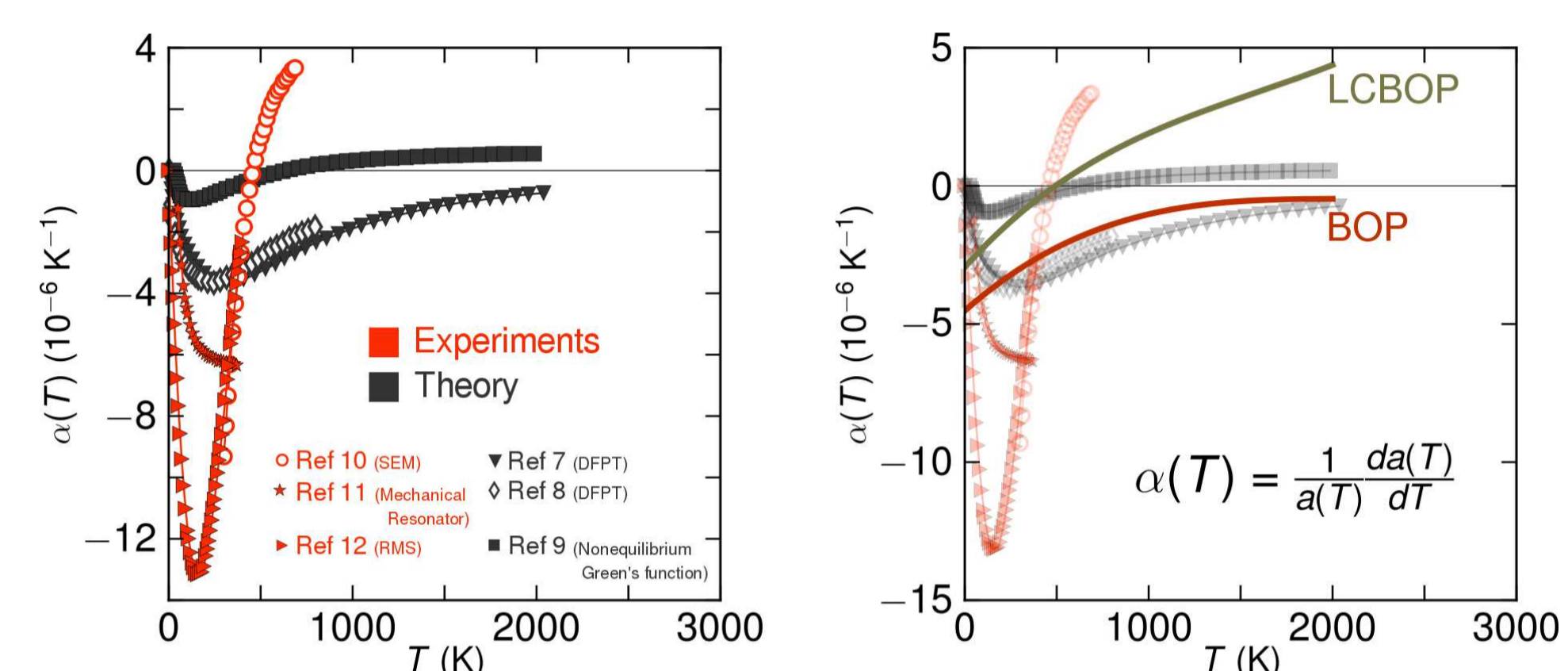
Thermal excitation causes **corrugation of graphene**.^[13] Consequently, increase of temperature induces the inplane lattice parameter a to decrease, which reflects in a **negative thermal expansion coefficient $\alpha(T)$** .

Finite Temperature behaviour



- Average bond distances d_{CC} increases with temperature: usual behaviour of classical solids
- Minor effects of simulation cell sizes
- BOP and LBOP present contraction of a in qualitative agreement with DFT^[6-8] but overestimate a over a large temperature range
- Only LCBOP exhibits an increase in a near 700 K although it is closest to DFT results

Thermal expansion coefficient



- Qualitative agreement of BOP and LBOP with references [6-8,11,12]
- Qualitative agreement of LCBOP with references [9,10]
- Sign of $\alpha(T)$ not consistent throughout literature (open question)

Remarks

Monte Carlo NPT simulations at $P=0$ reveal that various BOPs exhibit discrepancies in d_{CC} , a and $\alpha(T)$ depending on the potential used.

