Physisorption of hydrogen on graphene

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Outline

1. Context

2. Model

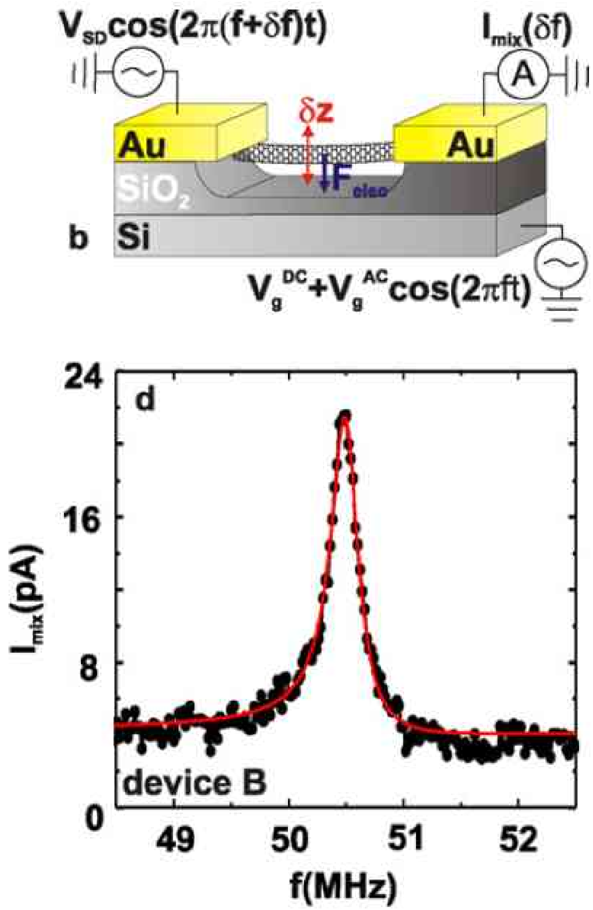
    H-graphene/graphite interaction potential
    Phonon model
    The specific problem of graphene
    H-phonon coupling model
    Dynamical methods

3. Physisorption of H on graphene

    Comparison RDM-CCWP
    Resonance processes
    Effect of the phonon model
    Effect of the number of layers (graphite)

Context : graphene

High sensitivity low Temperature Nano Electro Mechanical Systems (NEMS)



B. Lassagne, A. Bachtold / C. R. Physique 11 (2010) 355–361

Actuation : Oscillating electrostatic force induced by gate DC+AC voltage

→Mechanical oscillations of graphene (resonator).

Detection : current variation induced by vibration-dependant conductance.

Resonance : improvement of quality factor at low T

Mass detection : zepto-gramme (10-21 g) sensitivity

$$f = \sqrt{\frac{k}{m}}$$

Sticking properties central

Hydrogenation of graphene : what about physisorption ?

Control of Graphene's Properties by Reversible Hydrogenation: Evidence for Graphane

D. C. Elias,[1*] R. R. Nair,[1*] T. M. G. Mohiuddin,[1] S. V. Morozov,[2] P. Blake,[3] M. P. Halsall,[1]
A. C. Ferrari,[4] D. W. Boukhvalov,[5] M. I. Katsnelson,[5] A. K. Geim,[1,3] K. S. Novoselov[1]†

Although graphite is known as one of the most chemically inert materials, we have found that graphene, a single atomic plane of graphite, can react with atomic hydrogen, which transforms this highly conductive zero-overlap semimetal into an insulator. Transmission electron microscopy

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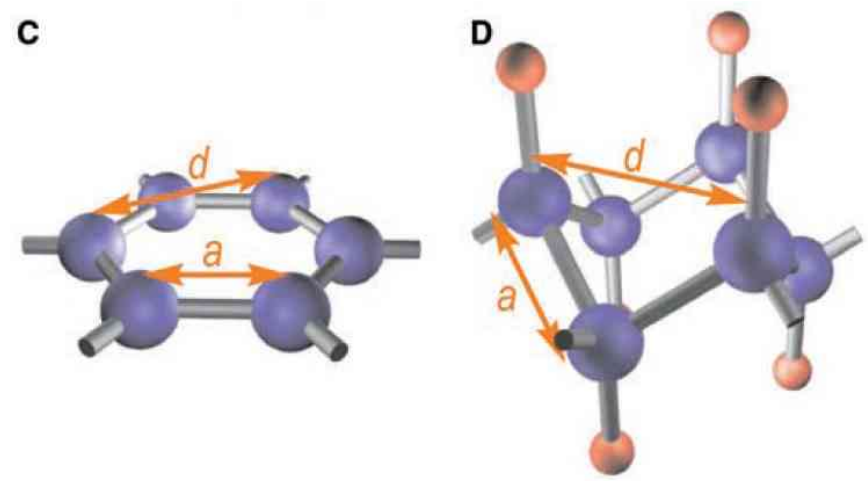
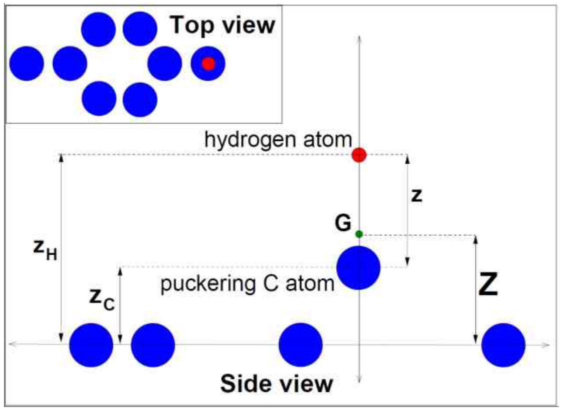
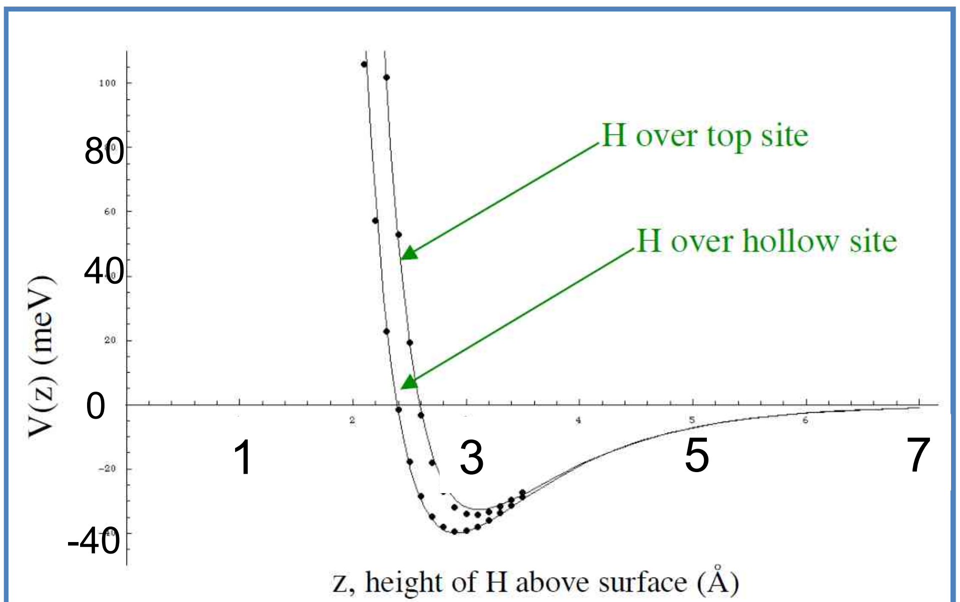


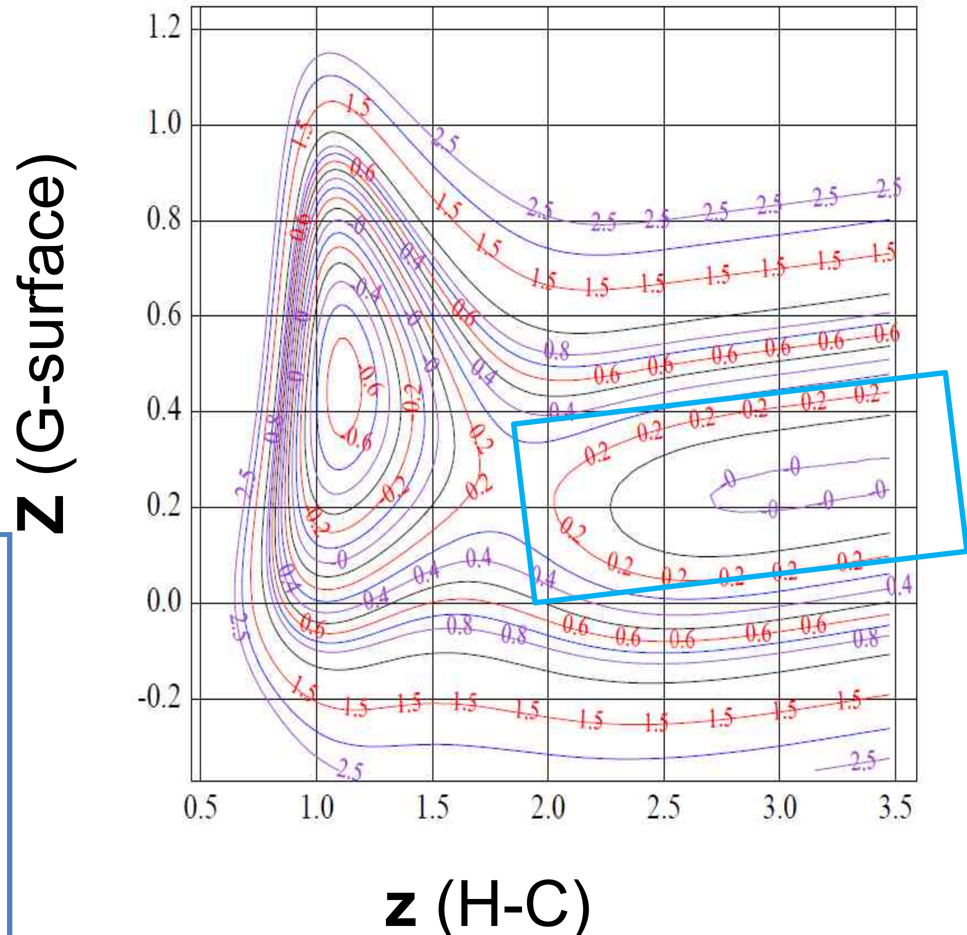
Graphene exposed to low pressure (0.1 mbar)
H2 (10%)-Ar for 2 hours

H-graphite/graphene interaction

Sha, Jackson, 2002







..... MP2 calculations of Bonfanti, Martinazzo, Tantardini and Ponti, J. Phys. Chem. C 111, 5825 (2007)

