Structure électronique d'un biplan de graphène couplage ab initio – liaisons fortes

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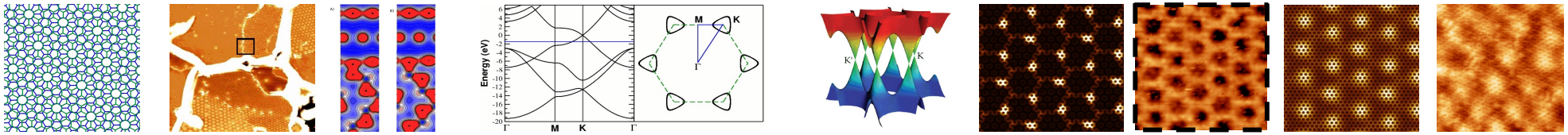
France

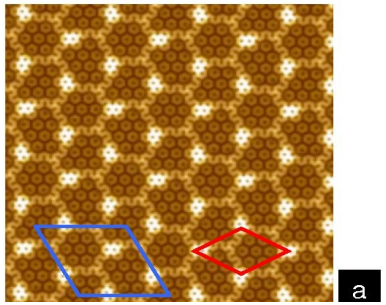


IDRIS

CIMENT
phynum project

Outline

1. **Interface graphène – Face Si de SiC**
   - **Données expérimentales**
   - **Plan tampon**



6√3x6√3 R30 (>1300 atomes)
approche DFT (VASP)
potentiel classique EDIP : C sp^2 et sp^3 + Si-C et C-C

2. **Biplan de graphène tourné**
   - **Données expérimentales**
   - **Calculs ab initio**
   - **Liaisons fortes**

3. **Conclusion et futur : croissance**

Introduction : Methods - technical details

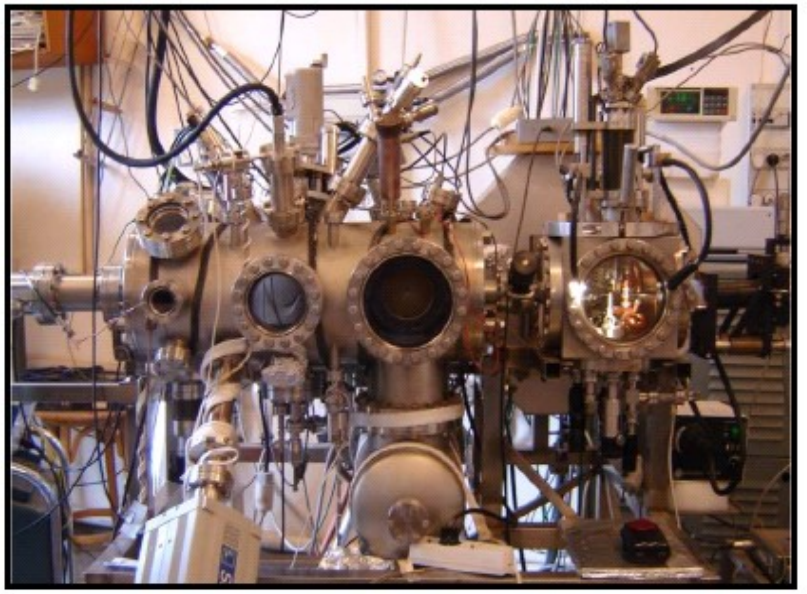
DFT calculations:

b-initio VASP ackage ienna imulation

DFT + GGA
pseudo potential + plane wave
large supercell (>1200 atoms)

F.Varchon, F.Hiebel, L.Magaud
IN and PHYNUM

Scanning tunneling microscope :



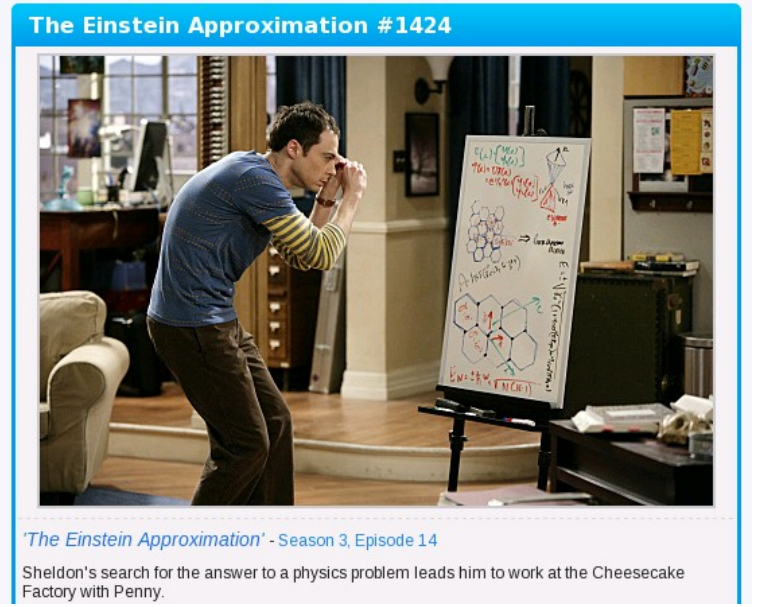
Home made UHV- STM
6H SiC (0001) and (000-1),
n doped

Si flux at 850 °C
progressive annealing
(900 -> 1100 °C)

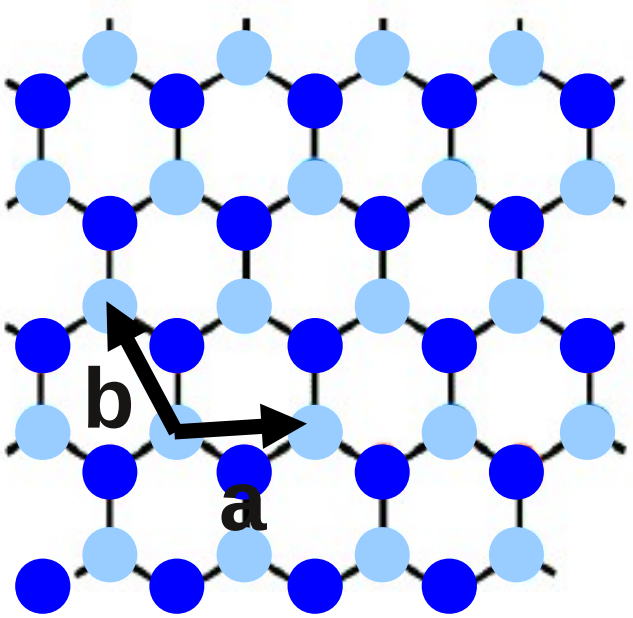
F.Hiebel, F.Varchon,
P.Mallet, J.-Y.Veuillen

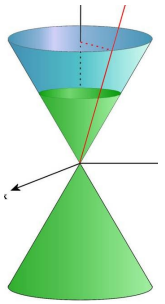
Le graphène :

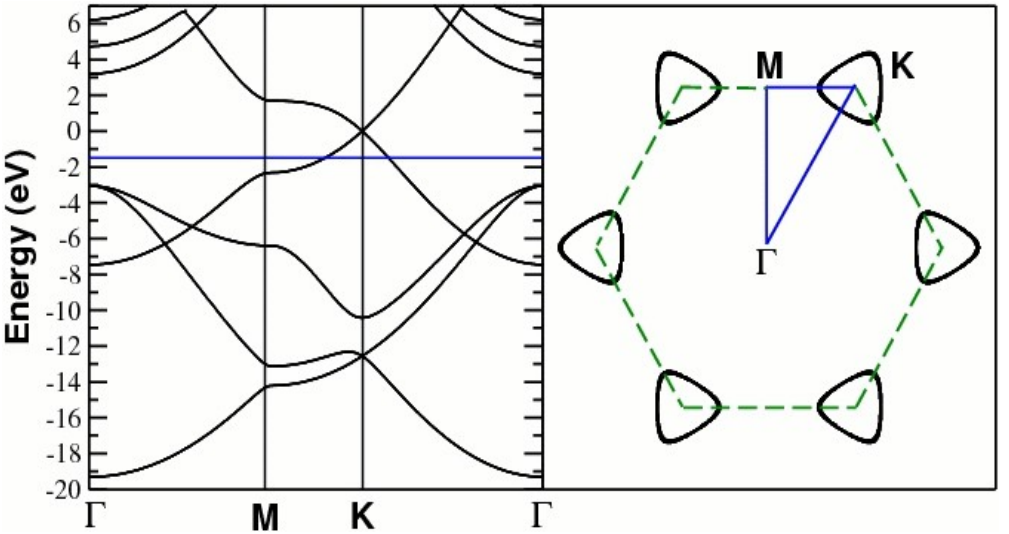
exfolié (Geim Novoselov, Kim)
sur SiC (de Heer)
sur métaux



1 plan de C en réseau nid d'abeille



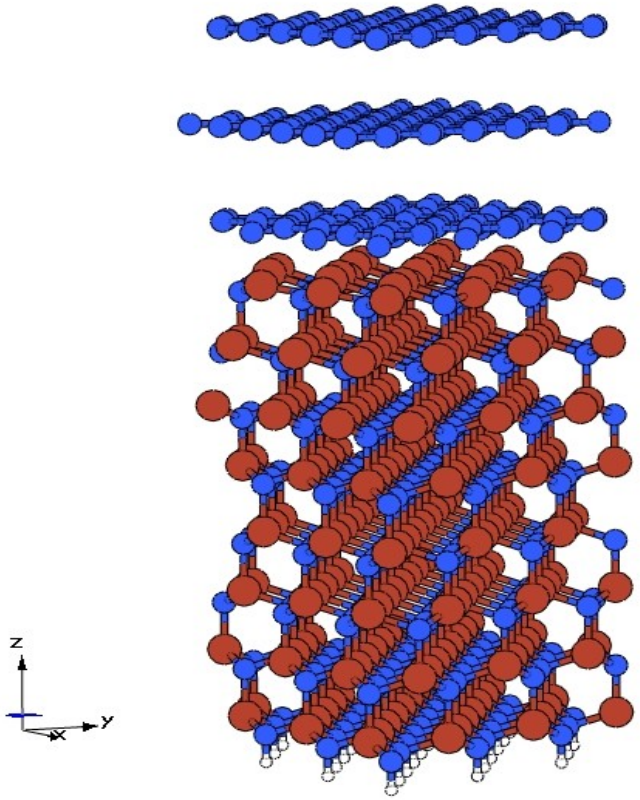




a=b,
θ=120°

Réseau de Bravais hexagonal

Faces polaires des polytypes hexagonaux de SiC



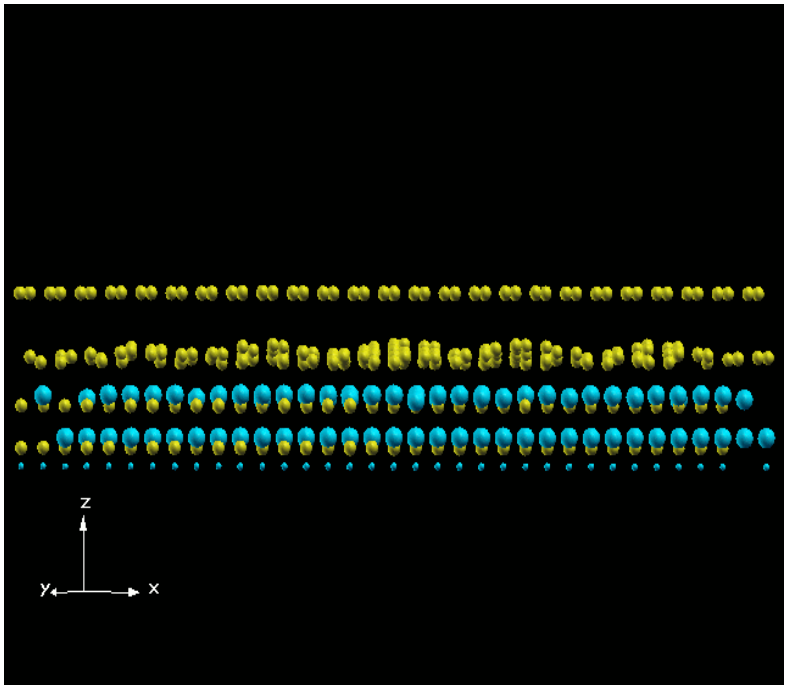
Si

C

Si face : strong interaction with substrate => buffer layer

Common cell graphene – SiC

6√3x6√3 R30

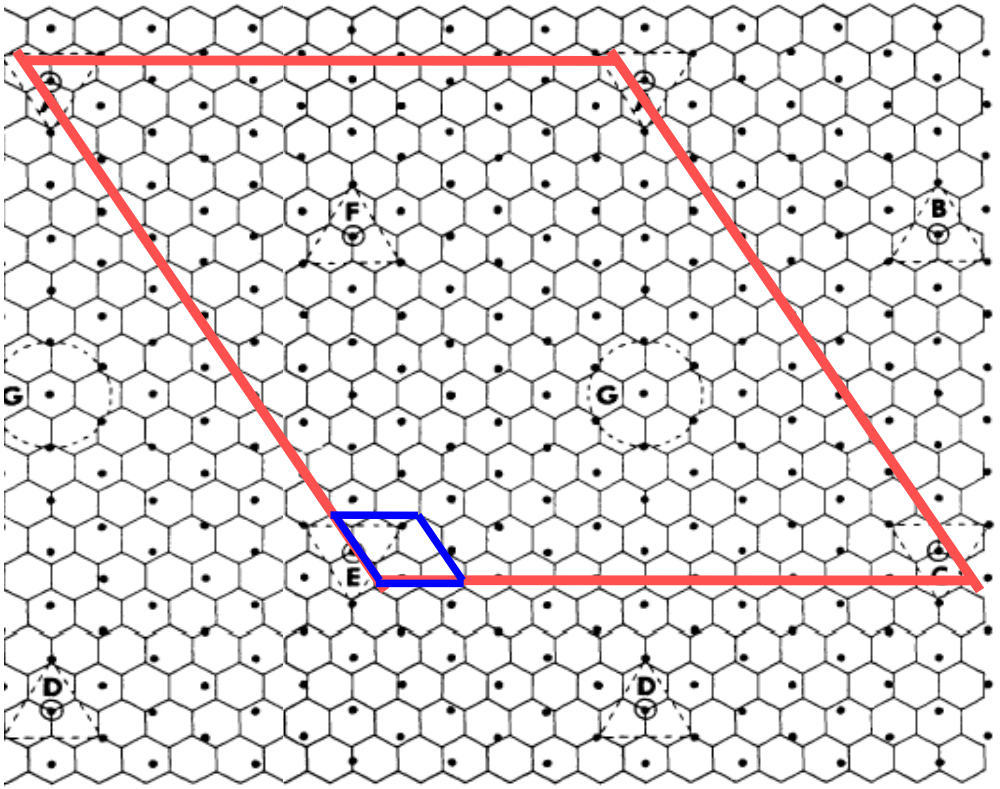


W.Chen et al Surf.Sci.596,176 (2005)
E.Rollings et al J.Phys.Chem. Sol 67, 2172 (2006)
F.Owman et al. Surf. Sci. 369, 126 (1996)
M.-H.Tsai et al. Phys. Rev. B45, 1327 (1992)
Th.Seyller et al Surf. Sci. 600, 3906 (2006)
E.K.Emtsev et al. Mater. Sci. Forum 556-557, 525 (2007)

