

# Phonon Properties of Multi-layered Graphene from Molecular Dynamics Simulations

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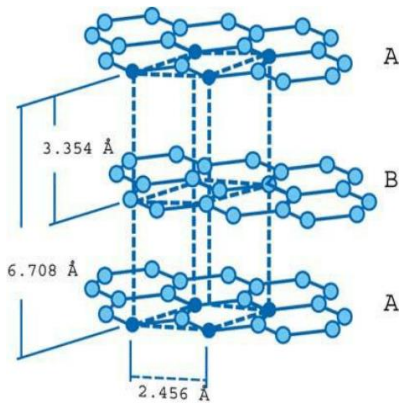
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# Objective of this work

- **Phonon properties** of single- and multi-layered graphene: dispersion curves, pDOS and dependence of  $\omega(T)$  and  $\tau(T)$  of  $\Gamma$ -point phonons
- Influence of the **number of layers N**
- Influence of the **interlayer interaction modelling/strength** on the phonon properties

# Interlayer interaction in multilayered graphene

## Classical interatomic potentials for Molecular Dynamics



Bernal Stacking (ABA)

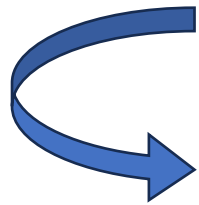
- **Intra-layer:**  $sp^2$  covalent C-C bonds (Tersoff)
- **Inter-layer:** Van der Waals interaction (non-polar materials)

### $\pi$ -orbital overlap (Pauli)

- Short-range
- Repulsive
- Anisotropic
- Non-local + many-body
- **Responsible for rugosity!**

### Dispersion (London)

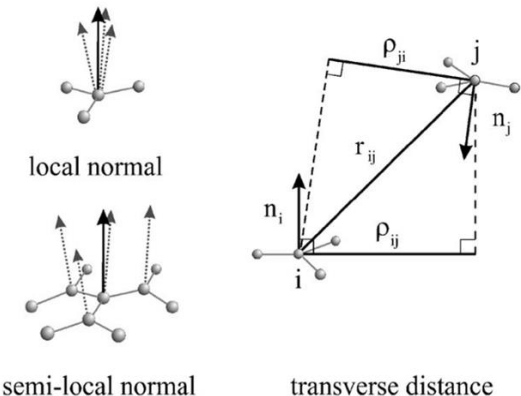
- Long-range
- Attractive
- Two-body  $\sim \left(-\frac{1}{r^6}\right)$



Lennard-Jones (LJ) potential (2body+radial)  
 “too smooth” for short-range part



complex, many-body potential:  
**Kolmogorov-Crespi (KC)**

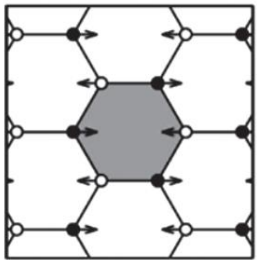


# $\Gamma$ -point phonons in Multilayered graphene

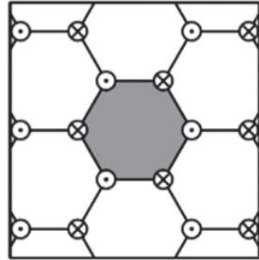
From 1L to Graphite

Single-layer

**Optical Modes**

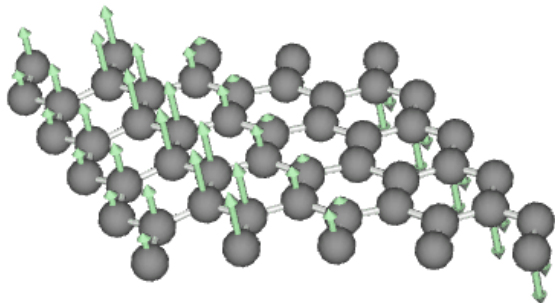


G (In-Plane)



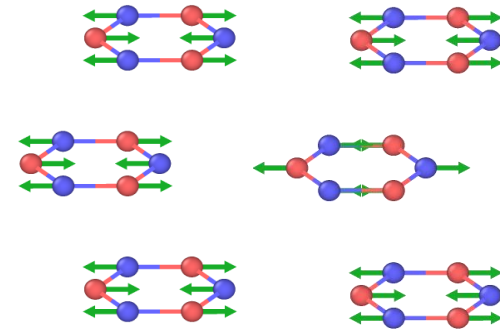
ZO (out-of-plane)

**Acoustical Modes**



N-layers

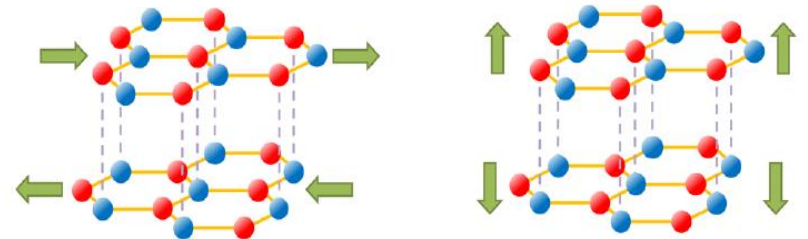
**N-Davydov multiplets**



G in-phase

G out-of-phase

**(N-1) Interlayer modes**



(N-1) Shear Modes (C)

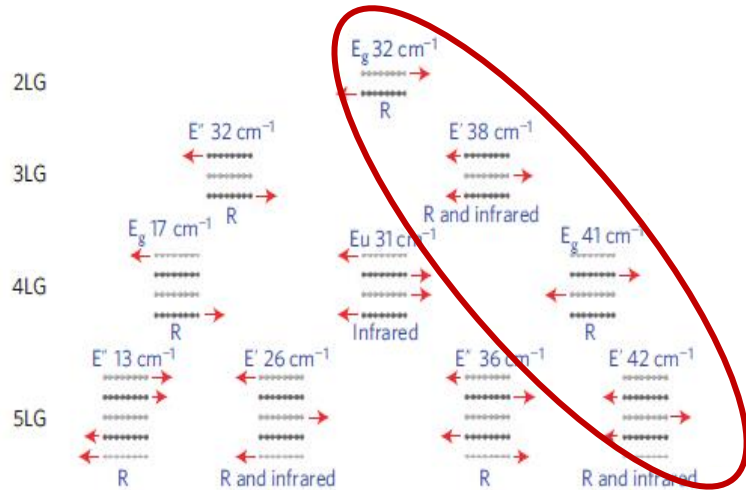
(N-1) Layer Breathing Modes (LBM)

# $\Gamma$ -point phonons in Multilayered graphene

## Choosing the mode representatives

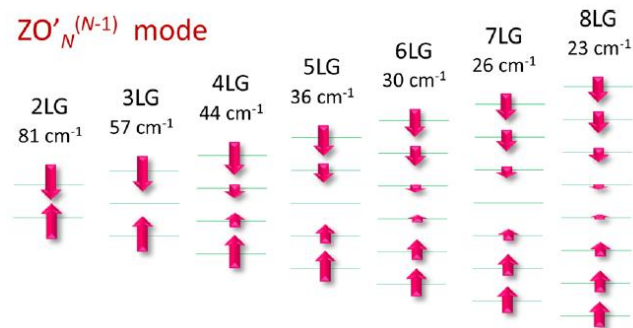
### Inter-layer

#### Shear Mode



Tan et al, Nat. Mat. 11, 3245 (2012)