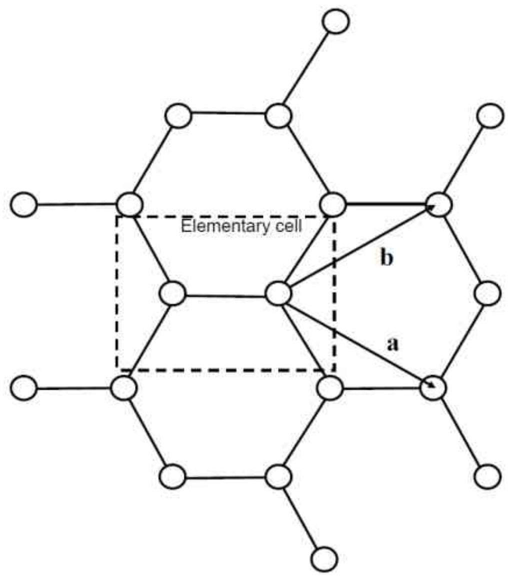
___ model PES

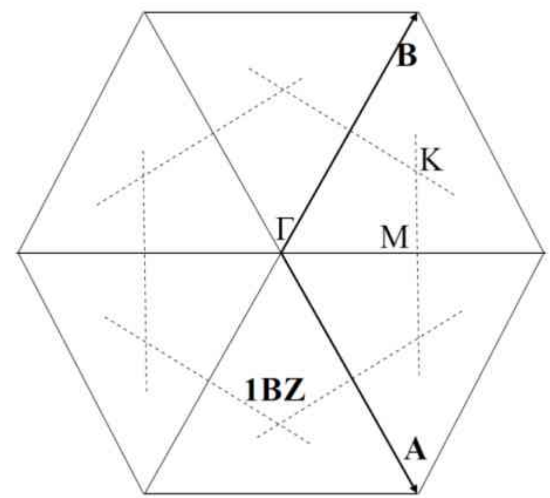
DISSIPATIVE MECHANISMS NECESSARY FOR STICKING :

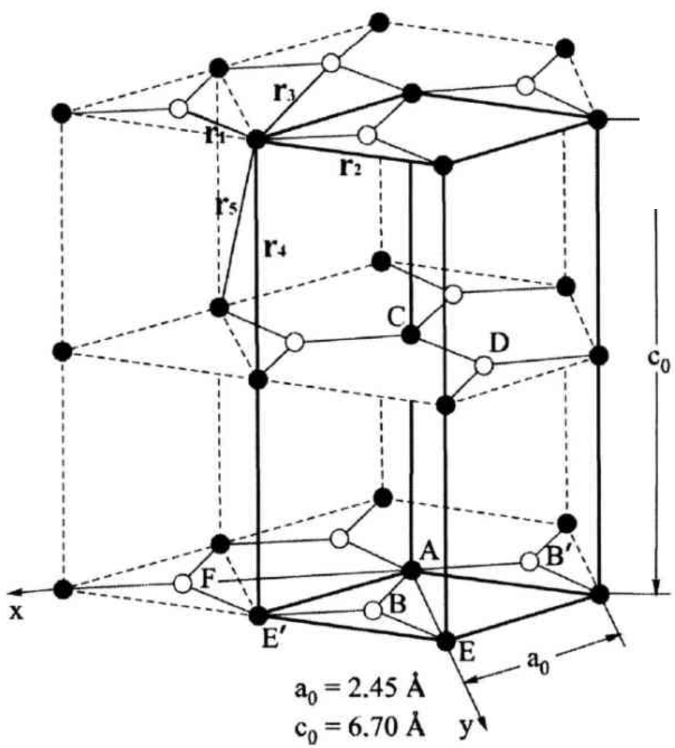
- electron-hole excitation ?

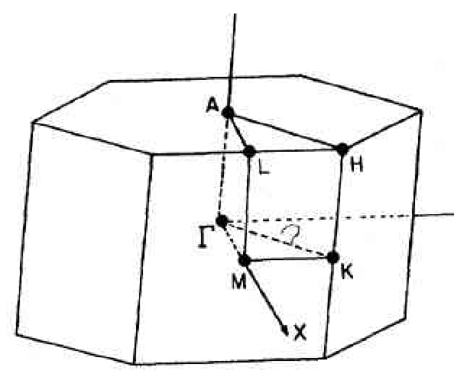
- phonon excitation ?

GRAPHENE/GRAPHITE STRUCTURE





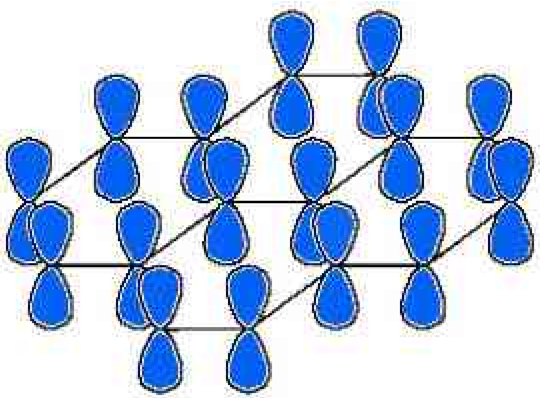


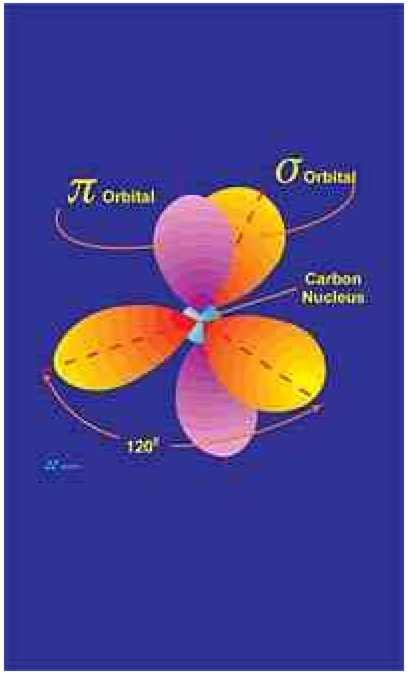


ELECTRONIC STRUCTURE OF GRAPHENE

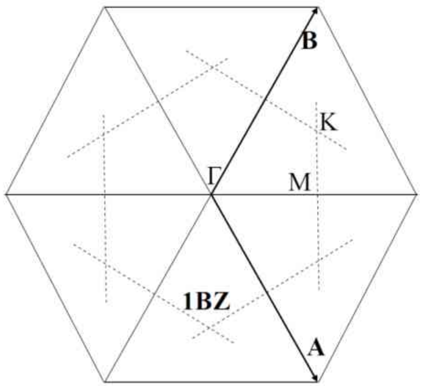
sp2 hybridization : 1s2 2s2 2p2 ✳ 1s2 σ3 π

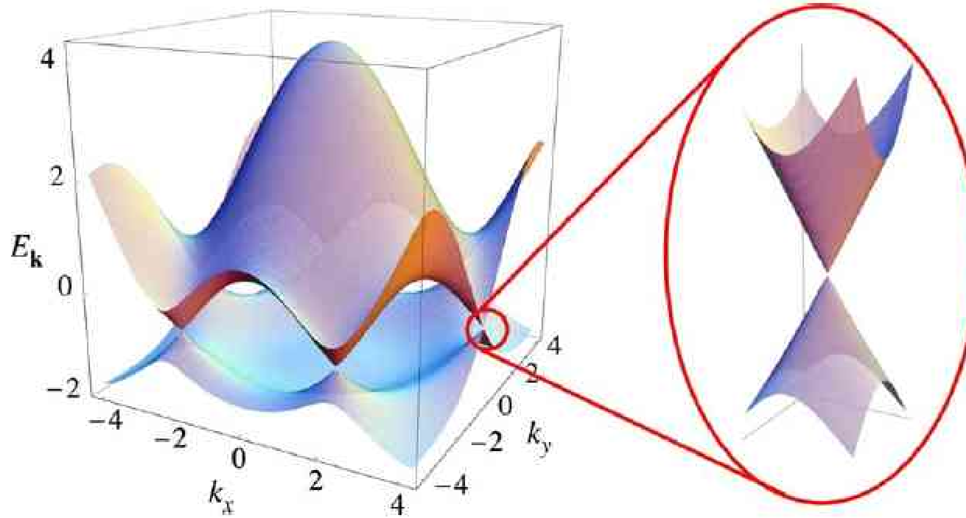
Network of conjugated π bonds ✳ conductivity





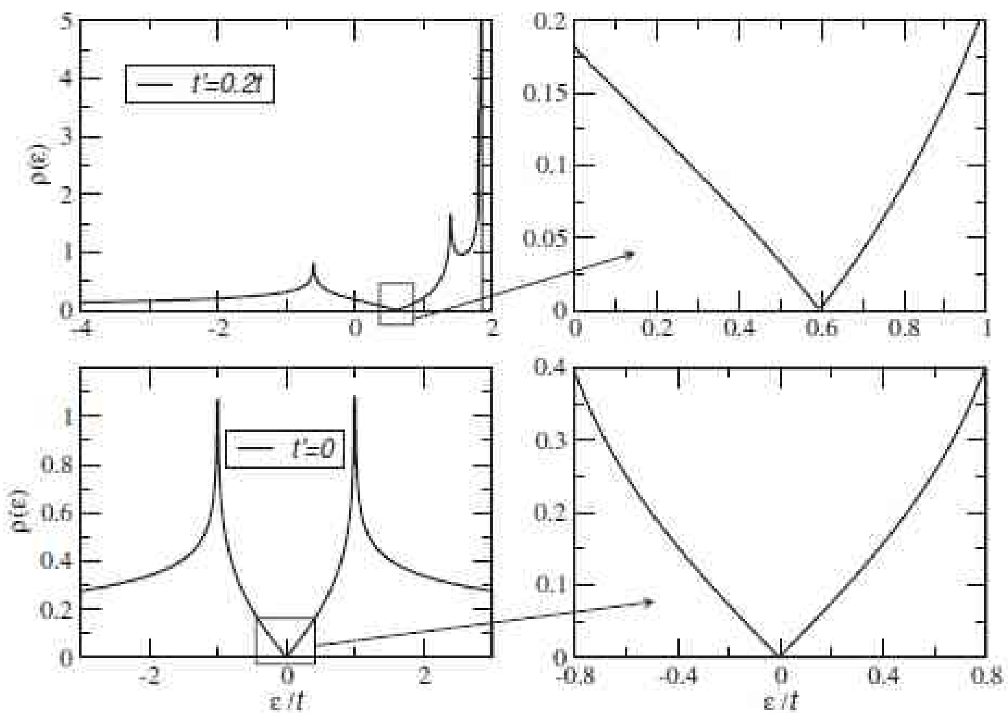
BAND STRUCTURE





DENSITY OF STATES

t=2.8 eV



REVIEWS OF MODERN PHYSICS, VOLUME 81, JANUARY–MARCH 2009

The electronic properties of graphene

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Graphene is a semi-metal :

no band gap but 0 density of states at Fermi level

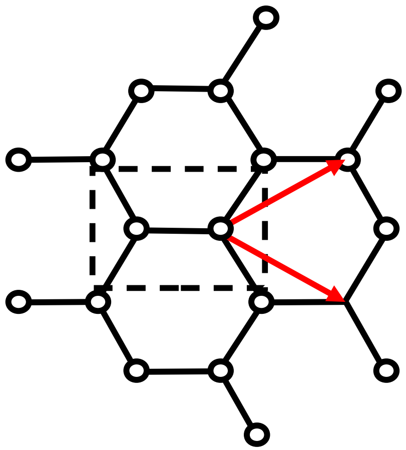
Because of the low density of states near Fermi level,