√3x√3 R30

*F.Varchon et al., PRL. **99**, 126805, (2007)*

*A.Mattausch et al. PRL**99**, 076802, (2007)*



6√3x6√3 R30

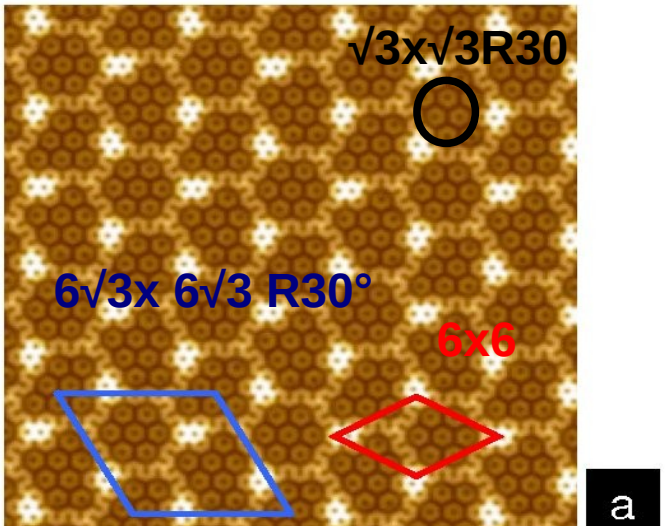
F.Varchon et al., Phys.Rev.B 77, 235412 (2008)

S.Kim et al. Phys. Rev.Lett 100,176802 (2008)

Nanostructuration of the first C layer

Ab initio

F.Varchon et al, Phys. Rev. B (2008)



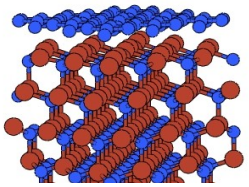
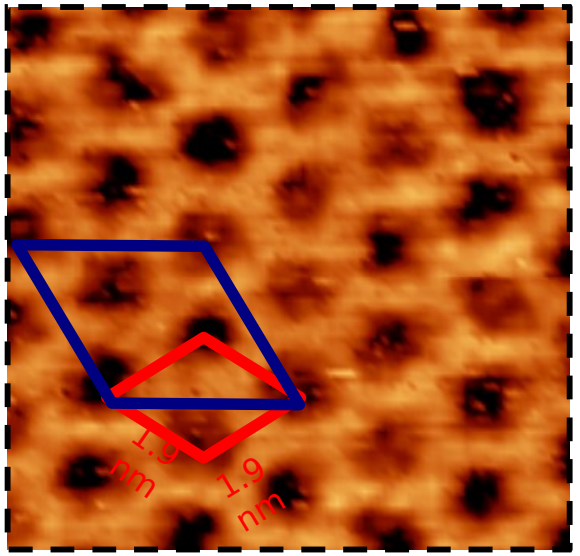


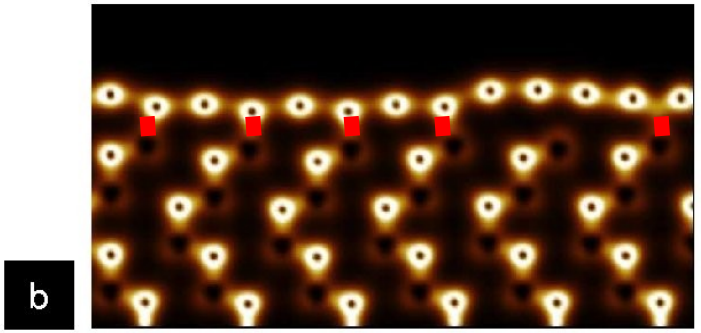
Image STM (0.2 V, 300 K)

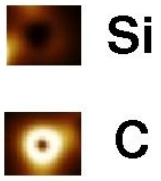
P.Mallet et al., Phys Rev B74, 041403 (R) (2007)

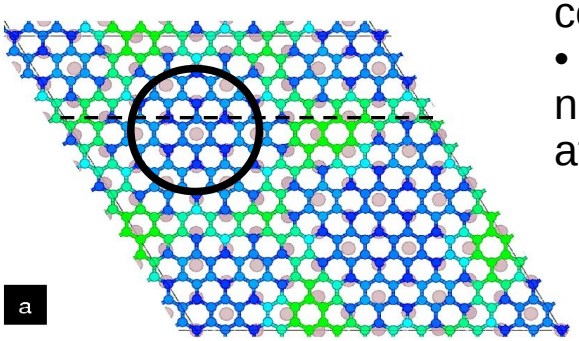


10 × 10 nm²

- mosaic pattern with local **√3x√3R30**
- apparent 6X6 reconstruction
- Corrugation : 1.2 Å (STM : 1-1.5 Å)





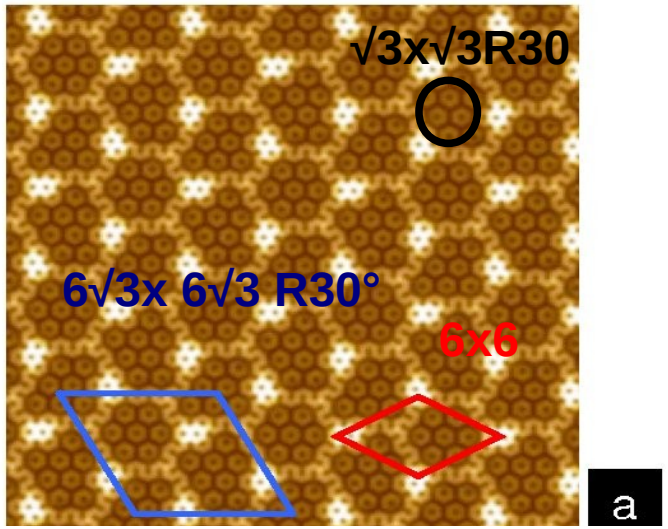


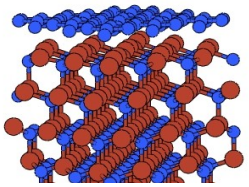
• grains : **√3x√3R30** matching regions
covalent bond
• frontier : not in register
no bond
atom higher

Nanostructuration of the first C layer

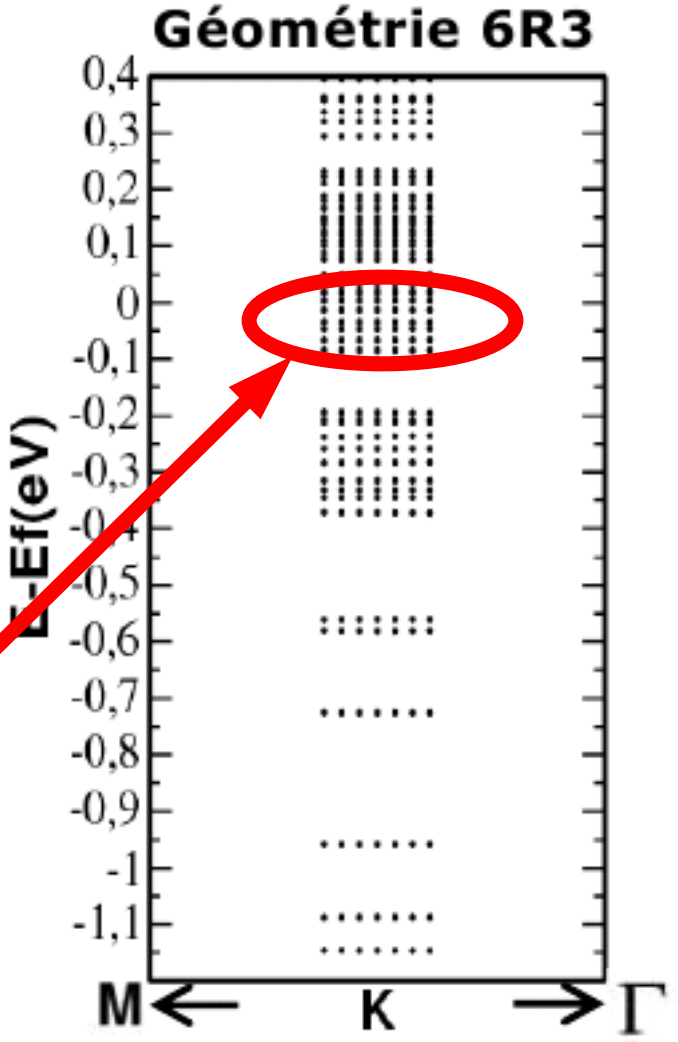
Ab initio

F.Varchon et al, Phys. Rev. B (2008)



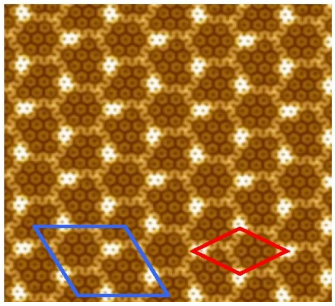


F.Varchon PhD, 2009



Interface states : dangling bonds

VASP : 1316 atomes : 13x13 graphène sur 4 biplans de SiC en $6\sqrt{3}x6\sqrt{3}$ R30



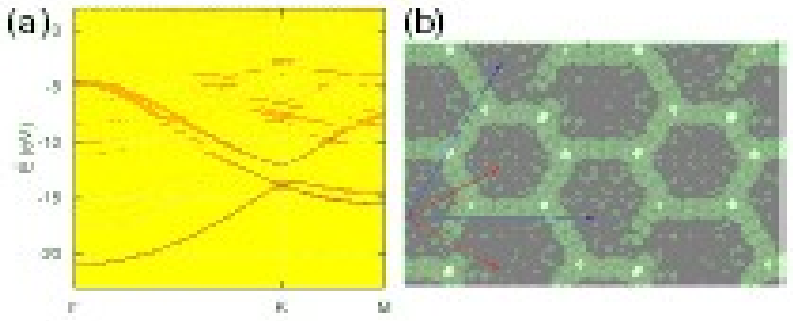
Un an de calcul sur une SGI 350 avec 8 processeurs (6 mois réels)

deuxième plan de C : limite SiC à 2 biplans
essais de modification des états d'interface, de diffusion, de croissance .... trop long

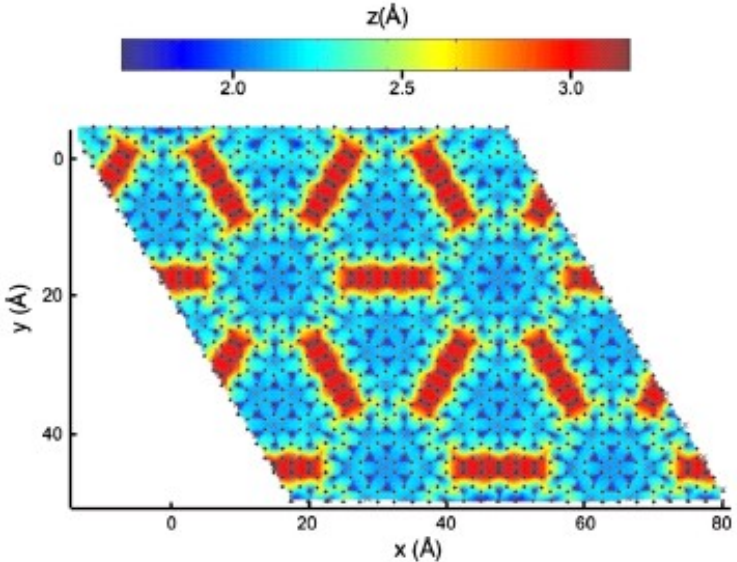
SIESTA :

Origins of anomalous electronic structures of epitaxial graphene on silicon carbide

Seunghul Kim,[1] Jisoon Ihm,[1] Hyoung Joon Choi,[2] and Young-Woo Son[3,*]



EDIP



Potentiels classiques

E.Lampin et al, J.Appl. Phys. 107, 103514 (2010)

C sp^2 et sp^3 + liaisons Si-C et C-C

G.Lucas et al JPCM 22, 035802 (2010)

EDIP : environment dependent interatomic potential

E.Lampin, IEMN

E.Lampin, C.Priester, C.Krzeminski, LM J.Appl. Phys. 107, 103514 (2010)

M.Z.Bazant, E.Kaxiras, PRL 77, 4370 (1996) pour Si
G.Lucas, M.Bertolus, L.Pizagalli JPCM 22, 035802 (2010) adaptation pour SiC

$$E = \sum_i E_i,$$

$$E_i = \sum_{j \neq i} V_2(\vec{r}_i, \vec{r}_j, Z_i) + \sum_{j \neq i} \sum_{k \neq i, k > i} V_3(\vec{r}_i, \vec{r}_j, \vec{r}_k, Z_i).$$

$$Z_i = \sum_{m \neq i} f(r_{im})$$

$$\text{f(r)} = \begin{cases} 1, & r < c \\ \exp\left[\alpha / \left(1 - \left(\frac{a-c}{r-c}\right)^3\right)\right] \Delta(r), & c < r < a \\ 0, & r > a. \end{cases}$$

$$V_2(r_{ij}, Z_i) = A\left[\left(\frac{B}{r_{ij}}\right)^{\rho} - p(Z_i)\right]\exp\left(\frac{\sigma}{r_{ij} - a}\right)$$

$$p(Z) = \exp(-\beta Z^2)$$

$$V_3(\vec{r}_{ij}, \vec{r}_{ik}, Z_i) = g(r_{ij})g(r_{ik})h(l_{ijk}, Z_i)$$

$$l_{ikj} = \cos\theta_{ijk} = \vec{r}_{ij} \cdot \vec{r}_{ik}/r_{ij}r_{ik}$$

$$g(r) = \exp\left(\frac{\gamma}{r - a}\right)$$ Stillinger-Weber

$$h(l, Z) = \lambda[(1 - \exp(-Q(Z)(l + \tau(Z))^2)) + \eta Q(Z)(l + \tau(Z))^2],$$

$\tau(Z)$ angle d'équilibre

$$\tau(Z) = l_0(Z) = -\cos\theta_0(Z)$$

$$\omega(Z)^{-2} = Q(Z) = Q_0\exp(-\mu Z)$$

$\omega(Z)$ force de l'interaction

$$\tau(Z) = u_1 + u_2(u_3\exp(-u_4 Z) - \exp(-2u_4 Z))$$

13 paramètres pour Si

SiC

A : garde Si optimise C
Si-C moyenne
+ correction

$$\Delta(r) = \begin{cases} 1, & r < c \\ \exp\left(\dfrac{\alpha}{1-x^{-3}}\right), & c < r < a-\delta \\ 0, & r > a-\delta, \end{cases}$$