Deviation from harmonic (bending) to anharmonic (stretching) coupling modes has been proposed to explain the sign change of $\alpha(T)$.^[13] However this has been questioned by a recent approach based on classical elasticity theory.^[14]

All BOPs present a qualitative agreement with DFT below 700 K in a and d_{CC} .

Graphene on metal

Atomistic potential and its parameters for graphene on Ru(0001)

Pure carbon

- Brenner BOP^[3] with original parameters

Pure ruthenium

- Embedded Atom Model (EAM), form as in Cleri and Rosato^[15]
- Additional dispersion force correction for semi-infinite substrate
- Parameters for Ru adjusted via Monte Carlo fit to experimental data
- Reproduced quantities: lattice constants, cohesive energy, elastic constants
- Consistent description of the entire system by rewriting the EAM potential in the form of Brenner BOP

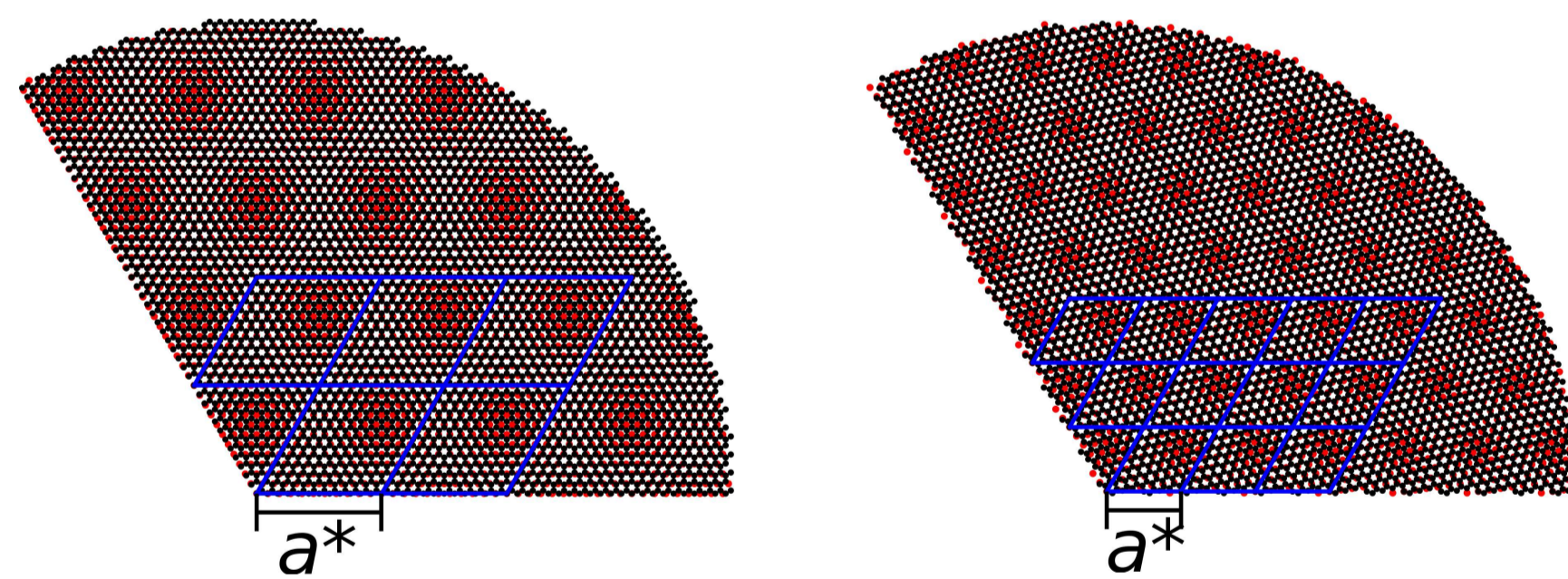
Ruthenium-Carbon

- Brenner BOP form plus a dispersion force correction for semi-infinite Ru substrate.
- Parameter adjustment via Monte Carlo fit of several equilibrium structures determined by DFT^[2]
 - Match the zero forces
 - Reproduce adsorption energies of the graphene layer and adatoms

