Thermal Transport in Two-dimensional Silicon Calls for Accurate Force Field

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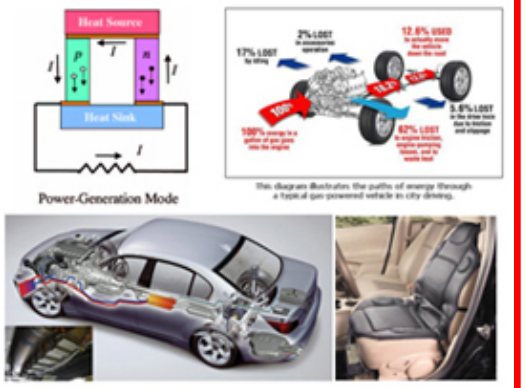
Critical Role of Thermal Transport in Novel Energy Application

Thermoelectrics
Energy Conversion Cars Efficiency

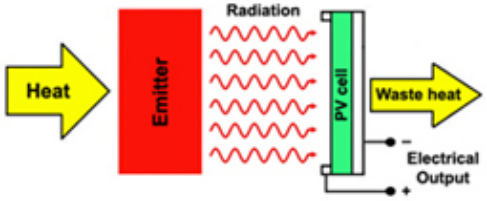


Thermal Insulators
Building Energy Efficiency

Electronics
Efficient Laptops Supercomputers

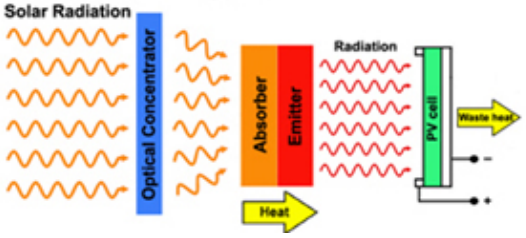
Optoelectronics
Laser Diodes Reliability and Failure