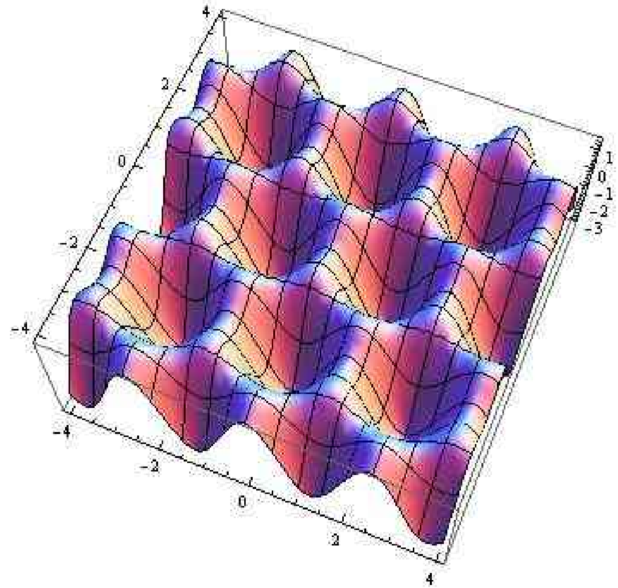
electron-hole formation

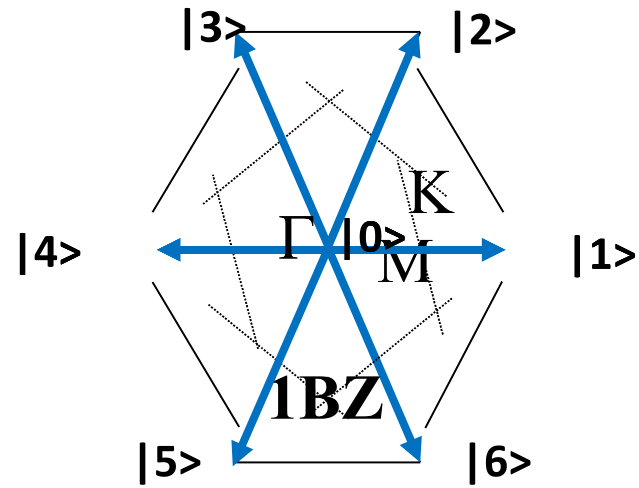
should not be efficient at low energy

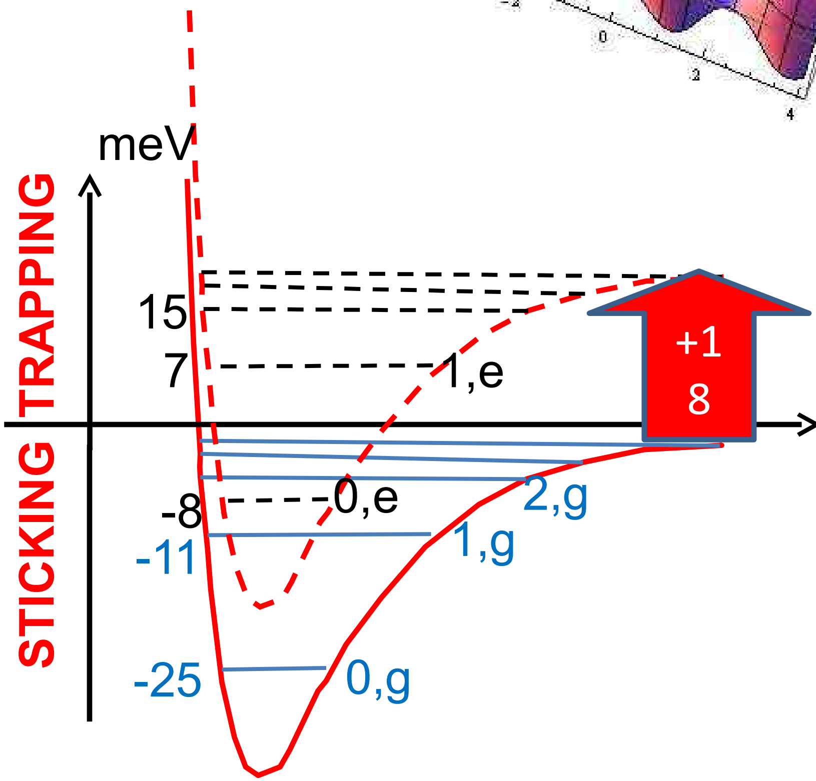
Its efficiency may increase with increasing energy

The model : H-graphite interaction









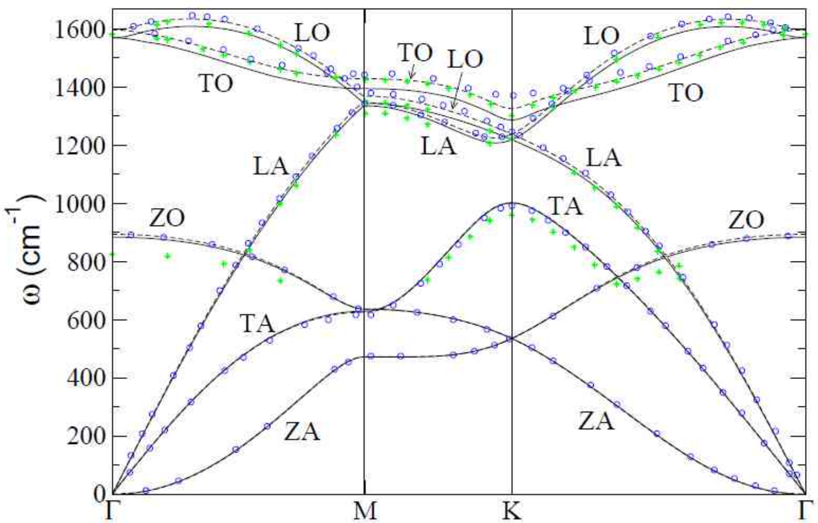
Normal incidence :
2 diffraction states

|g>=|0>

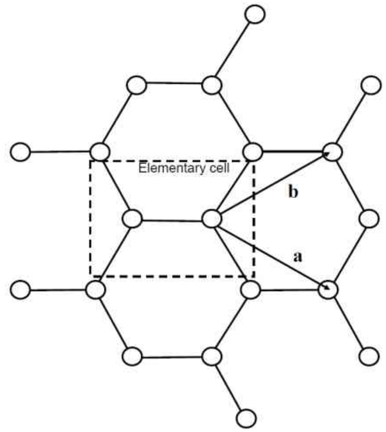
|e>=(|1>+|2>+|3>+|4>+|5>+|6>)/61/2

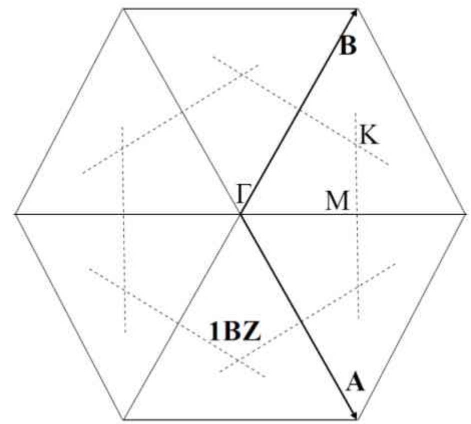
The model : phonons

Graphene

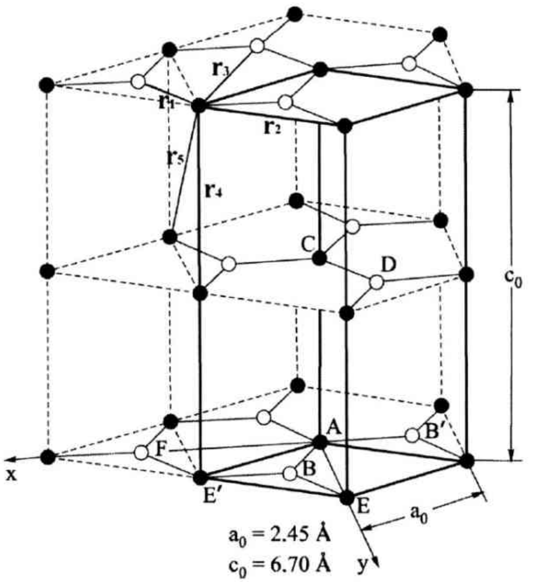


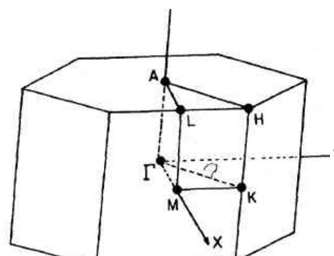
L. Wirtz, Rubio, Solid. State Com., 131, 141 (2004)

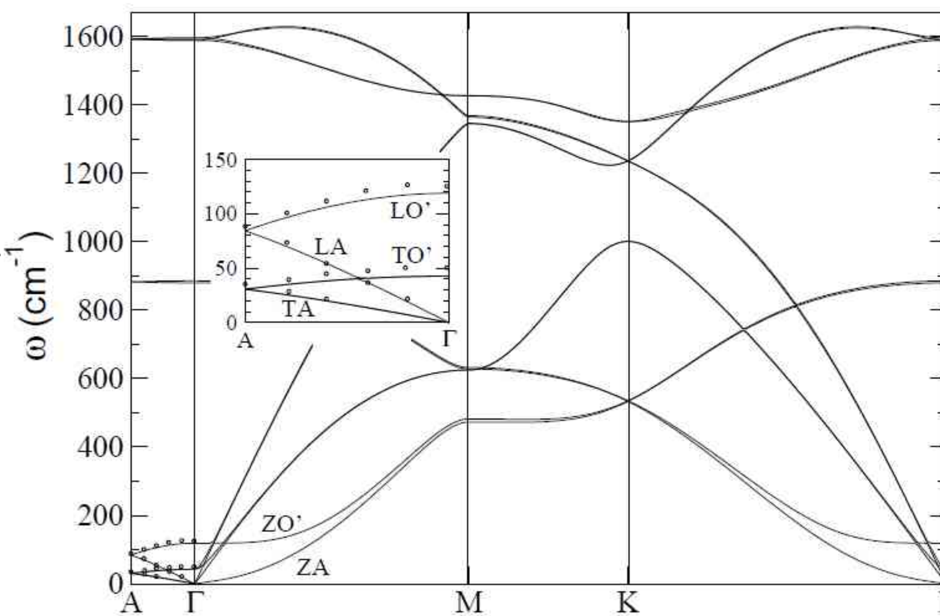




Graphite







The model : phonons

For flexural modes (perpendicular to the surface)

