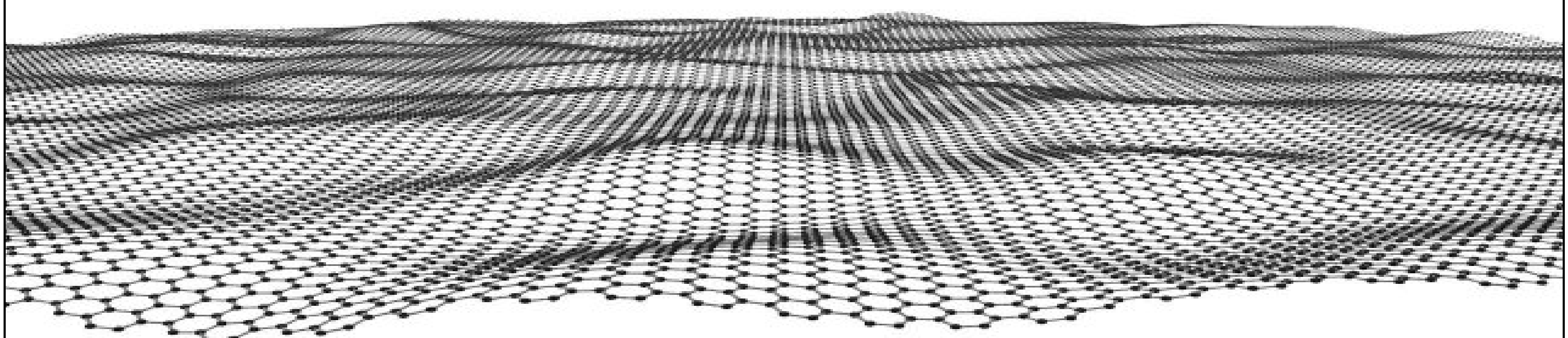
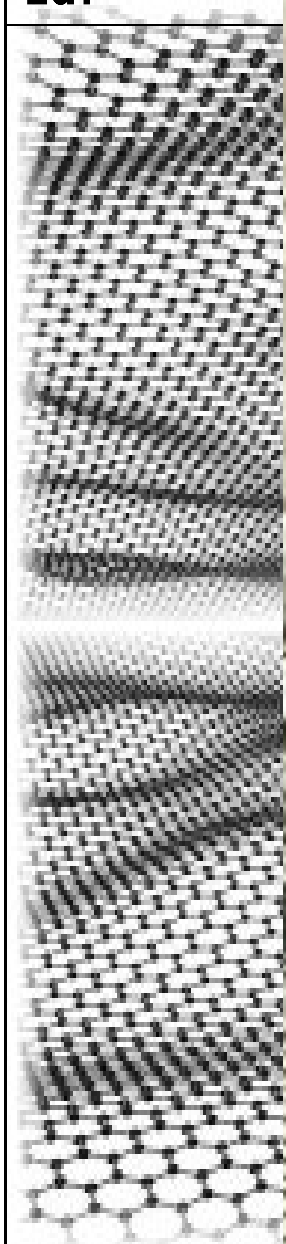
Universität Konstanz

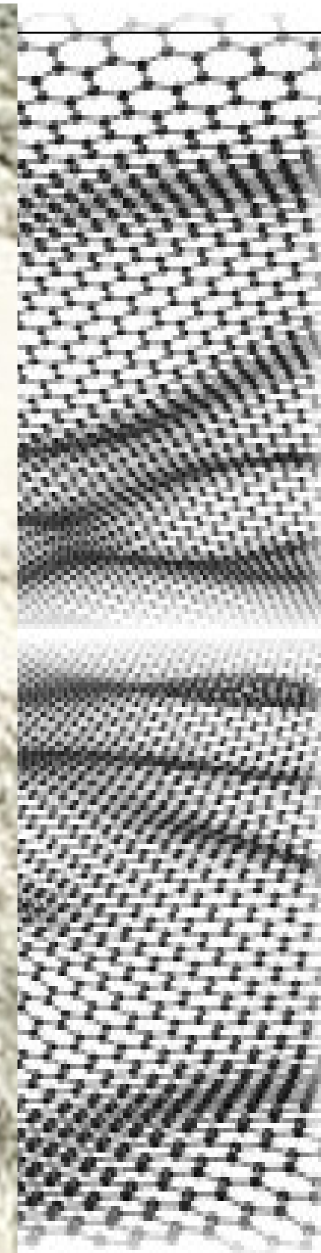
Theory-Seminar: Graphene

Phonons, Elasticity and Crumpling of Graphene






GRAPHENE –
TO BE OR NOT TO BE
... IN 2D?



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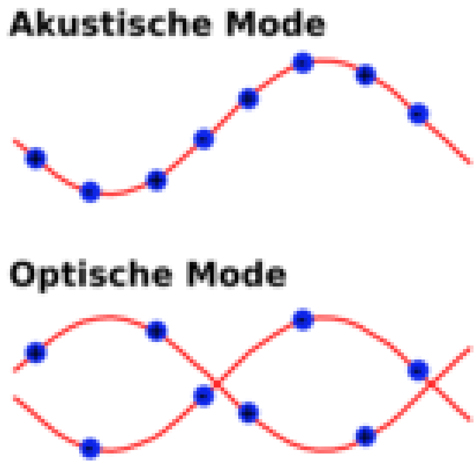
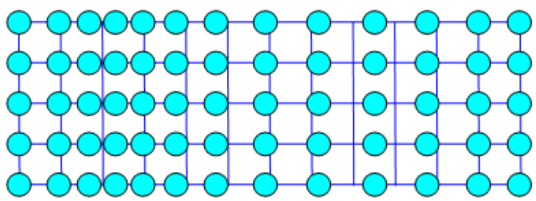
Phonons in crystal lattices