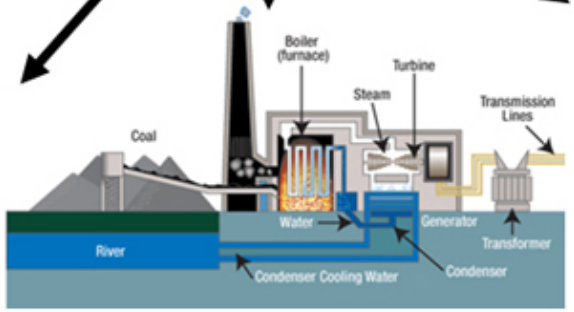
Thermal Photovoltaics
Energy Conversion



Heat

Solar Thermal Photovoltaics
Energy Conversion



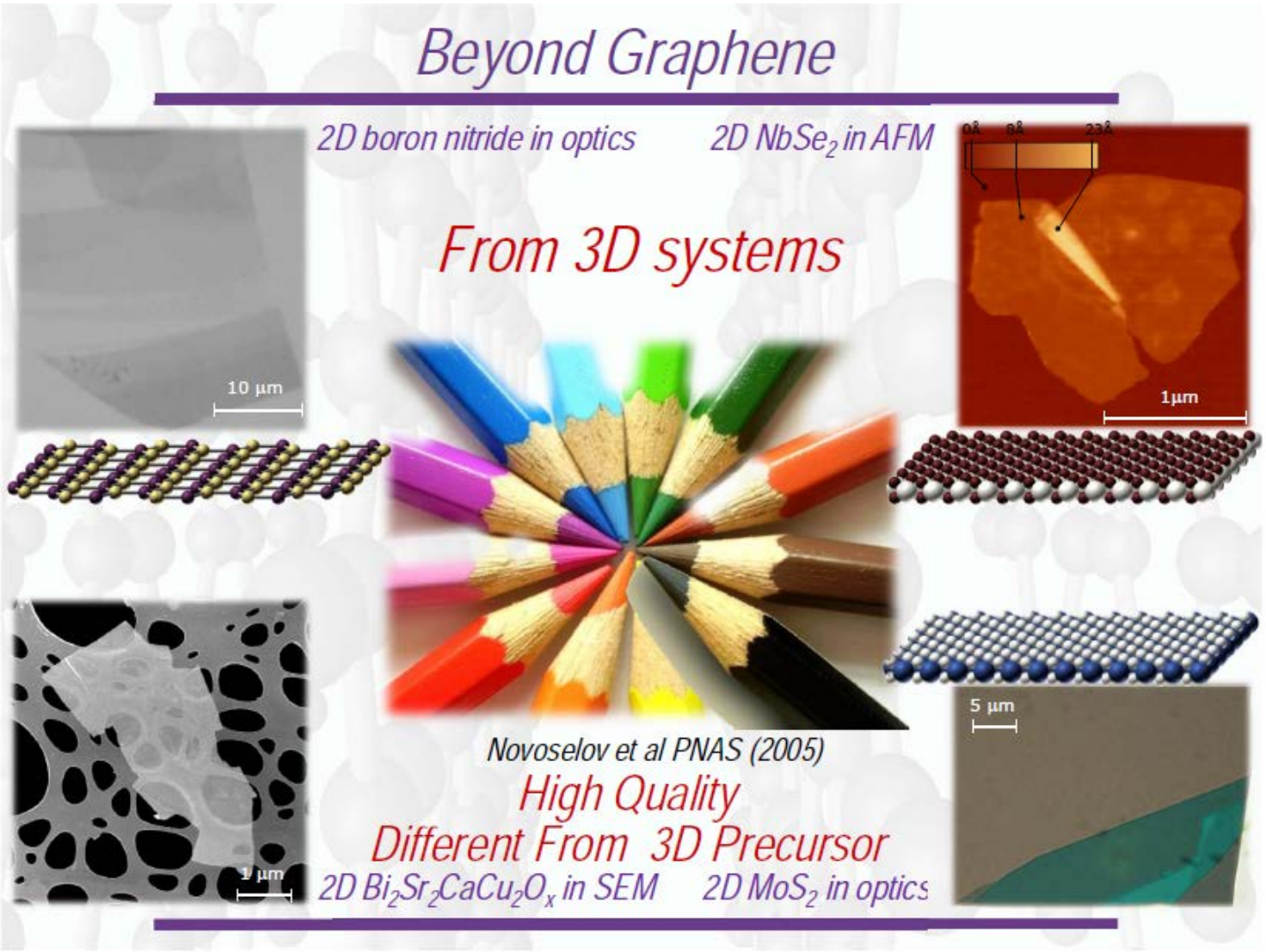


Waste Heat Capture Engineered Thermal Fluids

Coal and Nuclear Power Plants

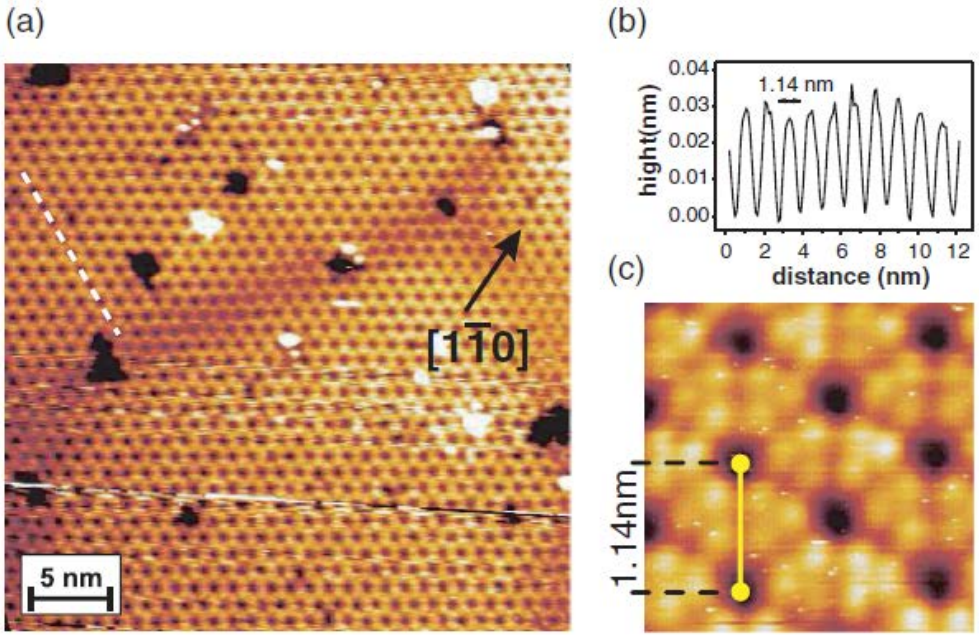