B: tout réoptimisé

δ=0.3 Å

$$f(r) = \begin{cases} 1, & r < c \\ \exp\left[\alpha/\left(1-\left(\dfrac{a-c}{r-c}\right)^3\right)\right] \Delta(r) & c < r < a \\ 0, & r > a. \end{cases}$$

$$V_2(r_{ij}, Z_i) = A\left[\left(\frac{B}{r_{ij}}\right)^{\rho} - p(Z_i)\right]\exp\left(\frac{\sigma}{r_{ij}-a}\right) \quad \Delta(rij)$$

$$V_3(\vec{r}_{ij}, \vec{r}_{ik}, Z_i) = g(r_{ij})g(r_{ik})h(l_{ijk}, Z_i)\Delta(rij)\ \Delta(rik)$$

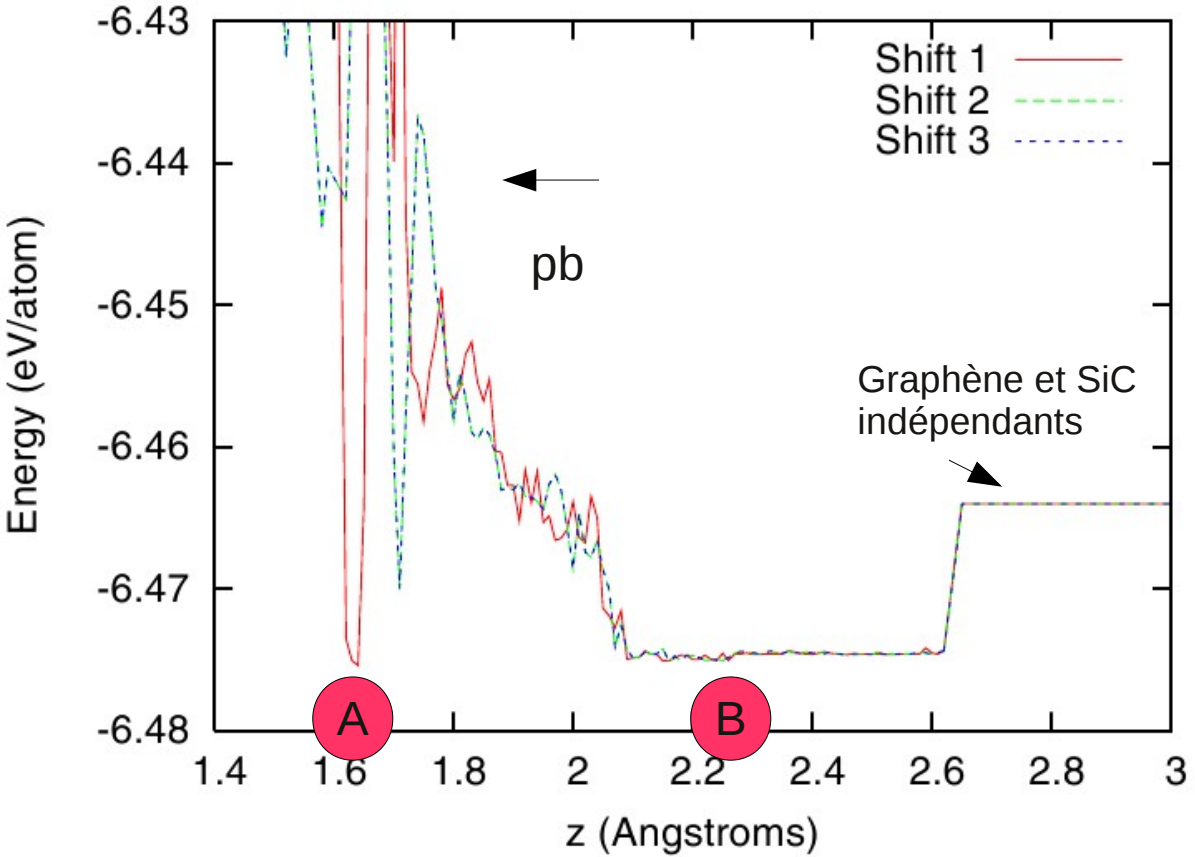
13X13 graphène sur 6√3x6√3 R30 SiC (6 biplans)

biplan du bas gelé
gradients conjugués

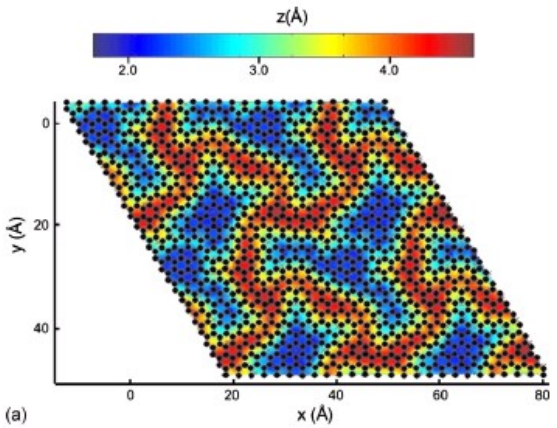
Fait varier la distance initiale plan de graphène – SiC de 1.5 à 3 Å par pas de 0.01 Å

1 : C au dessus Si
2 : centre hexagone au dessus Si
3 : milieu C-C graphène au dessus Si

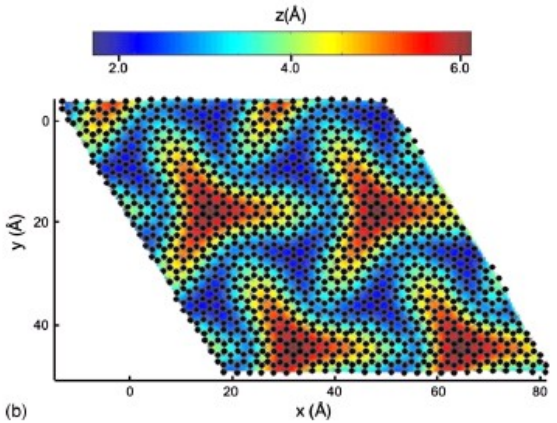
2et 3 même résultat



A
1.63

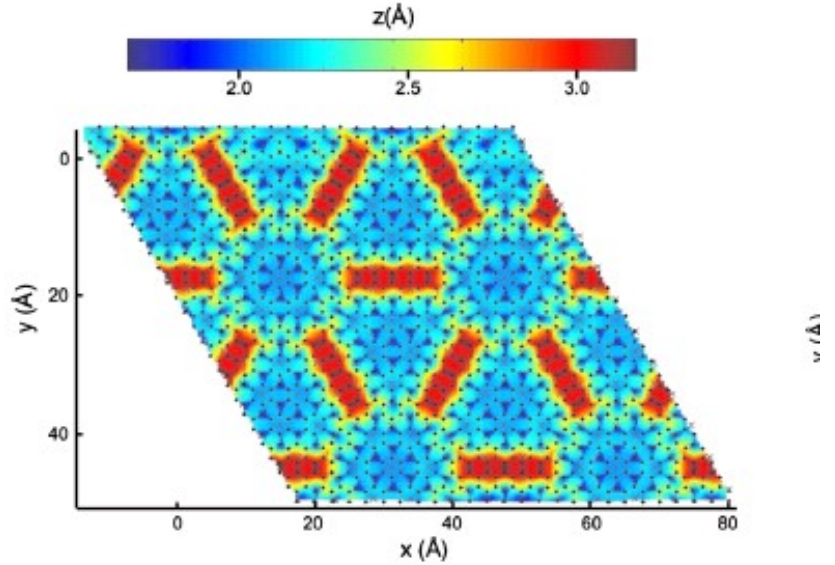


B
2.26

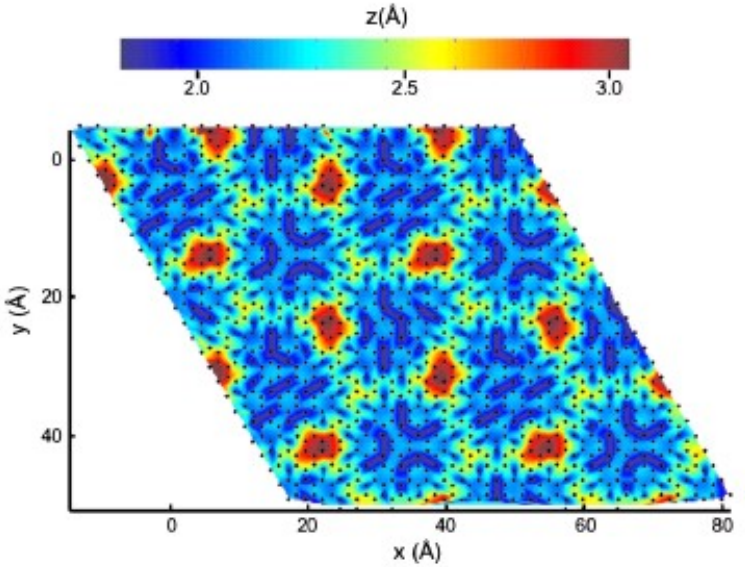


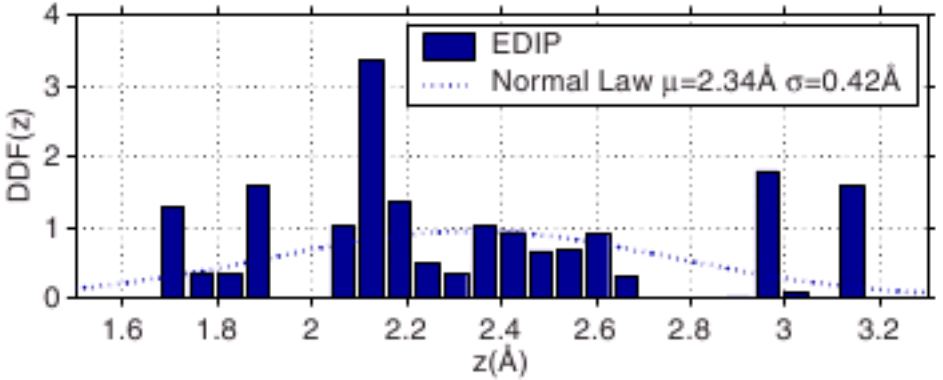
Pré-relaxation du graphène : descend les C qui sont proches voisins de Si

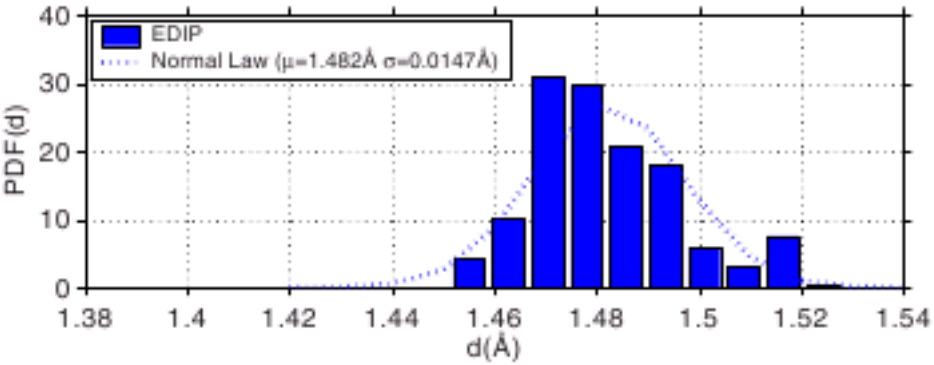
EDIP

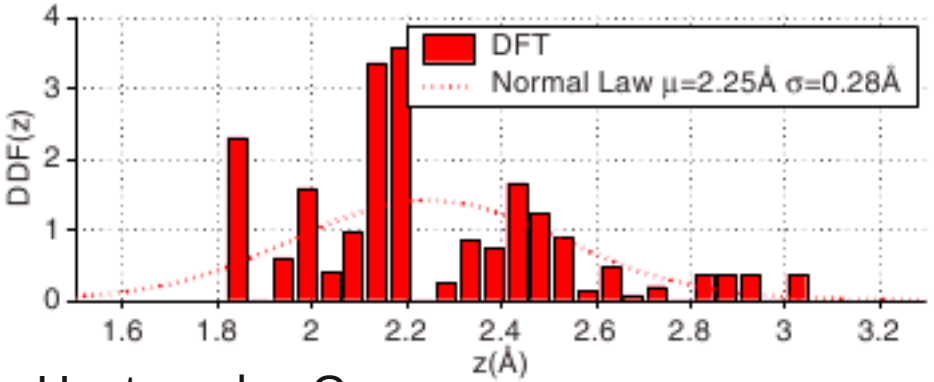


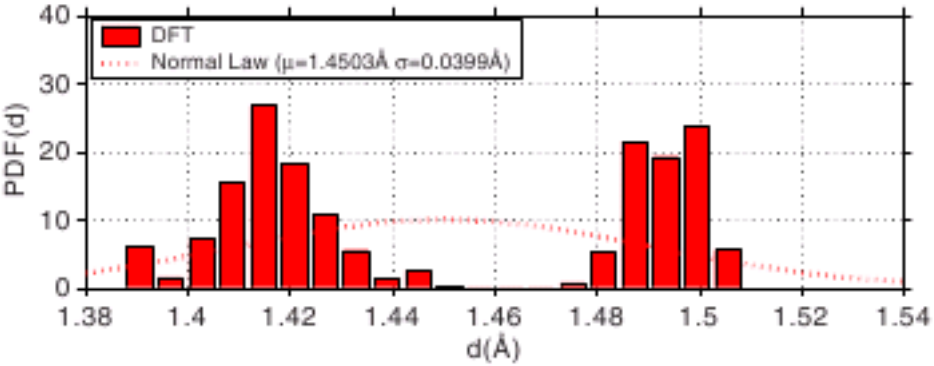
Ab initio











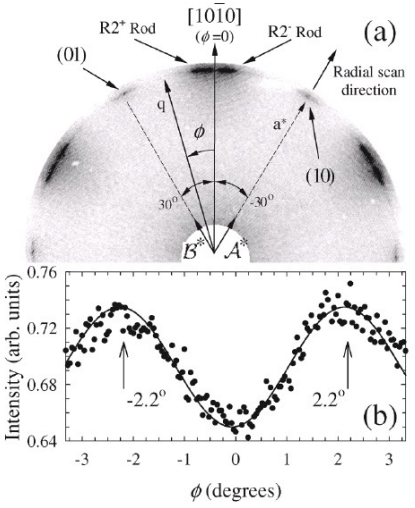
Hauteur des C

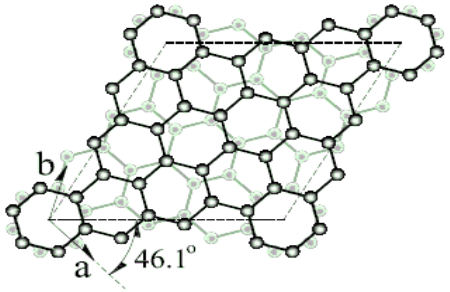
Distance C-C dans le plan

2. C Face : Rotated bilayers

Van Bommel 1975

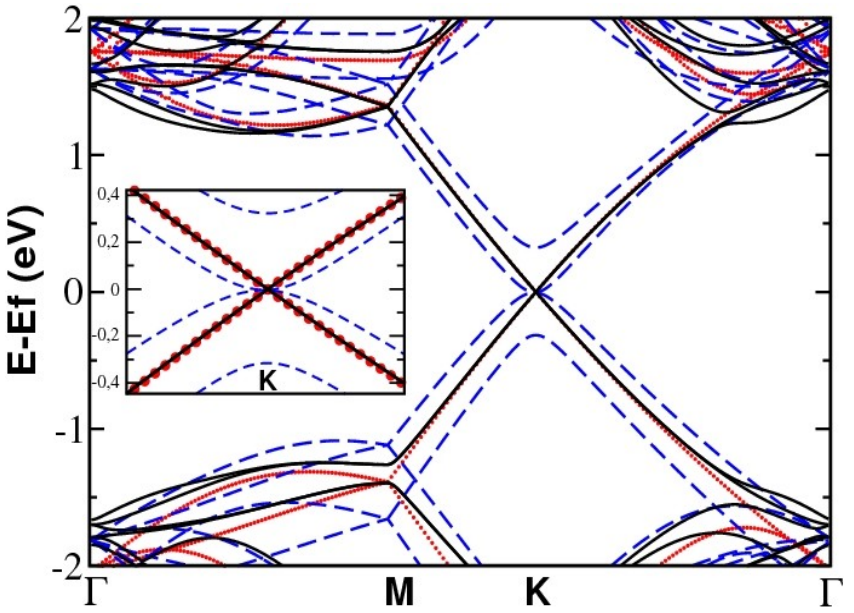
Weak interaction : no long range order for growth
no Bernal stacking (**twisted layers**)