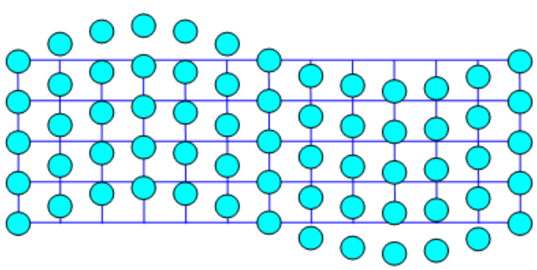


Branches of a **lattice base with r atoms** in **D dimensions:**

D	acoustic branches
$D \cdot r - D$	optical branches

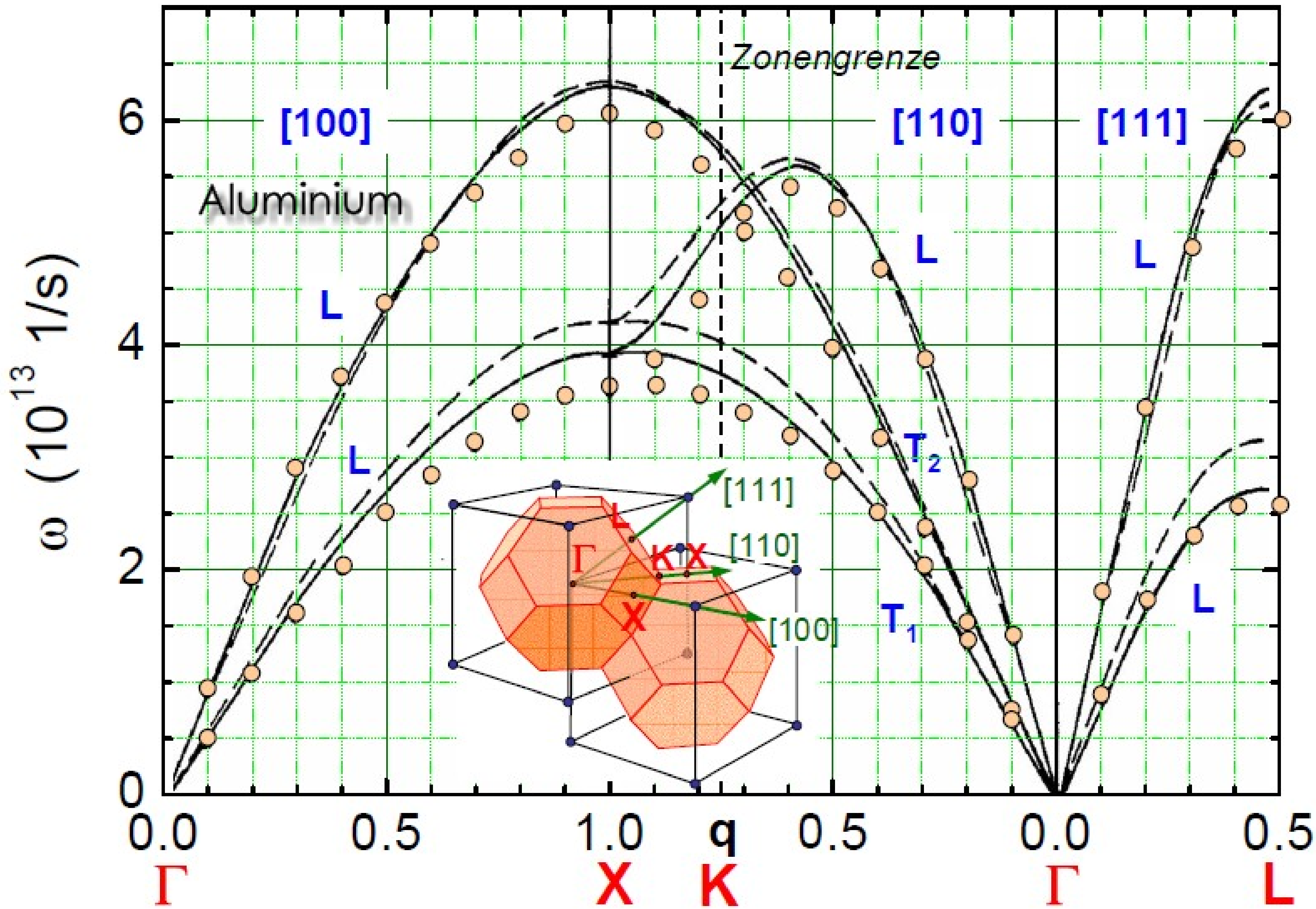


Longitudinal mode

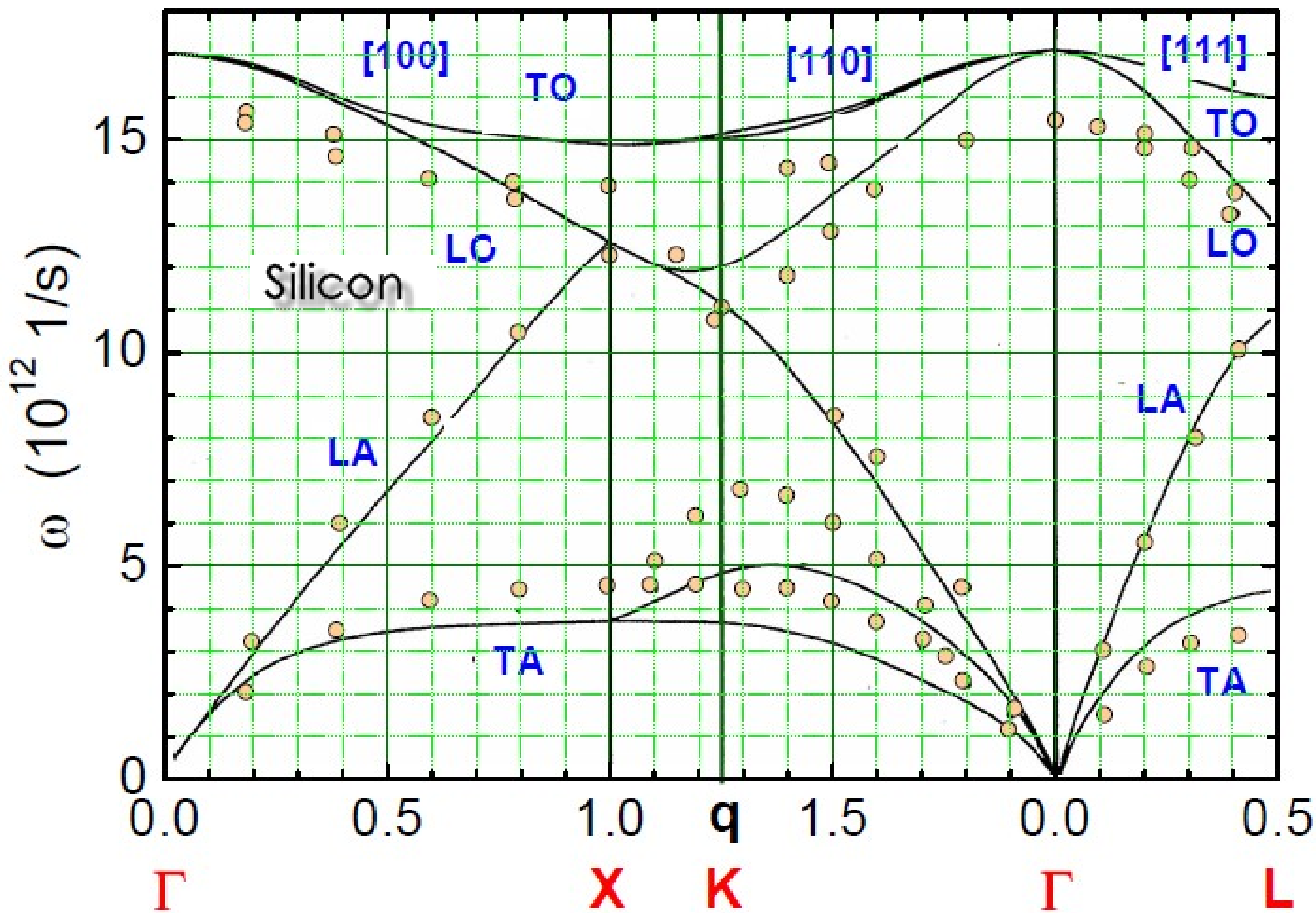


transversal mode

Phonons in 3D (one atom in base)



