Effects of strain in MoS_2: band gap engineering & funnel effect

Rafael Roldán

Instituto de Ciencia de Materiales de Madrid CSIC

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Transition Metal Dichalcogenides: new players

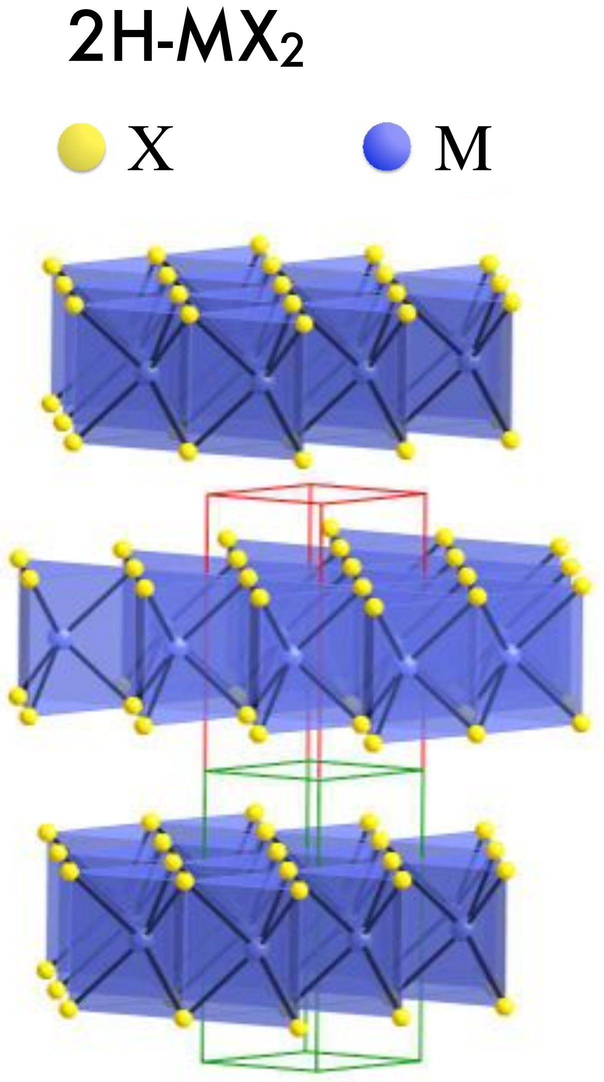
- Van der Waals 2D materials: Exfoliation from Bulk to 1 layer and few layers
- Semiconductor with *large* gap (~1.9 eV single-layer, ~1.3 eV bulk)
- Electronic structure highly sensitive to pressure/strain
- Strong Spin-Orbit coupling (~0.15eV MoS_2/ ~0.4eV WS_2)
- Strong photoluminescence
- Controllable valley and spin polarization
- Large on-off ratio in field effect transistors

For a (short) recent review, see R.Roldán *et al.*, arXiv:1410.2154

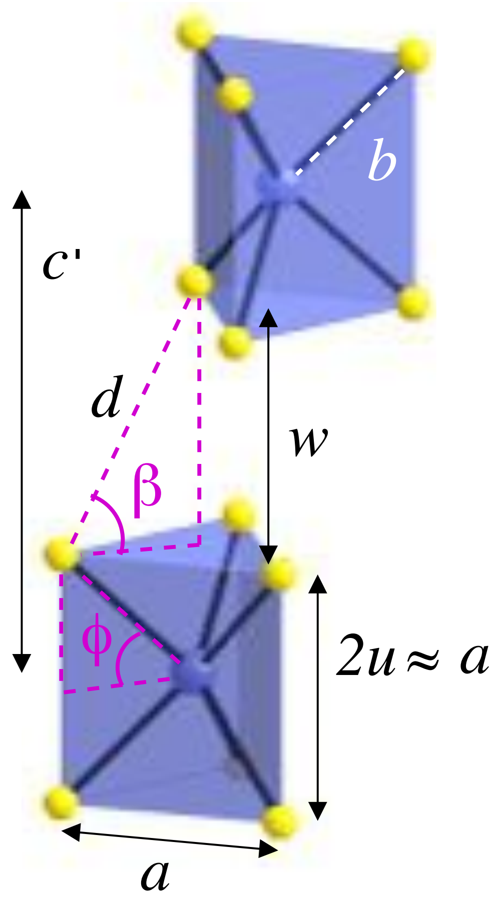
Our focus

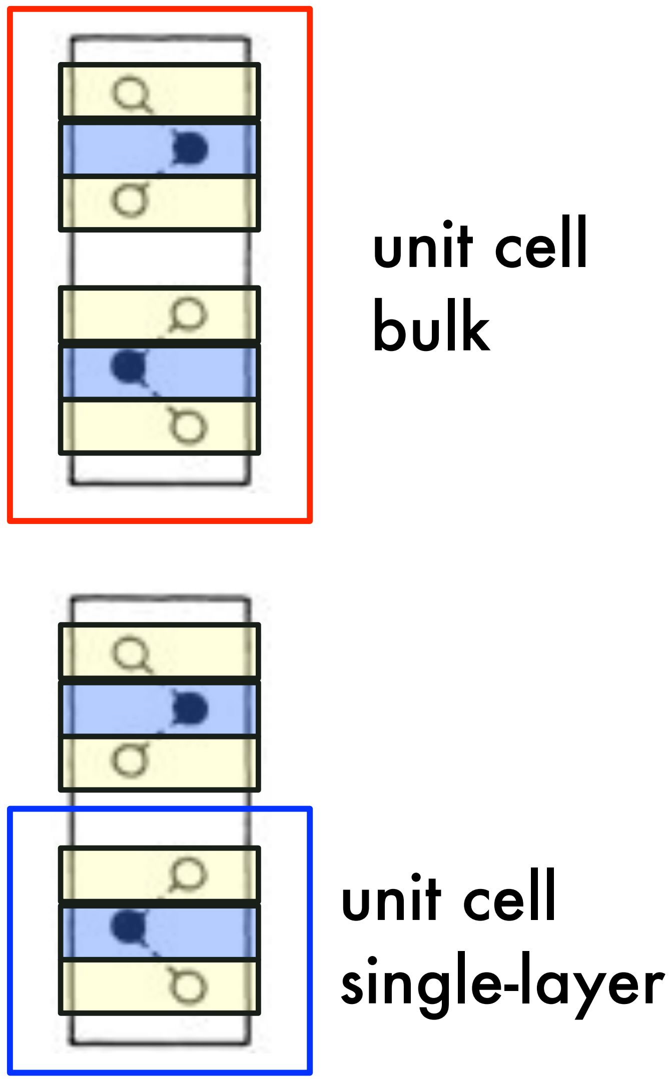
- Analytical tight-binding and DFT methods [E. Cappelluti *et al.*, PRB 2013]
- Effects of spin-orbit interaction [RR *et al.*, 2D Materials (in press)]
- Local strain-induced gap tuning [A. Castellanos *et al.*, Nano Letters 2013]
- Screening properties [A. Castellanos *et al.*, Advanced Materials 2013]
- Superconductivity [RR *et al.*, PRB 2013]
- Spin relaxation [H. Ochoa and RR, PRB 2013]
- Optical and transport properties of disordered MoS_2 and WS_2 [S. Yuan *et al.*, PRB(R) 2014]
- ......