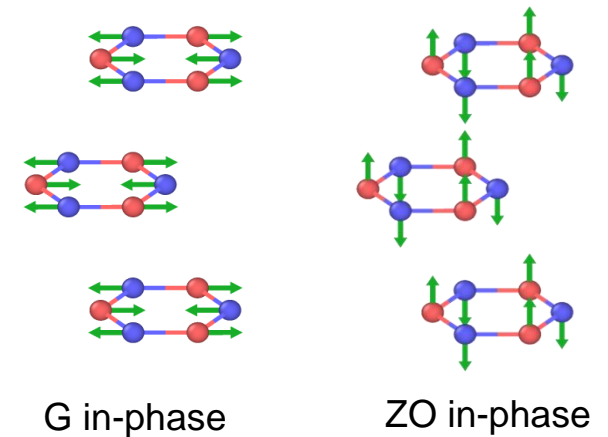
#### Breathing Mode



Lui et al, Nano Lett. 14, 4615 (2014)

### Intra-layer

#### Optical Modes



Always Raman active<sup>1</sup>  
(for comparison with experiment)

<sup>1</sup>Saha et al, Phys. Rev. B, 78, 165421 (2008)

# The kVACS method

k-VACS: **k**-space **V**elocity **A**utocorrelation **S**equence  $Z_x^p(\mathbf{k}, \omega)$

$$Z_x^p(\mathbf{k}, \omega) = \int d\tau e^{i\omega\tau} \langle v_x^p(\mathbf{k}, \tau) v_x^{p*}(\mathbf{k}, 0) \rangle$$

- $\langle \dots \rangle$  denotes time-average
- $v_x^p(\mathbf{k}, t) = \sum_j v_x^p(l, t) e^{-i\mathbf{k}\mathbf{R}^p(l)}$
- $\mathbf{R}^p(l)$ : equilibrium position of atom  $p$  in unit cell  $l$
- $l$ : unit cell,  $i$ : time,  $p$ : atom species,  $x$ : cartesian coordinate,  $*$ : complex conjugate

$$Z_{total}(\mathbf{k}, \omega) = \sum_x \sum_p m_p Z_x^p(\mathbf{k}, \omega)$$

➤ Wiener-Khintchin Theorem (ergodic processes):  $Z_x^p(\mathbf{k}, \omega) \propto \Phi_x^p(\mathbf{k}, \omega)$  (Power Spectral Density)

$$\Phi_x^p(\mathbf{k}, \omega) = \frac{1}{\tau} \left| \sum_l \sum_i v_x^p(j, t) e^{-i[\mathbf{k}\mathbf{R}^p(l) - \omega t_i]} \right|^2$$

$\tau$ : total simulation time

# The kVACS method

- $Z(\mathbf{k}, \omega)$  is a superposition of Lorentzian functions, centered at the phonon eigenfrequencies and **FWHM** equal to double the phonon decay rates<sup>1</sup>

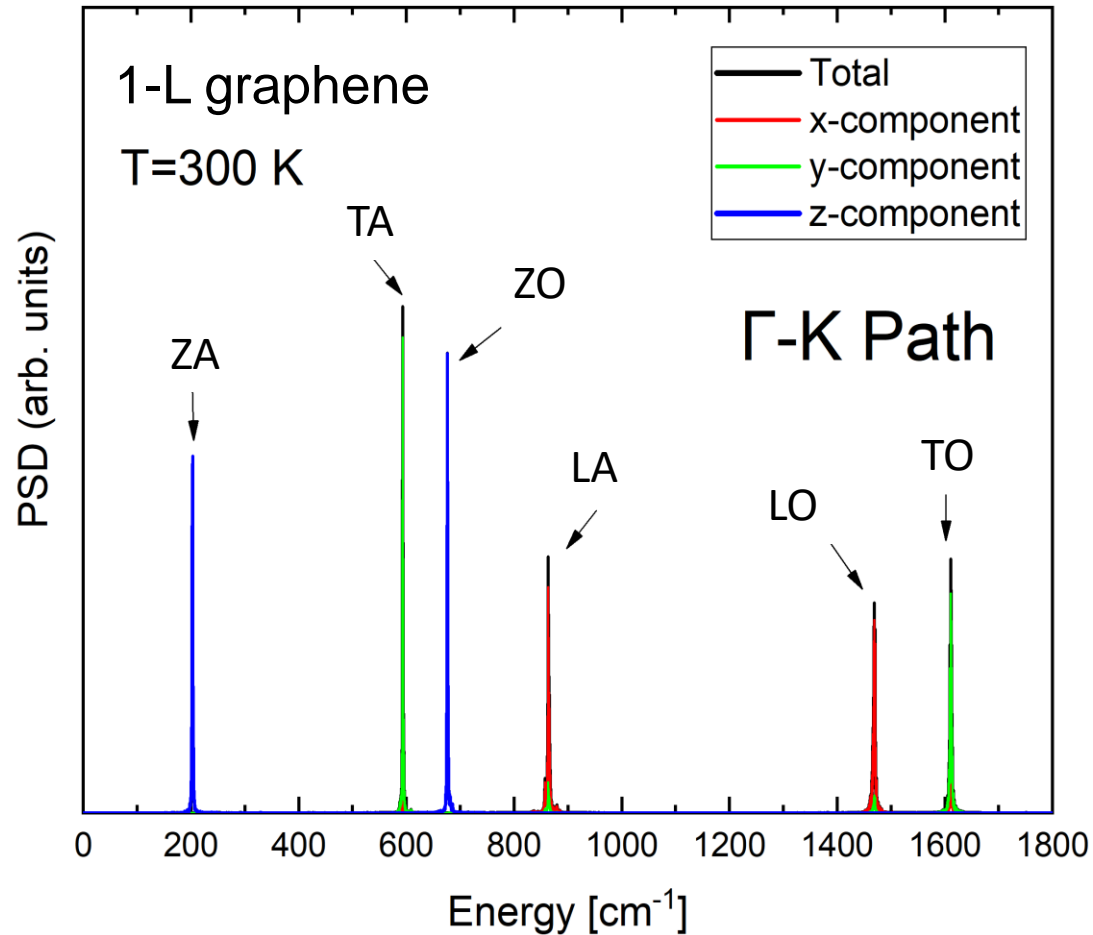
$$Z(\mathbf{k}, \omega) = \sum_j C(\mathbf{k}, j) \frac{\Gamma^2(\mathbf{k}, j)}{[\omega - \omega_R(\mathbf{k}, j)]^2 + \Gamma^2(\mathbf{k}, j)}$$

- The decay rates obtained are only due to ph-ph interactions ( $\Gamma_{ph-ph}$ )
- Applicable to all kinds of systems (non-periodic, amorphous, defects, dislocations, strain, etc.)
- **Inherently includes all orders of anharmonicity + thermal lattice expansion!**