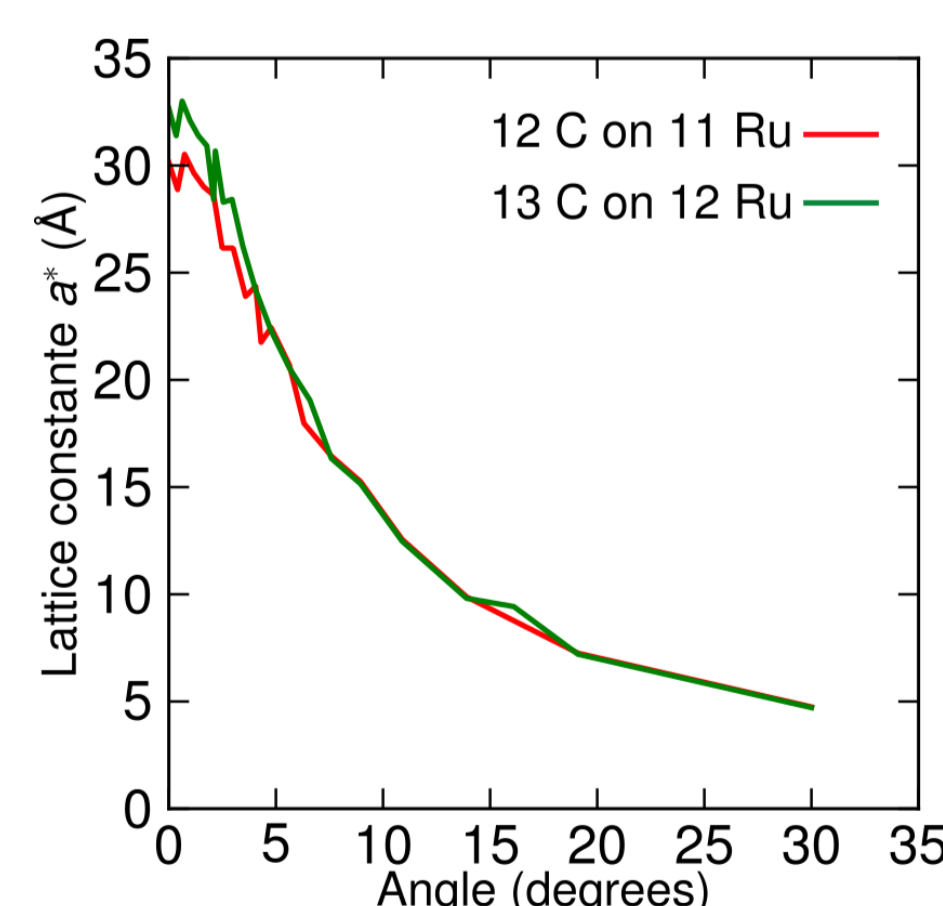
Quantity	DFT results	Reproduced values
Corrugation of graphene layer	1.44 Å	1.63 Å
Corrugation of topmost ruthenium layer	0.04 Å	0.23 Å
Smallest separation of graphene and topmost graphene layer	2.24 Å	2.12 Å
Average spacing of the uppermost metal layers	2.07 Å	2.14 Å
Adsorption energy of graphene layer	-3.9 eV	-3.88 eV
Interaction energy of graphene layer	-10.0 eV	-11.99 eV
Adsorption energy of an adatom at fcc site	-2.6 eV	-3.97 eV

Moiré geometries for graphene on Ru(0001)