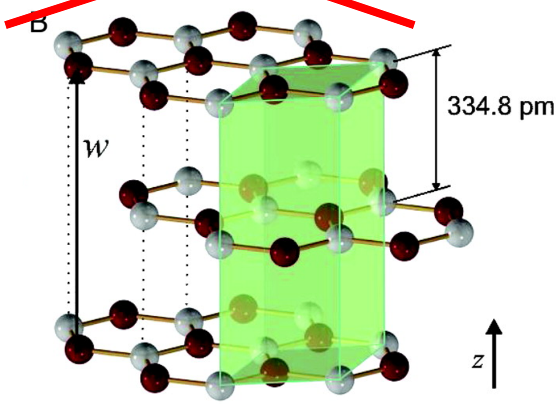
Phonons in 3D (two atom in base)



<u>Phonons in 3D</u> (four atom in base)

3	acoustic branches
$3 \cdot 4 - 3 = 9$	optical branches
12	branches

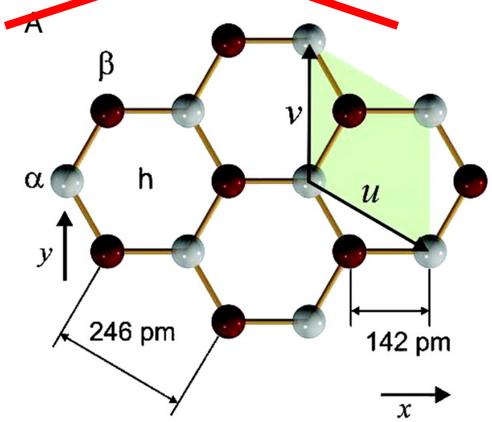
~~like „**graphite**“~~



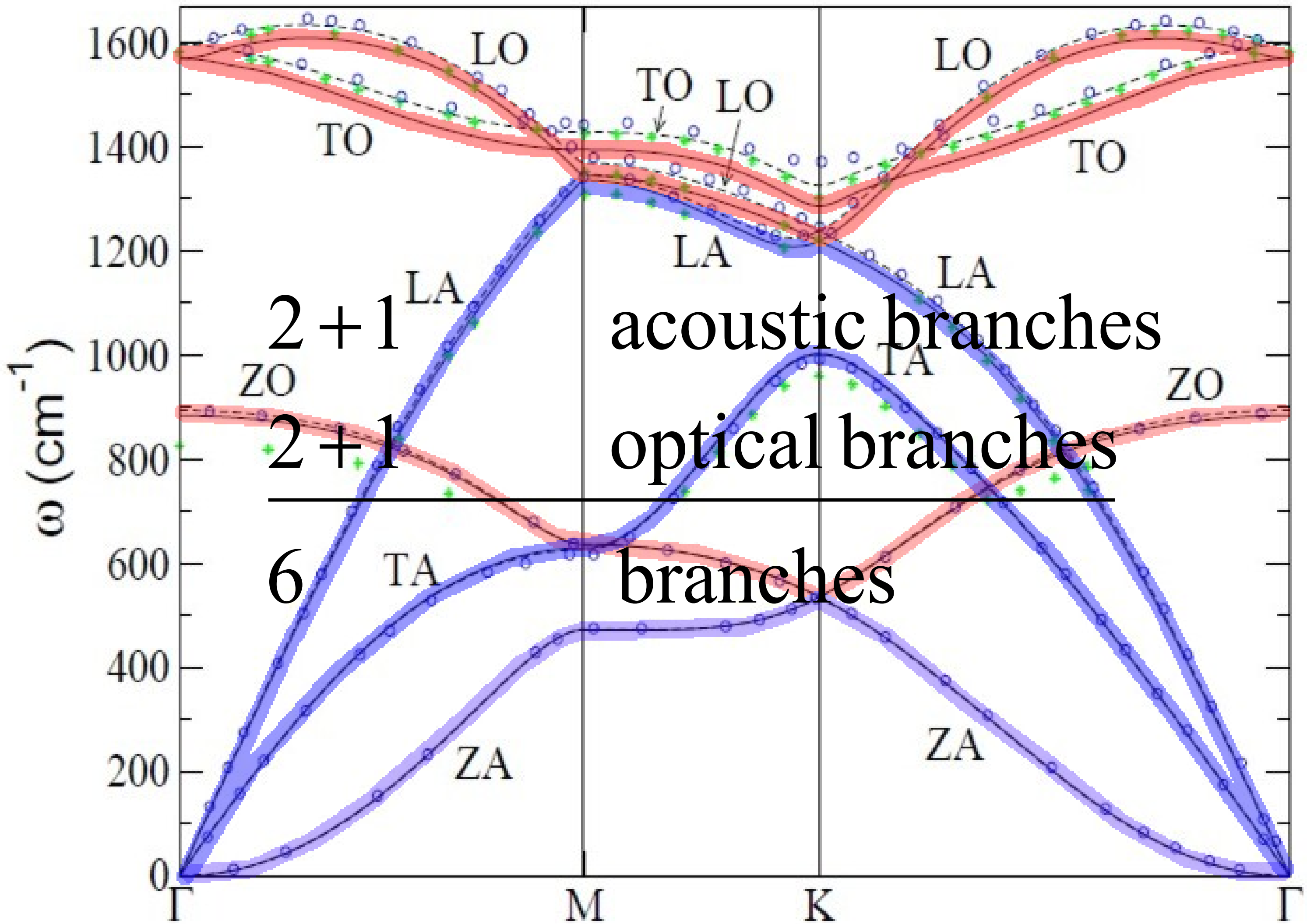
<u>Phonons in 2D</u> (two atom in base)