<sup>1</sup>Poulos et al (2024) *Manuscript submitted to Physical Review B*

# The kVACS method

## Example kVACS spectrum

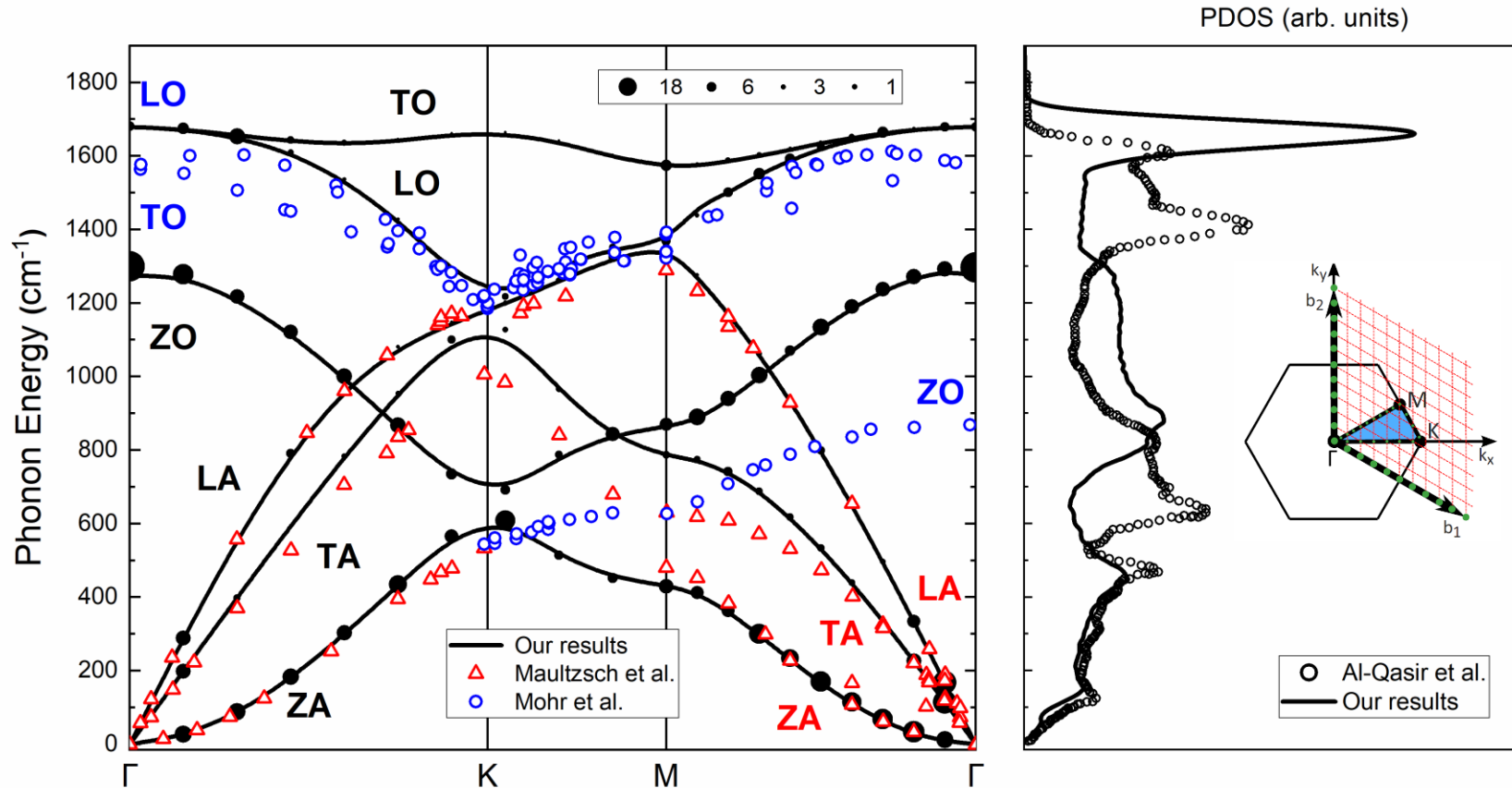


Polarization of  $\Phi(\mathbf{k}, \omega)$  gives the polarization of the phonon peaks!



# Dispersion Curves and density of states

Bulk Graphite @ T = 300K



- Excellent agreement for acoustic branches
- **Z-phonons have larger  $\tau$**

- 40% overestimation of ZO
- 12% overestimation of LO/TO
- $\omega_{LO} < \omega_{TO}$

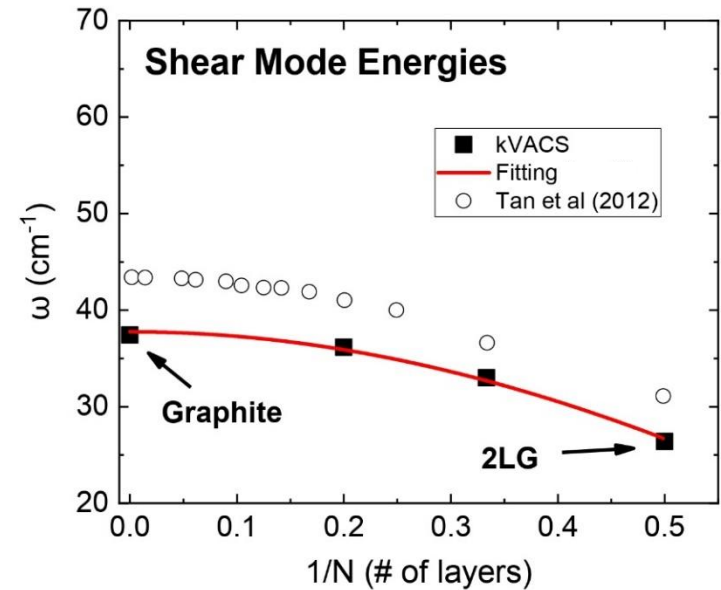
- Unable to capture Kohn anomaly at K and M (no *el-ph*)
- Reflected in PDOS

# Dependence on # of Layers

## Inter-layer optical phonons

$$k_{shear} = 0.96 \times 10^{19} \text{ Nm}^{-2}$$

$$k_{shear}^{exp} = 1.26 \times 10^{19} \text{ Nm}^{-2}$$



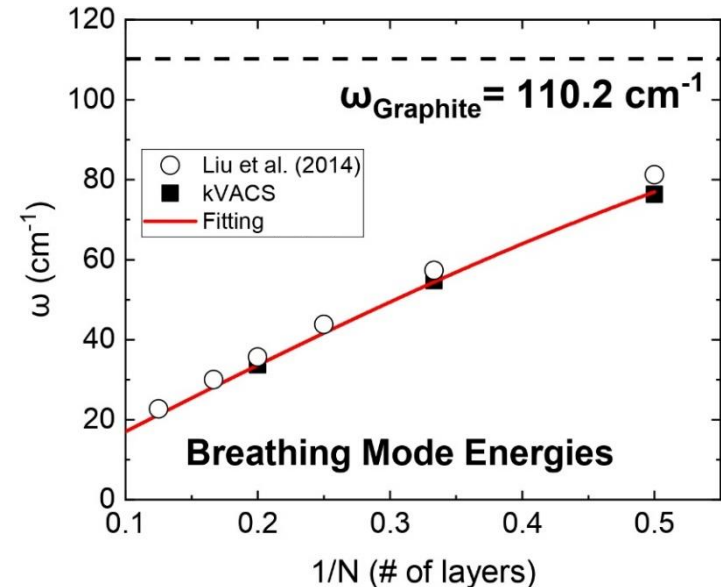
Linear Chain Model:  
3(N-1) Optical Modes

$$\omega_{\nu}^{(i,N)} = \sqrt{\frac{2k_{\nu}}{\mu} \left\{ 1 - \cos \left( \frac{(i-1)\pi}{N} \right) \right\}}$$

(N-1) Longitudinal (LBM)  
(N-1) 2bly degenerate Transverse (Shear)