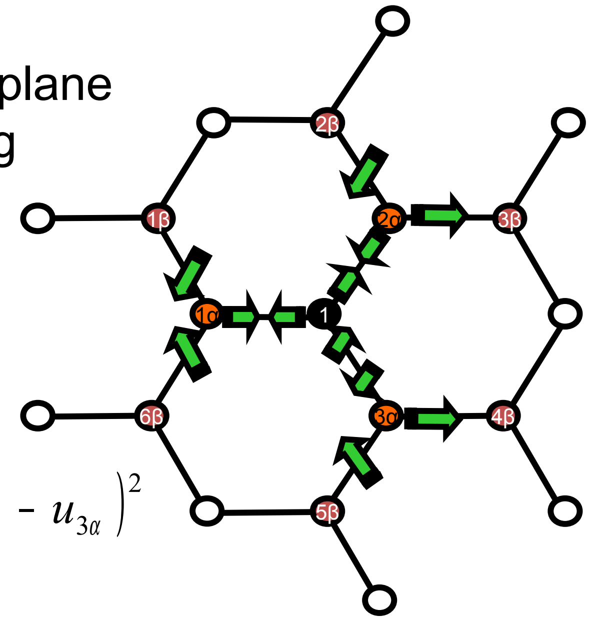
Intra-layer :

Valence-force-field with 2 « spring constants » :

out-of-plane bending+twisting

T. Aizawa, R. Souda, S. Otani, Y. Ishizawa, C. Oshima, Phys. Rev. B 42 (1990) 11469

Out-of-plane bending

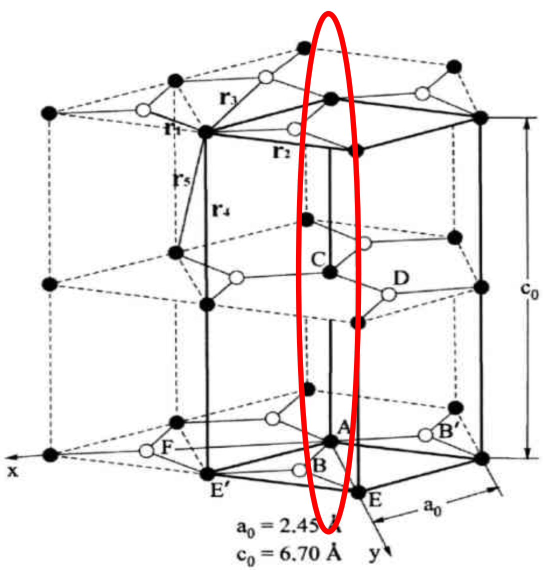


$$\frac{3\gamma}{2a^2}\left(3u_1 - u_{1\alpha} - u_{2\alpha} - u_{3\alpha}\right)^2$$

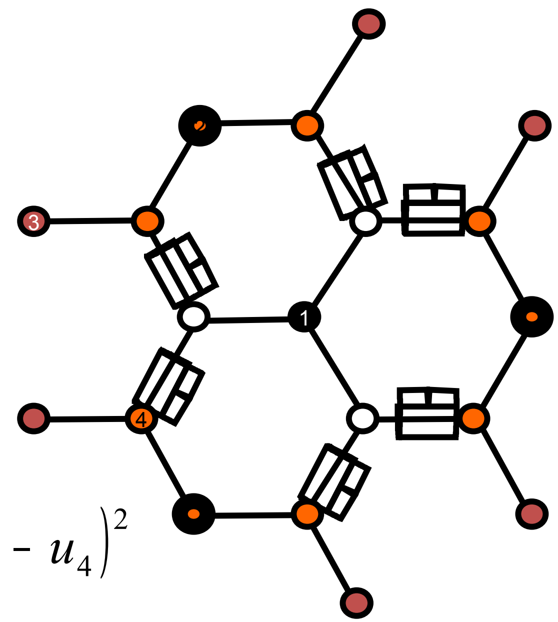
Inter-layer :

1 nearest-neighbor « spring constant »

R. Nicklow, N. Wakabayashi, H.G. Smith, Phys. Rev. B 5 (1972) 4951

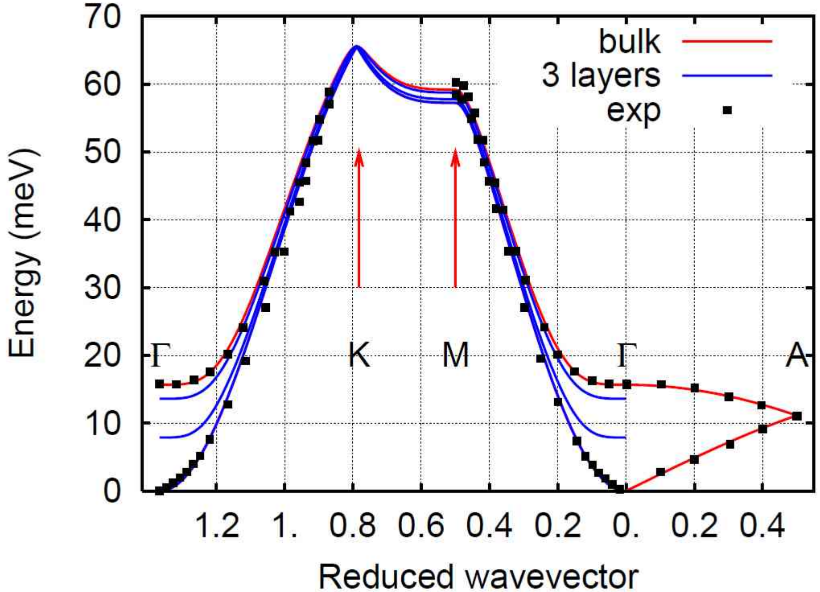


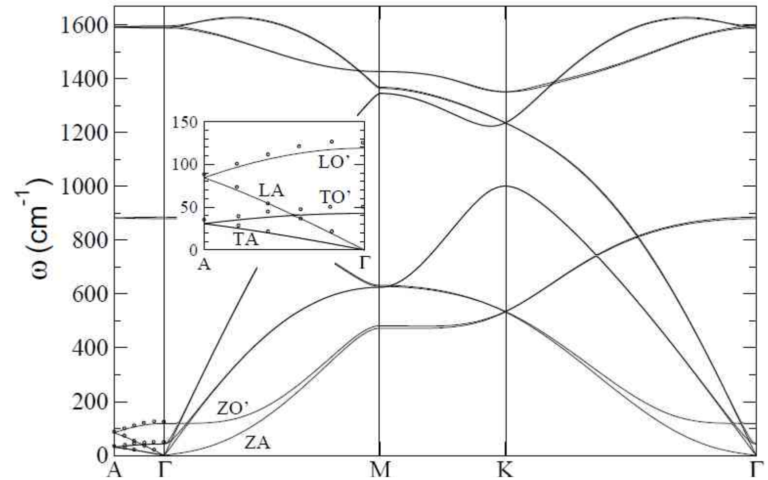
Twisting

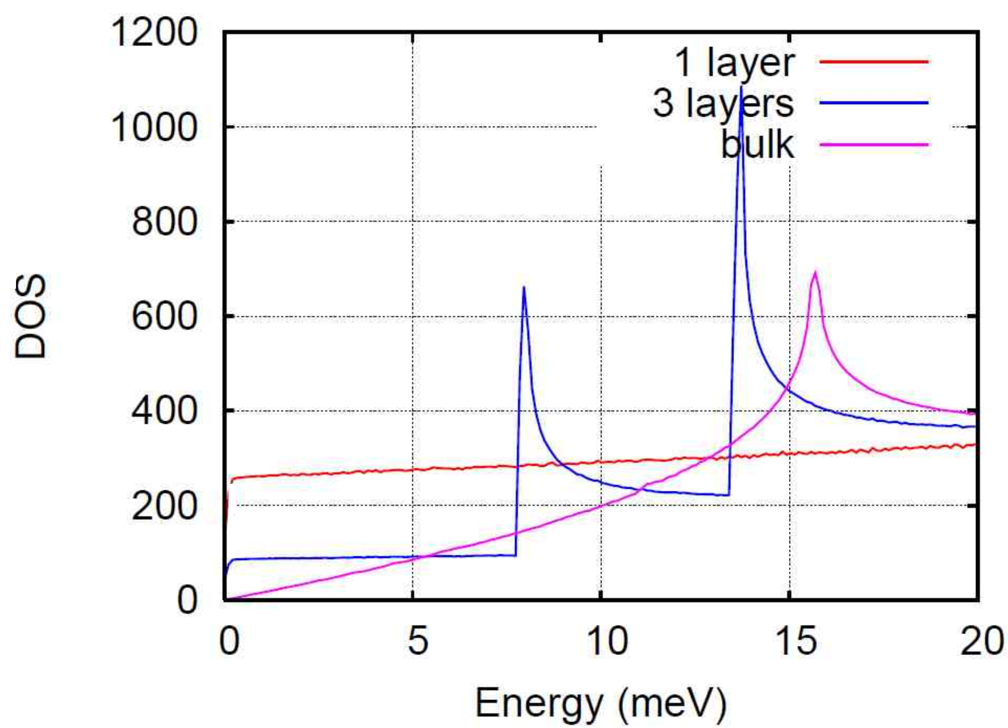


$$\frac{\delta}{2a^2}\left(u_1 + u_3 - u_2 - u_4\right)^2$$

The model : phonons







$$DOS = \rho(\omega) = \frac{\Delta^D Q}{\Delta \omega}$$

D = 2 : graphene, D = 3 : graphite

GRAPHENE : PHONON PROBLEM

$$u_i = \frac{1}{(MN)^{\frac{1}{2}}} \sum_{Q\sigma} U_{Q\sigma}\, \varepsilon_{Q\sigma}^{s_i}\, e^{iQ(l_i + s_i)}$$

Thermal average : $n_\omega(T) = \dfrac{1}{e^{\frac{\hbar\omega}{kT}} - 1}$

Correlation between displacements at different point = measure of long range order :

$$\langle (u_i - u_j)^2 \rangle = \frac{\hbar}{MN} \sum_{Q\sigma} \frac{1}{\omega_{Q\sigma}} \left(n_{Q\sigma}(T) + \frac{1}{2} \right) \left| \varepsilon_{Q\sigma}^{s_i} \right|^2 \left(1 - \cos(Q(r_i - r_j)) \right) \rightarrow \frac{kT}{M} \int d\omega\, \rho(\omega) \left(\frac{Q}{\omega} \right)^2$$

R. Peierls,
Quelques propriétés typiques des corps solides
Annales de l'IHP, 5 (1935) 177

Integrand	LA, TA	ZA
GRAPHITE	ω^2	ω^0
GRAPHENE	ω^0	ω^{-1}

graphene , ZA : singular integrand

✳ No order, even at short range

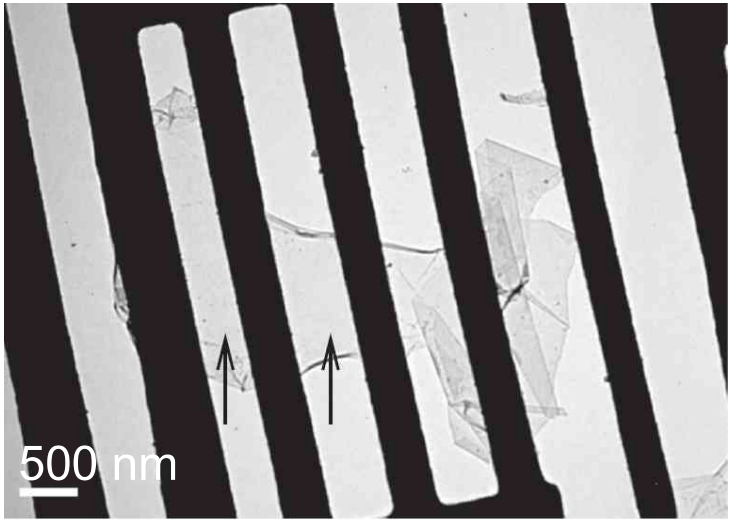
✳ instability : crumpling, buckling

- Stabilization role of coupling between bending and stretching (anharmonicity)
- Stabilization role of substrate ?
- Even for suspended graphene ?

