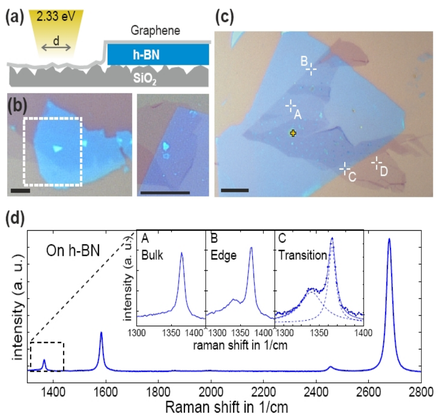
Substrate dependence of the Raman 2D line of graphene

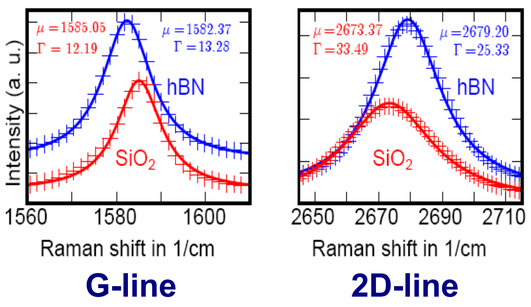
Alejandro Molina-Sánchez and Ludger Wirtz

UNIVERSITY OF LUXEMBOURG
Physics and Material Sciences Research Unit

Motivation



Raman measurements : Florian Forster, Christoph Stampfer,
BN-samples : K. Watanabe and T. Taniguchi



Hexagonal boron nitride is a promising substrate of graphene due to the lattice-match, the low surface roughness or the low density of charge traps.

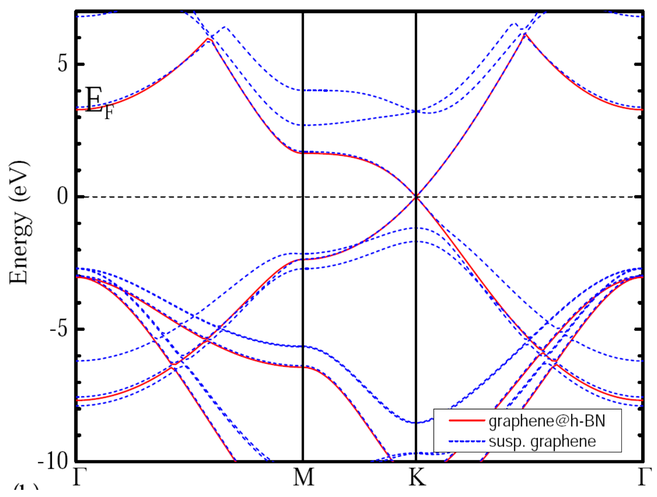
Raman spectroscopy is a powerful tool to explore the interaction of graphene with the substrate.

The G-line frequency (left) of graphene on hexagonal boron nitride is smaller than that of graphene on SiO_2. Effect of charging through impurities.

The 2D-line of **graphene@h-BN** is at higher energy than graphene@SiO_2 and suspended graphene [1].

Theoretical study of the electronic structure at the GW approx. level and calculation of the electron-phonon coupling.

Band structure of graphene@BN

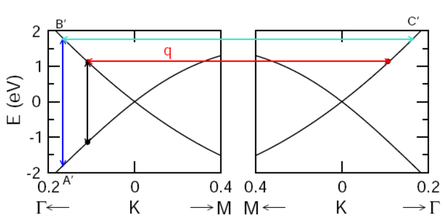


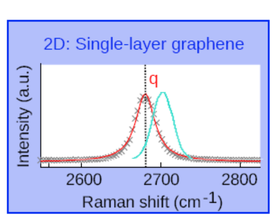
LDA band structure of suspended graphene and **graphene@hBN**.

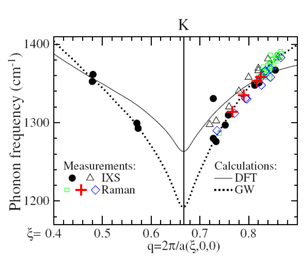
The linear crossing of the bands at the Dirac point is reproduced in both cases.

Both bands match almost perfectly around the **K** point.