√13 x √13 R±46.1°
commensurate with SiC

AB bilayer
Monolayer
Twisted bilayer



Twist preserves linear dispersion

J. Hass et al.,PRL 100, 125504 (2008)

*J. M. B. Lopes dos Santos et al., PRL 99, 256802 (**2007**)*
*S. Latil et al., Phys. Rev B76, 201402(R) (**2007**)*
S.Shallcross et al, Phys. Rev. Lett. 101, 056803 (2008)

2. Rotated bilayers: renormalisation of the velocity

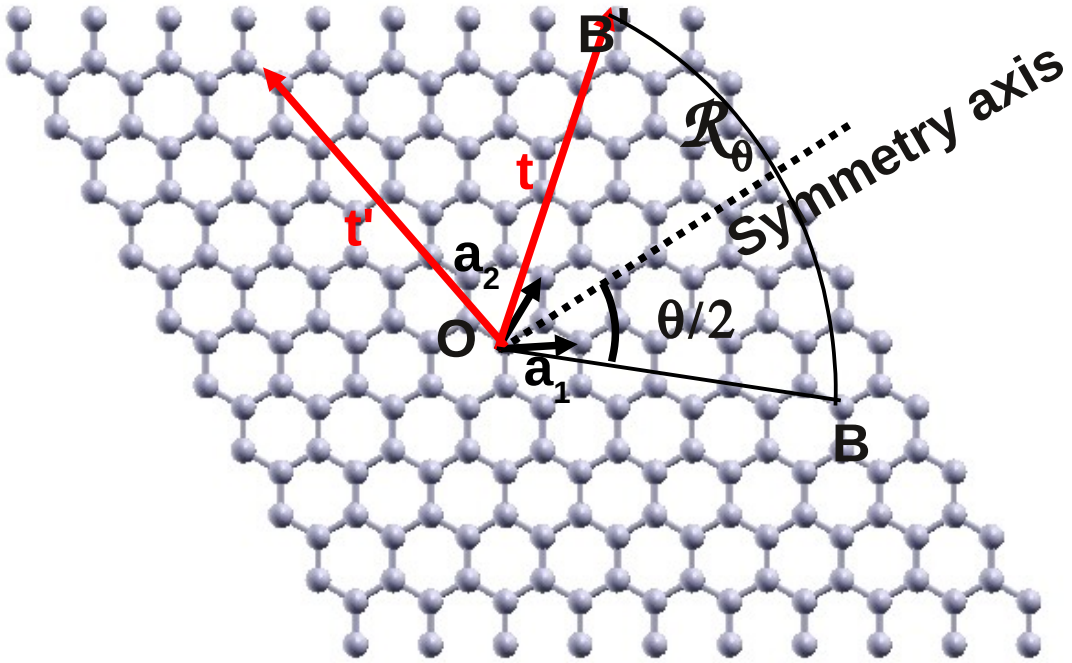
L.Magaud, D.Mayou, G.Trambly de Laissardière

Ab initio (VASP) => periodic system
Common cell for two layers rotated by θ

Common cell defined by:
$t = na_1+ma_2$
$t' = ma_1+(n+m)a_2$

Rotation angle:

$$\cos(\theta)=2\cos^2(\theta/2)-1=\frac{n^2+4nm+m^2}{2(n^2+nm+m^2)}$$



ab initio calculation + TB fit: small angles/ shift / asymmetric bilayer

Small angles (6,7) θ=5.08°

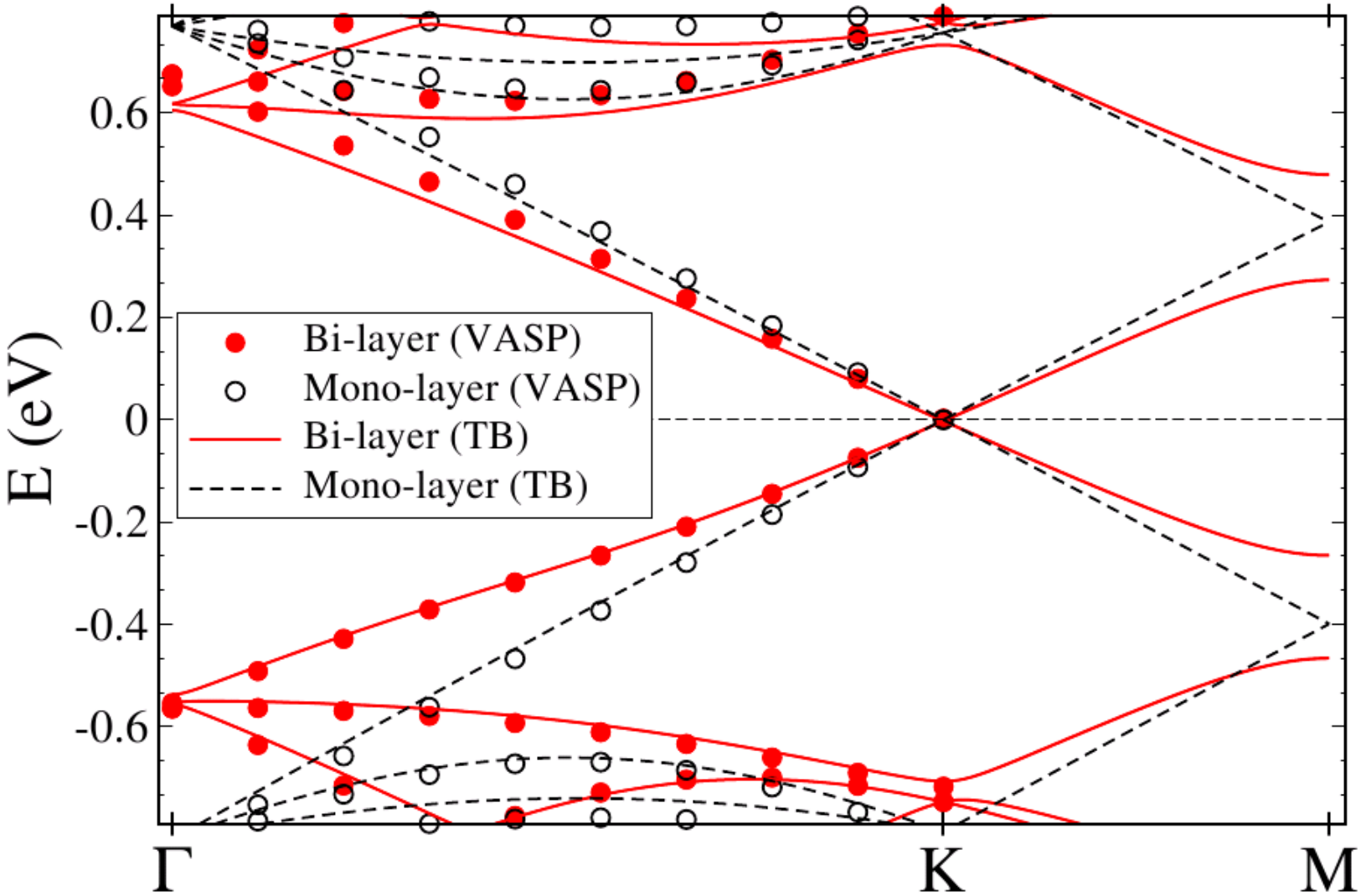
TB scheme

$$V_{pp\pi} = -\gamma_0 \exp\left(q_\pi\left(1-\frac{d}{a}\right)\right)$$

$$V_{pp\sigma} = \gamma_1 \exp\left(q_\sigma\left(1-\frac{d}{a_1}\right)\right) \quad \text{with} \quad \frac{q_\sigma}{a_1} = \frac{q_\pi}{a}$$

γ_0 = 2.7 eV, γ_1=0.48 eV
a=1.42 Å a1=3.35Å

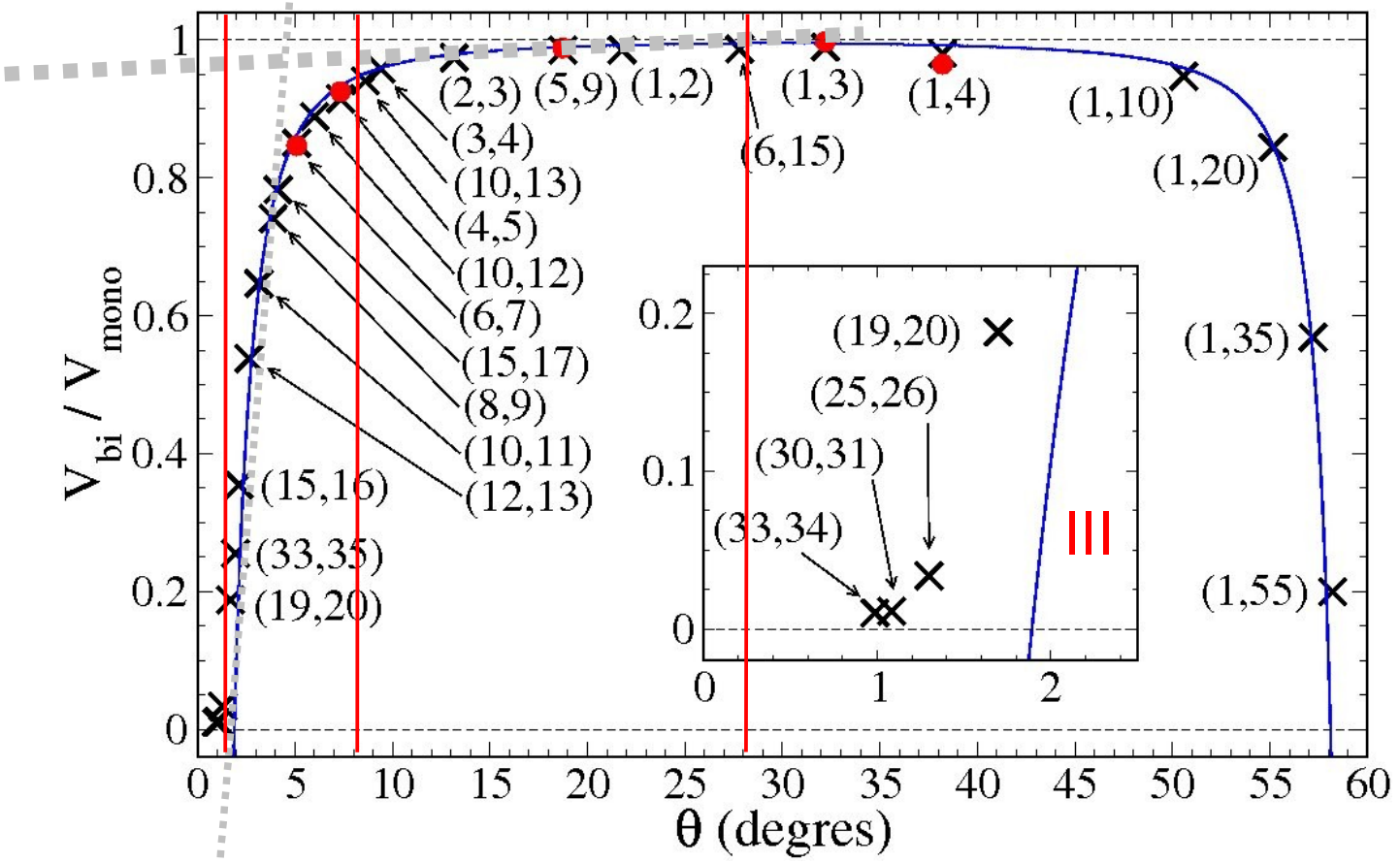
fitted on AA, AB, (1,3) et (1,4)