2	acoustic branches
$2 \cdot 2 - 2 = 2$	optical branches
4	branches

~~like „**graphene**“~~



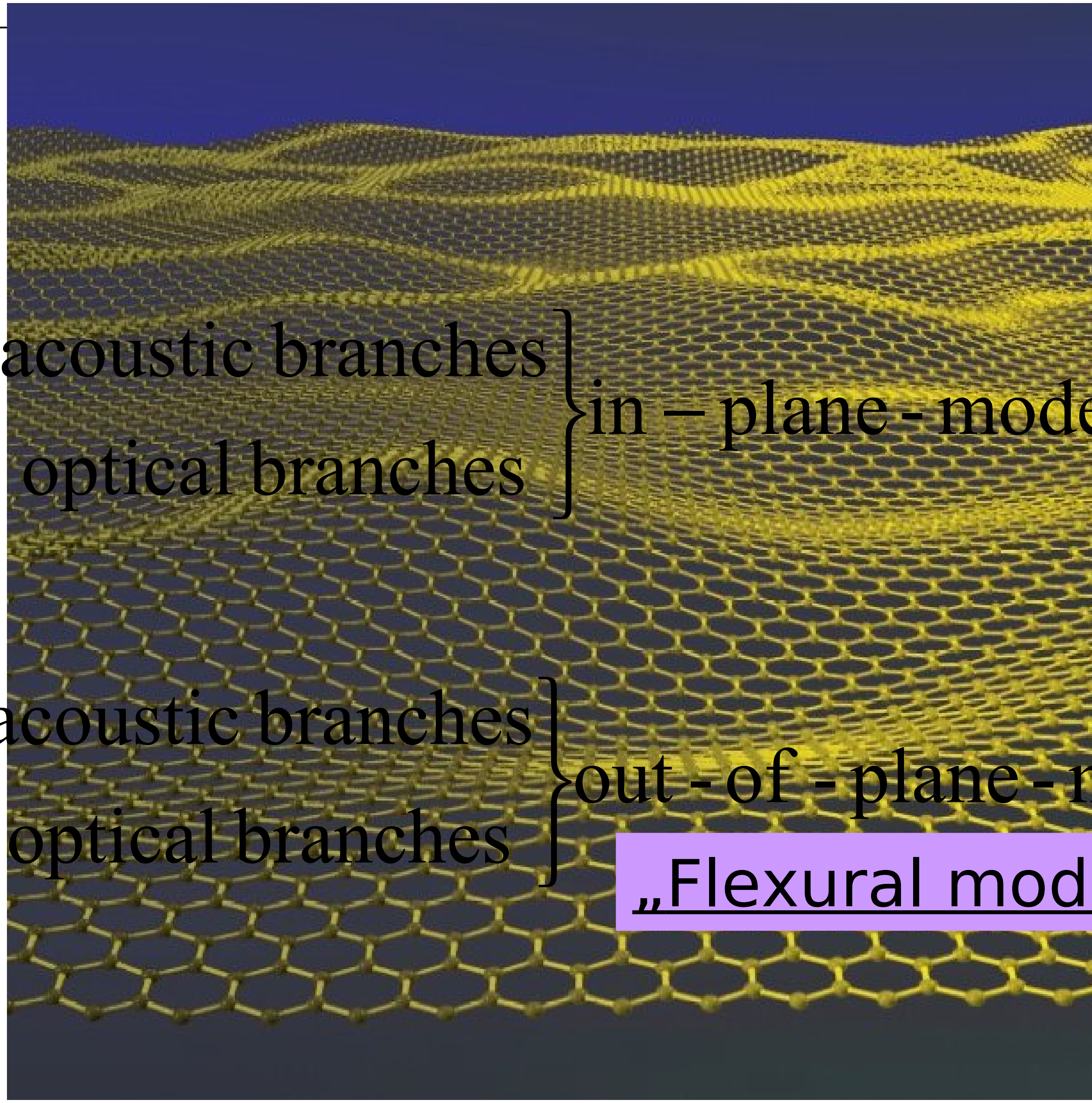
Phonons in Graphene



2 + 1 acoustic branches

2 + 1 optical branches

6 branches



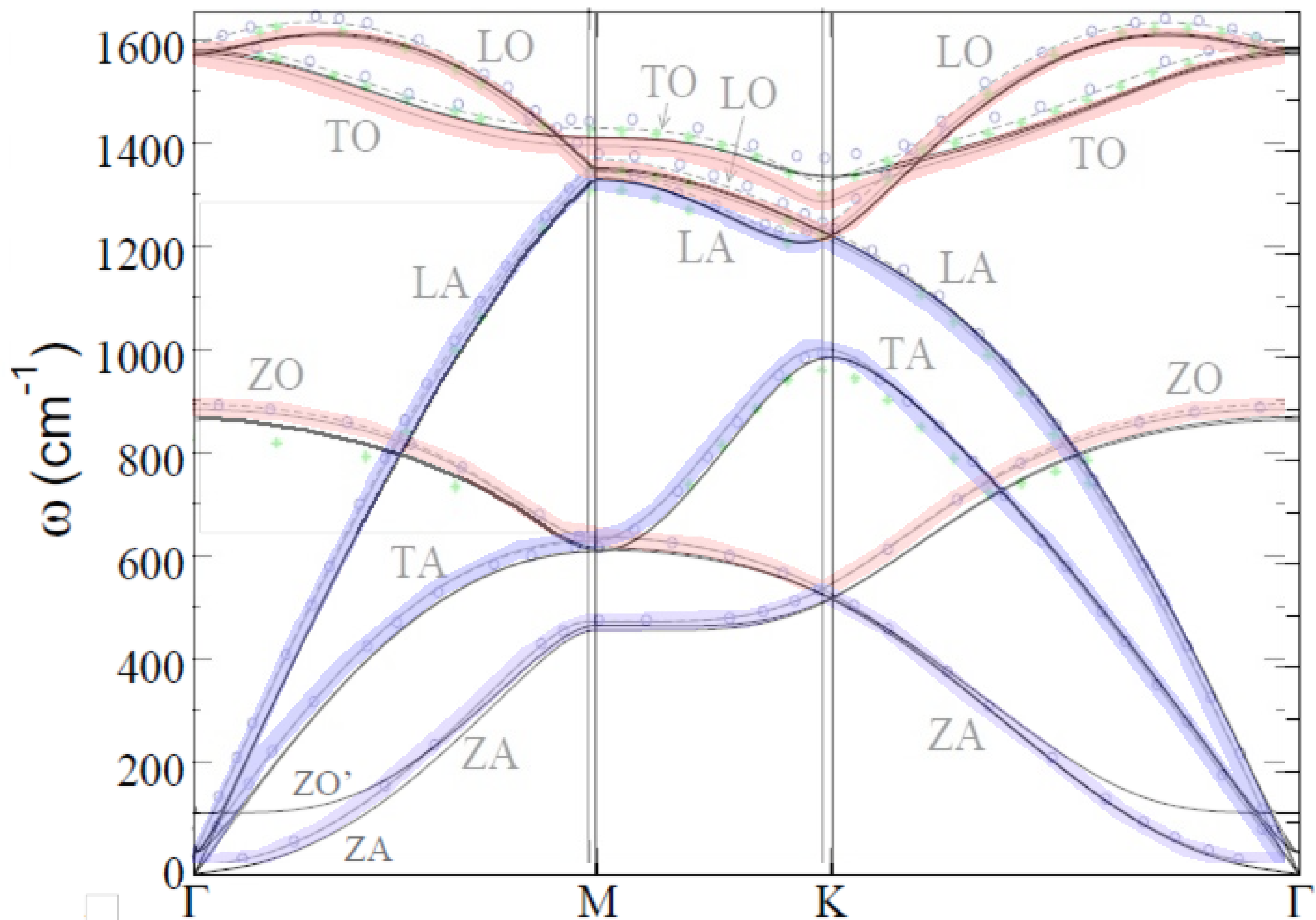
$$\left.\begin{cases} 2 & \text{acoustic branches} \\ 2 & \text{optical branches} \end{cases}\right\} \text{in} - \text{plane} - \text{modes}$$

