

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

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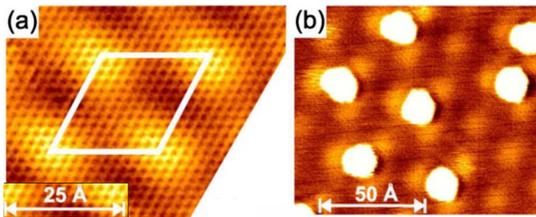
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## Introduction and background

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.<sup>[1,2]</sup>

## Experimental STM measurements<sup>[1]</sup>



(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<sup>[3]</sup>**: Interactions only between first neighbours

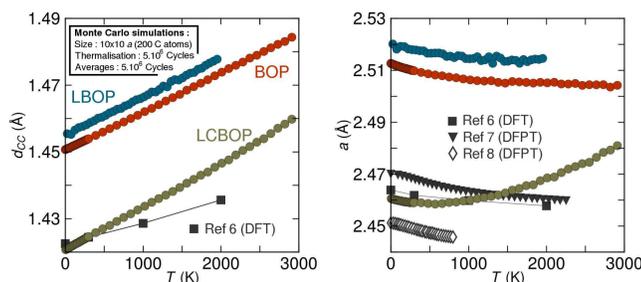
**LBOP<sup>[4]</sup>**: Brenner's BOP including long-range interactions

**LCBOP<sup>[5]</sup>**: BOP including long-range interactions, with a bond-order expression especially designed for carbon

## Graphene

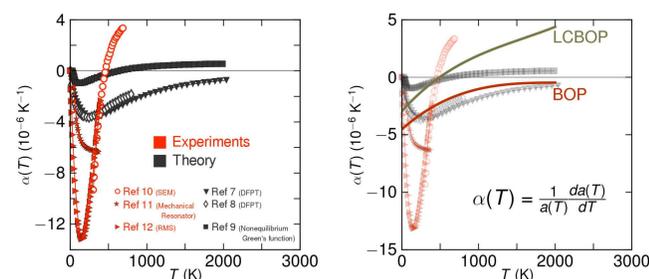
Thermal excitation causes **corrugation of graphene**.<sup>[13]</sup> Consequently, increase of temperature induces the inplane lattice parameter  $a$  to decrease, which reflects in a **negative thermal expansion coefficient  $\alpha(T)$** .

## 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<sup>[6-8]</sup> 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  $\alpha(T)$ .<sup>[13]</sup> However this has been questioned by a recent approach based on classical elasticity theory.<sup>[14]</sup>

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<sup>[3]</sup> with original parameters

#### Pure ruthenium

- Embedded Atom Model (EAM), form as in Cleri and Rosato<sup>[15]</sup>
- 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

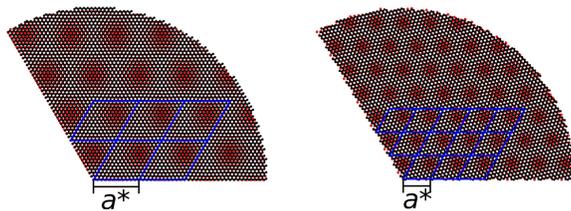
#### Ruthenium-Carbon

- 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<sup>[2]</sup>
  - Match the zero forces
  - Reproduce adsorption energies of the graphene layer and adatoms

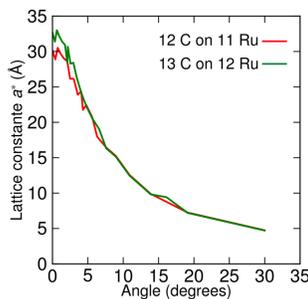
Quantity	DFT results	Reproduced values
Corrugation of graphene layer	1.44 Å	1.63 Å
Corrugation of topmost ruthenium layer	0.04 Å	0.23 Å
Smallest separation of graphene and topmost graphene layer	2.24 Å	2.12 Å
Average spacing of the uppermost metal layers	2.07 Å	2.14 Å
Adsorption energy of graphene layer	-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  $a^*$ :



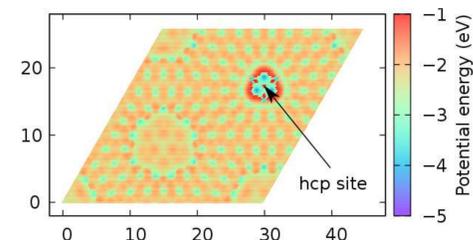
Graphene on Ru(0001), 12 carbon atoms matching 11 ruthenium atoms: lattices aligned  
Graphene on Ru(0001), 12 carbon atoms matching 11 ruthenium atoms: inplane angle of 6.3°



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

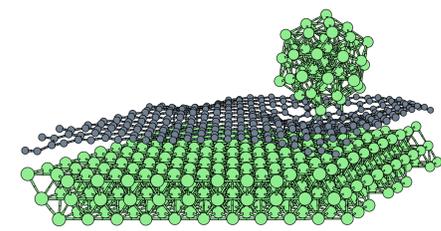
## Adsorption of clusters on GOM

- 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 Ru<sub>55</sub>-cluster: -4.47 eV



Ru<sub>55</sub>-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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