Aero Astro
Jet Engines Satellites

Introduction: 2-D Material

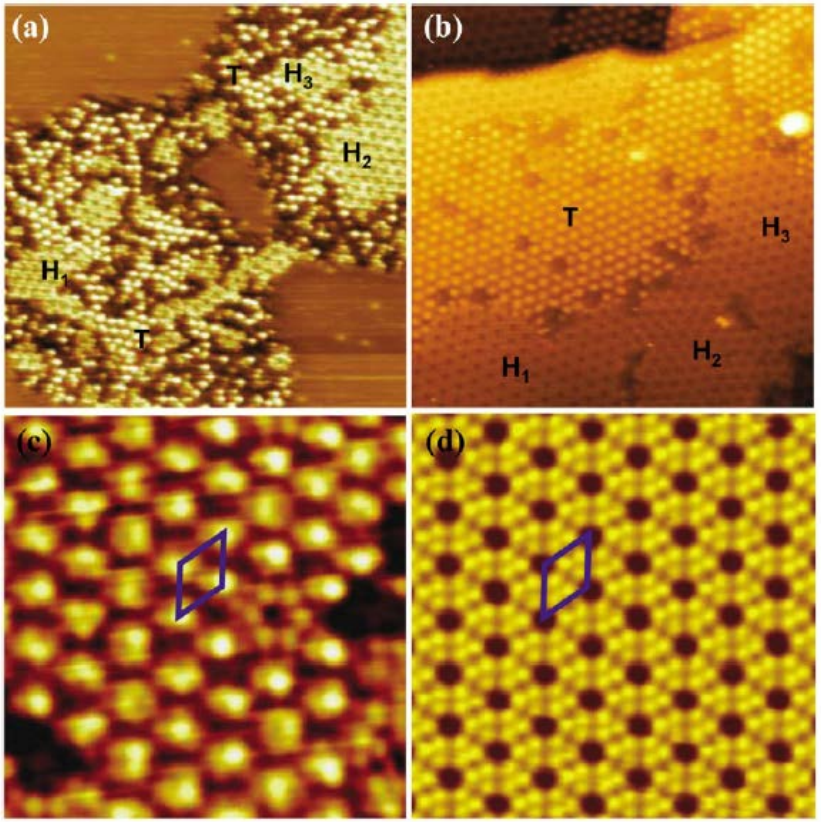


Experimental Evidence of Two-dimensional Silicon

Silicene on Ag substrate

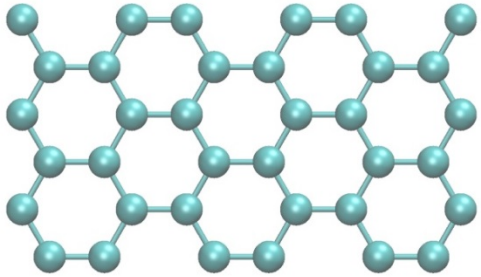


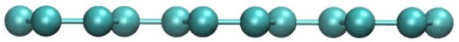
P. Vogt, et al, *Phys. Rev. Lett.* (2012)