$$+$$

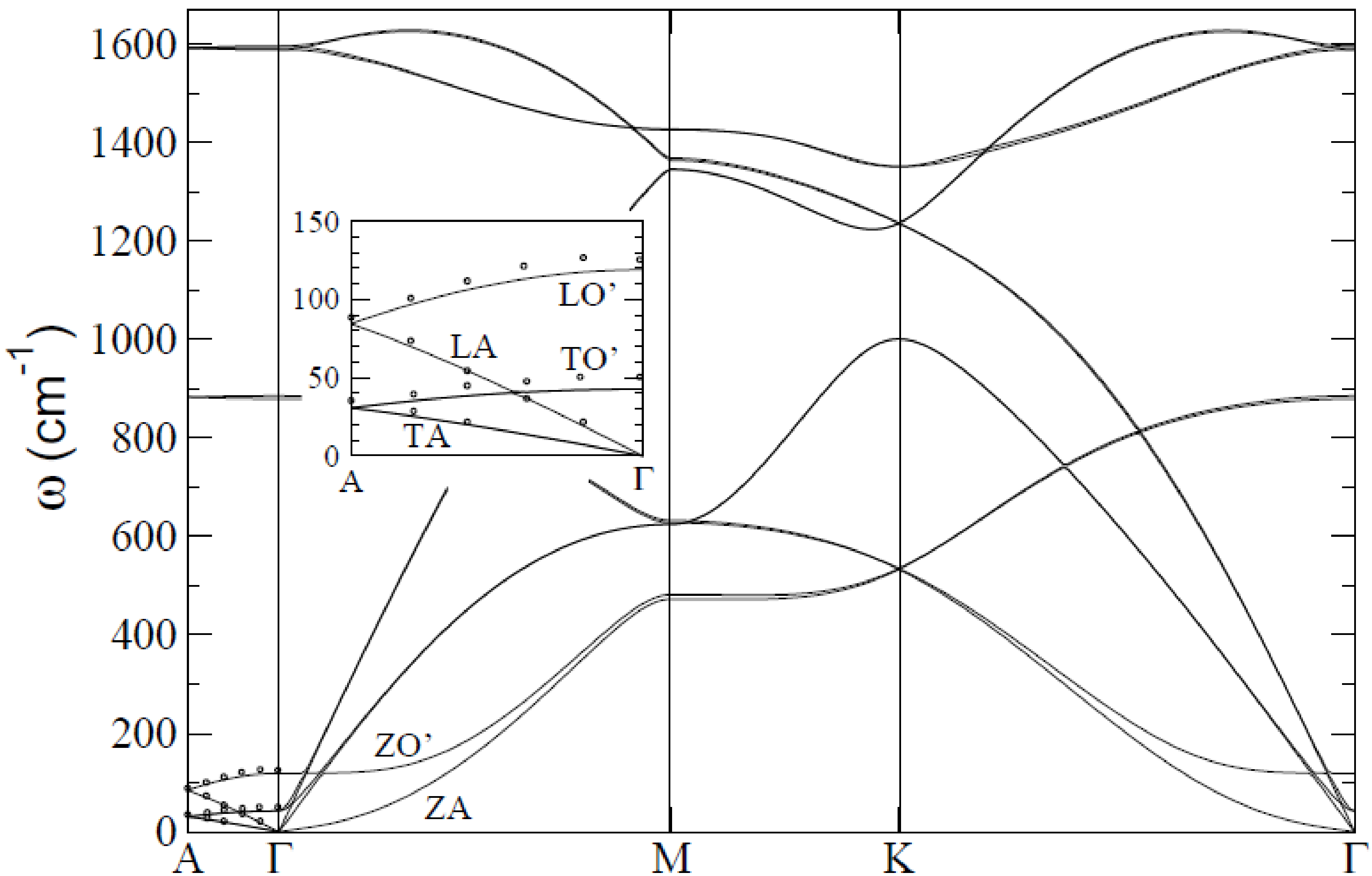
$$\left.\begin{cases} 1 & \text{acoustic branches} \\ 1 & \text{optical branches} \end{cases}\right\} \text{out} - \text{of} - \text{plane} - \text{modes}$$

„Flexural modes“

Phonons in Graphite



Phonons in Graphite



Dispersion Relation of Phonons in Graphene

Procedure:

- Create a **potential** for an oscillation in free floating graphene
- Put this potential into a **Hamilton-Operator**
- Solve the **equations of motion**

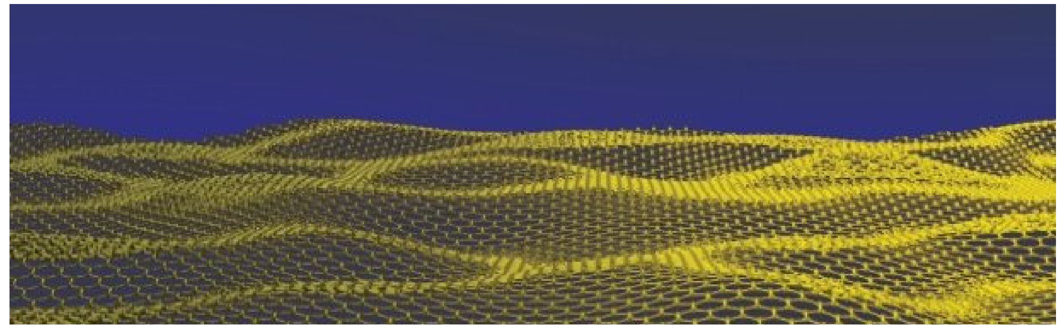
- Adapt the dispersion relation to **tension and substrate**

- Calculate the **number of phonons**

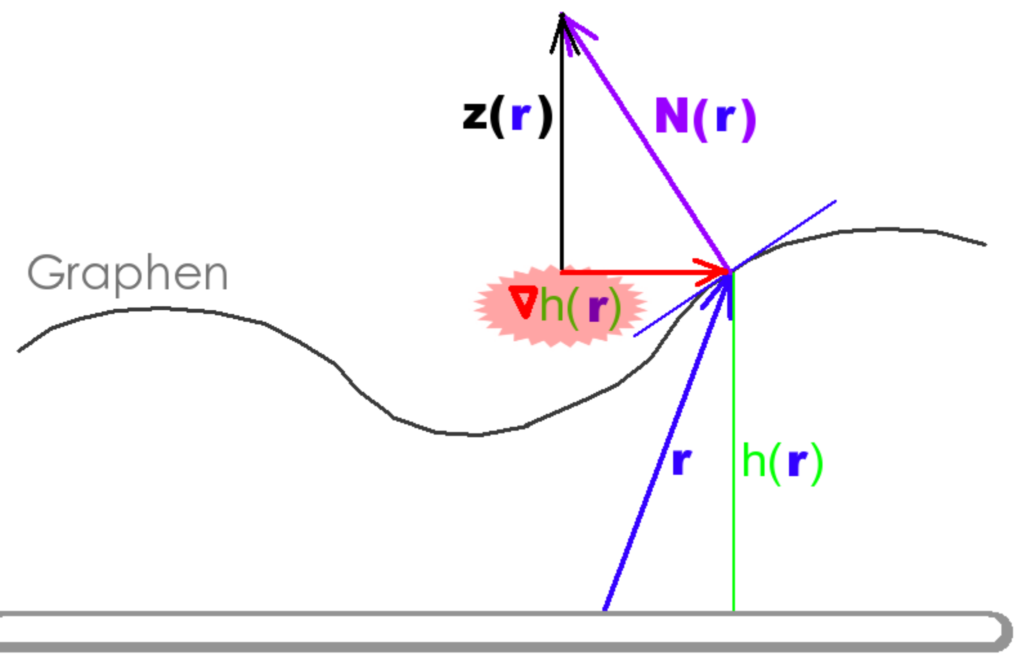
- Think about all the **approximations** you have done!

1. Potential for an oscillation

How to describe the elongation?



$$\vec{N} = \frac{\hat{z} - \nabla h}{\sqrt{1+(\nabla h)^2}}$$



1. Potential for an oscillation

Integration over microscopic springs:

$$E_0 = \frac{\kappa}{2} \int d^2 r \, (\nabla N)^2$$

For small bendings $(\nabla h)^2 << 1$ (**harmonic approximation**) we obtain

$$E_0 \approx \frac{\kappa}{2} \int d^2 r \, (\nabla^2 h)^2$$

Fourier-Transformation

$$h(\vec{r}) = \frac{1}{2\pi} \int d^2 \vec{k} \, e^{i\vec{k}\vec{r}} \, h_k$$

1. Potential for an oscillation

Adopt FT and divide into a r- and non-r-dependent part

$$(\nabla^2 h)^2 = \frac{1}{(2\pi)^2}\int d^2k\, k^2\, h_k \int d^2k'\, k'^2\, h_{k'}\, e^{i(k+k')r}$$

α

Solve integral

$$E_0 = \frac{\kappa}{2}\alpha \int dr\, e^{i(k+k')r}$$

$2\pi\delta(k+k') \Rightarrow k'=-k$

Use a discrete number of k‘s

$$E_0 = \frac{\kappa}{2}\sum_k k^4\, h_{-k}h_k$$

2. Hamilton-Operator

Define a momentum operator and put kinetic and the potential-energy term into the Hamilton-Operator

$$H = \sum_k \left\{ \frac{1}{2\sigma} P_{-k} P_k + \frac{\kappa k^4}{2} h_{-k} h_k \right\}$$

Compare with Hamiltonian of classical spring problem

$$H = \frac{p^2}{2m} + \frac{1}{2} m\omega^2 x^2 \qquad \Rightarrow \quad \sigma\,\omega^2 = \kappa k^4$$