The structure of suspended graphene sheets

Jannik C. Meyer[1], A. K. Geim[2], M. I. Katsnelson[3], K. S. Novoselov[2], T. J. Booth[2] & S. Roth[1]

NATURE | Vol 446 | 1 March 2007



Interaction with substrate for supported graphene

- Weak and not well known vdw interaction

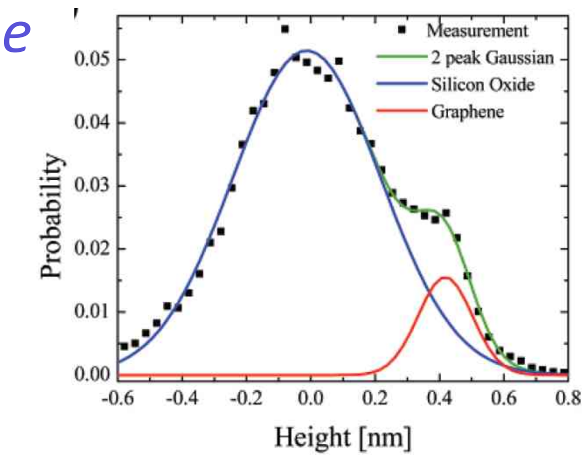
- Graphite :
  - interlayer distance : 3.4 Å
  - interlayer energy : 20 meV/Å2 = 50 meV/atom

- Graphene supported on SiO2 :
  - SiO2-graphene distance : *h0= 4.2 Å*
  - SiO2-graphene interaction energy
    - *Γ0≈ 6 meV/Å2 = 0.1 J/m2*

- Force constant for vibration of graphene on SiO2

$$U_{vdW}(h) = -\Gamma_0\left[\frac{3}{2}\left(\frac{h_0}{h}\right)^3 - \frac{1}{2}\left(\frac{h_0}{h}\right)^9\right]$$

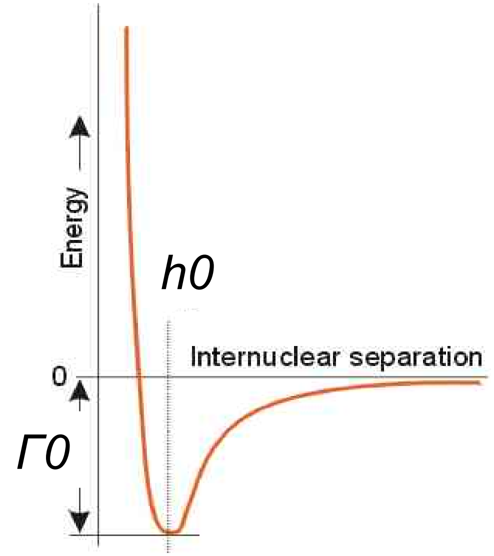
KZA = 2 d2UvdW/dh2=27Sa Γ0 /h0 ≈ 0.8 N/m



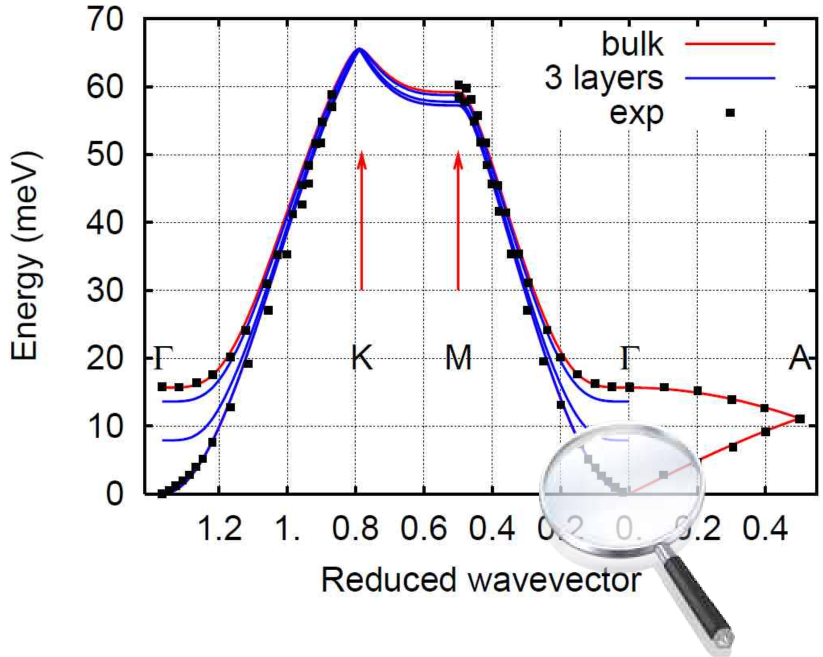
NANO LETTERS
2007
Vol. 7, No. 6
1643–1648

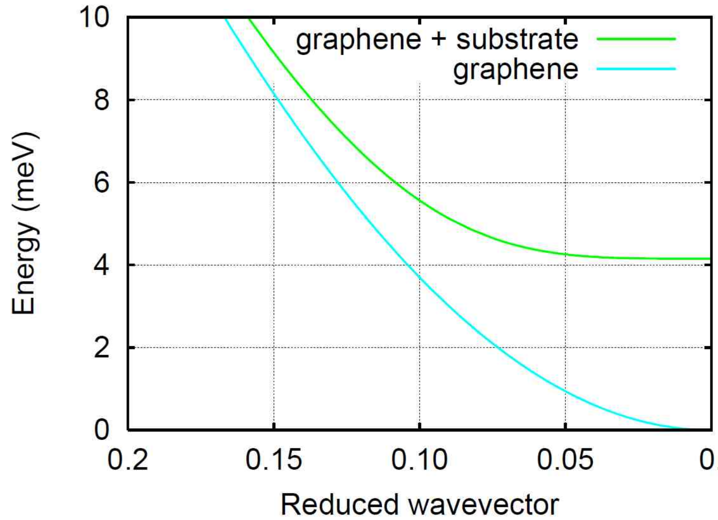
Atomic Structure of Graphene on SiO_2

Masa Ishigami,*,†,‡ J. H. Chen,†,‡ W. G. Cullen,†,‡ M. S. Fuhrer,‡,§ and E. D. Williams†,‡



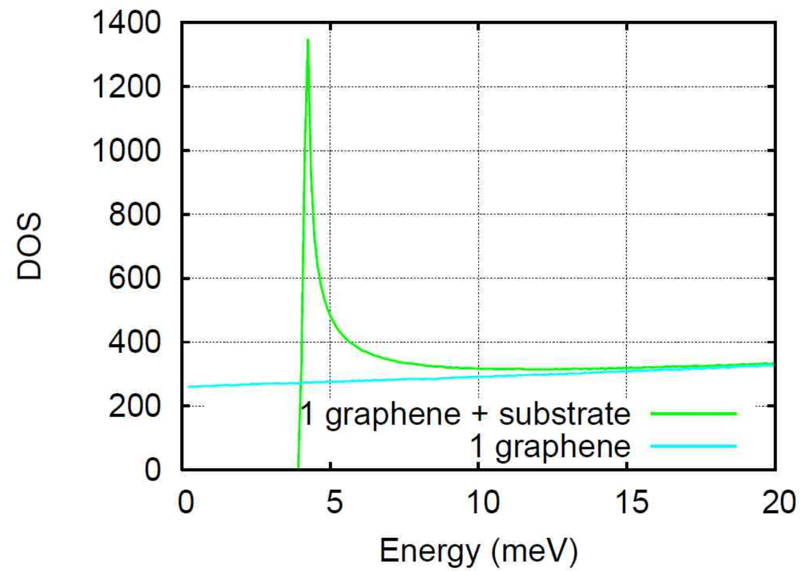
Interaction with substrate for supported graphene



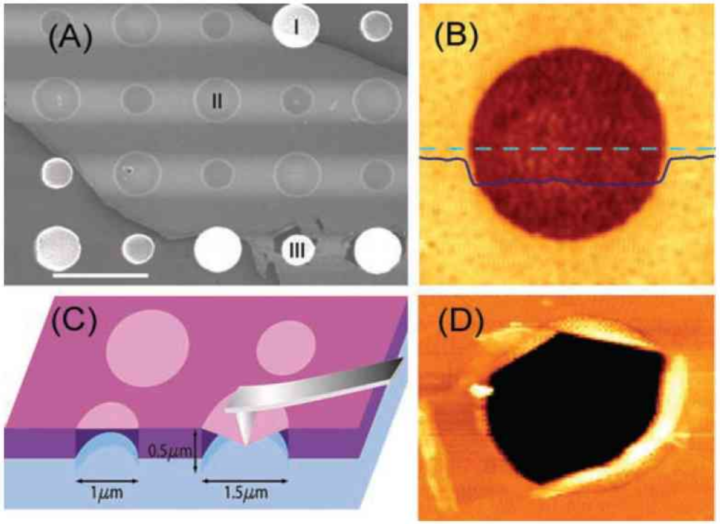


- Shift of the dispersion curve
- singularity integrable (van Hove)