Renormalisation of velocity

3. Rotated bilayers: renormalisation of the velocity

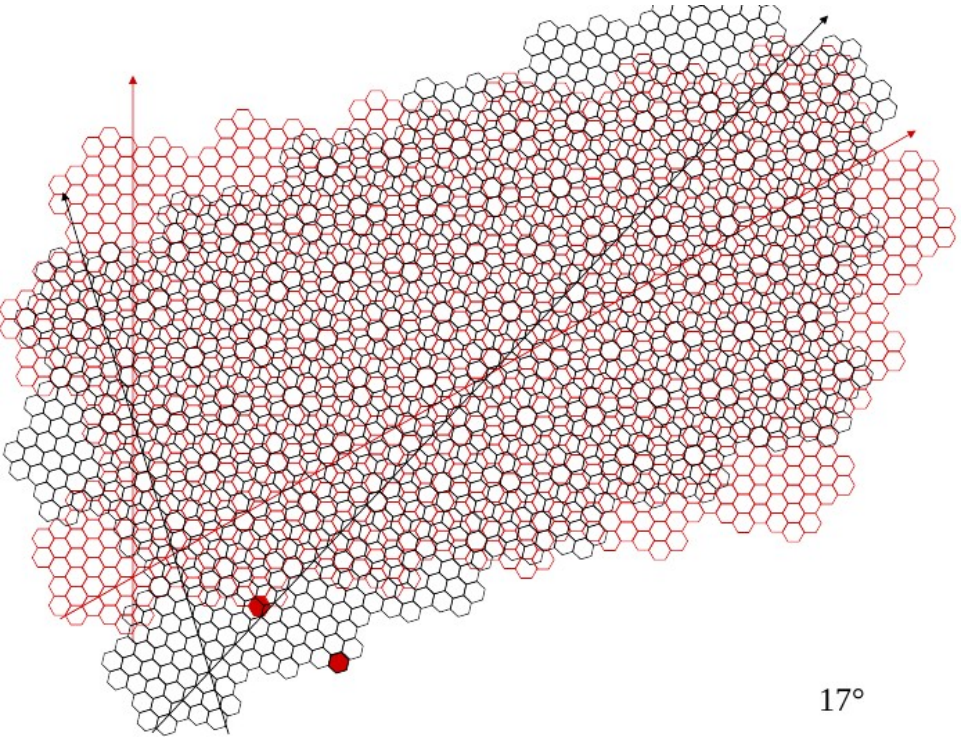
I : decoupling
II : Renormalisation of velocity
III : localization v-> 0

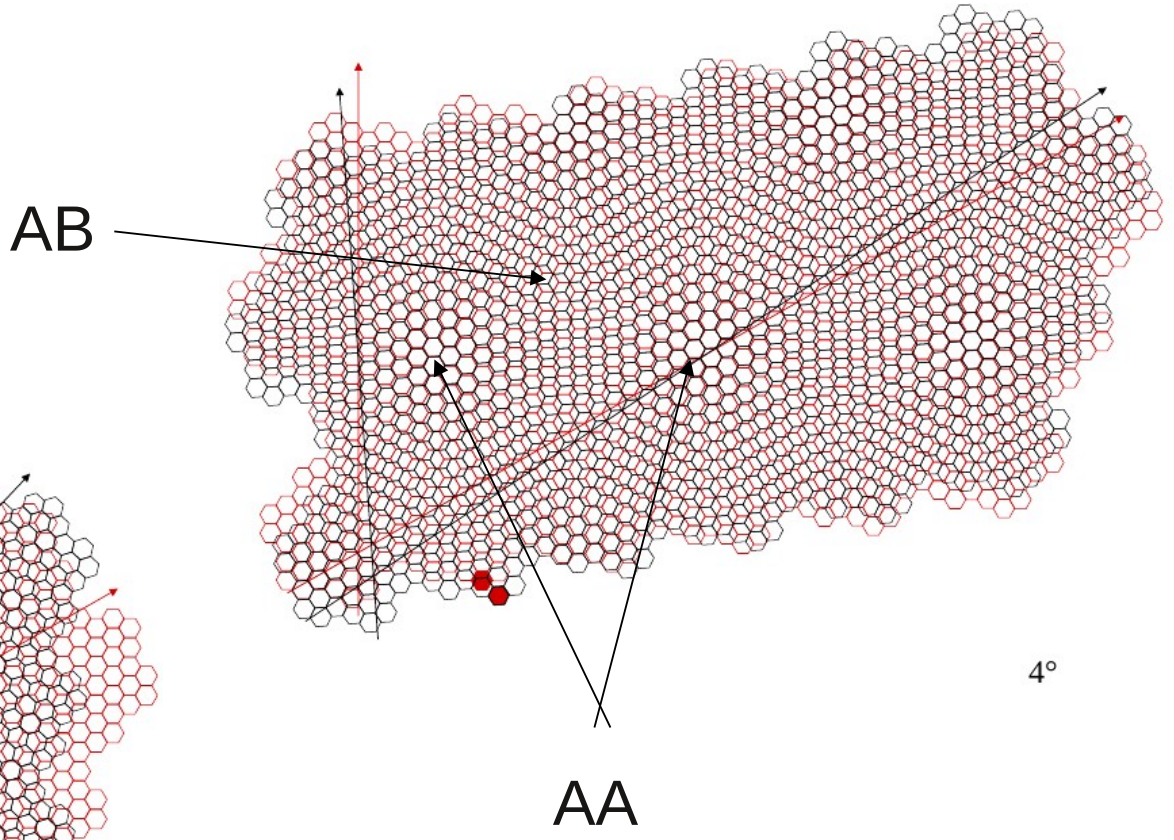


G.Trambly, D.Mayou, L.Magaud,
ArXiv : 0904.1233
NanoLetters 10, 804 (2010)

Lopez dos Santos et al ,PRL 99, 256802 (2007)

3. Rotated bilayers: renormalisation of the velocity





Change θ~10°

Campanera et al PRB 75, 235449 (2007)

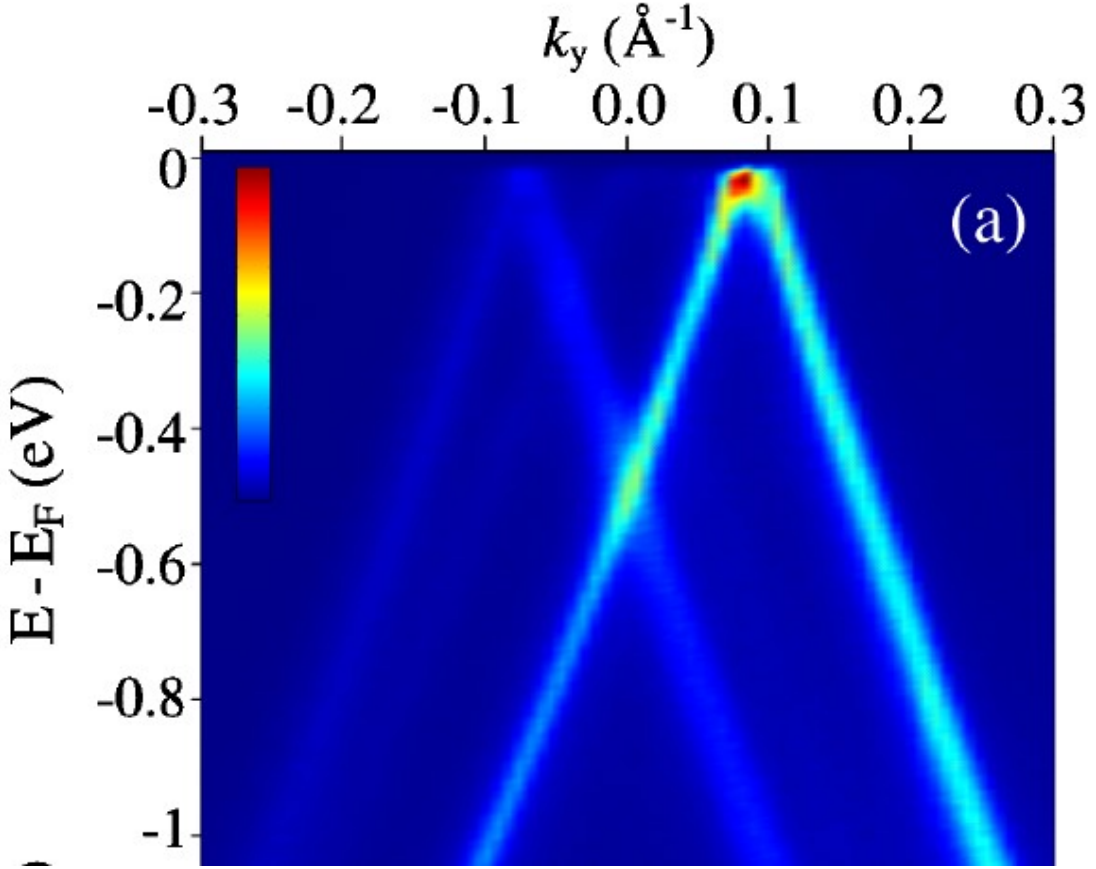
First regime :

- two decoupled graphene layers
- no change of velocity

PRL 103, 226803 (2009) PHYSICAL REVIEW LETTERS week ending 27 NOVEMBER 2009

First Direct Observation of a Nearly Ideal Graphene Band Structure

M. Sprinkle,[1] D. Siegel,[2] Y. Hu,[1] J. Hicks,[1] A. Tejeda,[3,4] A. Taleb-Ibrahimi,[5] P. Le Fèvre,[4] F. Bertran,[4] S. Vizzini,[6,7] zara,[2] and E. H. Conrad[1]

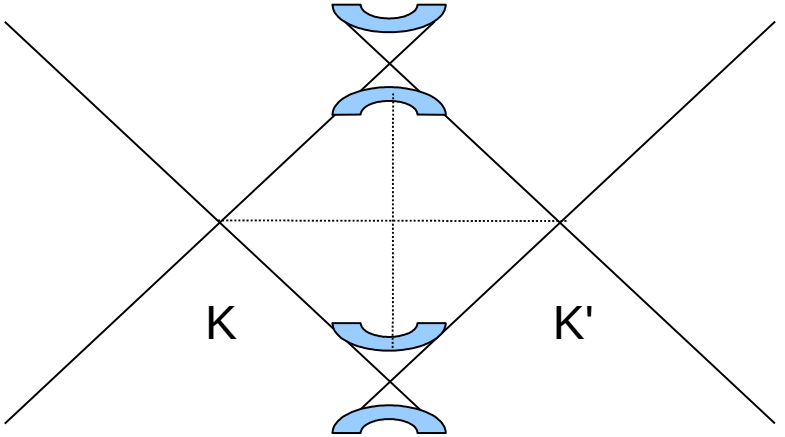


11 layers

Multilayer graphene=
isolated graphene sheets

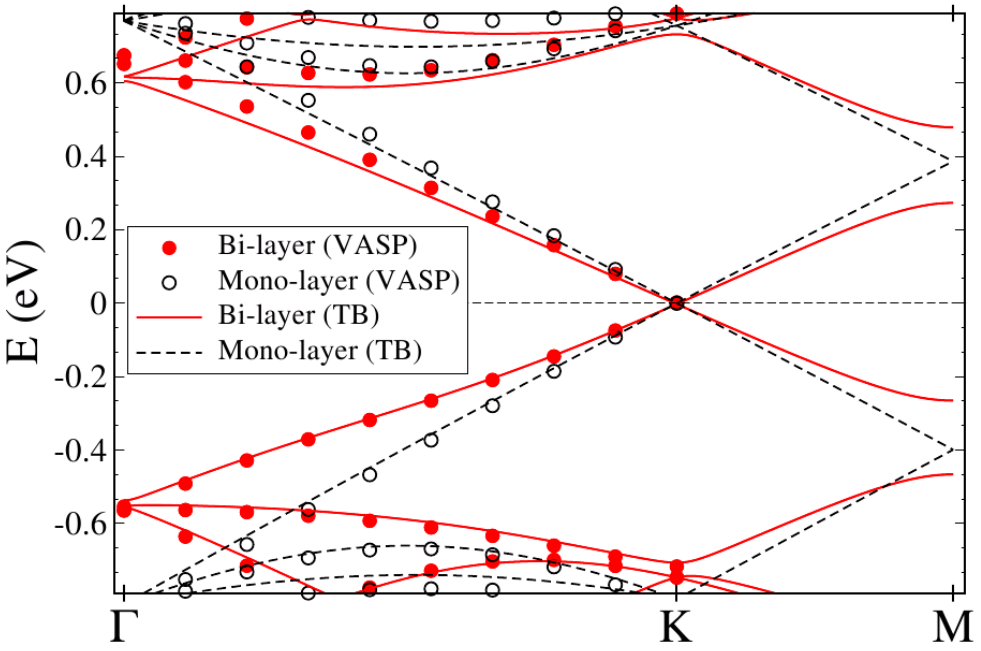
Second anf third regime :

- Renormalization of velocity
- Two coupled graphene layers



Single Layer Behavior and Its Breakdown in Twisted Graphene Layers

A. Luican[1], Guohong Li[1], A. Reina[2], J. Kong[3], R. R. Nair[4], K. S. Novoselov[4], A. K. Geim[4,5], E.Y. Andrei[1]

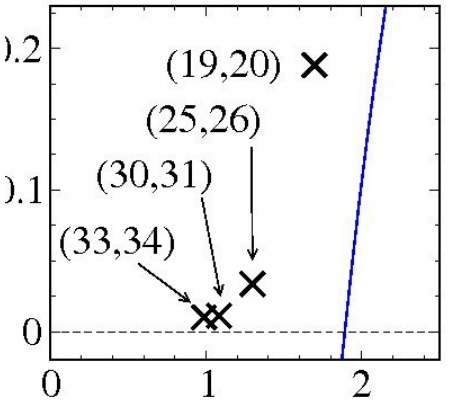


Twisted layers from growth on Ni
STS LL

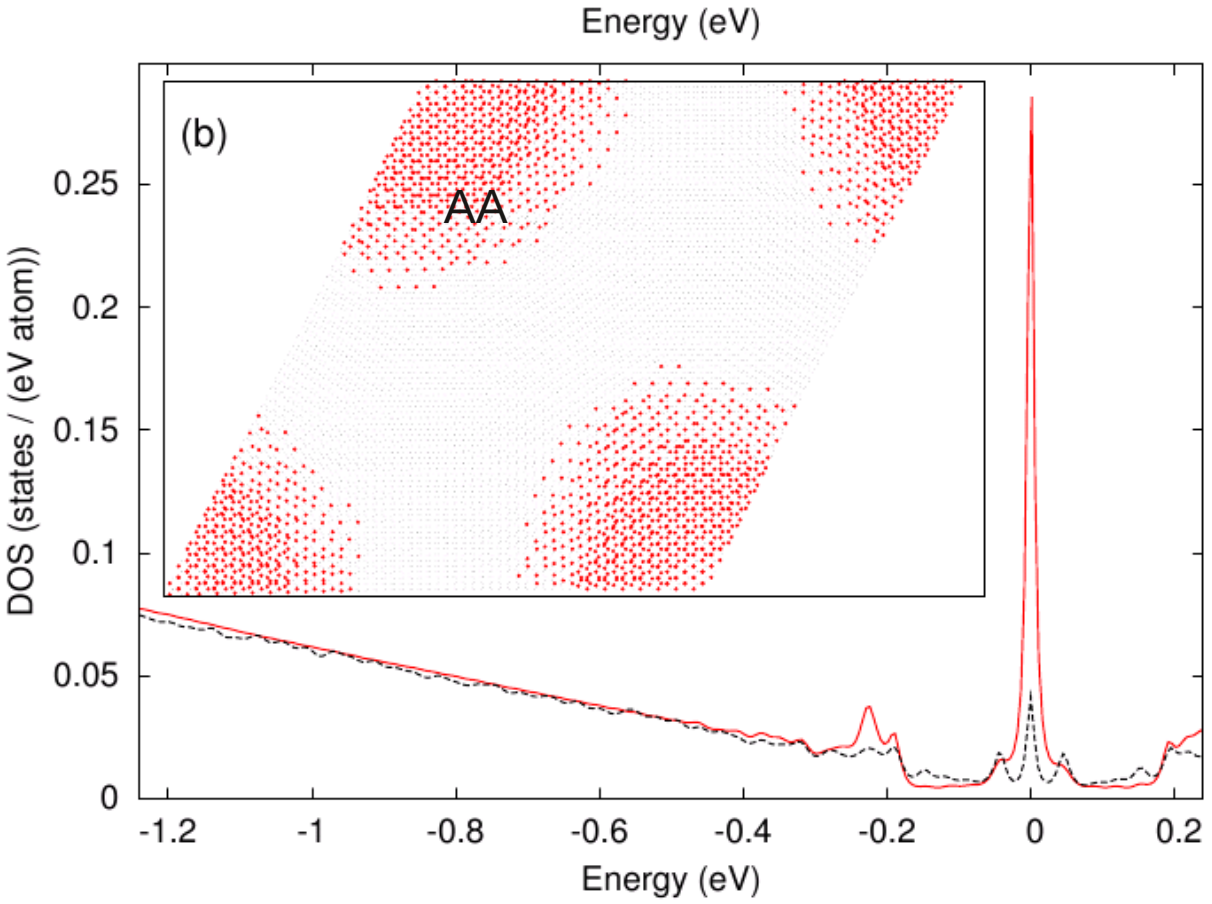
θ>20° decoupling
3<θ<20° renormalisation of velocity
θ<3° van Hove singularity and localisation

third regime :