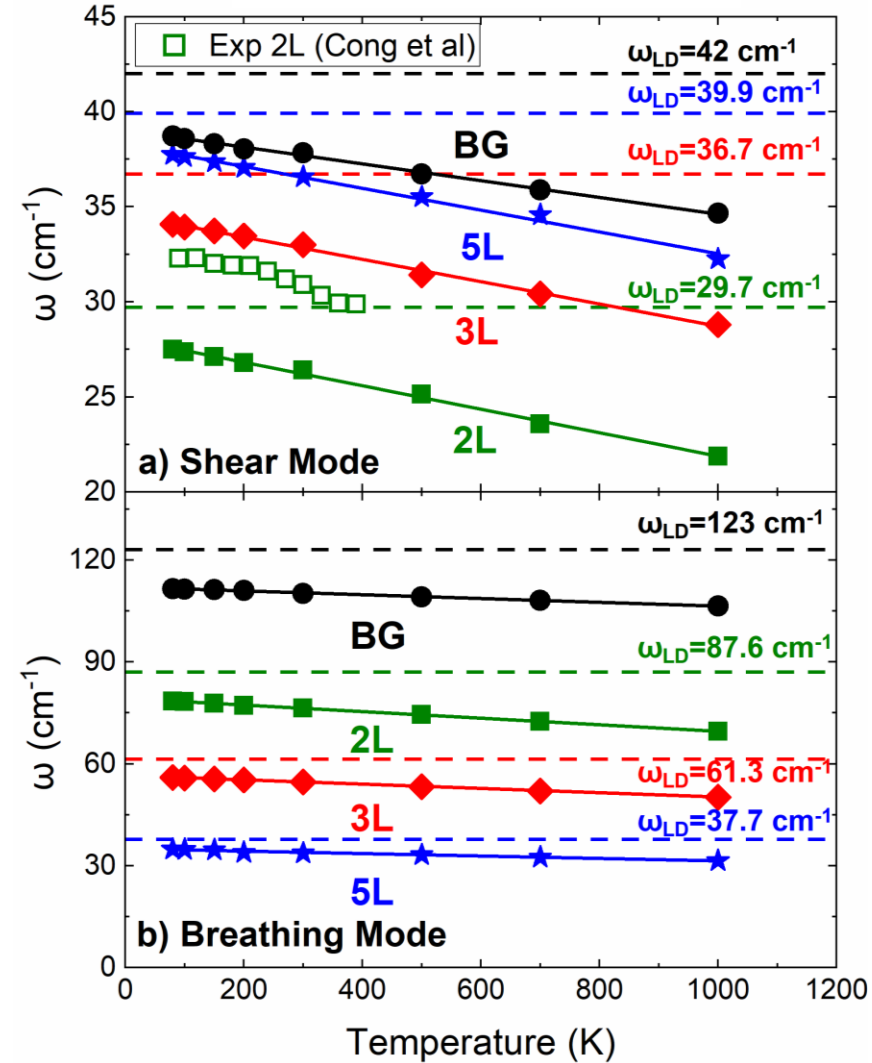
$$k_{LBM} = 7.97 \times 10^{19} \text{ Nm}^{-2}$$

$$k_{LBM}^{exp} = 8.84 \times 10^{19} \text{ Nm}^{-2}$$



# Dependence of energies on temperature

## Inter-layer



N

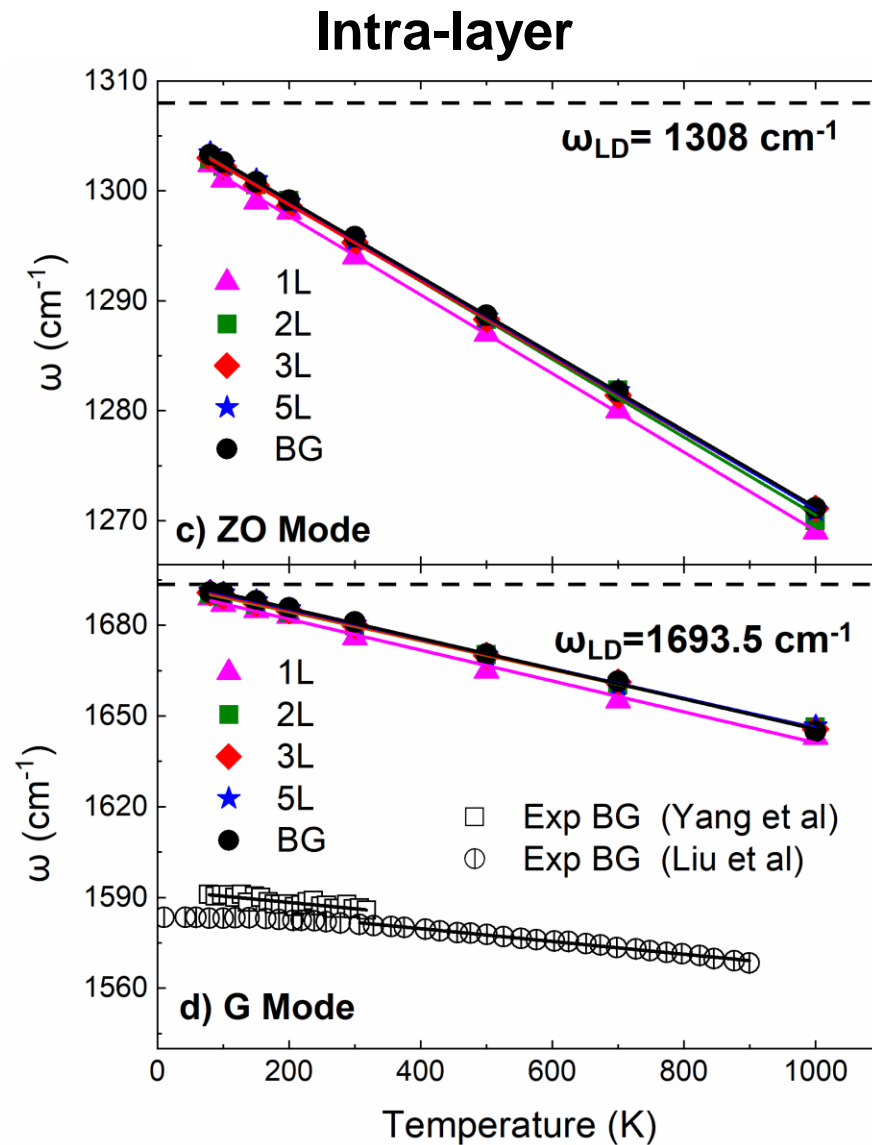


N

# Dependence of energies on temperature

↑ **N** ( $\sim 1-5 \text{ cm}^{-1}$ )

**Practically independent of N**



# Dependence of energies on temperature

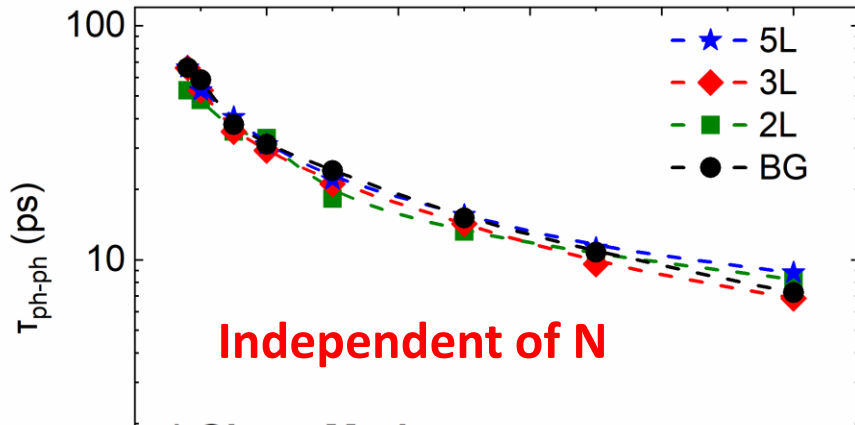
Temperature slope  $\chi(T)$

# of Layers	Inter-layer		Intra-layer	
	Shear	LBM ( $\times 10^{-3} \text{ cm}^{-1} \text{ K}^{-1}$ )	ZO	G
1	–	–	-36	-51
2	-6.2	-9.7	-35	-47
3	-5.9	-6.3	-34	-48
5	-5.7	-3.6	-35	-49
BG	-4.4	-5.6	-35	-50
Exper.	–	–	–	-21

- One order of magnitude lower
- # of layers affects slope of interlayer, but not for intra-layer