- The periodicity of the **moiré superlattice** is about one order of magnitude lower than the one of graphene
- In the case of graphene on Ru(0001) two types of moiré are relevant:
 - 12 carbon atoms matching 11 ruthenium atoms
 - 13 carbon atoms matching 12 ruthenium atoms
- An inplane angle between graphene and the Ru(0001) surface reduces the size of the moiré supercell a^* :



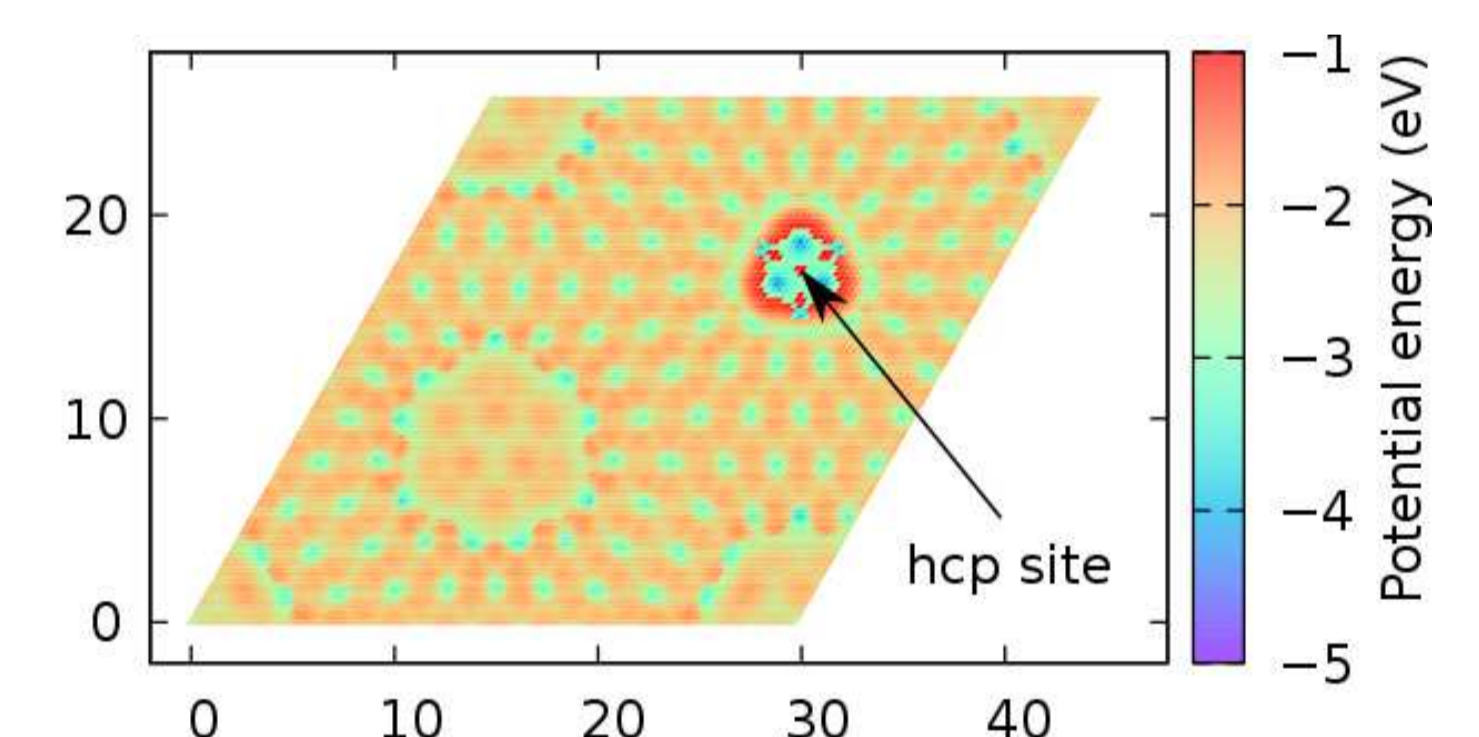
Graphene on Ru(0001), 12 carbon atoms matching 11 ruthenium atoms: lattices aligned
Graphene on Ru(0001), 12 carbon atoms matching 11 ruthenium atoms: inplane angle of 6.3°