Lattice structure of $2H\text{-}MX_2$

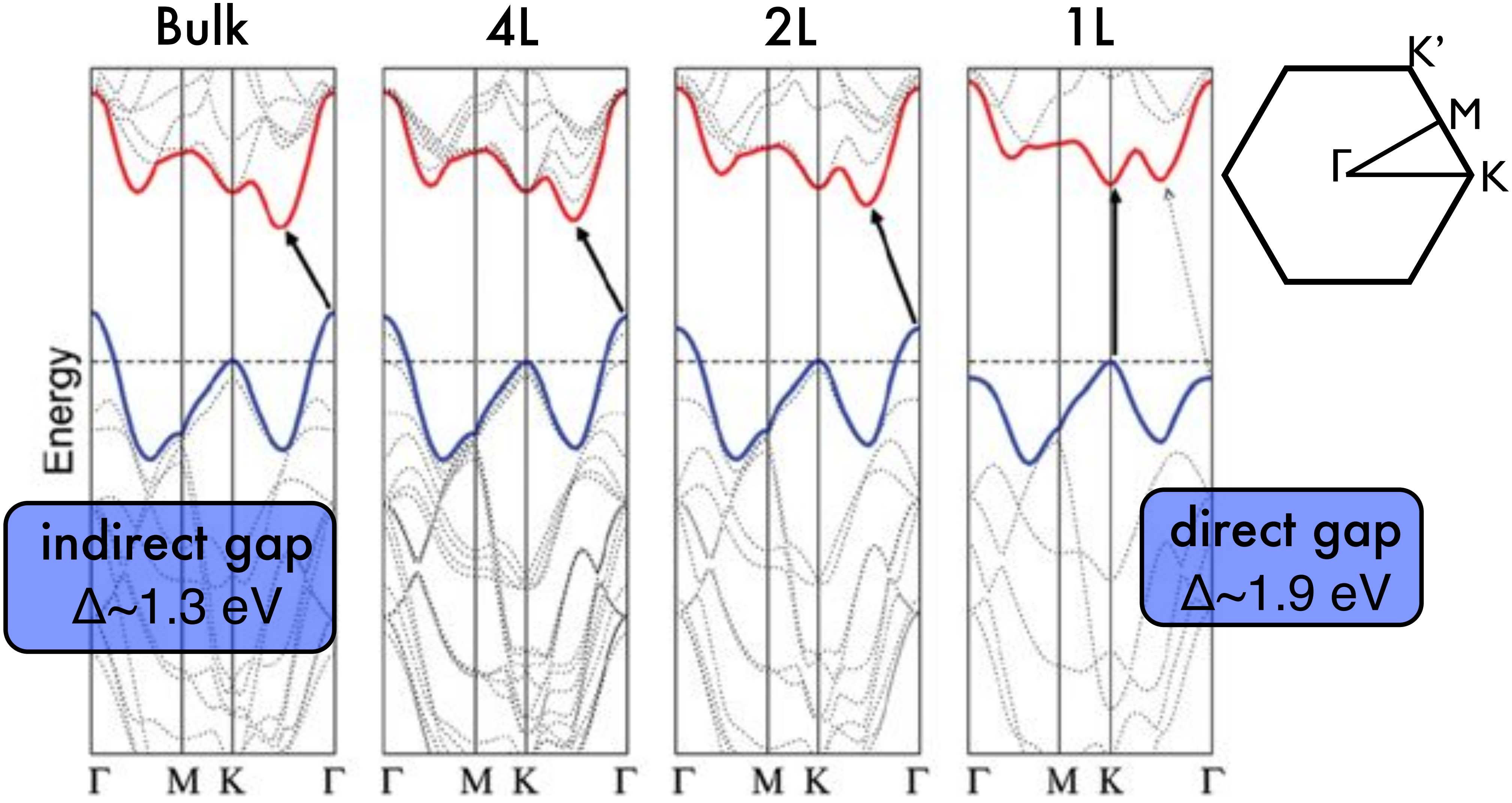


M = Mo, W
X = S, Se



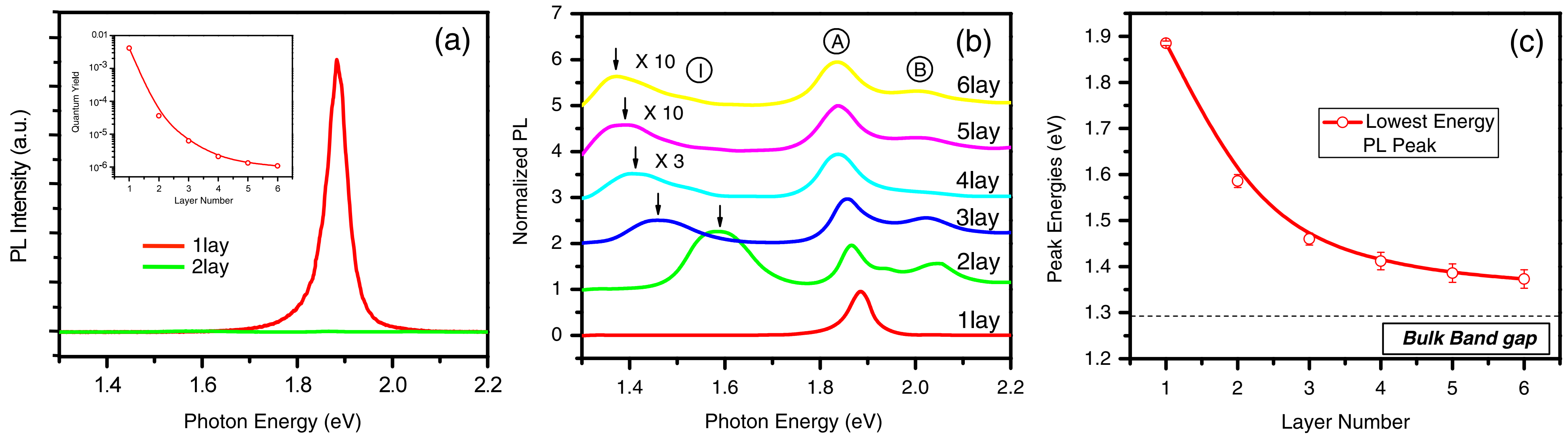


Band structure: from multi-layer to single-layer



Splendiani et al., Nano Lett 10, 1271 (2010)

Indirect to direct gap transition



- Huge increase of photoluminescence peak in 1-layer compounds signalizing direct gap optical transitions without phonon assistance.

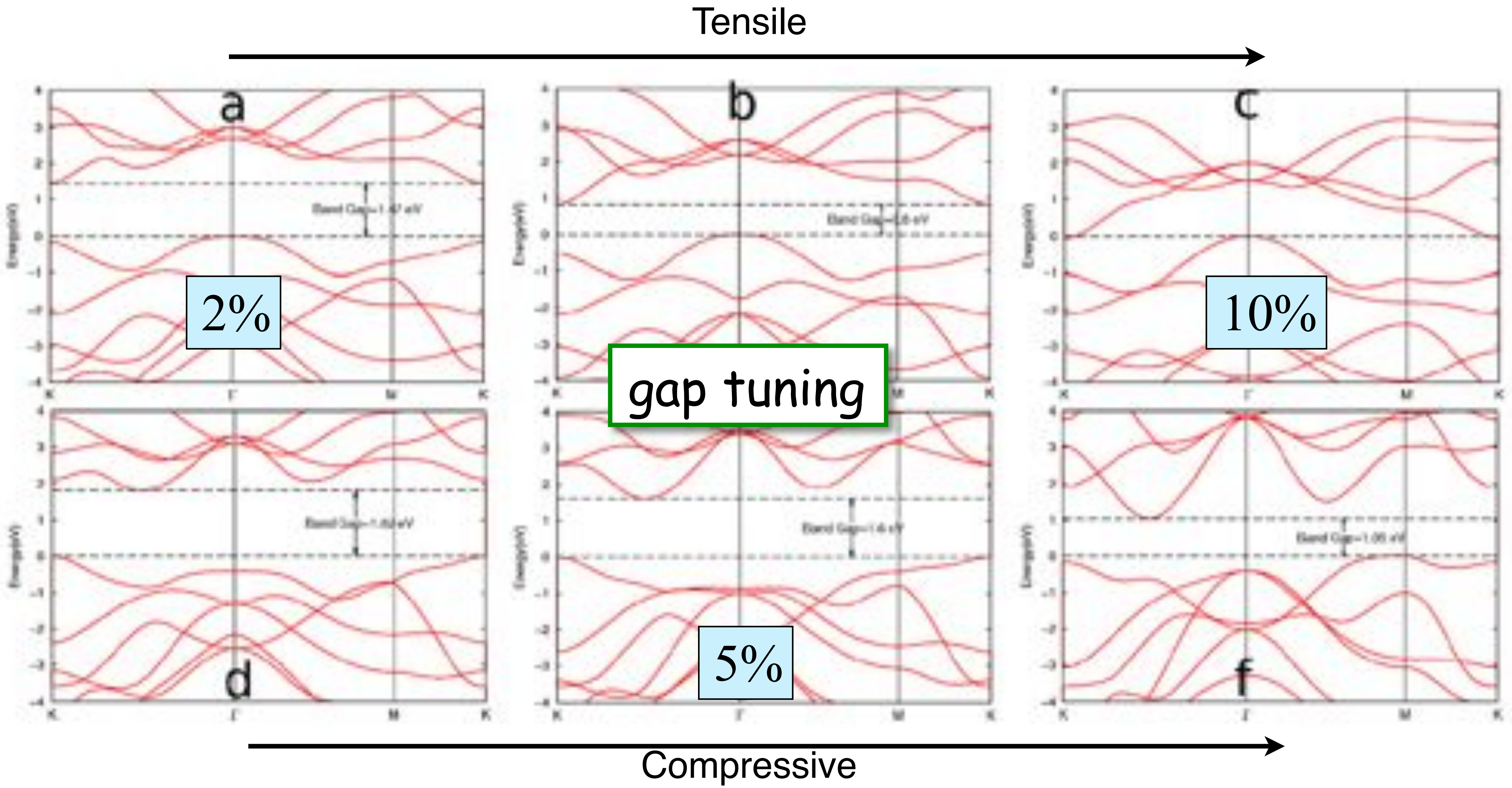
- Indirect gap probed from the **I** feature of the photoconductivity spectrum.