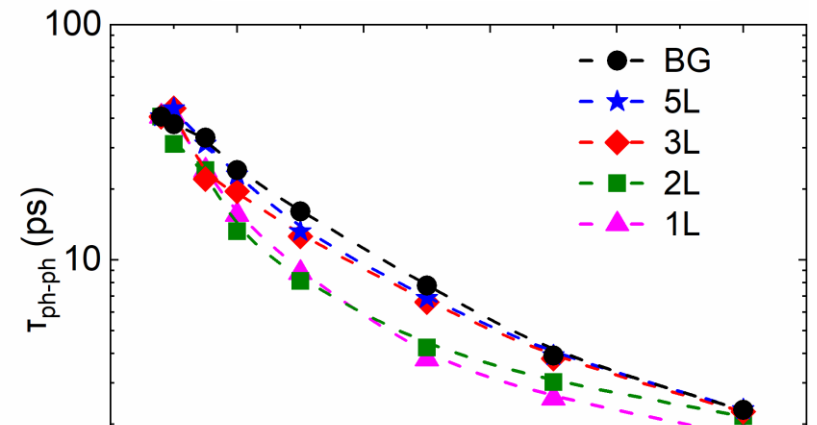
# Dependence of lifetimes on temperature

## Inter-layer

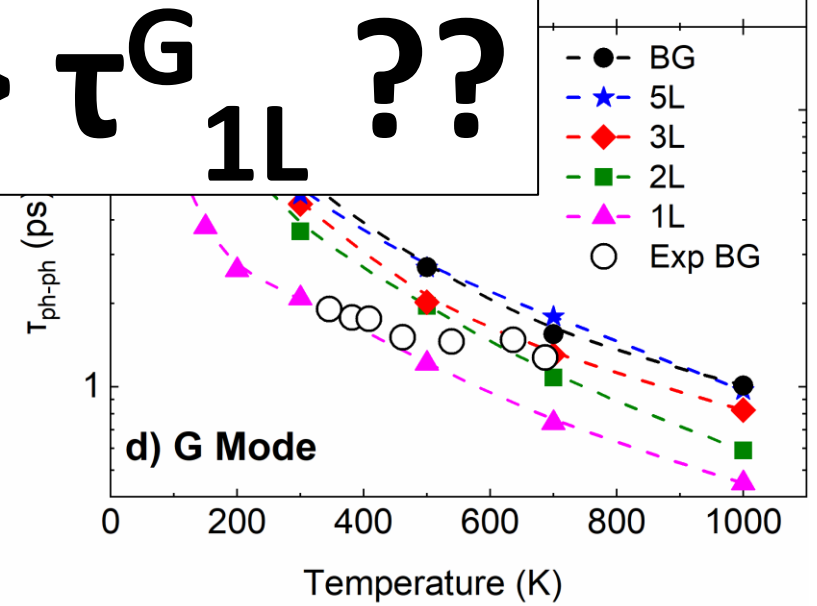
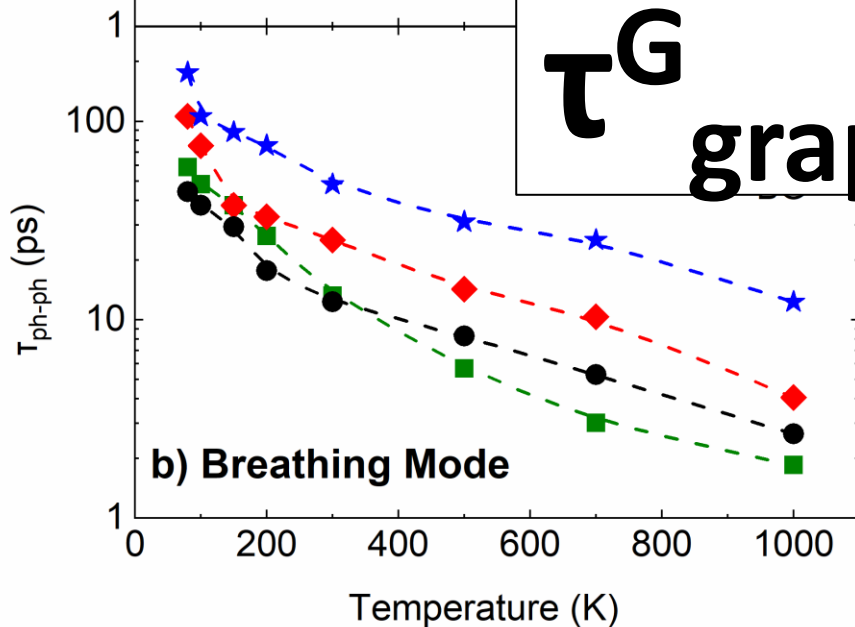


a) Shear Mode

## Intra-layer

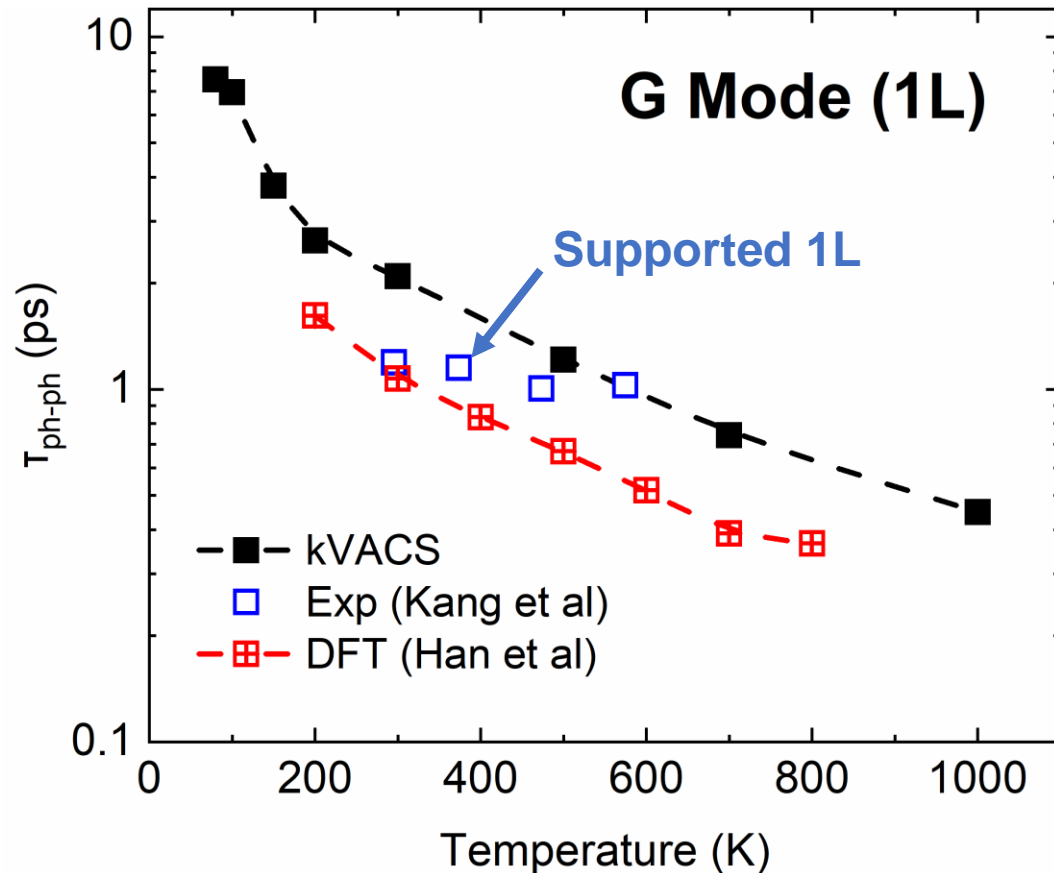


$\tau^G_{\text{graphite}} > \tau^G_{1L} ??$



# Dependence of lifetimes on temperature

Single-layer graphene,  $E_{2g}$  phonon (G-mode)