The 2D-line is dispersive, comes from a two-phonon process and is sensitive to changes in:
- Slope of the bands around **K**.
- Slope of the phonon branch around **K**.
- Excitation energy.





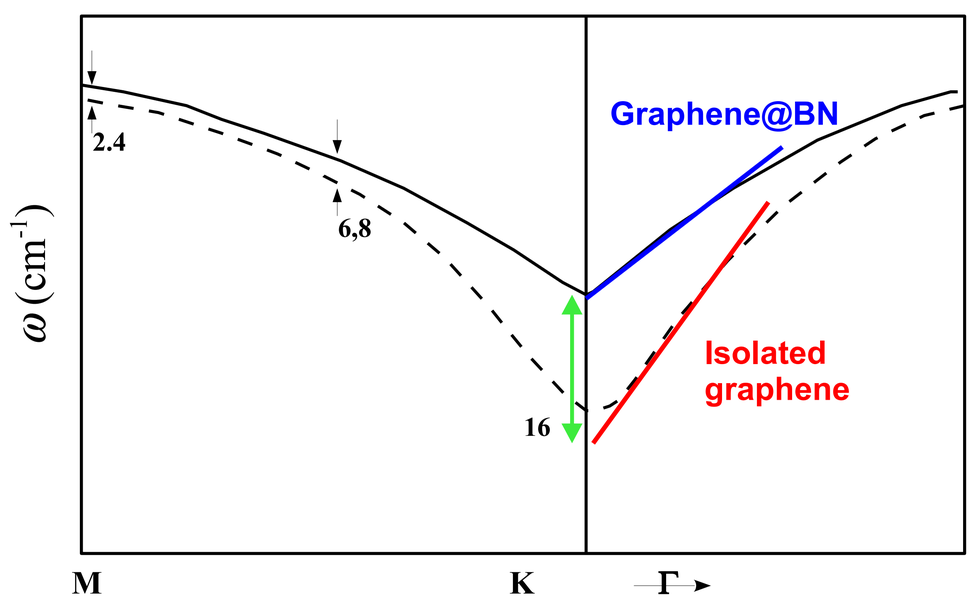


Electron-phonon coupling

$\langle D^2_K \rangle_F$ [eV^2/Å^2]

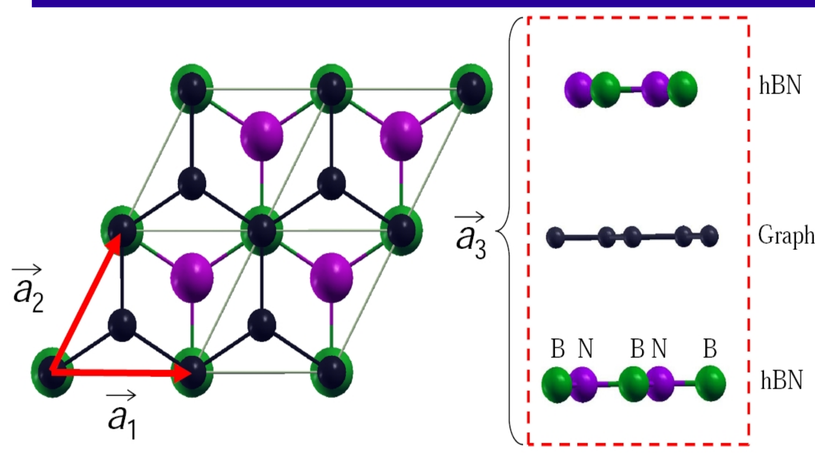
	LDA	GW
pure graphene	89.2	207.9
graphene@hBN	86	191.3

The presence of the dielectric substrate reduces the electron-phonon coupling by 3.5% (LDA), 8% (GW).

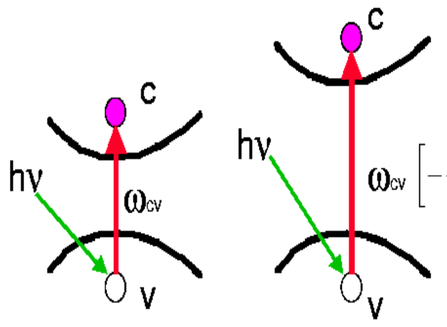


- A reduction of the slope of the Kohn-Anomaly by the dielectric substrate.
- Increase of the 2D-line phonon Frequency (around 5-7 cm^{-1}).