- Single-layer MoS_2 as the first atomically thin material that is an effective emitter of light.

Mak et al., PRL 105, 136805 (2010)

Strain in MoS_2

Electronic structure highly sensitive to pressure/strain

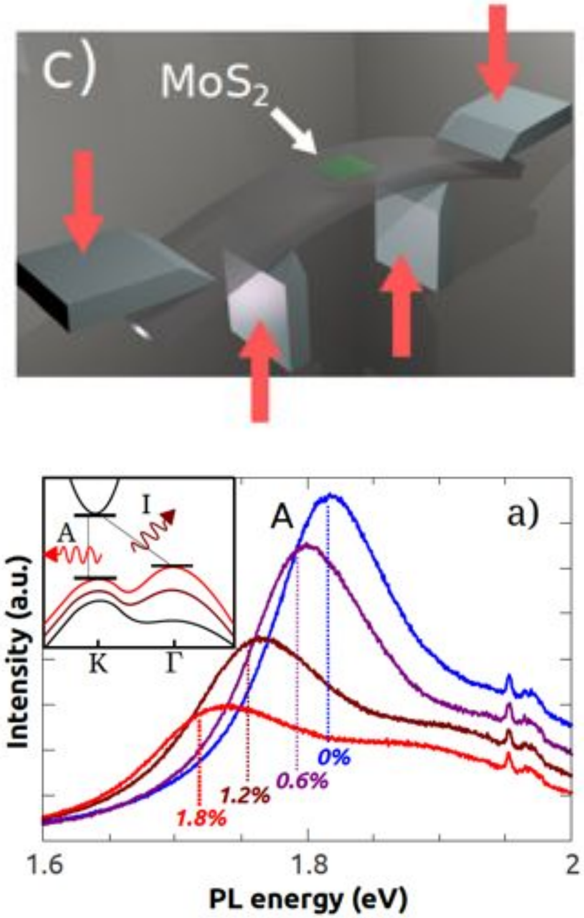


Scalise et al., Physica E (2012)

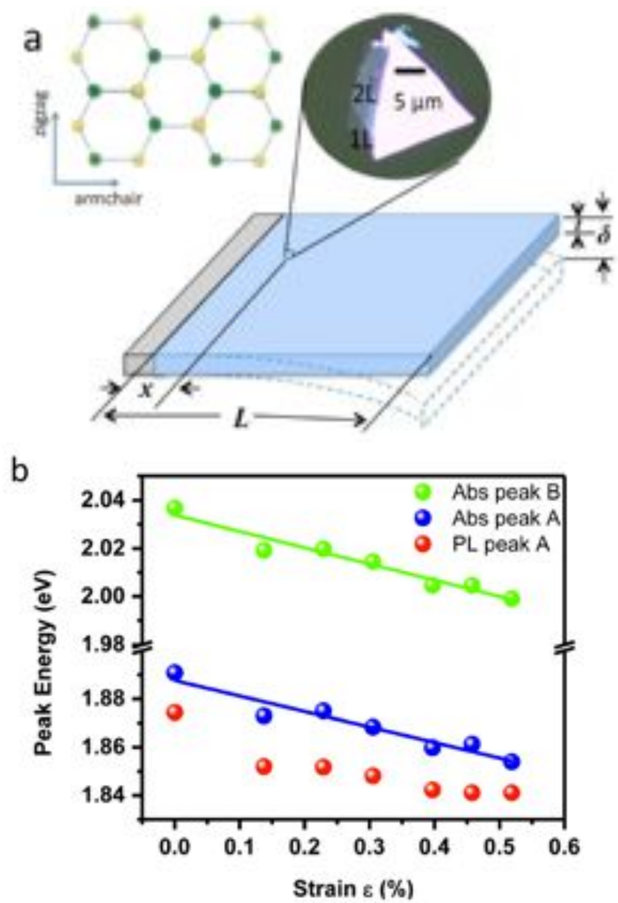
Strain engineering in MoS_2

- Interplay between mechanical deformations and electronic/optical properties
- Gap reduction from energy PL peaks
- Direct/indirect gap transition from peak intensities

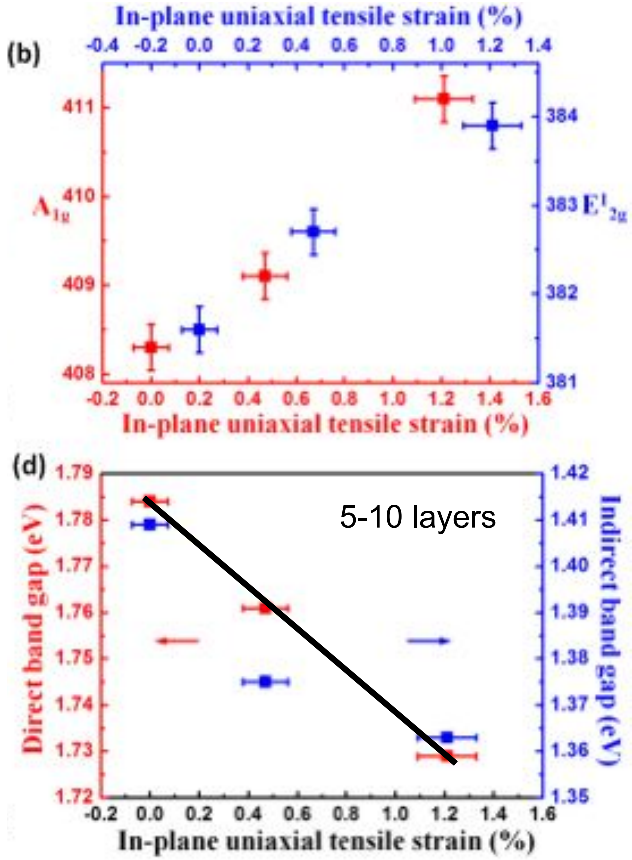
Experiments with uniform strain



Conley et al. Nano Lett 13, 3626 (2013)



He et al. Nano Lett 13, 2931 (2013)



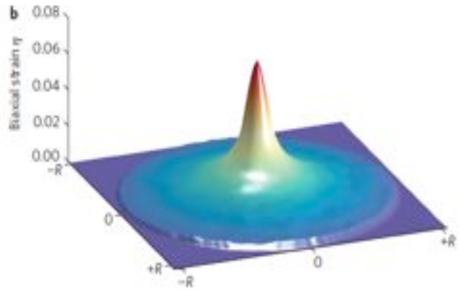
Yang et al., Scientific Reports (2014)

Strain engineering in MoS_2

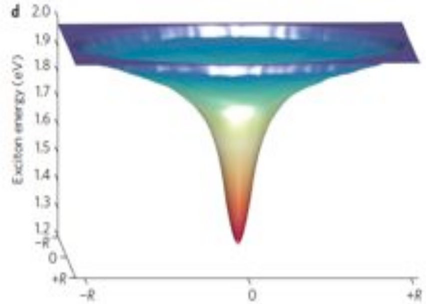
Possible at local scale?

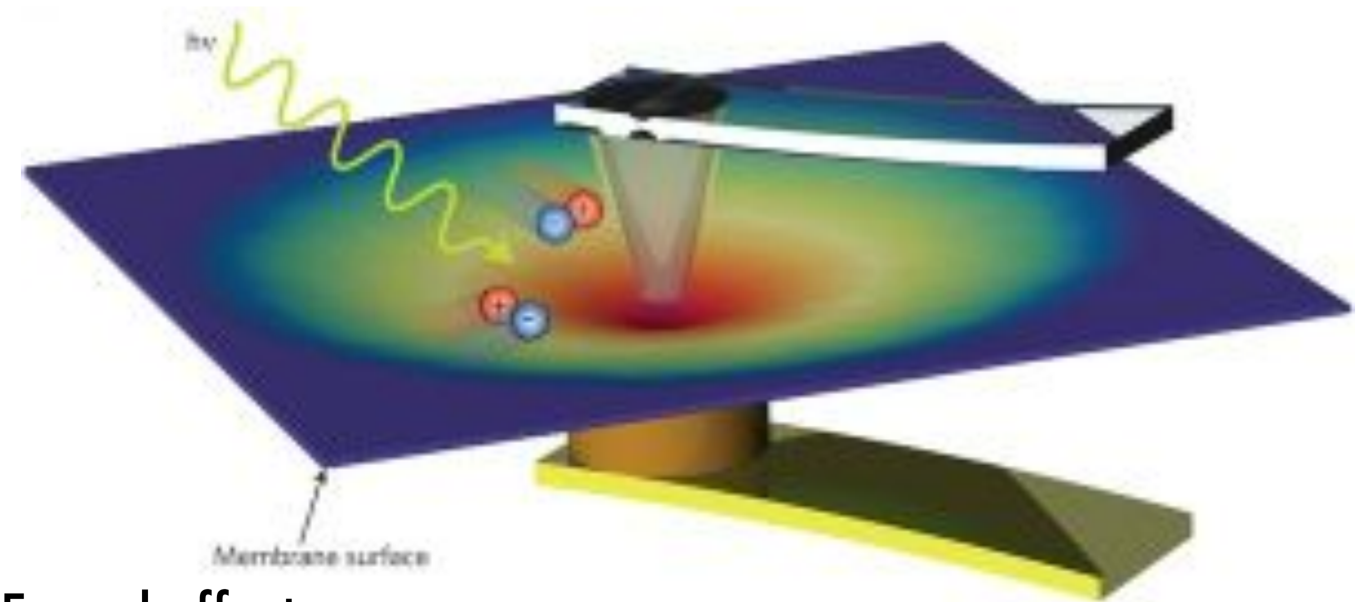
2D crystals can be subjected to inhomogeneous strain: relevant for solar cells