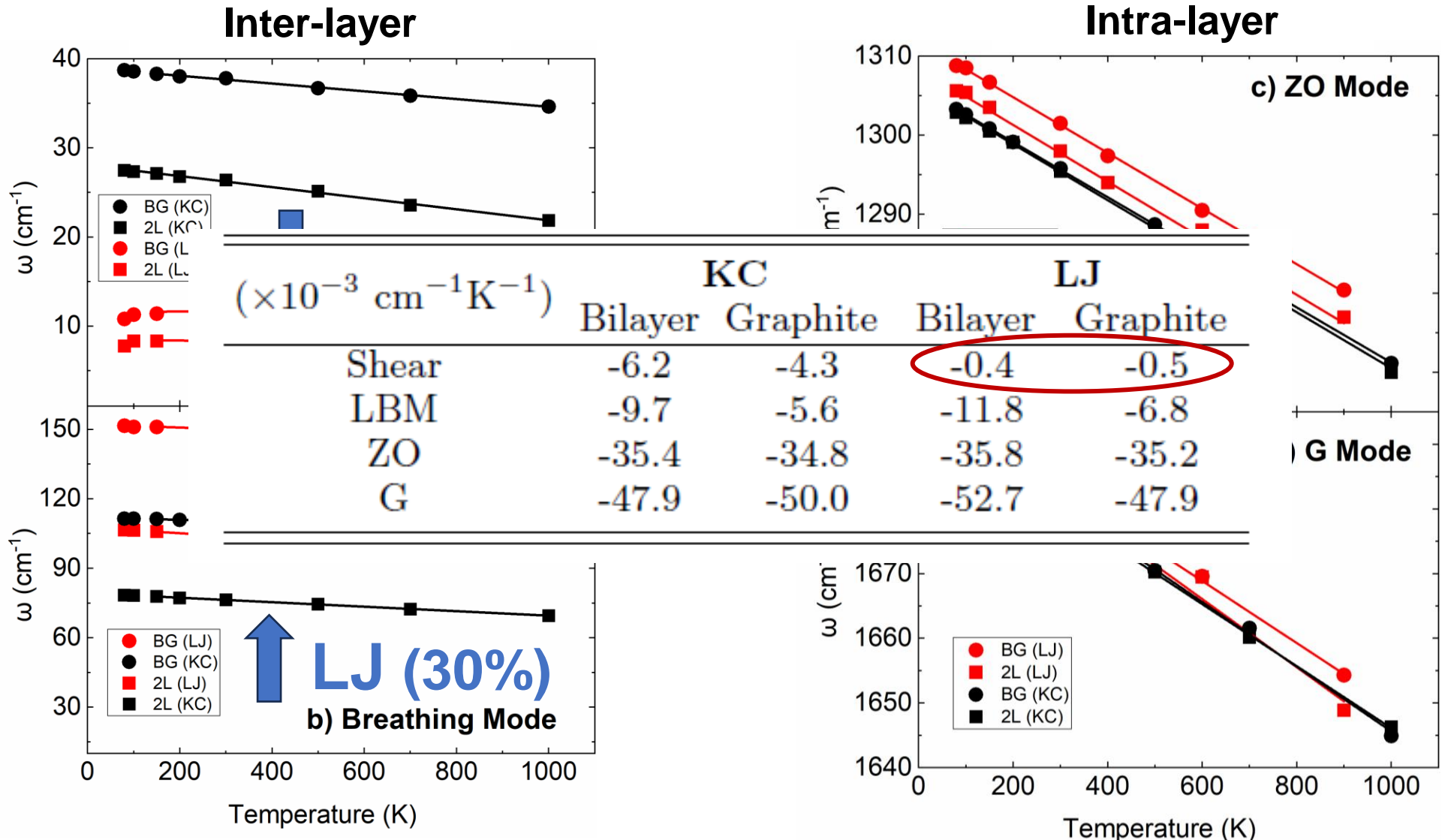


$$\gamma_G = \gamma_G^{ph-ph} + \gamma_G^{el-ph}$$

- $\gamma^{el-ph}$  dominant in graphene
- **Conventional Raman captures both mechanisms!**
- Only Time-Resolved Raman captures purely  $\gamma^{ph-ph}$  (challenging experiments)
- **No experimental data on multi-layered!**

# Dependence of energies on temperature

Different interlayer potential (Lennard Jones)

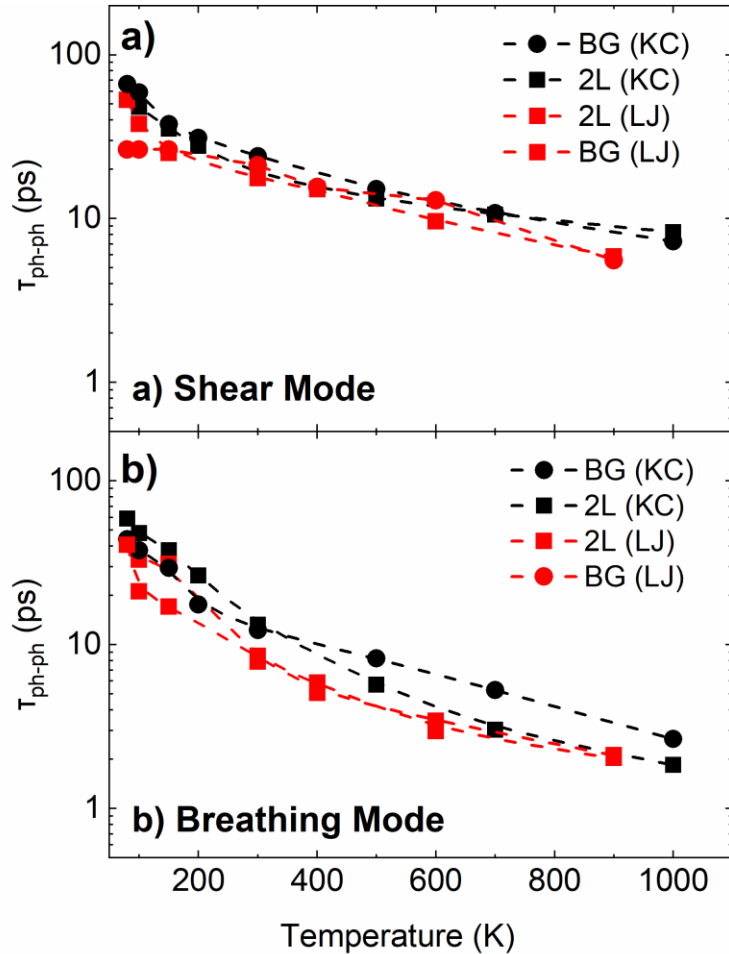




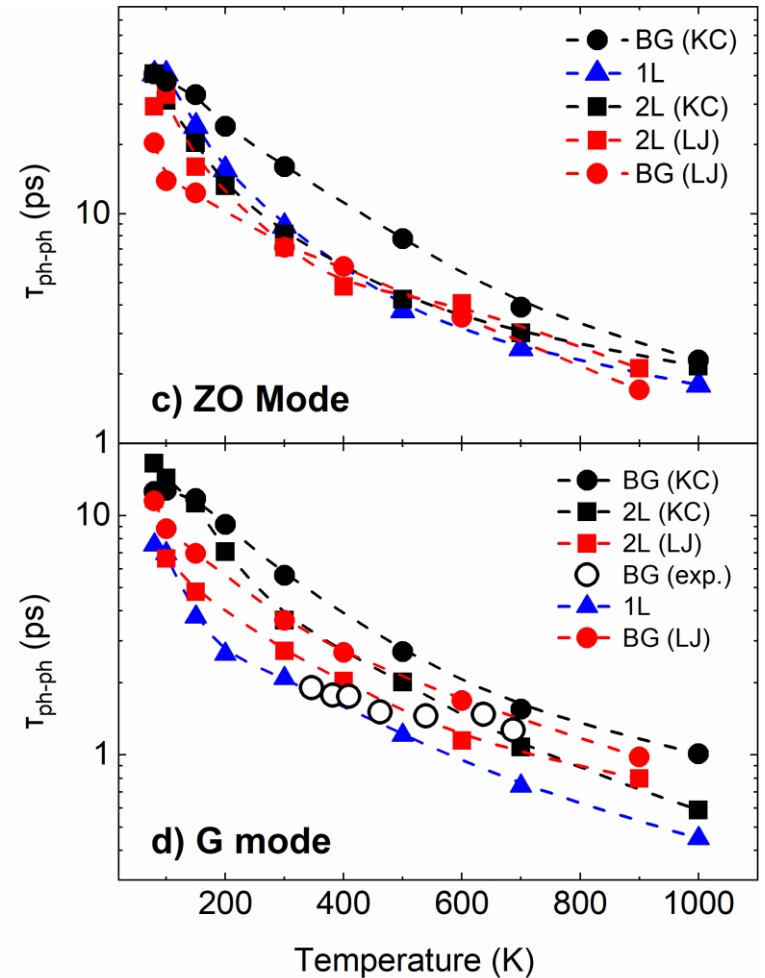
# Dependence of lifetimes on temperature