B. Feng, et al, *Nano Lett.* (2012)

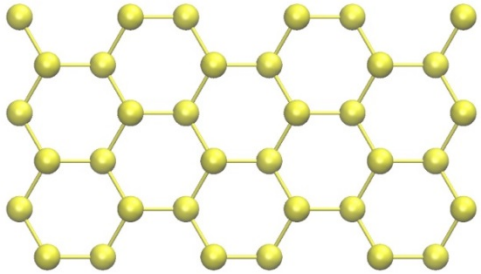
Silicene: Analog to Graphene





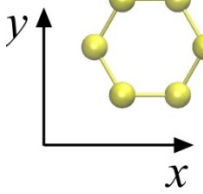
graphene

h ~ 0 Å



silicene

h ~ 0.42 Å



σ **High** Science **306**, 666 (2004).

S **Low** Science **328**, 213 (2010).

κ **High** Nano Lett. **8**, 902 (2008).

$$ZT = \frac{S^2 \sigma T}{\kappa}$$

σ **High** Nat. Nanotechnol. **3**, 206 (2008).

S **High** Phys. Rev. B **88**, 115404 (2013).

κ **Low** Phys. Rev. B **89**, 054310 (2014).

The Periodic Table of Elements

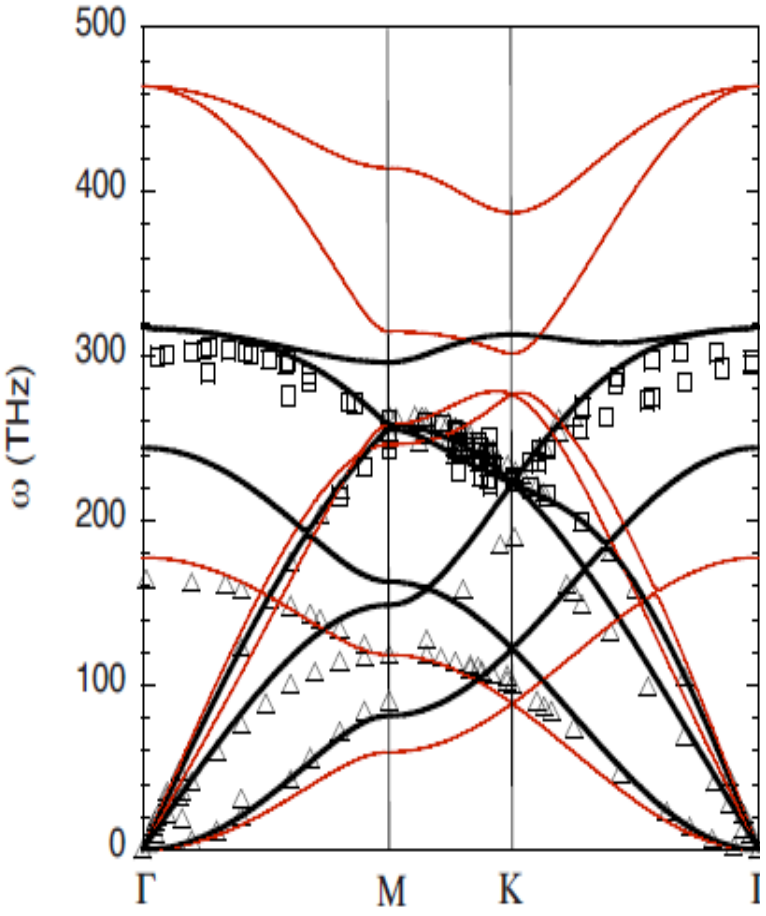
1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr

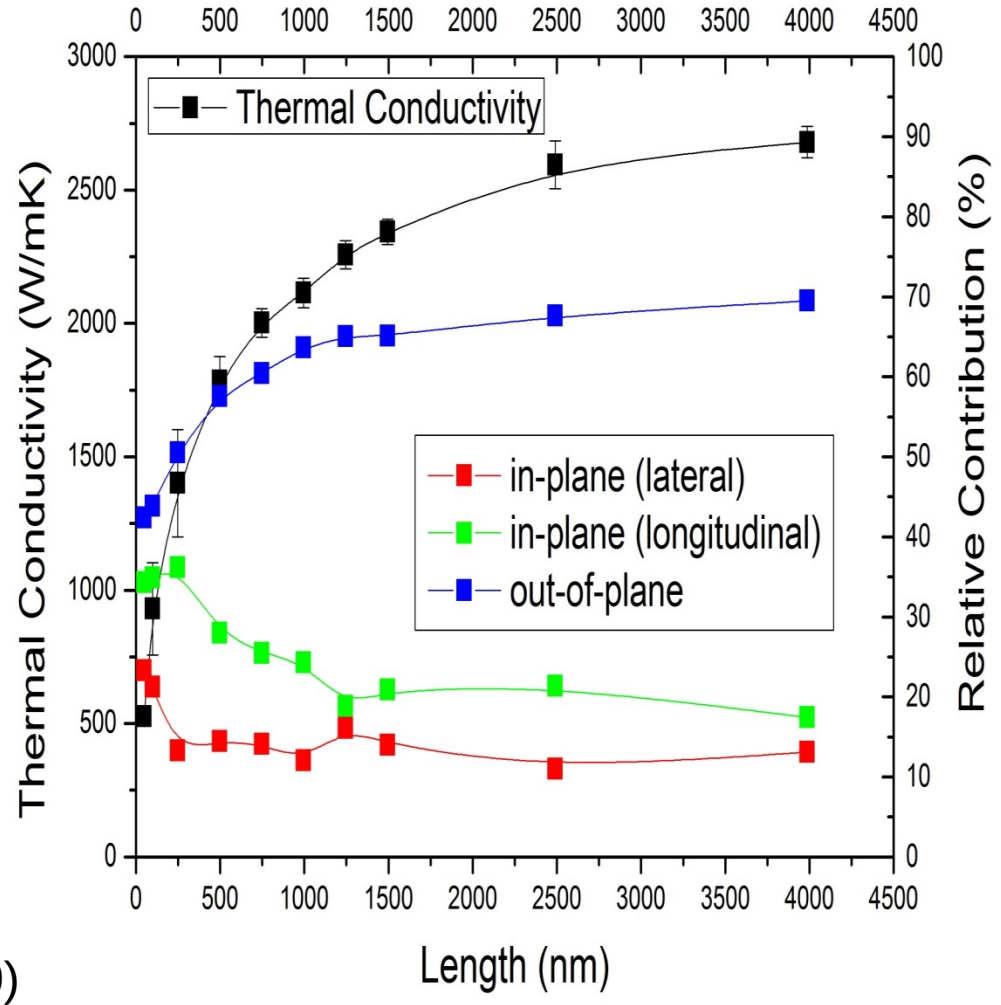
Silicene---Promising thermoelectrics !

Outline

- **Thermal conductivity of free standing silicene**
  - **Classical molecular dynamics simulation**
  - **First-principle based ALD/BTE study**
- **Thermal conductivity of functionalized silicene**
- **Thermal conductivity of supported silicene**