Strain



Exciton energy





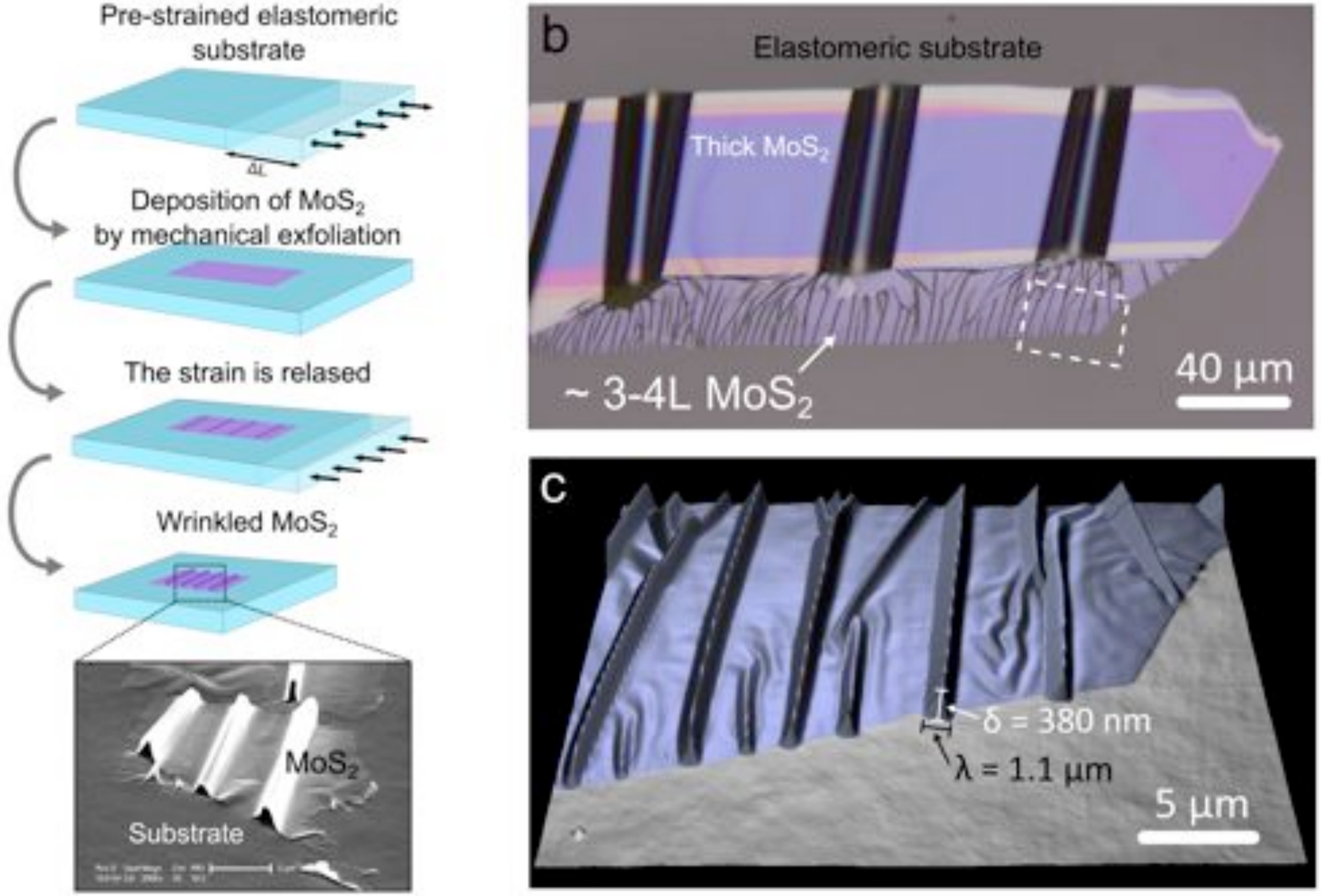
No experimental works on **local** strain engineering in MoS_2

Funnel effect:
Gap modulation → spatial migration of particle-hole pairs

Feng et al., *Nature Photonics* **6**, 866 (2012)

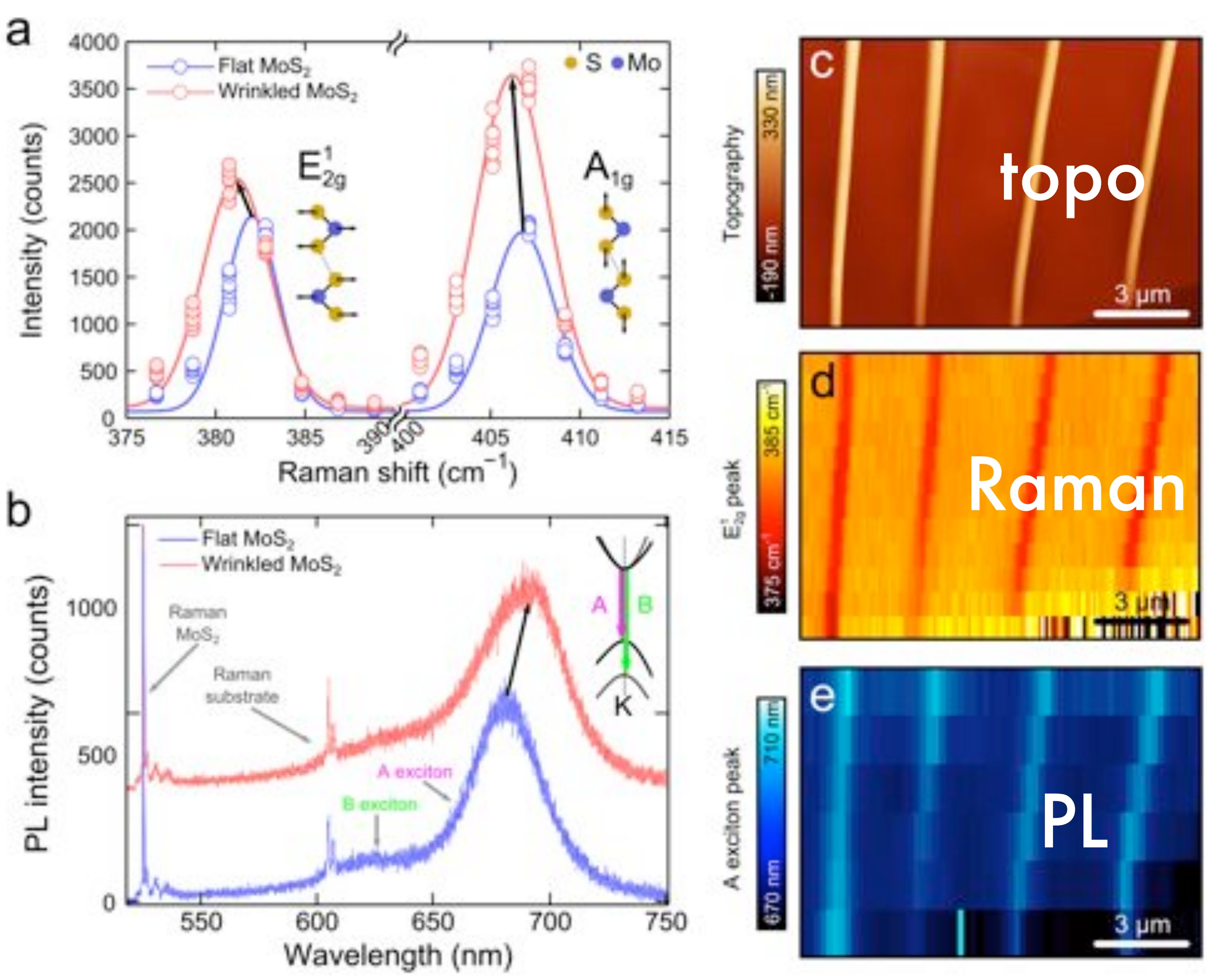
Local strain-induced gap engineering in MoS_2