- Localization v->0



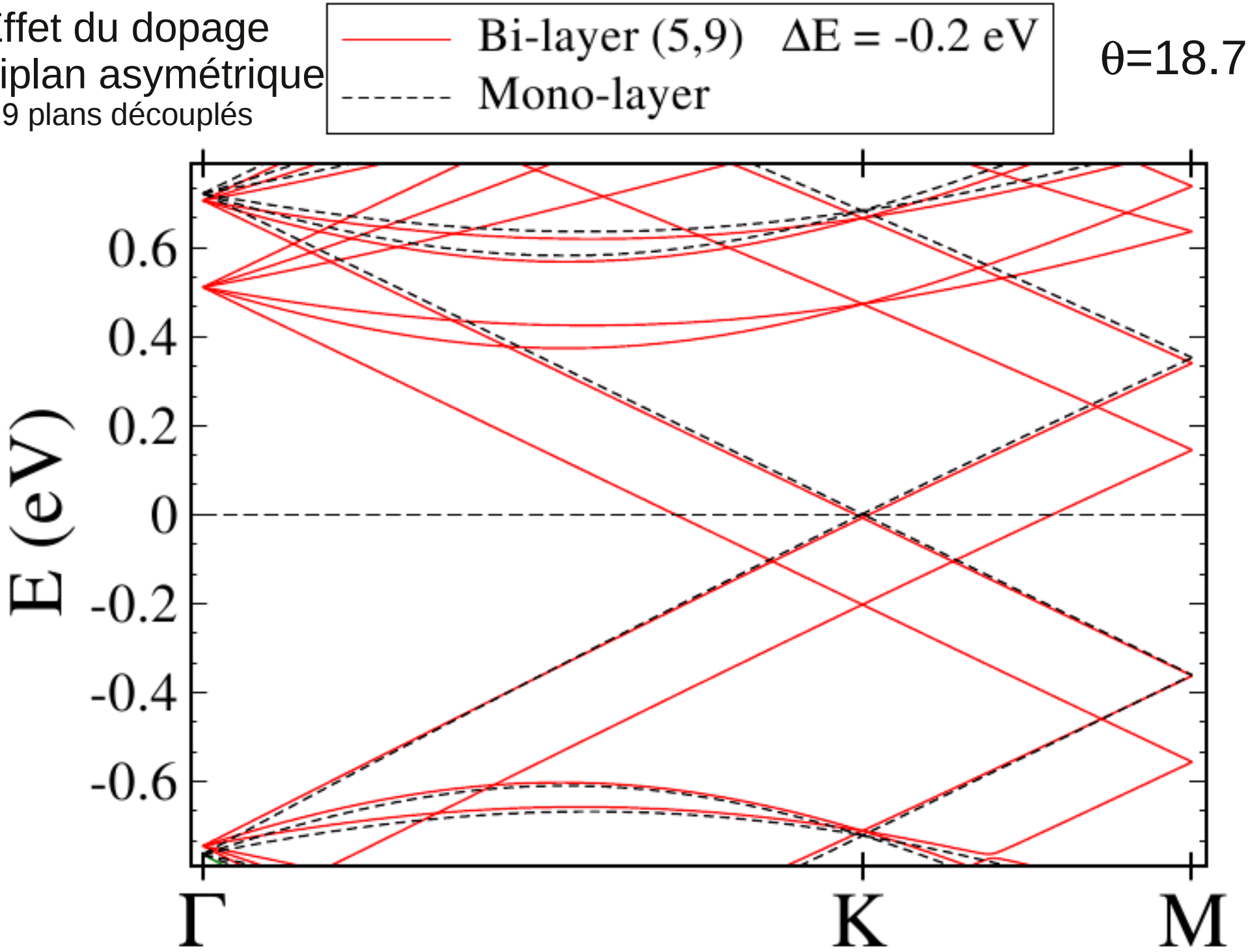
(30,31) (1.08°)



Peak at Dirac point

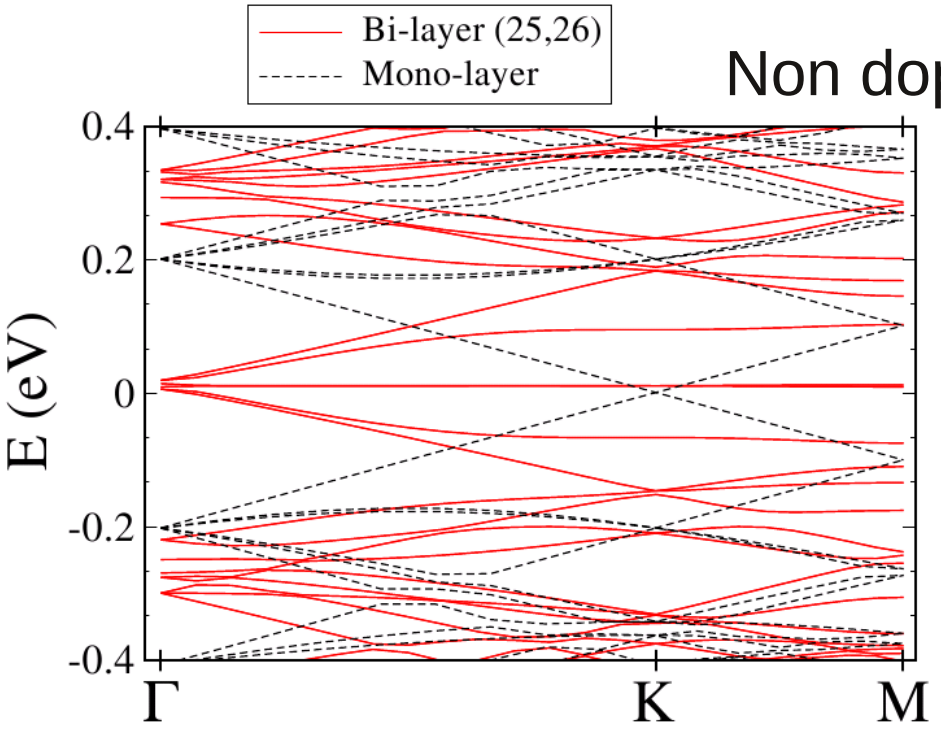
G.Trambly, D.Mayou, L.Magaud,
ArXiv : 0904.1233
NanoLetters 10, 804 (2010)

Effet du dopage
biplan asymétrique
5,9 plans découplés

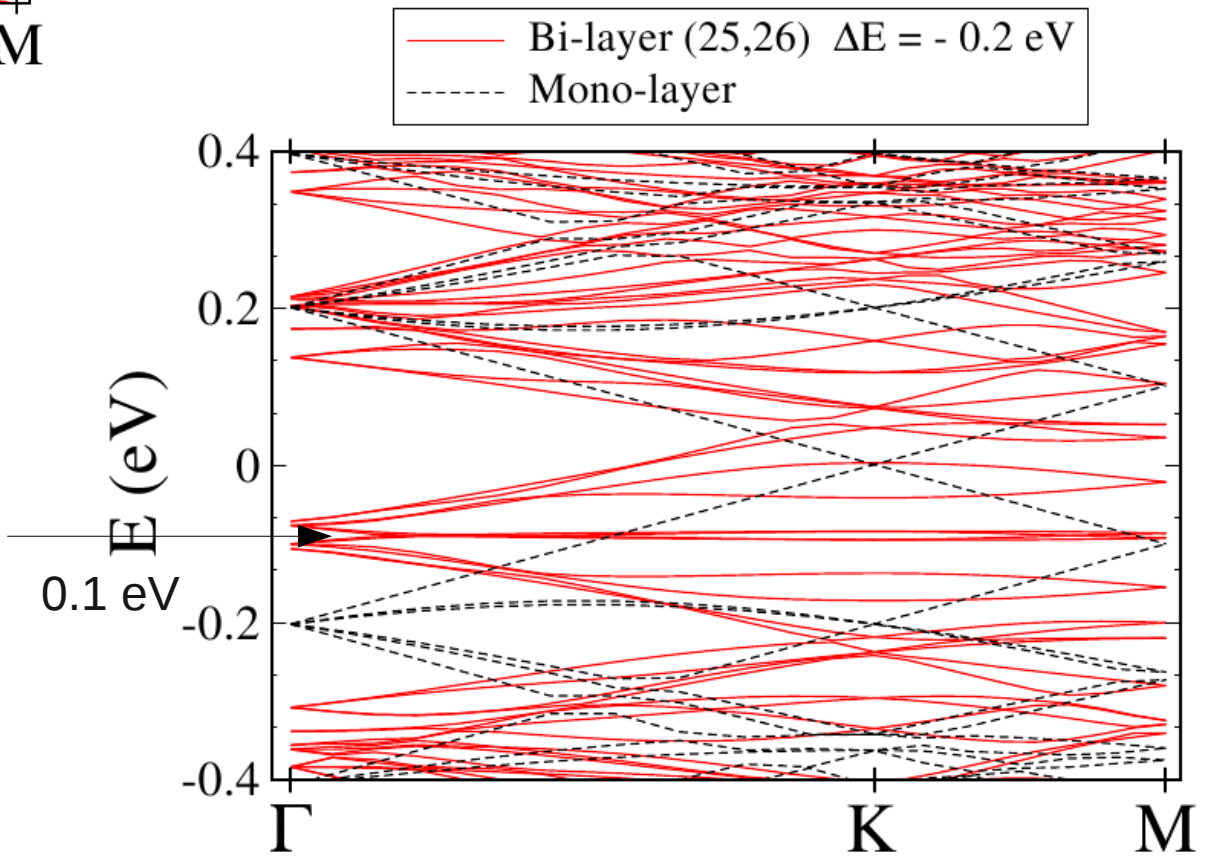


Non dopé

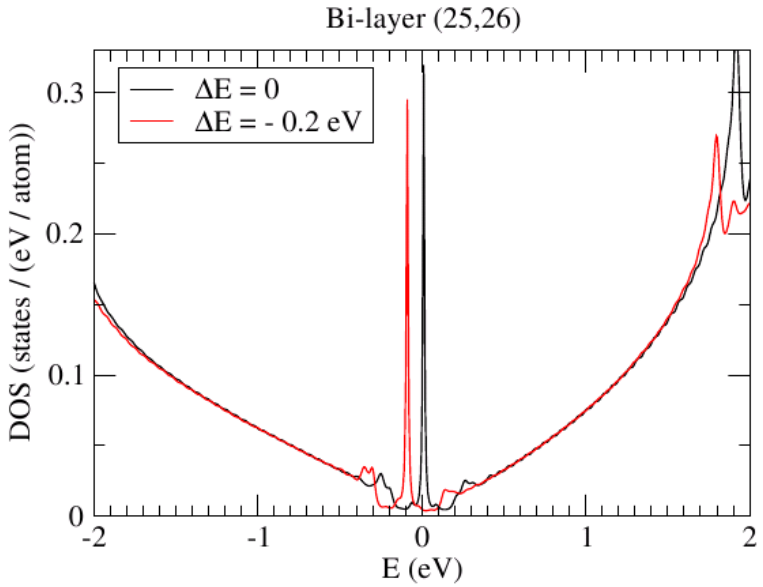
(25,26) θ=1.26°



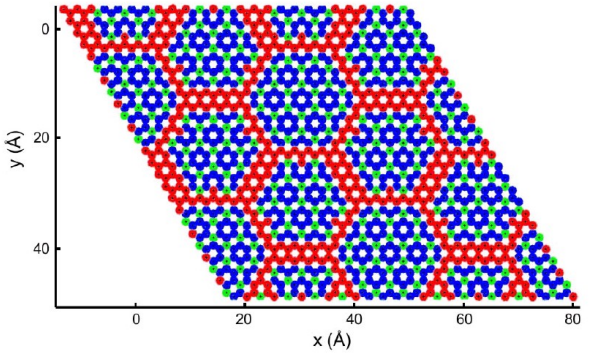
dopé



0.1 eV



Conclusion



EDIP

- **Si - face**

- strong coupling

- 1rst layer = bufferlayer

E.Lampin et al, J.Appl. Phys. 107, 103514 (2010)

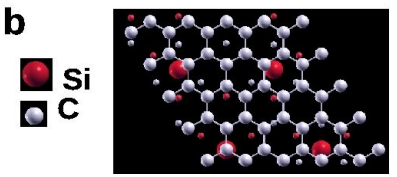
- **C - face**

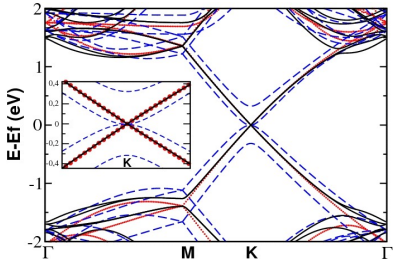
- weak coupling : passivation by surface reconstruction

- graphene = 1rst C layer

- no epitaxy : rotated grains

- twist : from decoupling to localization





Collaborations :