Theory. GW calculation of the TO mode at K



Calculations are done in suspended graphene and graphene symmetrically sandwiched between hexagonal boron nitride layers, using *ab initio* methods [2].

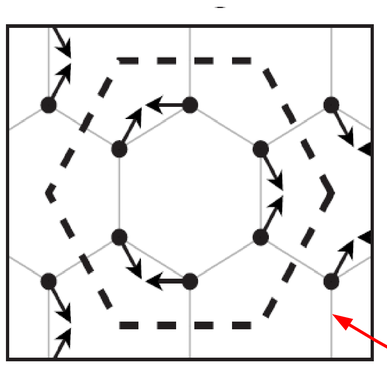


1.) DFT : underestimation of the band-gap
2.) GW-approximation (including electron-electron interaction) : "opening" of the band gap

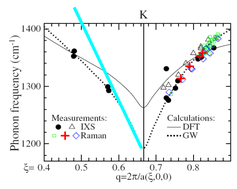
$$\omega_{cv}\left[-\frac{\nabla^2}{2}+V_{ext}(\mathbf{r})+V_{Hartree}(\mathbf{r})\right]\psi^{qp}_{n\mathbf{k}}(\mathbf{r})+\int d^3\mathbf{r}'\Sigma(\mathbf{r},\mathbf{r}';E^{qp}_{n\mathbf{k}})\psi^{qp}_{n\mathbf{k}}(\mathbf{r}')=E^{qp}_{n\mathbf{k}}\psi^{qp}_{n\mathbf{k}}$$

Self energy: $\Sigma = iGW$ — **screened Coulomb potential**

Evaluation of the influence of the dielectric screening on the bandgap opening



The electron-phonon coupling is proportional to:
- the **slope** of the TO phonon branch close to K
- the softening of the TO mode at **K**.



The e-p coupling can be calculated with the expression [3]:

$$\langle D^2_{\mathbf{K}} \rangle_F = \lim_{d\to 0}\frac{1}{8}\left(\frac{\Delta E_{\mathbf{K}}}{d}\right)^2 \qquad \Delta E_{\Gamma} = \epsilon_{\mathbf{K},\pi^*} - \epsilon_{\mathbf{K},\pi}$$

Band-gap calculated within the GW approx.

Displacement according to the phonon eigenvector (TO mode at **K**)

Estimation of the phonon dispersion with hybrid B3LYP functional

$$Exc = (1\text{-}\mathbf{a})(E_{LDA,x} + bE_{BECKE,x}) + \mathbf{a}E_{HF,x} + (1\text{-}\mathbf{c})E_{VWN,c} + \mathbf{c}E_{LYP,c}$$

A changes of parameters a and c is equivalent to a change in the dielectric Screening.

We can fit the paramterers *a* (admixture of HF exchange) and *c* (compesate the changes in the bond-strength) with the information given by the GW calculations of the electron-phonon coupling.

Once the exchange-correlation energy is found, the phonon dispersion is calculated around the K-point.

Isolated graphene: a = 0.157 ; c = 0.1
graphene@BN ; a = 0.139 ; c = 0.81

Conclusions

We find a significant substrate dependence of the 2D-line frequency of the graphene Raman spectrum.

The effect of the dielectric screening can be evaluated by calculating the Self-energy and the quasi-particle eigenvalues in the GW approximation.

From the calculation of the electron-phonon coupling for **suspended graphene** and **graphene@h-bn**, one can predict a larger softening of the TO mode for suspended graphene.

The slope of the TO phonon branch at **K** will be also larger in the case of **suspended graphene** and consequently the 2D-line frequency will be higher in the case of **graphene@h-bn**.

References

Calculations done with ABINIT http://www.abinit.org and YAMBO http://yambo-code.org

[1] S. Berciaud, S. Ryu, L. E. Brus, and T. F. Heinz, Nanolett. 9, 346 (2009).

[2] A. Molina-Sánchez, L. Wirtz, *et. al.*, *in preparation*.

[3] M. Lazzeri, C. Attaccalite, L. Wirtz, and F. Mauri. Phys. Rev. B 78, 081406R (2008).