Buckling induced delamination process



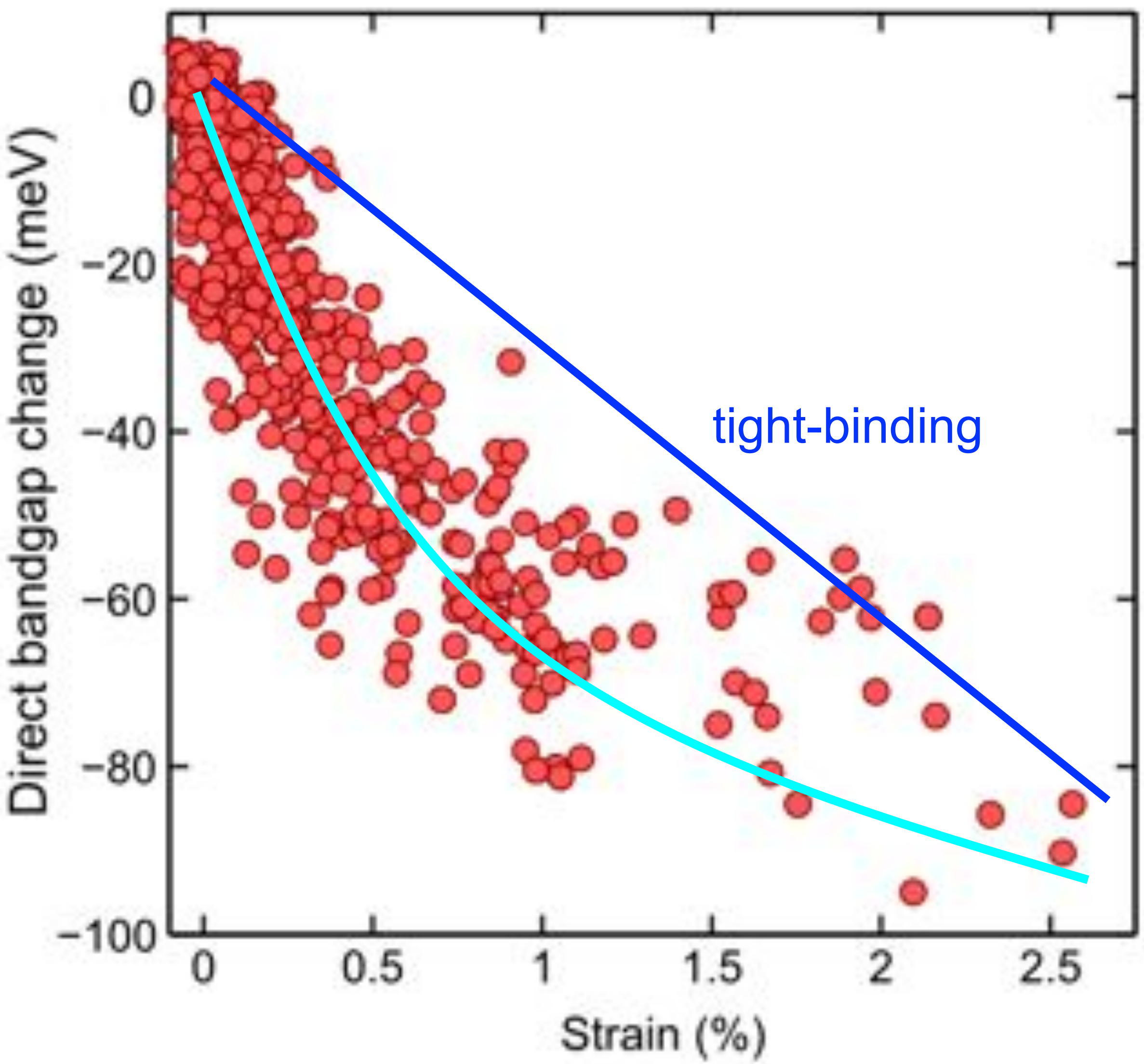
A.Castellanos-Gómez, RR, E.Cappelluti, G.Steele, F.Guinea & H. van der Zant, Nano Letters **13**, 5361 (2013)

Raman & Photoluminiscence spectra of strained MoS_2



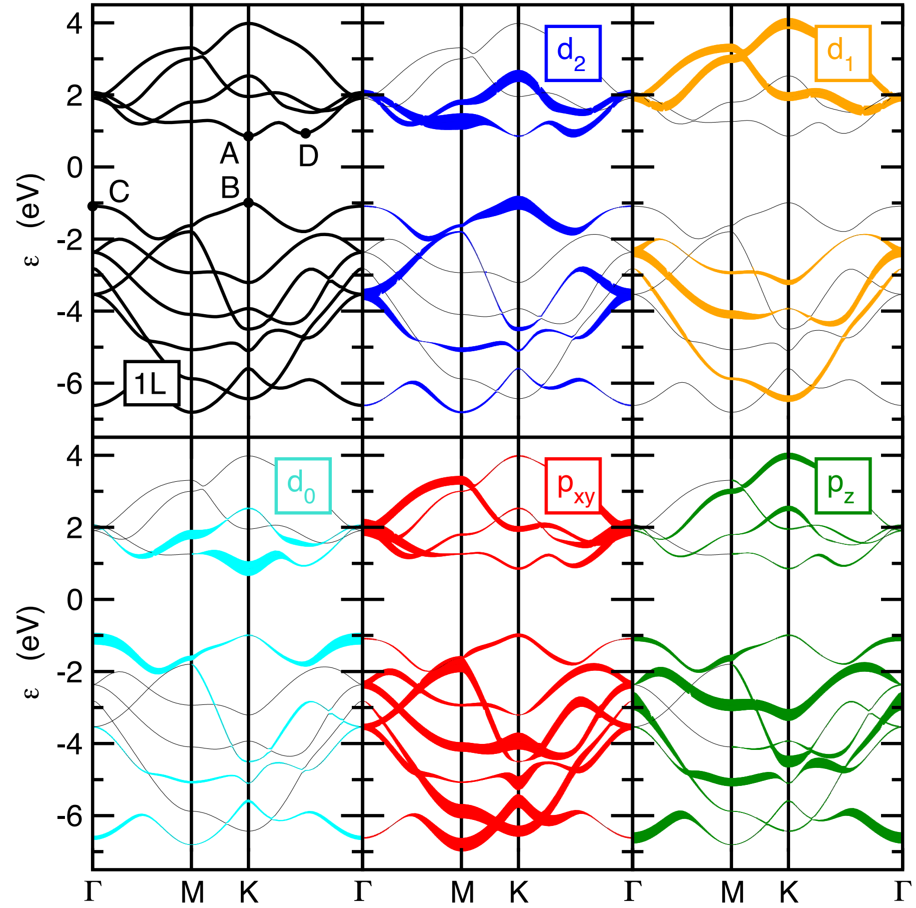
- Simultaneous scanning Raman microscopy and photoluminescence
- Raman spectroscopy accounts for the changes of the vibrational modes induced by strain
- PL accounts for the direct transitions between the valence and conduction bands at the K point

Strain tuning the direct band gap trasition in MoS_2



- Direct local correlation between strain and bandgap
- The change in the direct gap is obtained from the shift of the A exciton in the PL spectra
- Theoretical tight-binding model (see later) predicts the right magnitude of the dependence (~ -36meV per % of strain) but linear behavior
- Origin of the non-linear behavior? Funnel effect

Tight-binding model for MoS_2



Mo:
$$d_0 \rightarrow d_{3z^2-r^2}$$
$$d_1 \rightarrow d_{xz}, d_{yz}$$
$$d_2 \rightarrow d_{xy}, d_{x^2-y^2}$$

S:
$$p_x$$
$$p_y$$
$$p_z$$

Theoretical model to account for non-uniform strain

- Formidable task for DFT: huge supercells!!
- Affordable with tight-binding

1st task: Build a robust strain-sensitive tight-binding description of MoS_2 (including Mo and S orbitals)

> Tight-binding for 1-layer MoS_2:
> 11 bands & 12 TB parameters

Suitable generalization to multi-layer systems in a LEGO model, by simply adding few inter-layer hopping