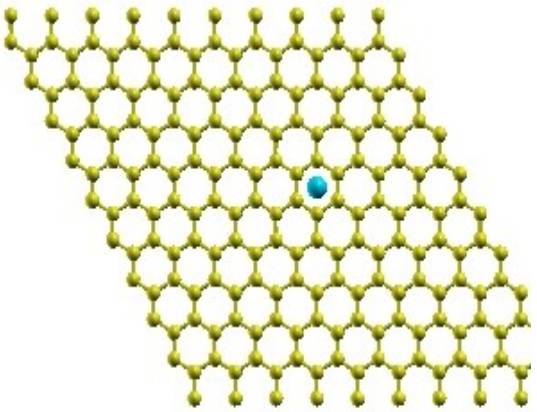
STM	**P.Mallet, J-Y.Veuillen, F.Hiebel, F.Varchon**
Theory	**LM, F.Varchon, D.Mayou, F.Hiebel,** **G.Trambly de Laissardière (Cergy-Pontoise)** **Driss Mouhamadou, Quentin Stainer**

Fundings : ANR Blanche GRAPHSIC
ANR P3N NANOSIM_GRAPHENE
Region : CIBLE 2007 and CIBLE 2008, Cluster recherche
Nanoscience Fundation grenoble : DISPOGRAPH

Growth

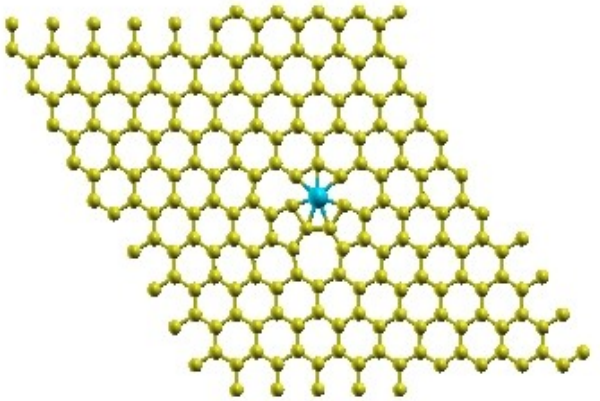
N.Camara et al, Appl. Phys. Lett. 93, 263102 (2008)

Perfect graphene



15 eV

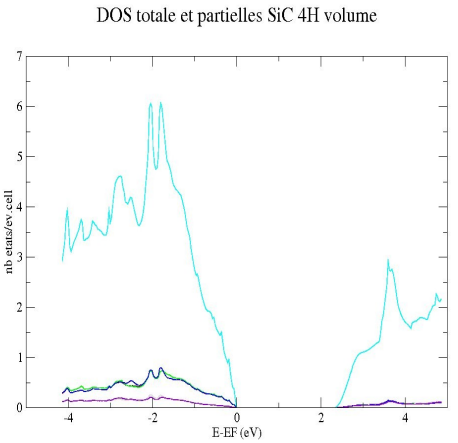
Stone Wales defect



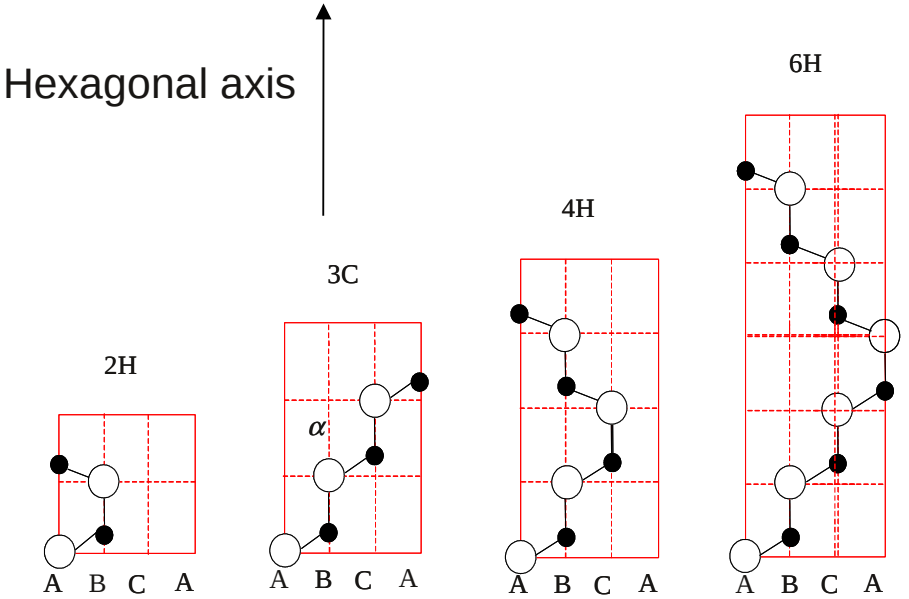
9 eV

The substrate SiC

SiC : large band gap semiconductor
Si – C bilayers similar to C bilayers or Si bilayers along the (111) axis in diamond structure

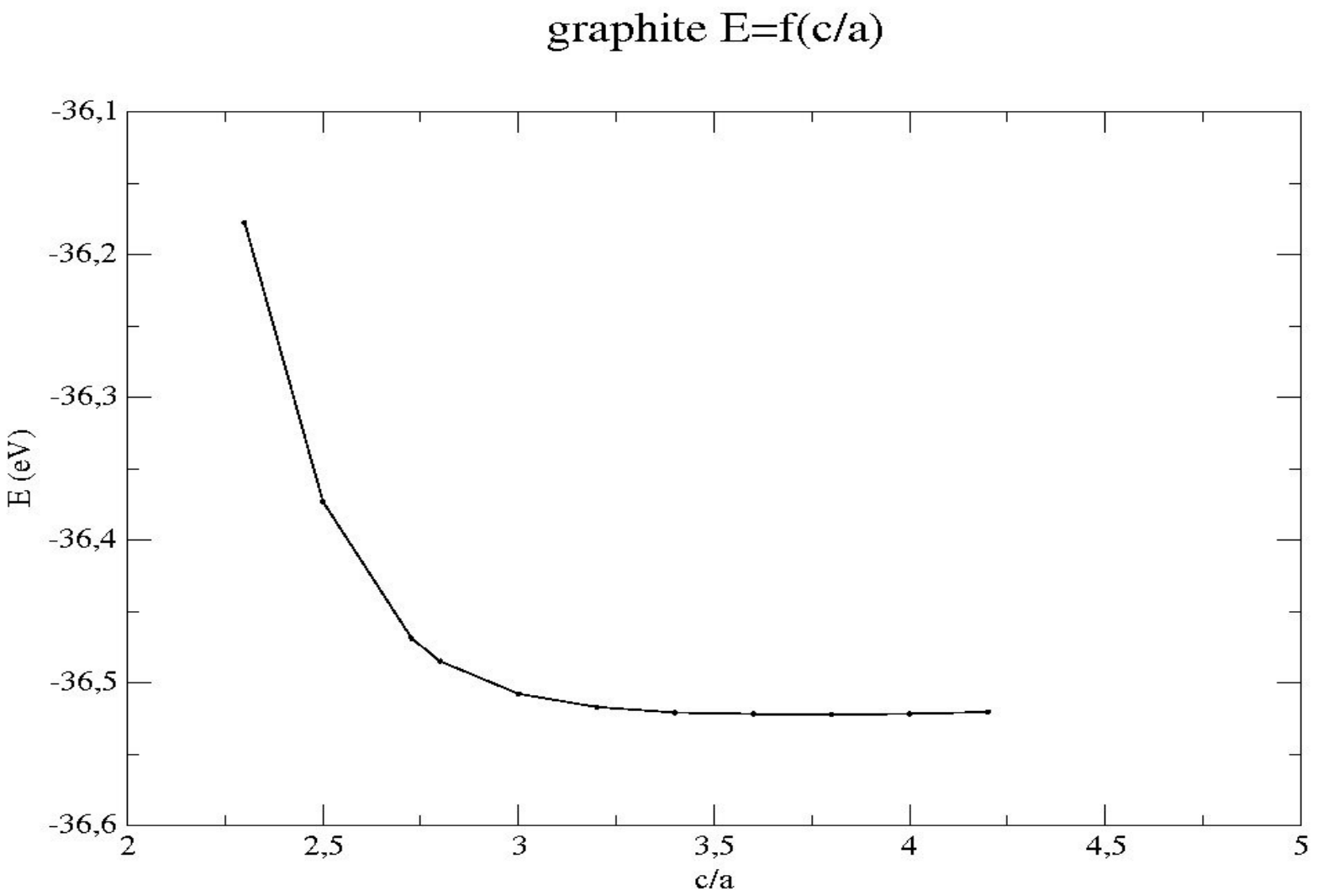


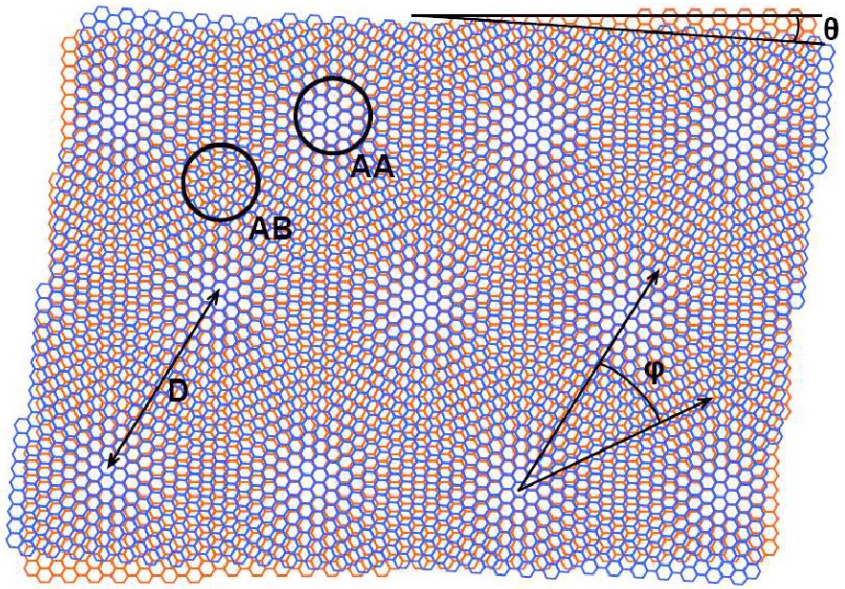
Polytypes :
how Si-C bilayers are stacked along the hexagonal axis.
Structures very close in E

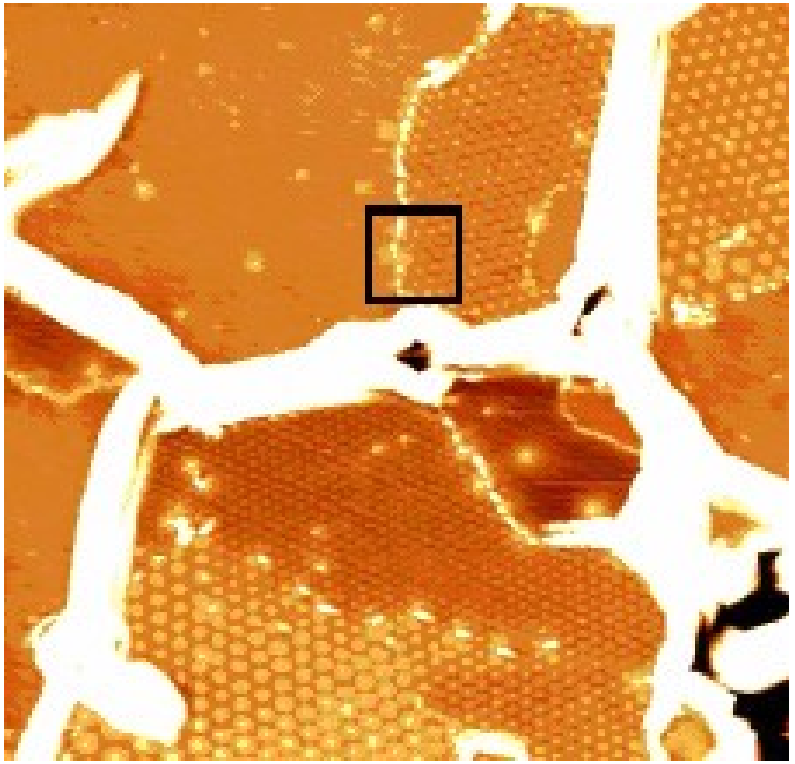


C terminated surface

Si terminated surface


graphite E=f(c/a)
-36,1
-36,2
-36,3
-36,4
-36,5
-36,6
E (eV)
2
2,5
3
3,5
4
4,5
5
c/a





F.Varchon et al, PRB 77, 235412 (2008)

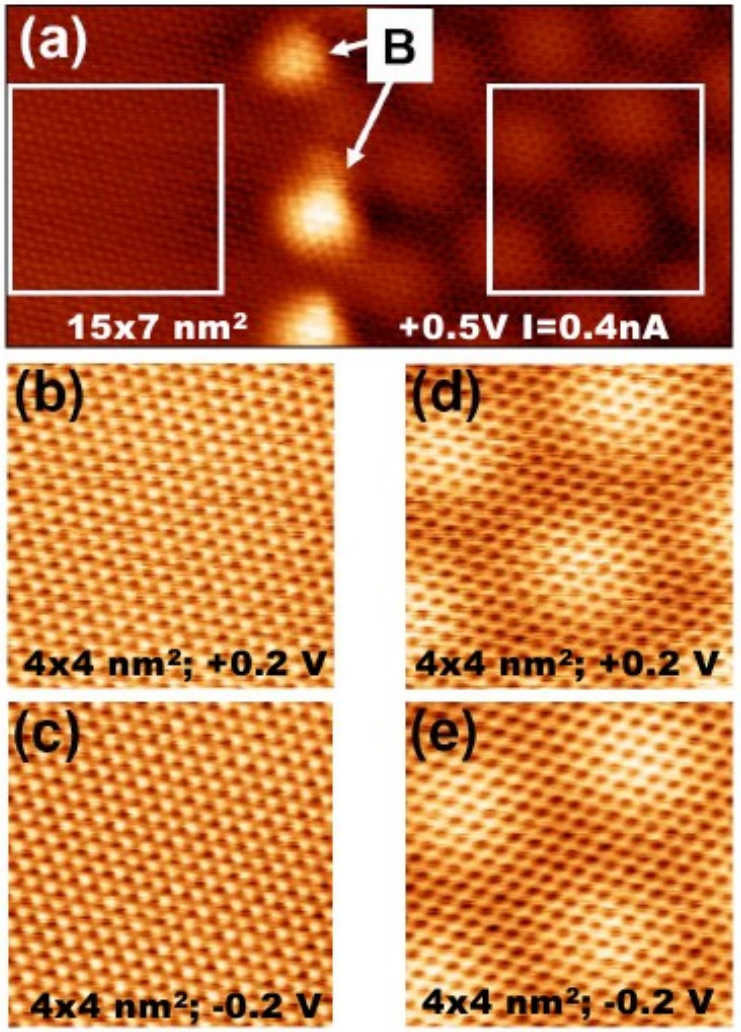
θ : rotation angle between two graphene layers
a lattice parameter
• period of the superlattice (moiré)

D = a/(2sin(θ/2))

•Angle **φ** between the moiré superlattice and graphene

φ= 30°-(θ/2)

Impact on atomic contrast



F.Varchon *et al.*, PRB **77**, 165415 (2008)

We observe, in a range of small biases (below and above E_F):

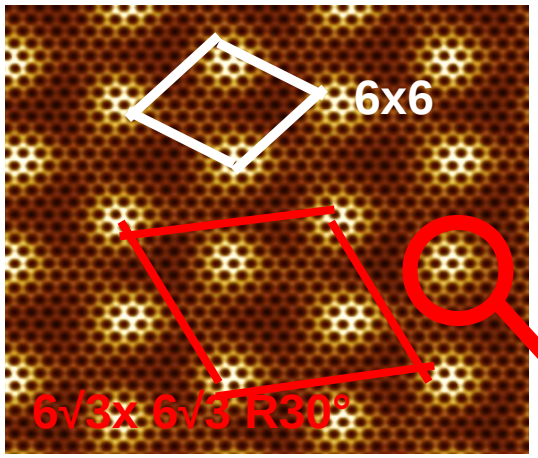
- **honeycomb pattern (or a significantly reduced A/B site asymmetry) on the Moire superstructure**
- **triangular pattern on the flat region (bernal stacking)**

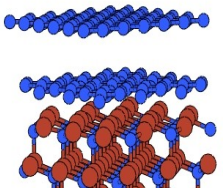
Valuable indication that a single layer-like behavior can be found on rotated graphene layers.