✳ stabilization



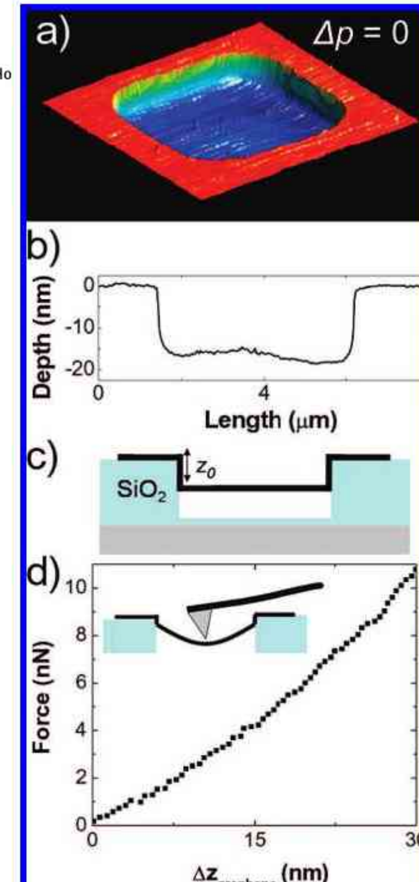
Self tension for suspended graphene



SCIENCE VOL 321 18 JULY 2008 385

Measurement of the Elastic Properties and Intrinsic Strength of Monolayer Graphene

Changgu Lee,[1,2] Xiaoding Wei,[1] Jeffrey W. Kysar,[1,3] James Ho



Impermeable Atomic Membranes from Graphene Sheets

J. Scott Bunch, Scott S. Verbridge, Jonathan S. Alden, Arend M. van der Zande, Jeevak M. Parpia, Harold G. Craighead, and Paul L. McEuen*

NANO LETTERS
2008
Vol. 8, No. 8
2458-2462

- Due to the attraction of the SiO2 substrate (vdw interaction ≈ 0.1 J/m2 = 16 meV/atom)
- Generates a dip z0 ≈ 2-20 nm
- Stabilizes graphene and reduces corrugation
- Self tension σ ≈ 0.1-1 N/m (from *F/Δz)*
- Strain < 1% (≈ $\sigma/E2D$, $E2D=E^*(c/2)$, $E \approx 1$ TPa)

Propagation of self tension

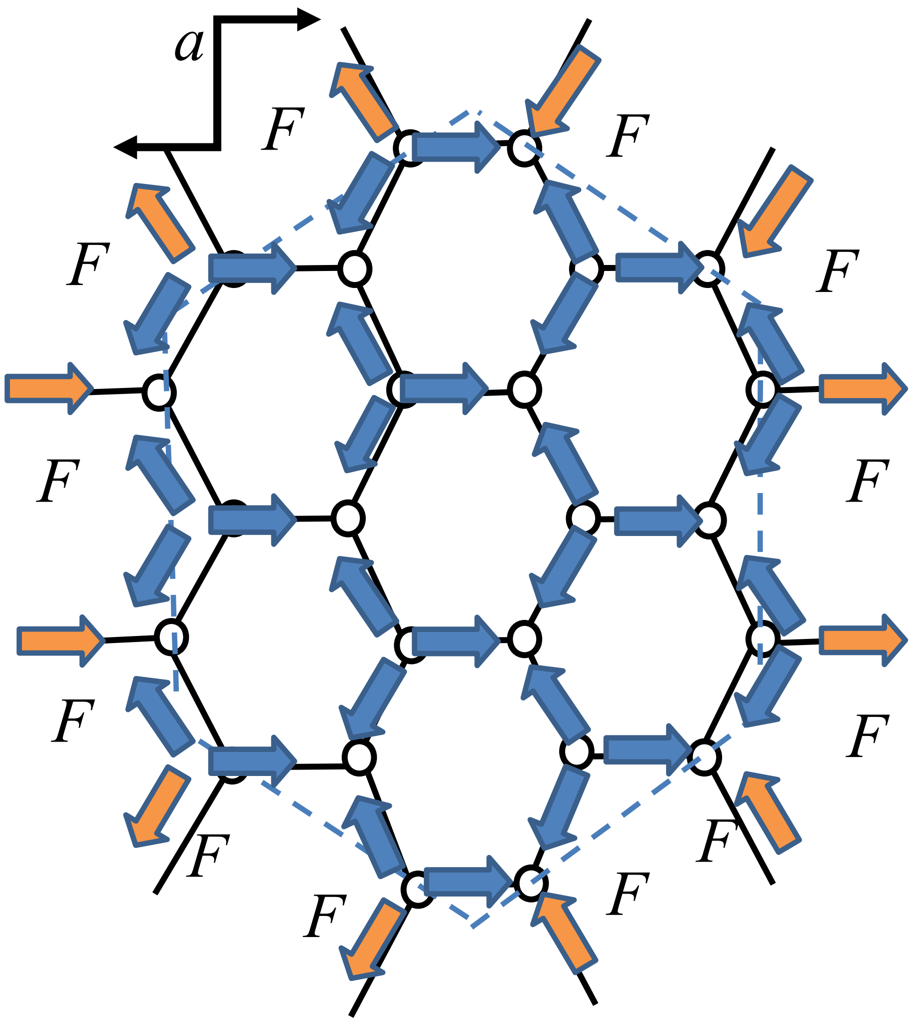
At equilibrium:

3 identical forces F /atom

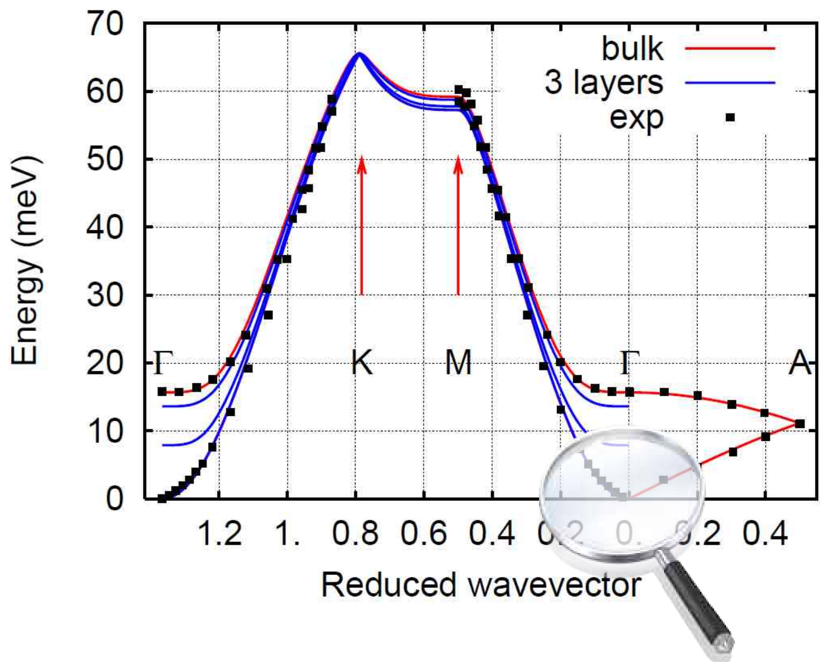
σ=12 F/perimeter$\ast$ F/a

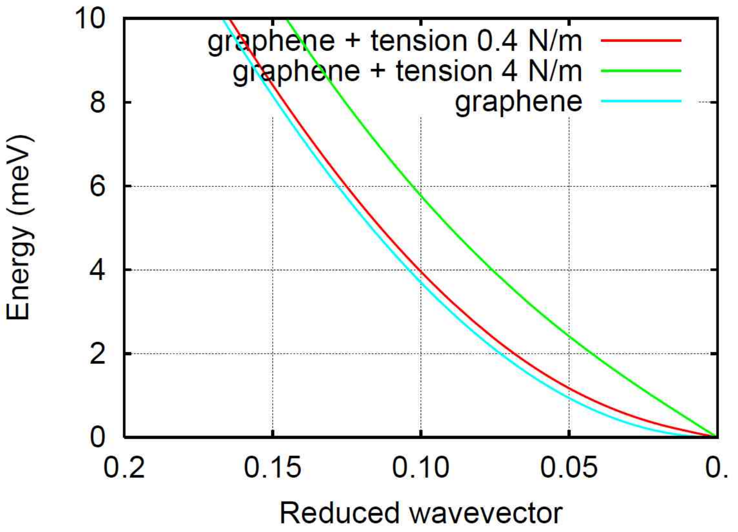
(for a large number of crowns)

This constant force F is added to the lattice dynamics model



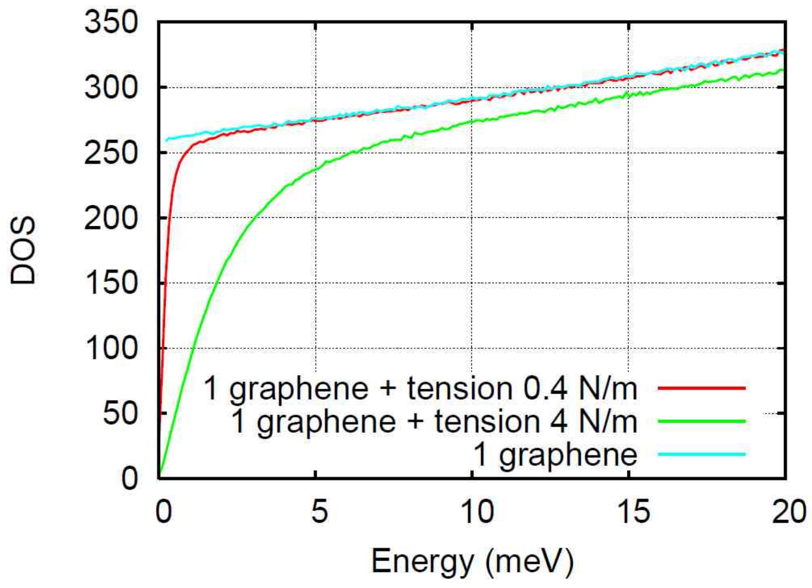
Effect of self-tension on DOS





- 0 DOS at Γ point
- removal of the singularity

✳ stabilization



Conclusions on graphene stability and role of substrate

1. As it is a 2D membrane, graphene has an anomalous acoustic phonon dispersion

2. This anomalous dispersion induces thermal instabilities

3. Stability as a flat membrane is restored by the presence of the substrate :

- supported graphene : direct force between substrate and membrane

- suspended graphene : tension induced by the surrounding attractive substrate contributes to stability

The model : Phonons

Models considered

$$C_{eff} = \sum_{\mathbf{Q}} \frac{n(\omega_{\mathbf{Q}}) e_z(\omega_{\mathbf{Q}})^2}{\omega_{\mathbf{Q}}} \ldots \propto \int d\omega \eta(\omega) \frac{n(\omega) e_z(\omega)^2}{\omega} \ldots$$

1. Lattice dynamics
- 1-3-5-10 layers
- With or without n+1 layer fixed
- Integrand of *Ceff* ≈ ω-1 (free-standing) or ω0 (on-substrate)

→strong coupling

e)

$$\omega_{\mathbf{Q}} = \omega_{max} \sin\left(\frac{\pi Q}{2Q_{max}}\right) \quad e_Z(\mathbf{Q}) = \left(\sin\left(\frac{\pi Q}{2Q_{max}}\right)\right)^{\frac{1}{2}}$$