E. Cappelluti, RR, J.A. Silva-Guillén, P. Ordejón and F. Guinea, *PRB* **88**, 075409 (2013)

Including strain in the tight-binding description

2nd task: generalization of TB in locally modulated strained samples

- Within a Slater-Koster framework, hopping processes between two atoms depend only on the relative angle and on the relative distance
- We assume that the main contribution comes from the modulation of the hopping integrals on the distance, and we neglect the weak dependence on the relative angles

$$V_{i,j,\mu,\nu}\left[R_{ij\mu\nu}(x,y)\right] \approx V_{i,j,\mu,\nu}\left(R^0_{ij\mu\nu}\right)\left[1-\beta_{i,j,\mu,\nu}\frac{\delta R_{ij\mu\nu}(x,y)}{R^0_{ij\mu\nu}}\right]$$

$$\mathbf{R}_{ij\mu\nu}(x,y) = \left[\hat{I}+\hat{\varepsilon}(x,y)\right]\cdot\mathbf{R}^0_{ij\mu\nu}$$

$$\beta_{i,j,\mu,\nu} = -\frac{d\log V_{i,j,\mu,\nu}(R)}{d\log R}$$

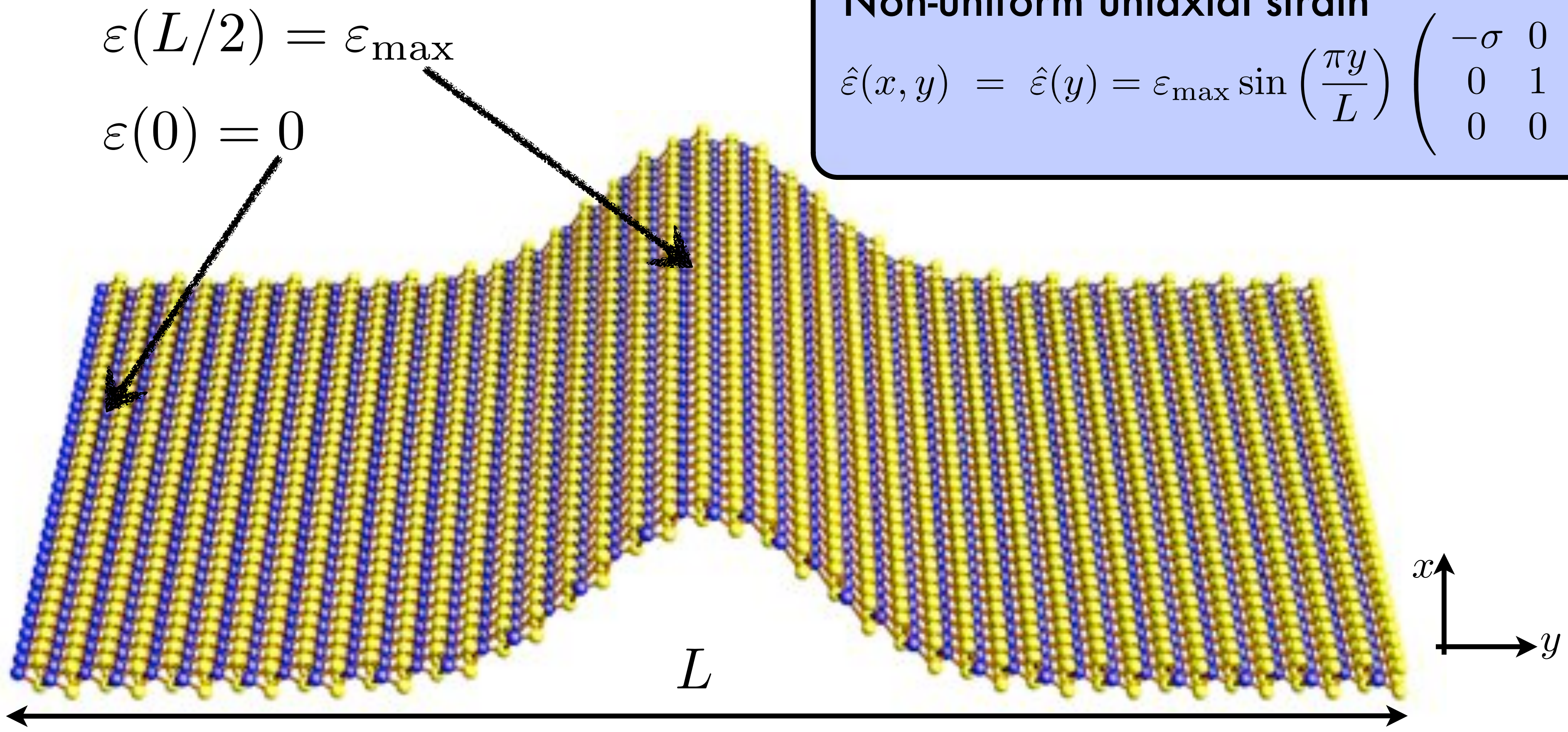
$$\delta R_{ij\mu\nu}(x,y) = R_{ij\mu\nu}(x,y) - R^0_{ij\mu\nu}$$

A.Castellanos-Gómez, RR, E.Cappelluti, G.Steele, F.Guinea & H. van der Zant, Nano Letters **13**, 5361 (2013)

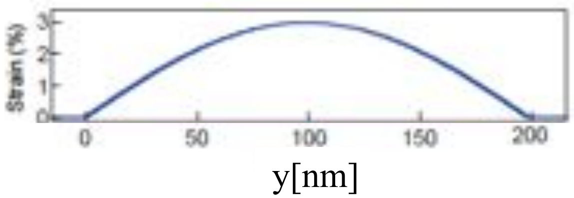
Including strain in a tight-binding description

Non-uniform uniaxial strain

$$\hat{\varepsilon}(x,y) \;=\; \hat{\varepsilon}(y) = \varepsilon_{\max}\sin\left(\frac{\pi y}{L}\right)\begin{pmatrix} -\sigma & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