Different interlayer potential (Lennard Jones)

Inter-layer

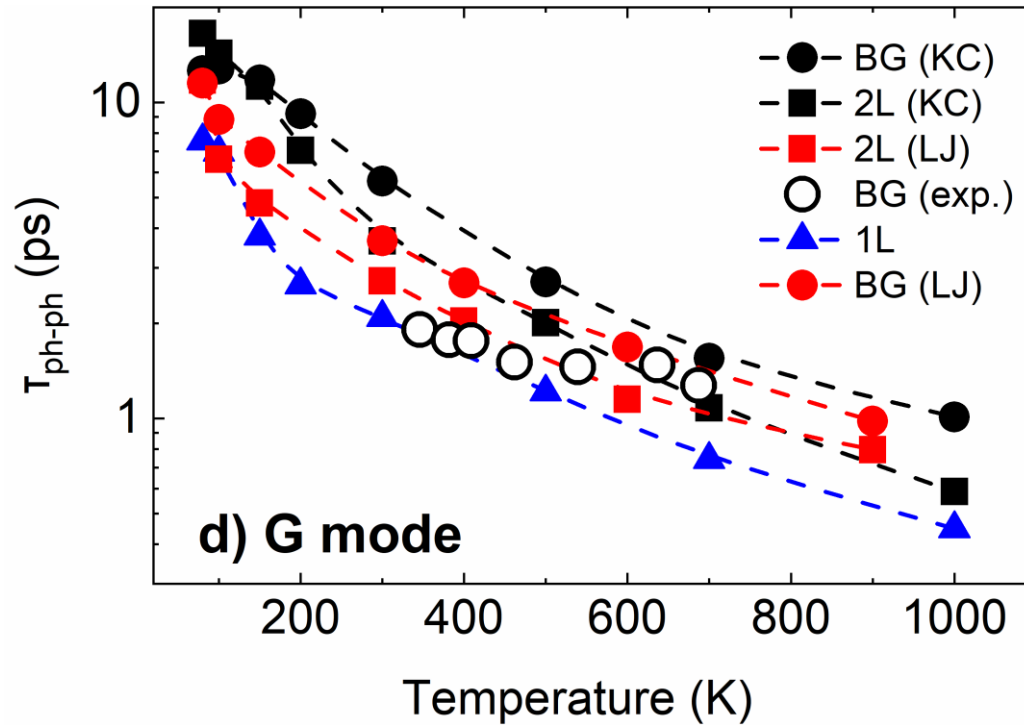


Intra-layer



# Dependence of lifetimes on temperature

Different interlayer potential (Lennard Jones)

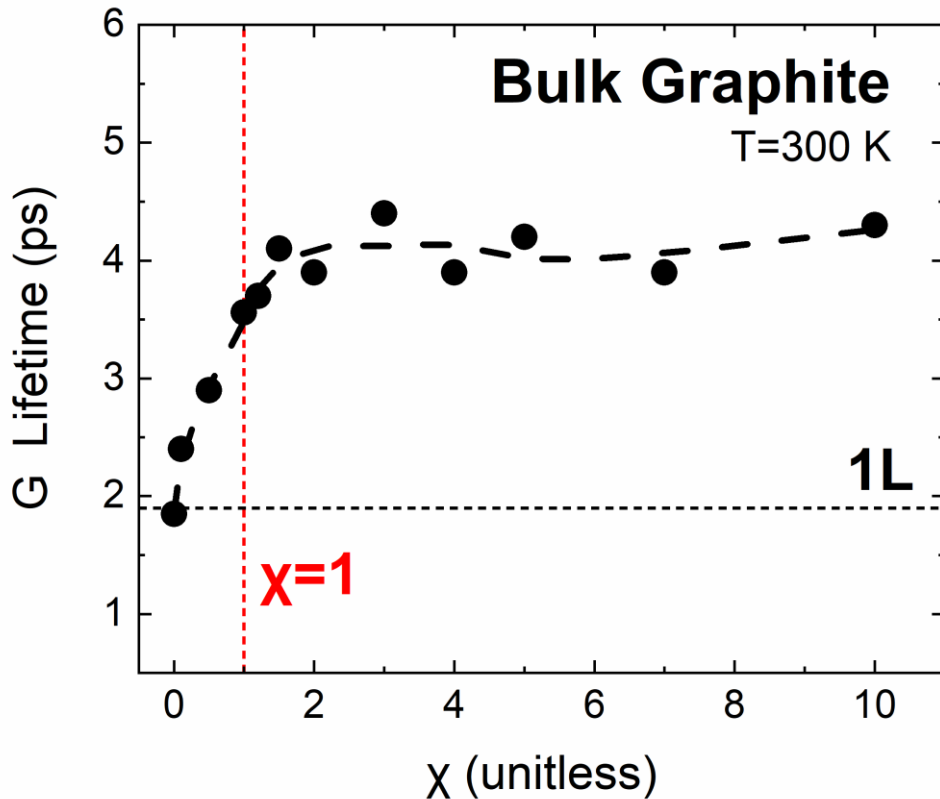


$$\tau_{\text{graphite}}^{\text{G}} > \tau_{1\text{L}}^{\text{G}}$$

# Effect of Interlayer Coupling Strength

## Effect of interlayer coupling strength (Lennard-Jones)

$$V(x) = \chi \cdot 4\varepsilon \left( \frac{\sigma}{x^6} - \frac{\sigma}{x^{12}} \right)$$



- $\tau^{\text{ph-ph}}$  increases with increasing the coupling strength
- For  $\chi \rightarrow 0$  it converges to the 1L value  
 $\tau^{\text{BG}} = 3.5 \text{ ps}$   
 $\tau^{1\text{L}} = 1.9 \text{ ps}$
- For  $\chi \geq 2$  it reaches a plateau (strong coupling limit)

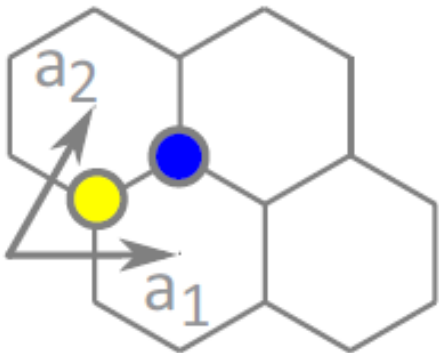
# Conclusions

- T-dependence of interlayer C and LBM, as well as intralayer ZO and G phonons for multi-layered graphene by classical MD
- Phonon lifetimes: Quantum-mechanical quantities calculated with classical physics! (Important parameters for transport phenomena)
- Inter- and intra-layer phonons have different behaviour: inter → strong N-dependence, while intra → N-independent
- Kolmogorov-Crespi potential superior in describing interlayer properties
- The dependence of  $\tau_G$  on #N is independent of the choice of the interlayer interaction:  $\tau_{\text{graphene}} < \tau_{\text{graphite}}$  !
- Strengthening the interlayer interaction **increases  $\tau$** !
- Experimental confirmation is challenging → we invite the experimental community to be involved!