- Integrand of *Ceff* ≈ ω1

✳ milder coupling

The model : H-phonons interaction

Linear coupling approximation :

$$V_c(\mathbf{r}, \{\mathbf{u_i}\}) = 2\alpha\Delta(z) \sum_i \frac{\partial W(\mathbf{R}, \{\mathbf{u_i}\})}{\partial \mathbf{u_i}} \mathbf{u_i} \qquad \frac{\partial W(\mathbf{R}, \mathbf{0})}{\partial \mathbf{u_i}} = A e^{-\frac{1}{2} Q_c^2 (\mathbf{R} - \mathbf{R_i})^2}$$

Bortolani, Franchini, Garcia, Nizzoli, Santoro, *Phys. Rev. B 28, 7358 (1983)*

Expansion on phonon modes :

$$V_c(\mathbf{r}, \{\mathbf{u_i}\}) = 2\alpha A \Delta(z) \frac{2\pi}{A_{uc} N_p^{\frac{1}{2}} Q_c^2} \sum_{\mathbf{Q}} \left(\frac{\hbar}{2M\omega_{\mathbf{Q}}} \right)^{\frac{1}{2}} e^{i\mathbf{QR}} \, e^{-\frac{1}{2} \frac{\mathbf{Q}^2}{Q_c^2}} e_Z(\mathbf{Q}) \left(a_{\mathbf{Q}} + a^{\dagger}_{-\mathbf{Q}} \right)$$

Effective coupling term (…Fermi Golden rule…) :

Density of Phonon states

Occupation number

Polarization vector

$$C_{eff} = \sum_{\mathbf{Q}} \frac{n(\omega_{\mathbf{Q}}) e_z(\omega_{\mathbf{Q}})^2}{\omega_{\mathbf{Q}}} \ldots \propto \int d\omega \eta(\omega) \frac{n(\omega) e_z(\omega)^2}{\omega} \ldots$$

η(ω) : density of phonon states

η(ω=0) crucial

The model : Dynamical methods

Reduced density matrix propagation (RDM) :

Corrugation

$$\frac{d\sigma_{\alpha i,\beta j}}{dt} = \frac{i(E_\beta + \kappa_j - E_\alpha - \kappa_i)}{\hbar}\sigma_{\alpha i,\beta j}(t) - \frac{2i\alpha}{\hbar}\sum_{\gamma,l}[\Delta_{\alpha\gamma} W_{il}\sigma_{\gamma l,\beta j}(t) - \sigma_{\alpha i,\gamma l}(t)\Delta_{\gamma\beta} W_{lj}]$$

$$-\frac{1}{\hbar^2}\sum_{\gamma,\delta}[A^-_{\alpha\gamma}\Delta_{\alpha\gamma}\Delta_{\gamma\delta}\sigma_{\delta i,\beta j}(t) - A^+_{\alpha\gamma}\Delta_{\alpha\gamma}\sigma_{\gamma i,\delta j}(t)\Delta_{\delta\beta} - \Delta_{\alpha\gamma}\sigma_{\gamma i,\delta j}(t)A^-_{\delta\beta}\Delta_{\delta\beta} + \sigma_{\alpha i,\gamma j}(t)\Delta_{\gamma\delta}A^+_{\delta\beta}\Delta_{\delta\beta}]$$

Phonons $\frac{\eta(\omega)}{\omega}\ldots$

Close coupling wave packet (CCWP) :

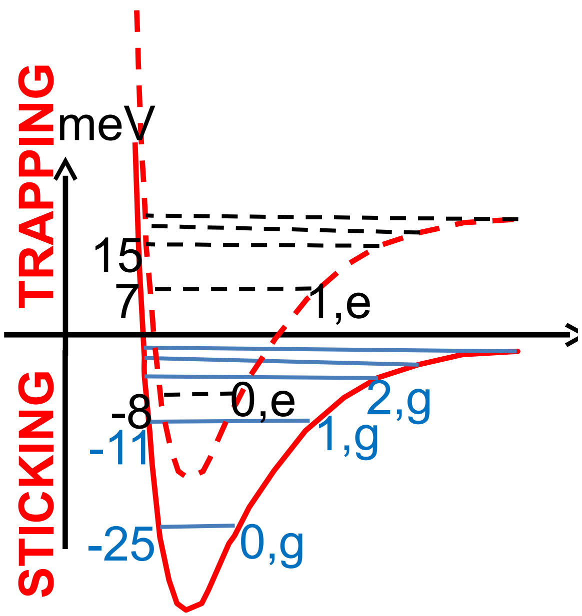
$$\psi(\mathbf{r},t) = \sum_{i=1-N_r,\lambda=0,\pm1,\mathbf{Q}} c_i^{\lambda\mathbf{Q}}(t)e^{-i\lambda\mathbf{QR}}\varphi_i(\mathbf{r})|\{n\}_{\lambda\mathbf{Q}} >$$

Phonon coupling

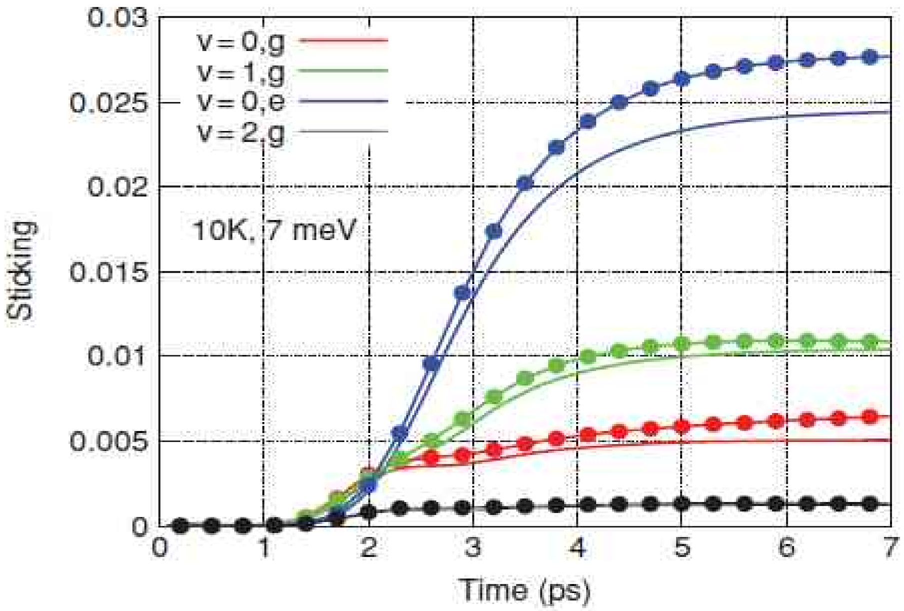
$$i\hbar\frac{dc_i^{\lambda\mathbf{Q}}(t)}{dt} = \left(\epsilon_i + \frac{\hbar^2\lambda^2 Q^2}{2m} + \lambda\hbar\omega_{\mathbf{Q}}\right)c_i^{\lambda\mathbf{Q}}(t) + \sum_{i',\lambda',\mathbf{Q}'} V_c^{\lambda\mathbf{Q}i\,\lambda'\mathbf{Q}'i'}\,c_{i'}^{\lambda'\mathbf{Q}'}(t)$$

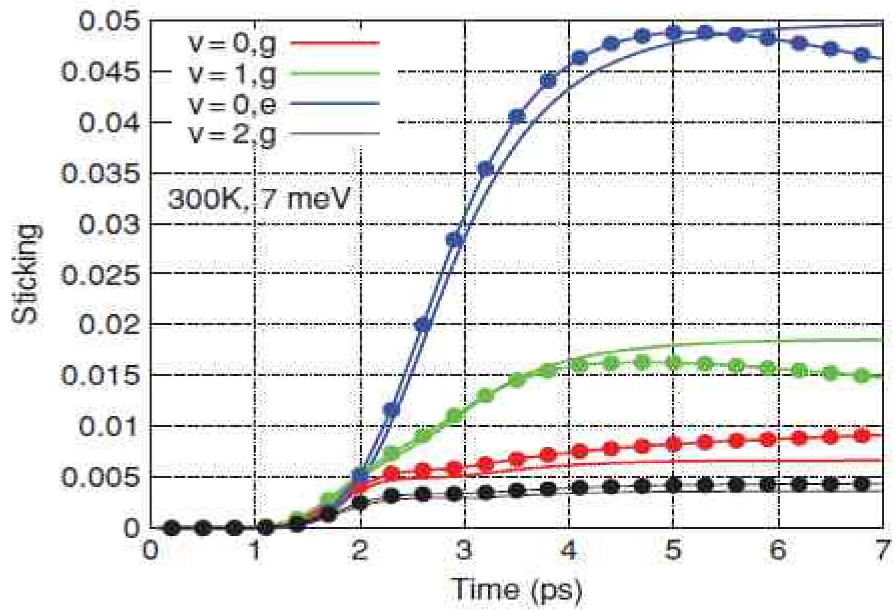
Perturbative treatment (PT) : $\lambda=0$ wavepacket not affected by phonons