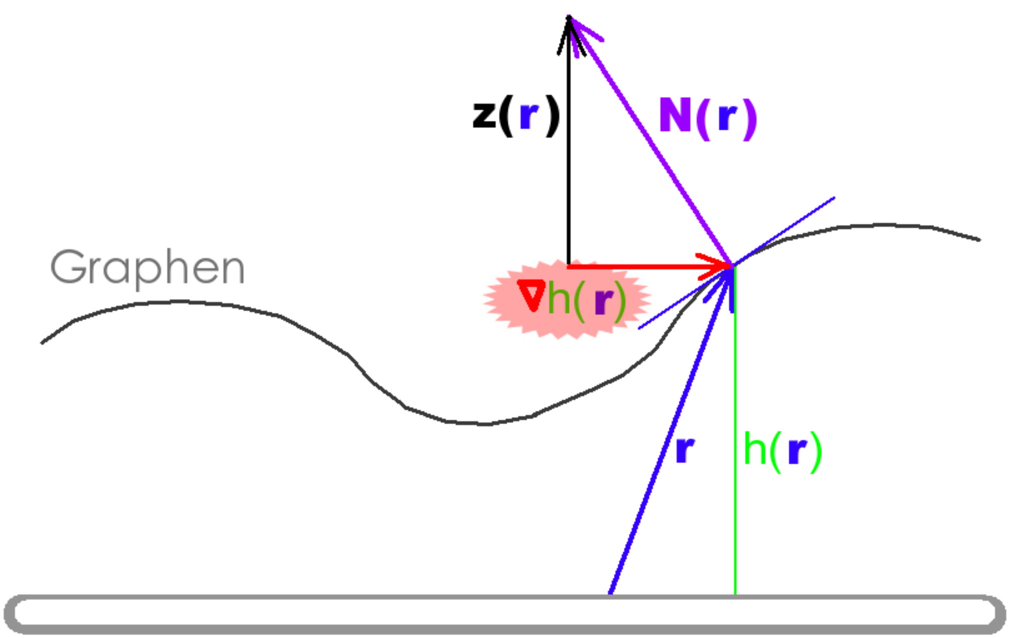
$$\Rightarrow \quad \omega_{flex}(k) = \sqrt{\frac{\kappa}{\sigma}} \cdot k^2$$

Dispersion relation for free floating graphene

3. Graphene under tension

Integration over microscopic springs:

$$E_T = \frac{\gamma}{2}\int d^2r\,(\nabla h)^2$$



3. Graphene under tension

Same calculation for graphene under tension ending up in a different Hamilton-Operator

$$H = \sum_k \left\{ \frac{1}{2\sigma} P_{-k} P_k + \frac{\kappa k^4}{2} h_{-k} h_k + \frac{\gamma k^2}{2} h_{-k} h_k \right\}$$

Compare with Hamiltonian of classical spring problem

$$H = \frac{p^2}{2m} + \frac{1}{2} m\omega^2 x^2$$

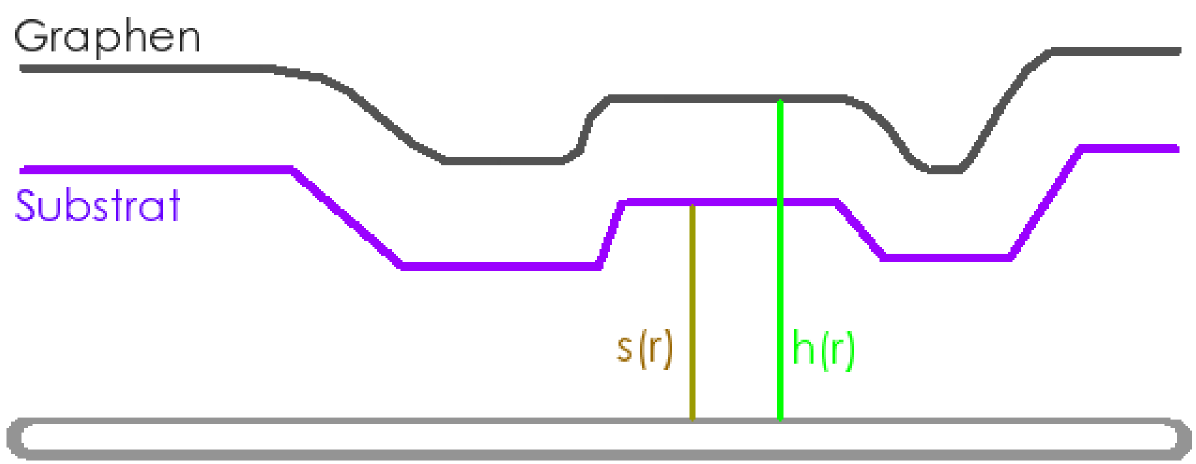
$$\Rightarrow \omega(k) = k \sqrt{\frac{\kappa}{\sigma} k^2 + \frac{\gamma}{\sigma}}$$

Dispersion relation for graphene under tension

4. Graphene on a substrate

Graphene in presence of a substrate

$$E_S \approx \frac{\nu}{2} \int d^2 r \, (s(r) - h(r))^2$$



5. Graphene as a Graphite layer

Is there any relation between the stiffness of graphene and graphite?

Weak Van-der-Waals forces between graphite-layers, thus a relation is possible

Lets measure the resonance frequency of a microscopic graphite sample

$$\nu(k) = \sqrt{\frac{Y}{\sigma} t k^2}$$

Compare v(k) to $\omega_{flex}(k) = \sqrt{\frac{\kappa}{\sigma}} \cdot k^2$

$$\kappa = Yt^3$$

This value fits to the measurements with graphene

6. Number of Phonons

a) Free floating graphene

$$n_k = \frac{1}{\exp(\beta(E)) - 1}$$

$$N_{ph} = \int \frac{d^2k}{(2\pi)^2} \cdot n_k$$

$$= \int_0^\infty \frac{dk}{2\pi} \cdot \frac{k}{\exp(\beta\sqrt{\kappa/\sigma} \cdot k^2) - 1}$$

$$\omega_{flex}(k) = \sqrt{\frac{\kappa}{\sigma}} \cdot k^2$$

Integral diverges in the infrared!!

That means graphene could not exist!!

Way out: Set the lower limit $2\pi/L$

6. Number of Phonons

Now the integral converges

$$N_{ph} = \frac{\pi}{L_T^{٢}} \ln\left(\frac{١}{١ - \exp(-L_T^{٢}/L^{٢})} \right)$$

With the thermal wavelenght $L_T = \frac{٢\pi}{\sqrt{k_B T}} \left(\frac{\kappa}{\sigma} \right)^{١/٤}$

6. Number of Phonons

$$N_{ph} = \frac{\pi}{L_T^2} \ln\left(\frac{1}{1 - \exp(-L_T^2 / L^2)} \right)$$

Have a closer look at $\left(\frac{L_T}{L} \right)$ Keep in mind: $L_T \propto \frac{1}{\sqrt{T}}$

1. $L >> L_T$

Number of phonons diverges Logarithmically with L

System cannot be structurally ordered at any finite temperature

6. Number of Phonons

$$N_{ph} = \frac{\pi}{L_T^2} \ln\left(\frac{1}{1 - \exp(-L_T^2 / L^2)} \right)$$

Have a closer look at $\left(\frac{L_T}{L} \right)$ Keep in mind: $L_T \propto \frac{1}{\sqrt{T}}$

2. $L << L_T$

Number of phonons goes to 0

System can be flat

if temperature is low enough

6. Number of Phonons

What means „low enough temperature“?