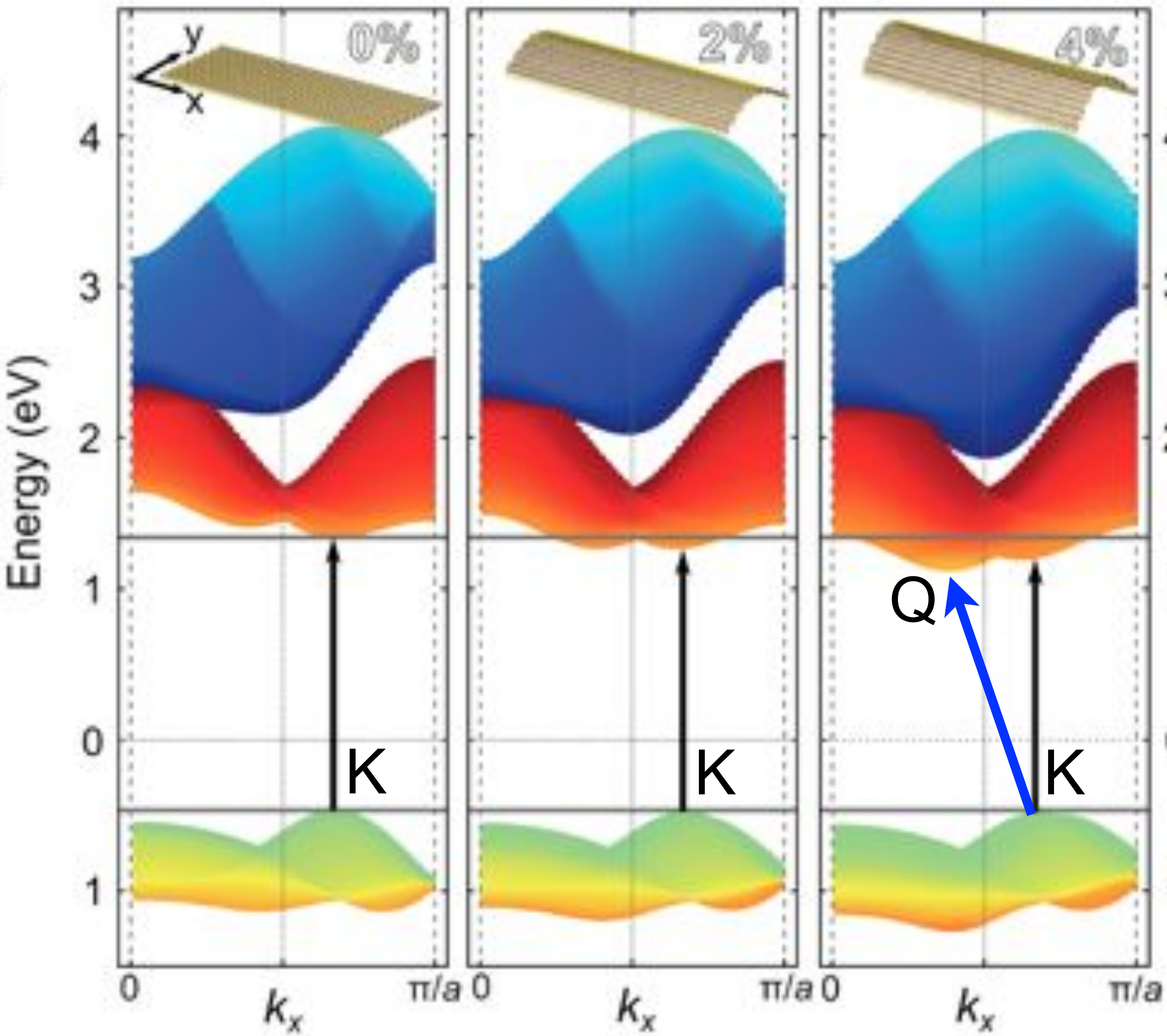


Tight-binding in locally strained MoS_2



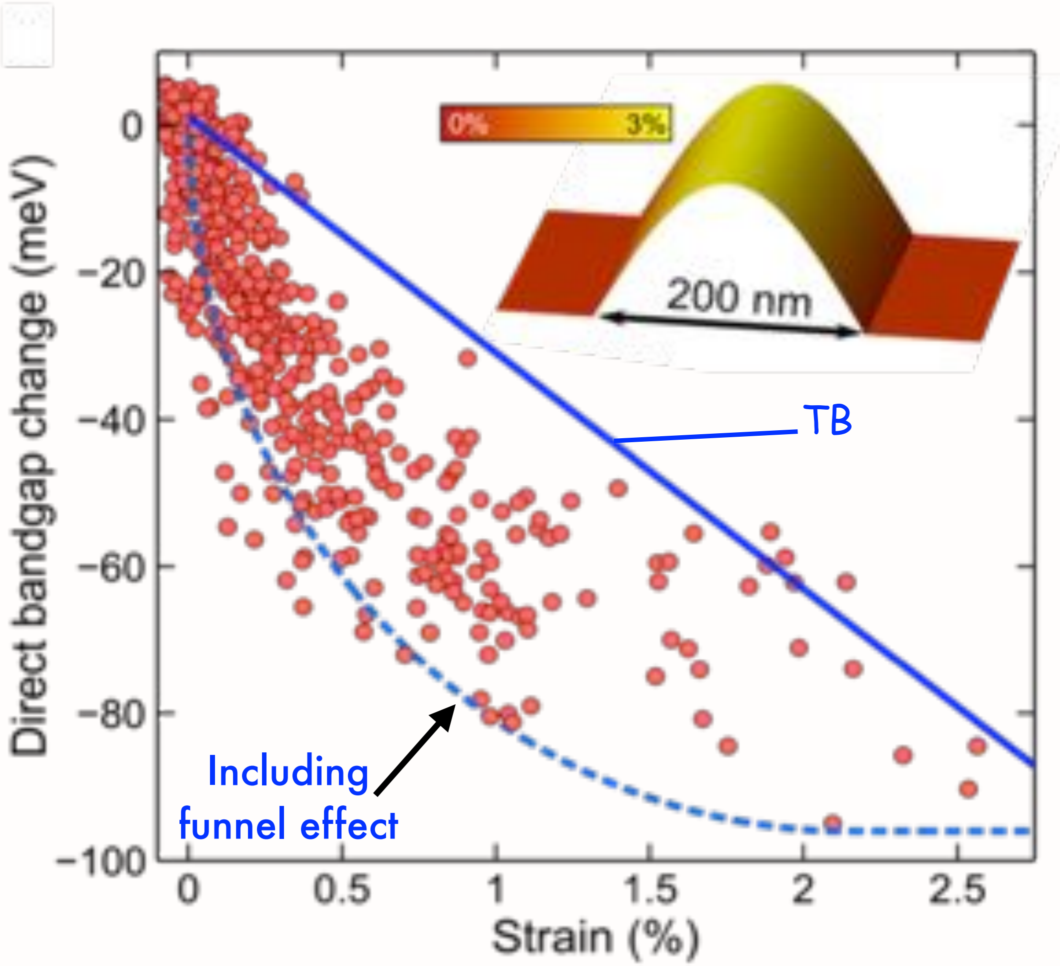
700 units cells ~ 200 nm

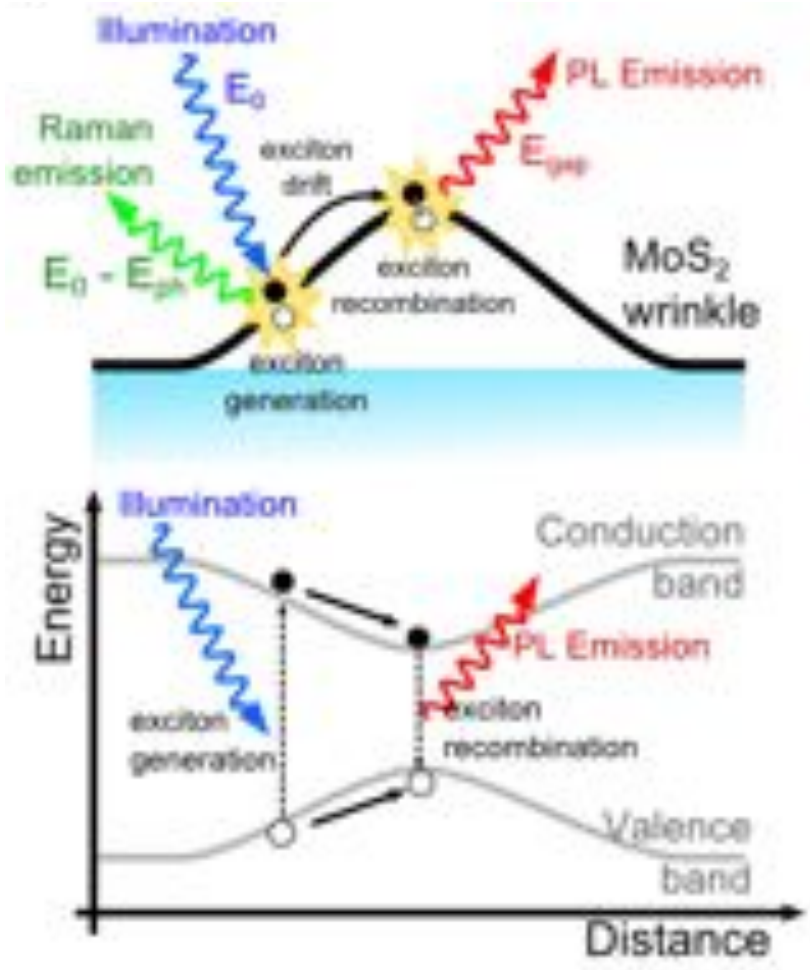
- Bandgap reduction upon strain
- Direct to indirect bandgap transition with strain



Assume β to be independent on the specific pair of atoms/orbitals: $\beta_{i,j,\mu,\nu} = \beta = 3$