*S. Latil et al., Phys. Rev B76, 201402(R) (**2007**)*

second C layer = graphene with soft ripples

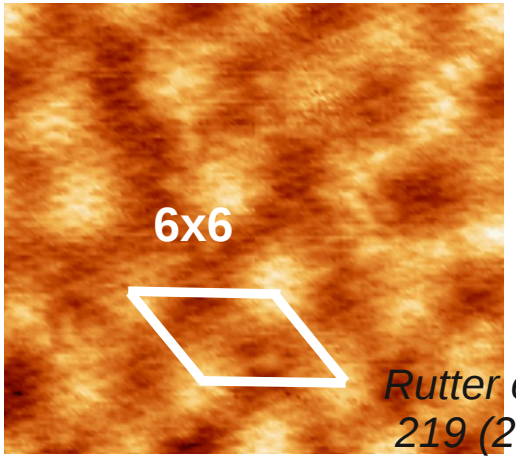
Ab initio

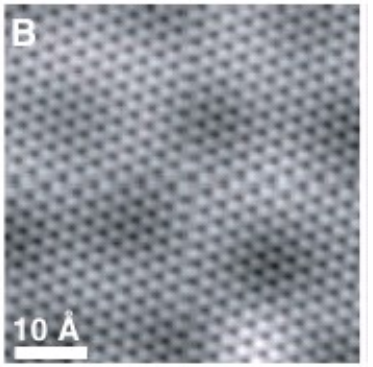




STM image (0.2 V, 300 K),

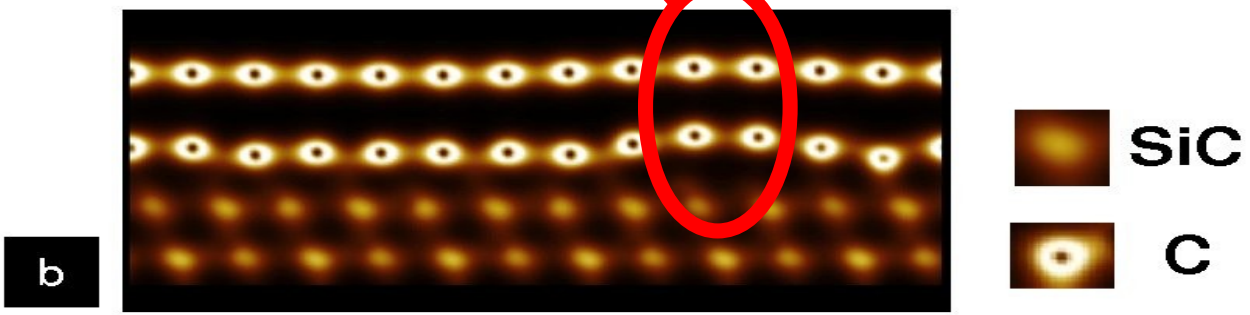
P.Mallet et al., Phys Rev B74, 041403 (R) (2007)

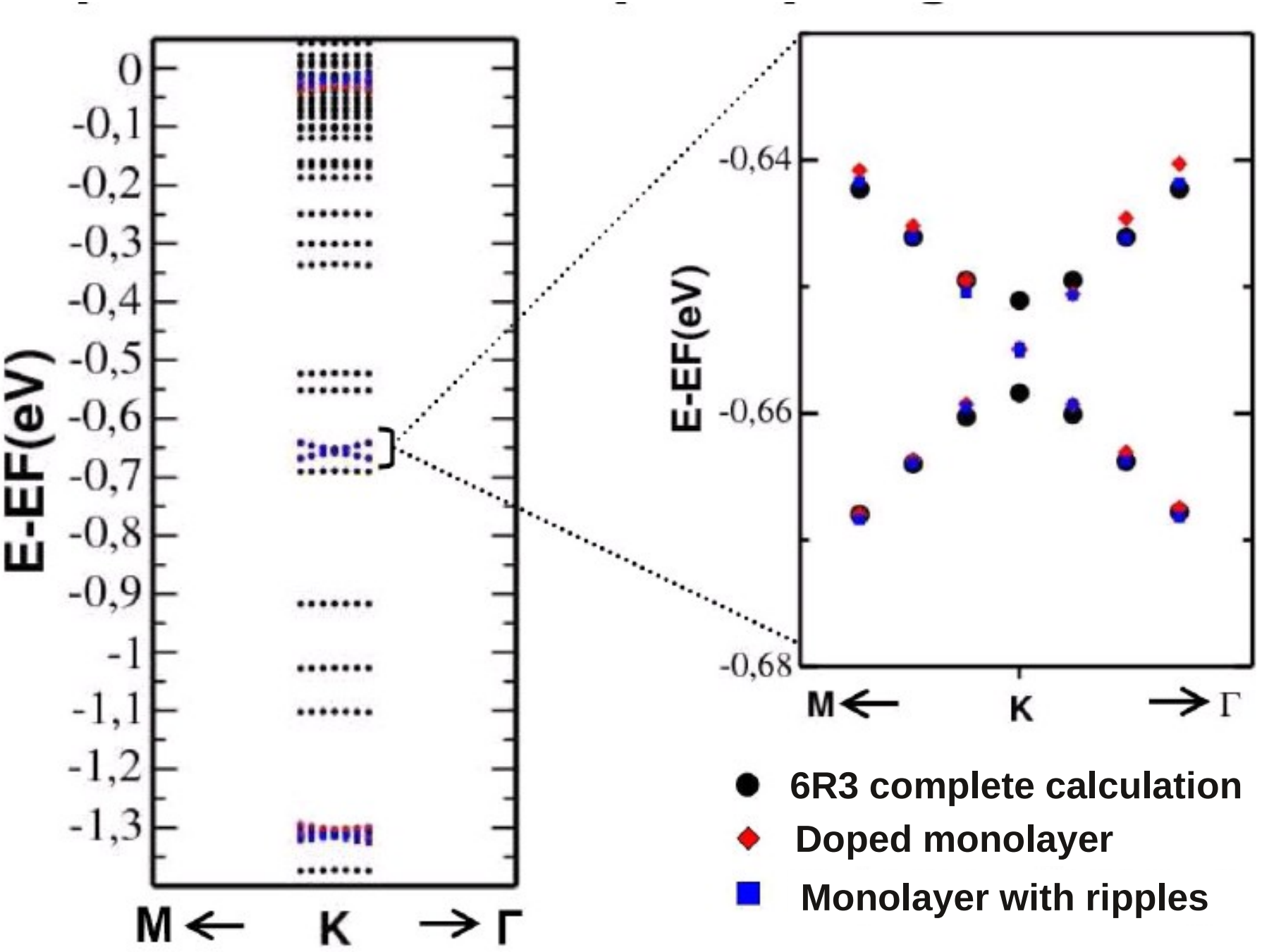




Rutter et al Science 317, 219 (2007)

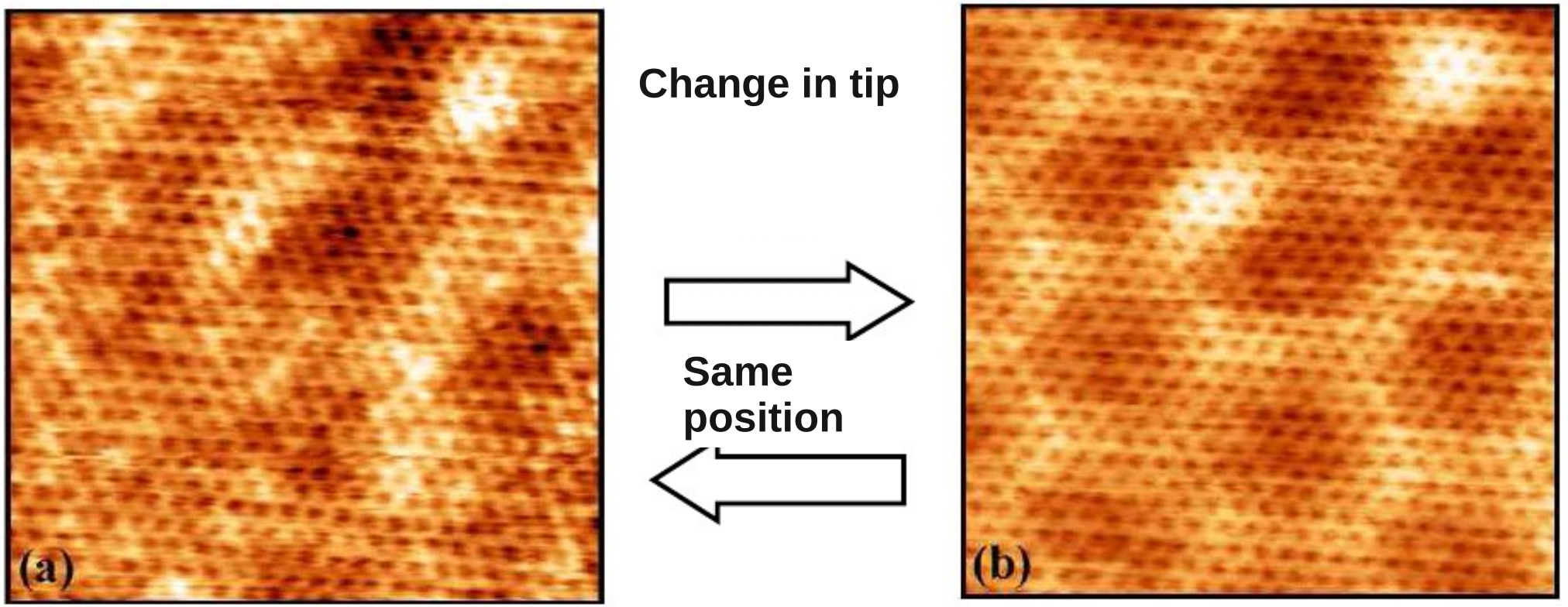
Corrugation : 0.5 Å (STM : 0.2 – 0.4 Å), roughly follows buffer layer geometry, generates soft 6x6 ripples
no C-C bond
graphene decoupled from the substrates thanks to the buffer layer




E-EF(eV)
0
-0,1
-0,2
-0,3
-0,4
-0,5
-0,6
-0,7
-0,8
-0,9
-1
-1,1
-1,2
-1,3
M
K
Γ
E-EF(eV)
-0,64
-0,66
-0,68
M
K
Γ
6R3 complete calculation
Doped monolayer
Monolayer with ripples

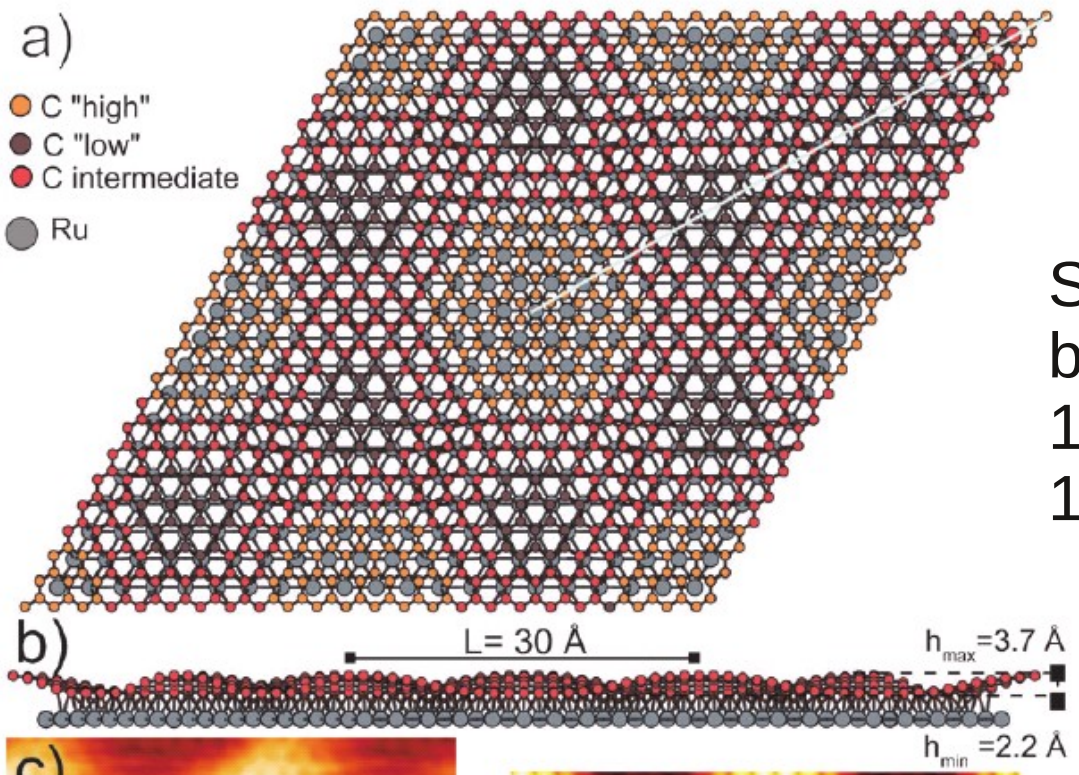
6R3 = complex model but actual interface even more complex

disorder
adatoms at interface



5.6 x 5.6 nm², +0.2 V

Graphene on Ru (0001)



Strong coupling bufferlayer
12x12 C on
11x11 Ru

STM
1mA, -0.05V
50x40 A
Marchini et al PRB 76, 075429 (2007)

Ab initio

Wang et al, Phys. Chem. Chem. Phys. 10, 3530 (2008)