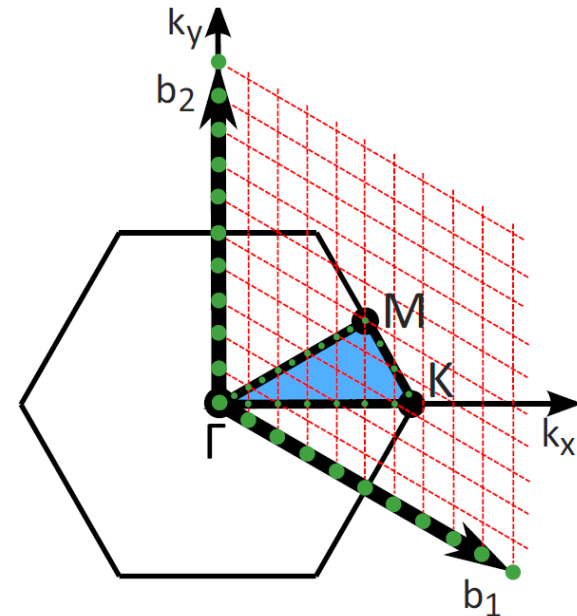
**Thank you!**

# Molecular Dynamics Modelling

- System Size: 10 x 10 nm (40 x 40 unit cells)
- Brillouin Zone Path:  $\Gamma \rightarrow K \rightarrow M \rightarrow \Gamma$
- Interatomic Potentials: **Tersoff-2010** for intra-layer, **Kolmogorov-Crespi (KC)** for inter-layer interactions
- Temperature: from 80 K to 1000 K
- Timestep: **0.5 fs**, Total Simulation Time: **328 ps**
- “Thermal averaging” of  $\Phi(\mathbf{k}, \omega)$  over 10 realizations at each T



- $\Gamma \rightarrow K$ : Zig-zag
- $K \rightarrow M$ : Armchair
- $\Gamma \rightarrow M$ : C-C Bond

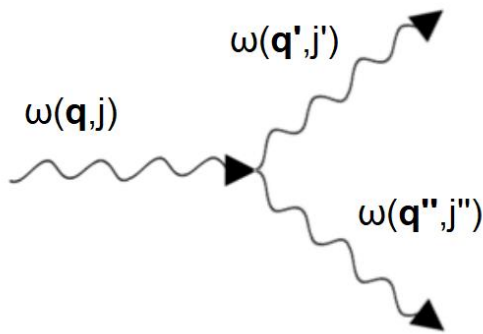


# Anharmonicity: ph-ph interactions

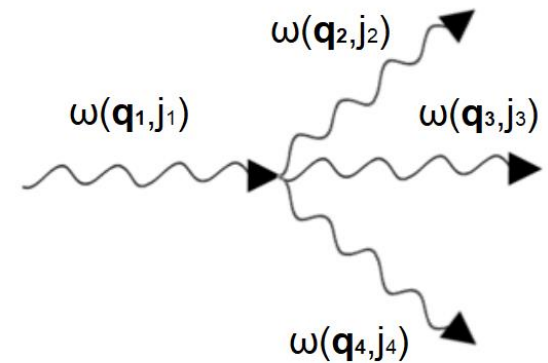
$$U(\bar{\mathbf{R}}) = U_0(\mathbf{R}_{\text{equil}}) + \frac{1}{2!} \sum_{i,j} \frac{\partial^2 U}{\partial \mathbf{u}_i \partial \mathbf{u}_j} \mathbf{u}_i \mathbf{u}_j + \frac{1}{3!} \sum_{i,j,k} \frac{\partial^3 U}{\partial \mathbf{u}_i \partial \mathbf{u}_j \partial \mathbf{u}_k} \mathbf{u}_i \mathbf{u}_j \mathbf{u}_k + \dots$$

**Harmonic Approximation**

Phonon Interactions: 3<sup>rd</sup>, 4<sup>th</sup> and higher order anharmonic terms



**Anharmonic Decay**



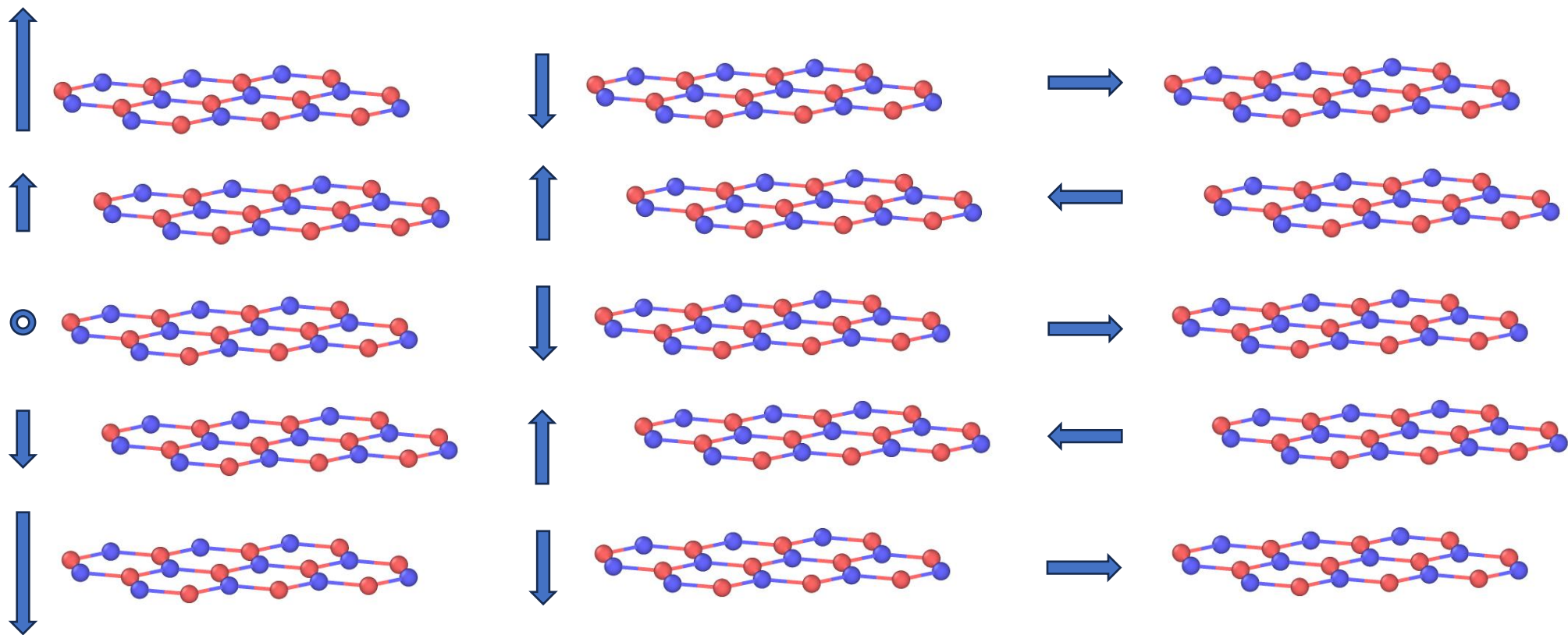
Perturbation theory: Phonon quasi-particle “dressed” in a virtual phonon cloud

$$\omega(\mathbf{q}, j) \rightarrow \omega(\mathbf{q}, j) + \Delta(\mathbf{q}, j) + i\Gamma(\mathbf{q}, j)$$

**Frequency Shift**

**Decay Rate**

# Interlayer Phonon Eigenvectors



**'True' LBM**

**Graphite LBM**

**'True' Shear Mode**



# Phonon Linewidth Fitting (1L vs 2L)