Moiré supercell edge as function of inplane angle between graphene and Ru(0001) surface

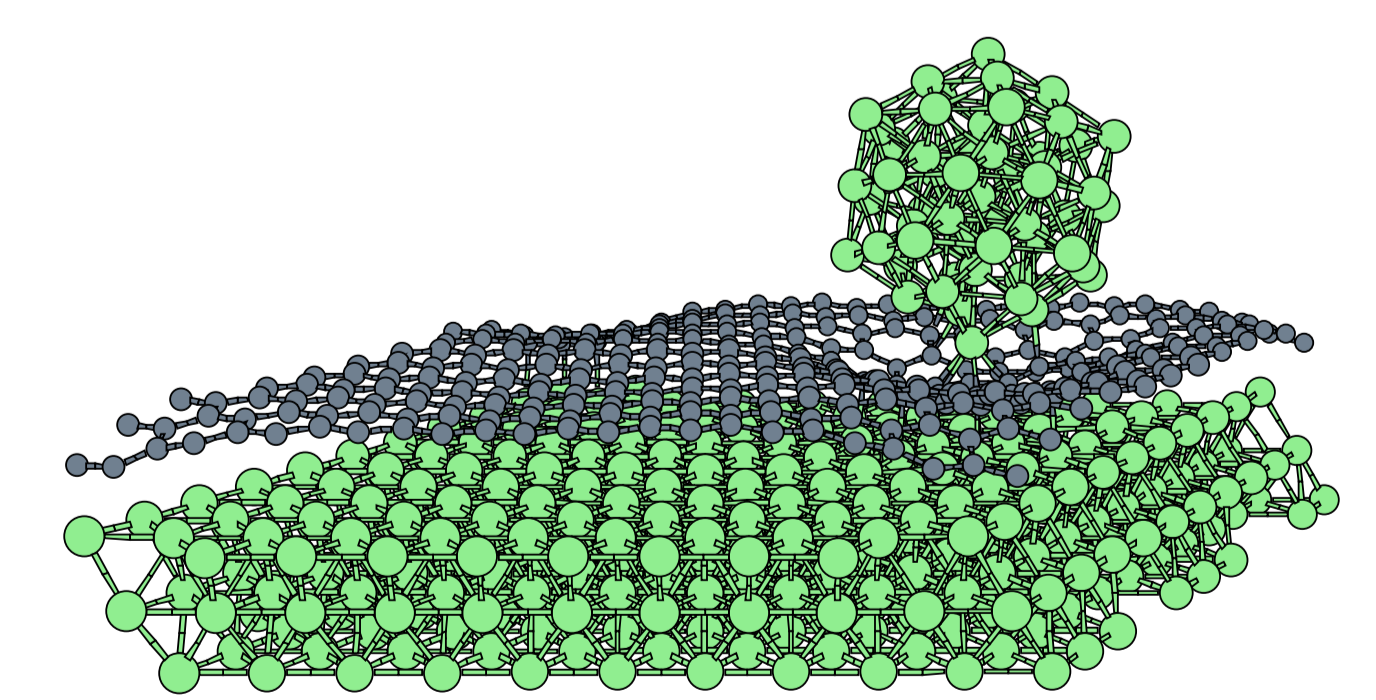
Adsorption of clusters on GOM

- Energy minimum for adatom is located at **hcp site** of the moiré supercell
- The graphene sheet is closest to the metal surface at the hcp site



Interaction energy of a Ru adatom with the substrate throughout the moiré supercell

Preliminary result: Adsorption energy of Ru₅₅-cluster: -4.47 eV



Ru₅₅-cluster adsorbed on graphene on Ru(0001) at hcp site

Perspectives and future research

- Further improvement of the parameters for the potential: refine Monte Carlo fitting procedure using replica exchange
- Establish an equivalent potential for systems presenting a lower corrugation (graphene on Ir(111))
- Relaxation of systems with adsorbed clusters
- Study of dynamics at finite temperature of individual and multiple clusters
- Replace the atomistic description of the cluster-substrate interaction by a continuous approximation

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