Results : Comparison of RDM/CCWP

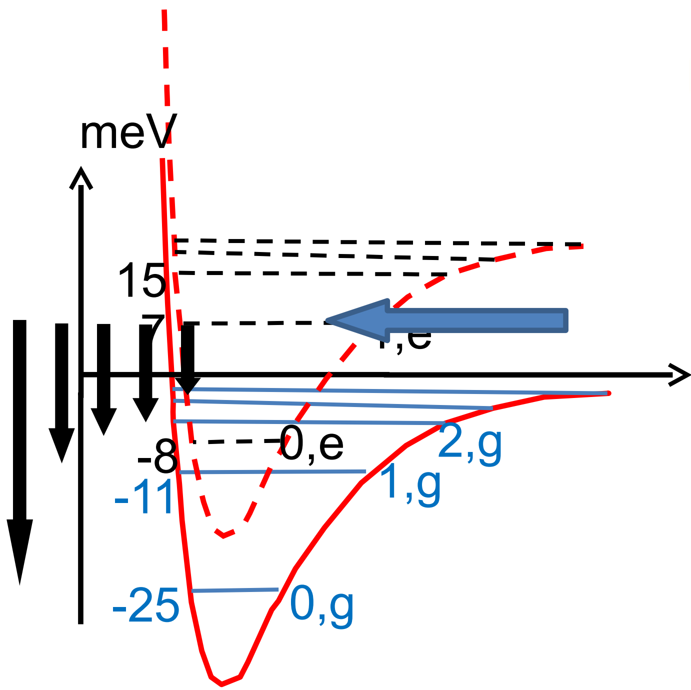


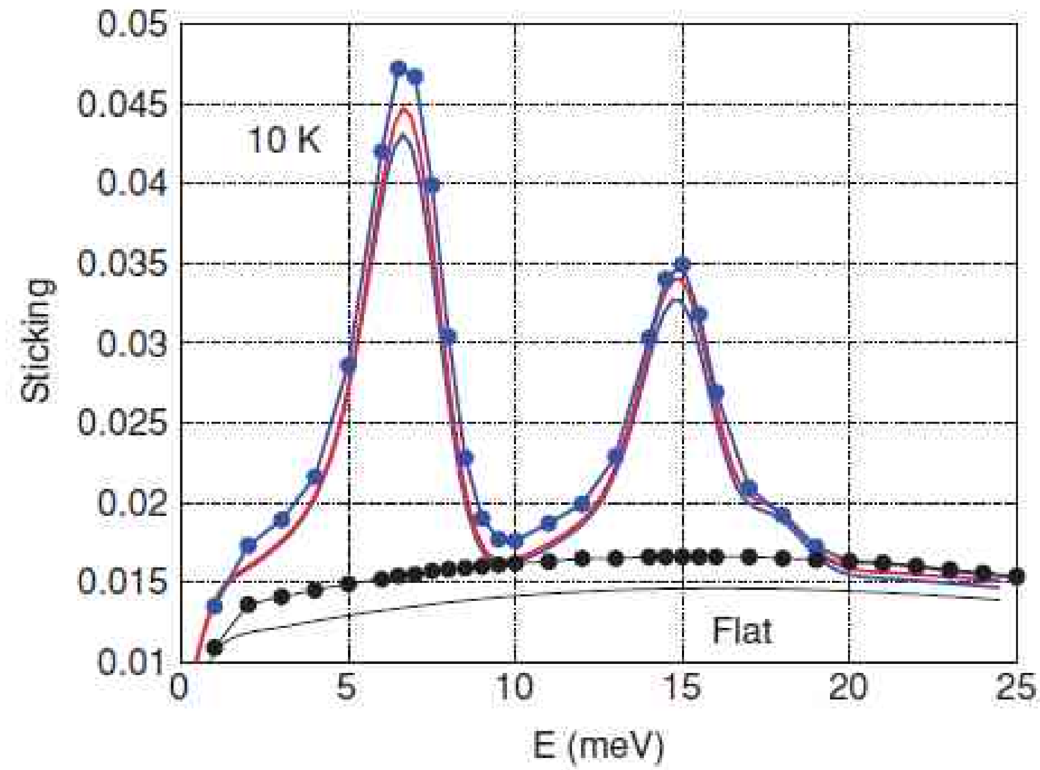
Initial state	Initial population decay (ps)	Stuck population decay (ps)
(0,g)	21	48
(1,g)	10	26
(0,e)	20	22
(2,g)	19	37



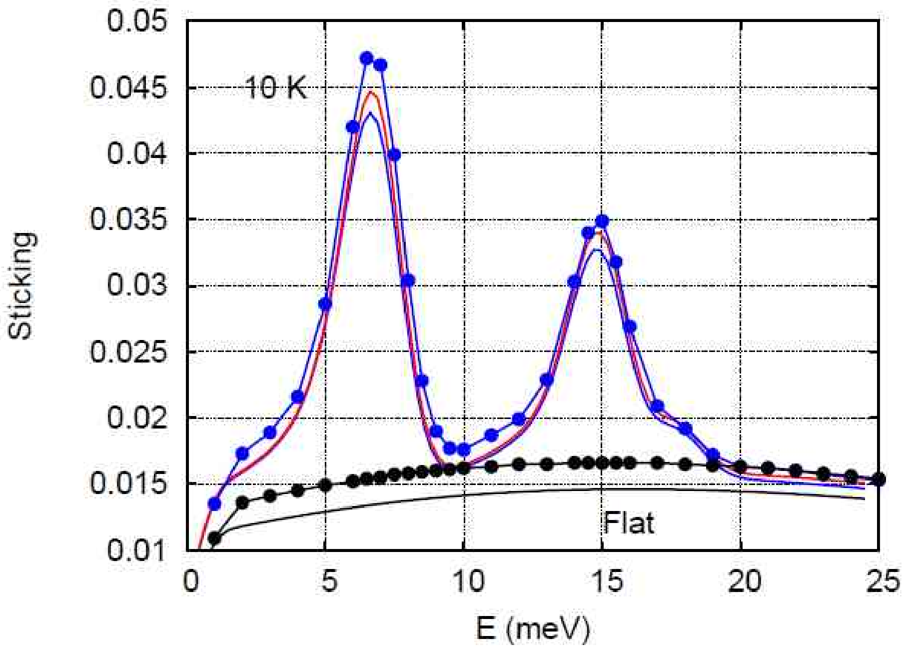


Results : Diffraction mediated selective adsorption

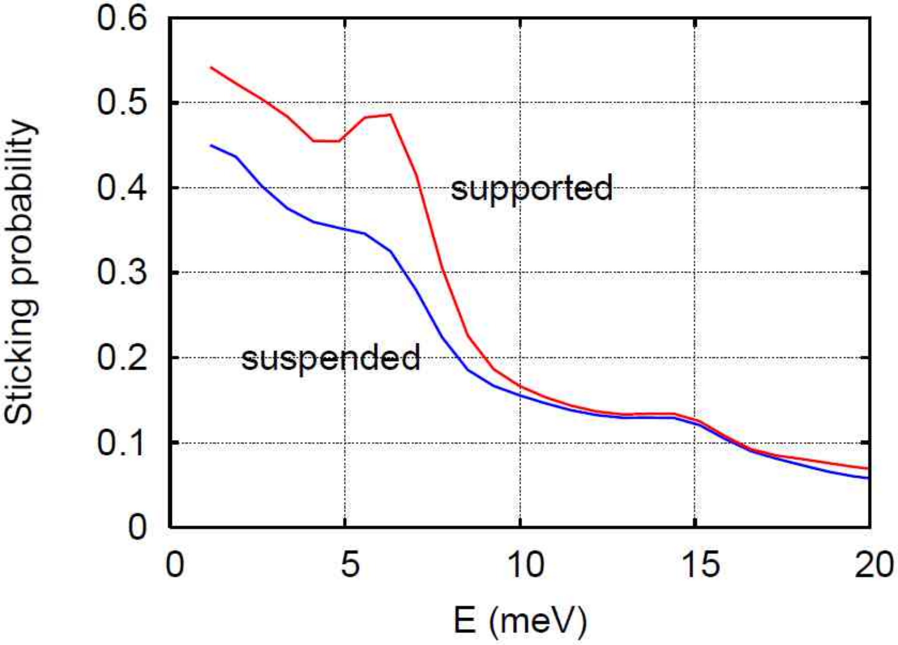




Results : effect of the choice of phonon model



Jackson model

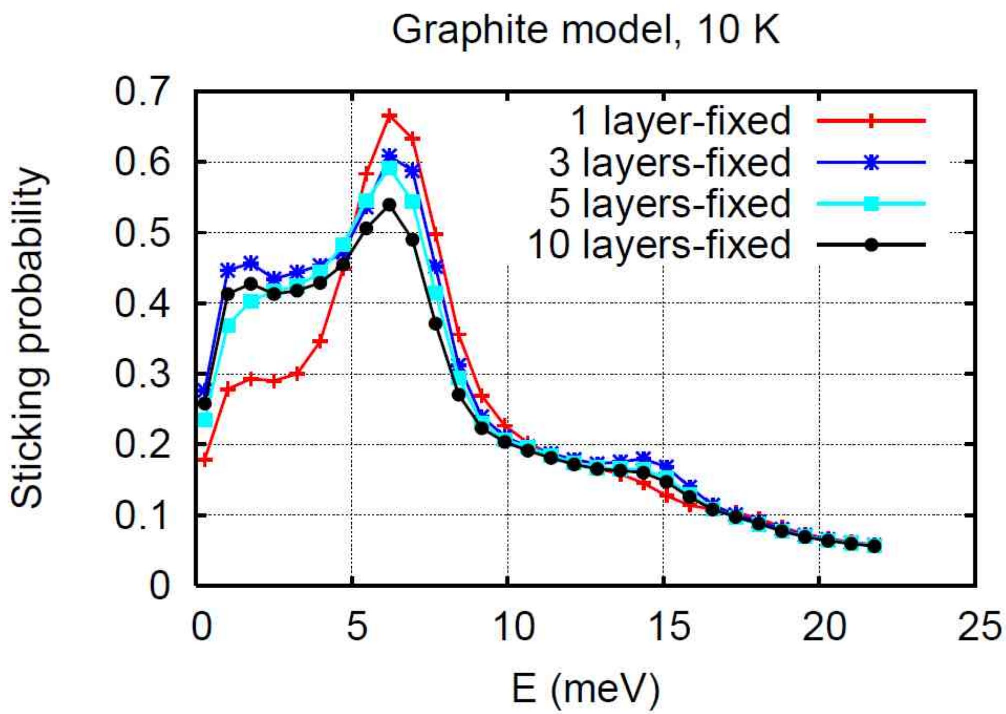


Lattice dynamics model

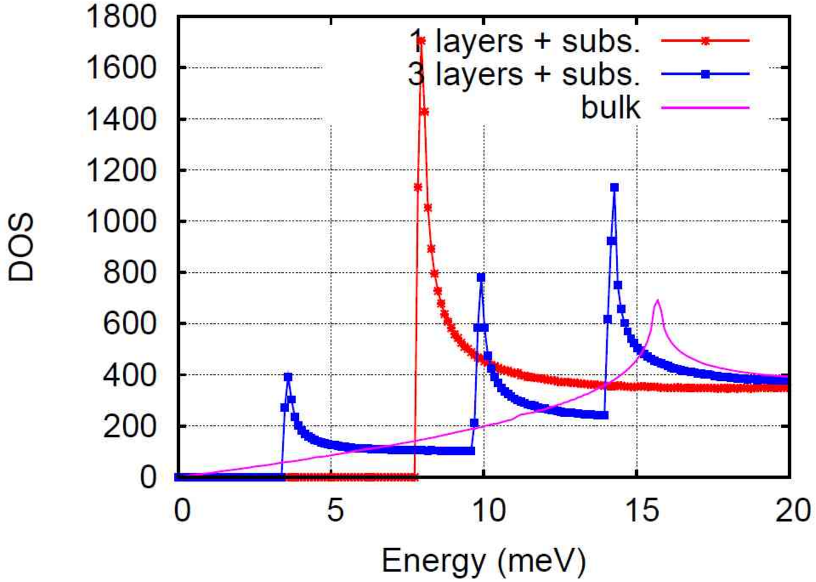
Strong dependence on phonon model : different density of states and polarisation vectors

DMSA resonances effective in both cases

Results : effect of the number of layers



Lattice dynamics model, on substrate



- Threshold effect for 1 layer : low energy phonons not available to stick to excited vibrational states at low energy
- Convergence for number of layers ≥ 3

Conclusions

1. Development of 3D (with corrugation) model for
   H sticking on graphite including a realistic lattice dynamics model

2. Corrugation : strong effect of DMSA resonances on sticking

3. Phonons : strong influence of the choice of model

4. Stabilizing of substrate to have flat graphene

5. Future work : chemisorption