1. **T = 300K**

   One obtain $L_T \approx 0{,}1nm \qquad \Rightarrow L_T << L$

2. **T = 0,01K**

   One obtain $L_T \approx 100nm \qquad \Rightarrow L_T << L$

The statement won!

System cannot be structurally ordered
At any finite temperature

6. Number of Phonons

b) How does graphene look like **under tension**?

$$N_{ph} = \int \frac{d^2k}{(2\pi)^2} \cdot n_k$$

$$n_k = \frac{1}{\exp(\beta(E)) - 1}$$

$$\omega(k) = k\sqrt{\frac{\kappa}{\sigma}k^2 + \frac{\gamma}{\sigma}}$$

Integral converges in the infrared.

That means it is independent from the size,

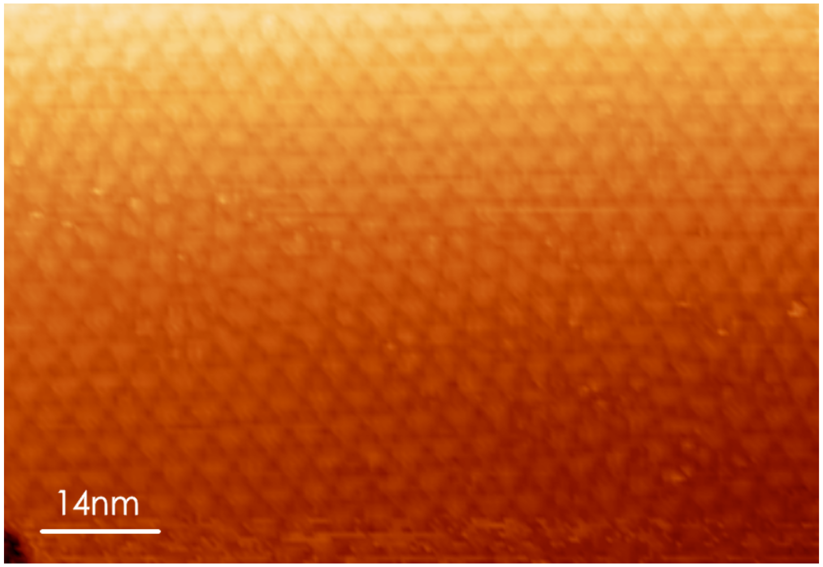
Just depends on the temperature.

Under these circumstances it is easier to find conditions, where **a graphene-sheet could be flat at finit temperatures.**

6. Number of Phonons

c) How does graphene look like **on a substrate**?

Substrate has a certain surface, descibed by s(r).
Graphene tries to follow the substrate surface to minimize potential energy.
Obviously, the graphene-sheet could have a static rippling.



7. Approximations and reality

1. We assumed that the **graphene-lattice is perfect**

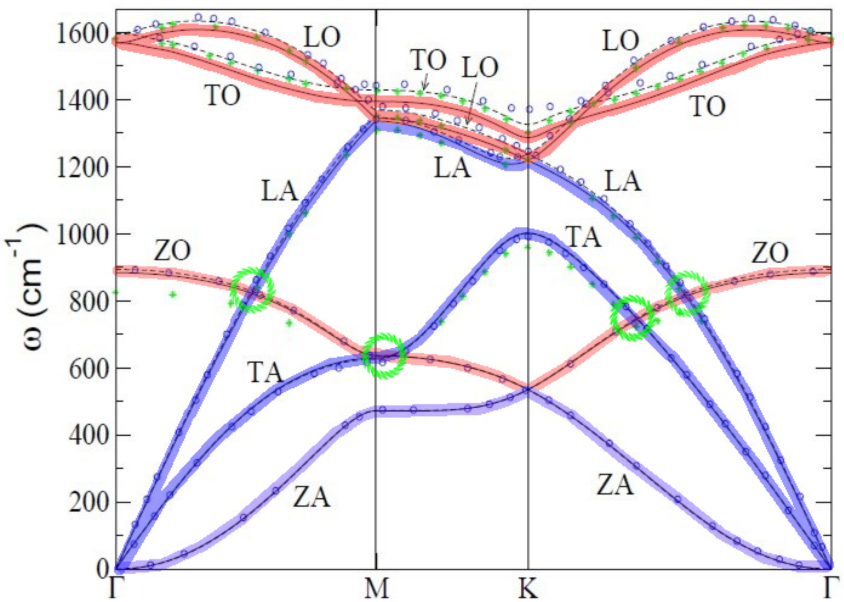
   BUT: there are topological defect: disclination, dislocation

2. We assumed **small bending deformations**

   BUT: What‘s small?

3. We assumed that there is **no coupling between the modes**

   BUT: Coupling exists



7. Approximations and reality

All these things lead to **non-linear effects**
and to such a **renormalization of the bending rigity**

that a flat graphene-phase is possible at low temperatures

Finally there can be **electon-phonon-interactions** between a metal gate and the flexural modes, which leads to a

damping of the flexural modes

Summary

- **Graphene does exist** – in theorie AND reality
- Graphene is a quasi-2D-system and has **flexural modes**
- One can get the dispersion relation by solving the linear problem of a **harmonic oscillator**
- There are different **dispersion relations** for different circumstances (**k^2 – free floating, linear in k – under tension**)
- **Number of phonons** tell us about the **structural order** of graphene
- **Flee floating** graphene **cannot be flat**, but **not free floating** graphene **can be flat** under certain condition

Literature

Author	Title	Year	Journal/Proceedings	Reftype
A.H. Castro Neto, F. Guinea, N.P.K.N. & Geim, A.	The electronic properties of graphene [BibTeX]	2009	Reviews of modern physics Vol. 81, pp. 109-162	article
A.K. Geim, A.M.	Graphene - exploring carbon flatland [BibTeX]	2007	Physics Today Vol. August 2007, pp. 35-41	article
A.K. Geim, K.N.	The rise of graphene [BibTeX]	2007	Nature Materials Vol. 6, pp. 183-191	article
Katsnelson, M.	Graphene: carbon in two dimensions [BibTeX]	2007	Materials today Vol. 10, no. 1-2, pp. 20-27	article
R. Gross, A.M.	Festkörperphysik - Vorlesungsskript zur Vorlesung im WS 2004/2005 [BibTeX]	2004		booklet

End