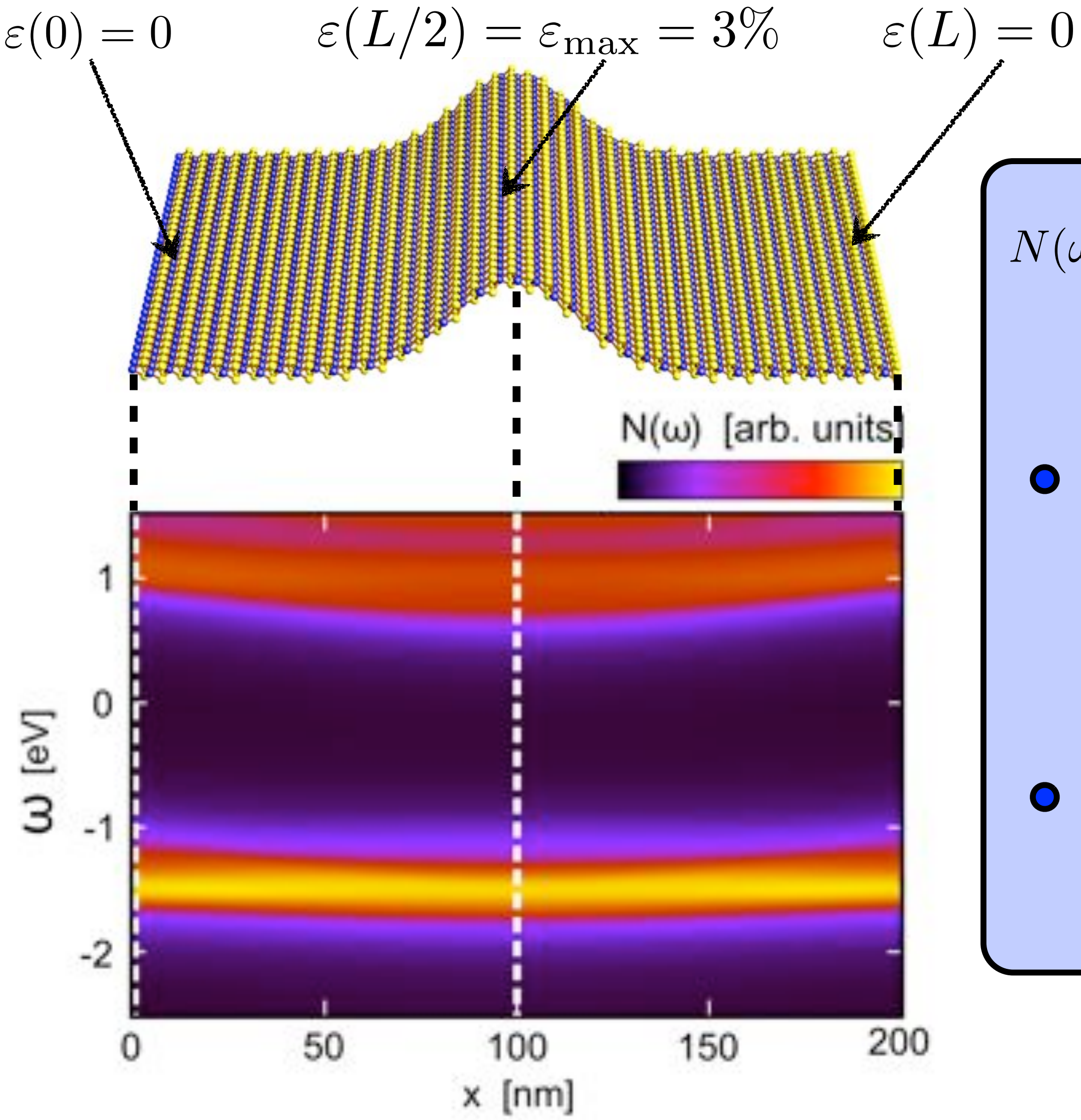
Funnel effect





- A.Castellanos-Gómez, RR, E.Cappelluti, G.Steele, F.Guinea & H. van der Zant, Nano Letters **13**, 5361 (2013)

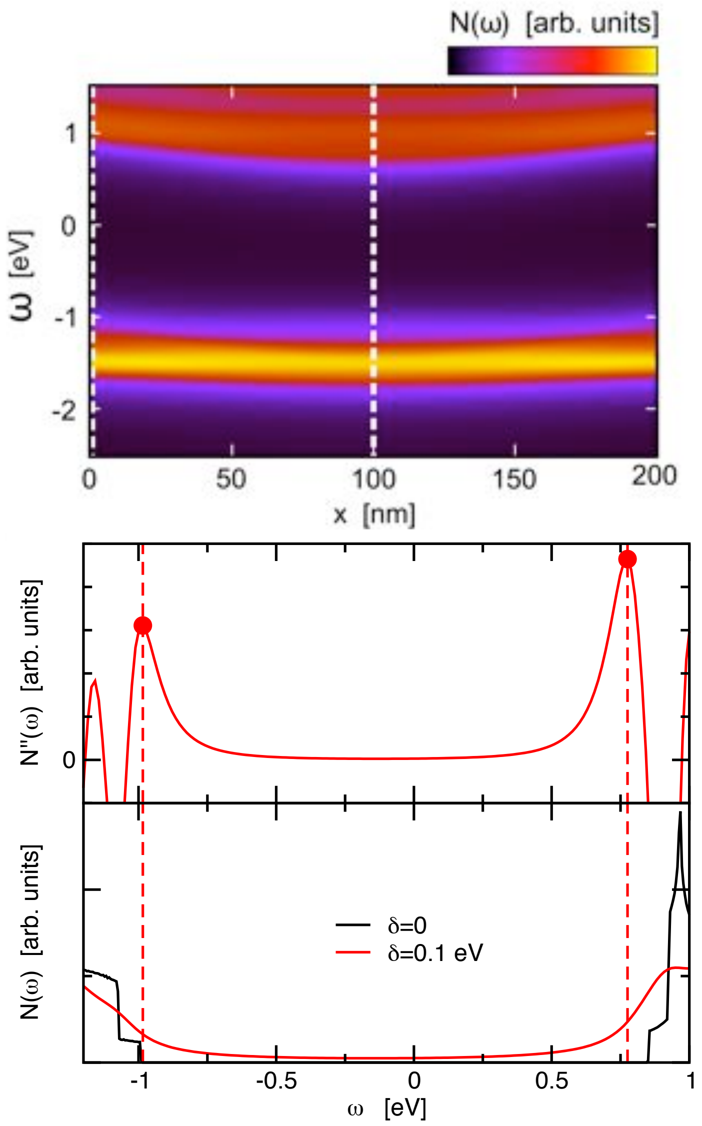
Local Density of States along the wrinkle



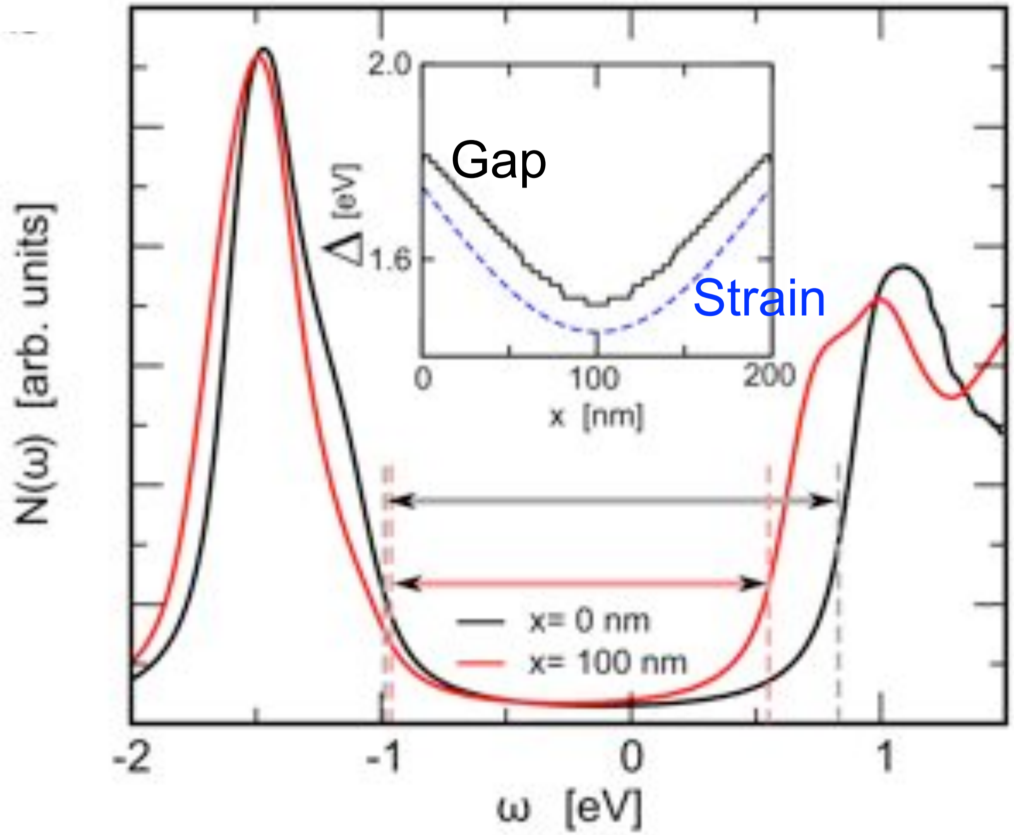
$$N(\omega, n) = \lim_{\delta \to 0} \sum_{k_x,\mu} \mathrm{Im} \left[\frac{1}{\omega \hat{I} - \hat{H}(k_x) + i\delta} \right]_{n,\mu;n,\mu}$$

- Clear correlation between the local strain and the modulation of the LDOS
- Closing of the band-gap in the center of the wrinkle

Estimation of the minimum gap from the LDOS



- Estimation of the band edges by looking at the inflection points
  $$d^2 N(\omega, n)/d\omega^2|_{\omega=E_I} = 0$$



Summary

- Transition Metal Dichalcogenides (MoS_2, WS_2,...) as a two-dimensional semiconducting crystals: Interesting from a fundamental point of view and for applications

- Full tight-binding model applicable for single-layer and multi-layer transition metal dichalcogenides

- Extension to finite systems: nonoribbons, nanotubes, etc.

- Strain engineering as a possible route to tune the bandgap

- Local strain yields exciton trapping (good for photovoltaic applications)

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Many thanks to...

Theory (Madrid)

E. Cappellutti
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Experiments (Delft)

A. Castellanos-Gómez
Michele Buscema
G. Steele
H. van der Zant

- A.Castellanos-Gómez, RR, E.Cappelluti, M. Buscema, G.Steele, F.Guinea & H. van der Zant, Nano Letters **13**, 5361 (2013)

...and thanks to you for your attention