New Optimized Tersoff Potential for Graphene



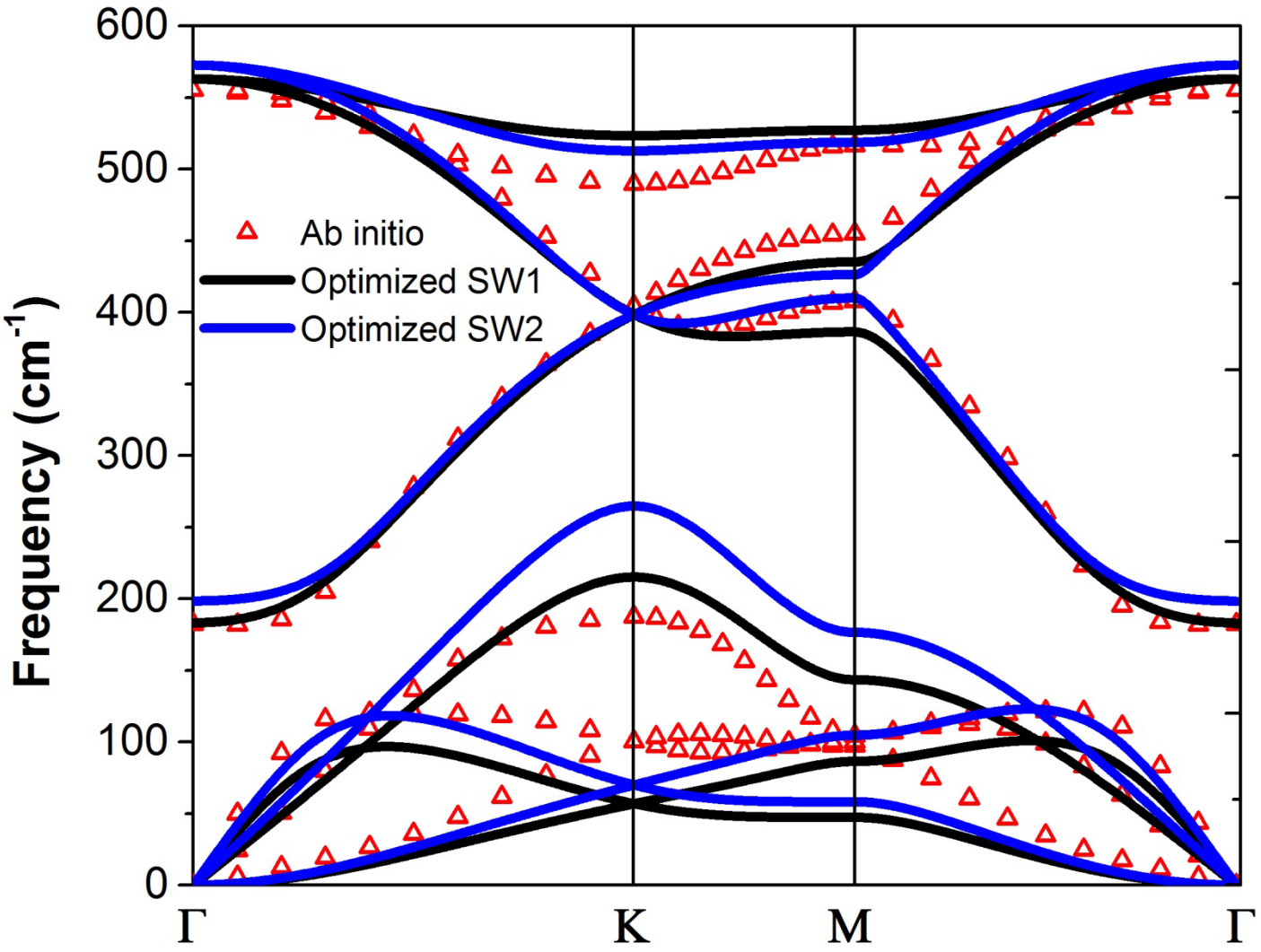


L. Lindsay, et al. *Phys. Rev. B* (2010)

Failure of Existing Potentials for Silicene

Potentials	Bond Length (Å)	Bond Angle (°)	Buckling (Å)
Tersoff (PRB1989, 5566)	2.304	120.00	0.00
Tersoff (PRB 1988, 9902)	2.305	120.00	0.00
Original SW (PRB 1985)	2.352	109.47	0.78
SW (PRB 2012 (GGA))	2.363	109.47	0.79
SW (PRB 2012 (LDA))	2.332	109.47	0.78
EDIP (PRB 1998)	2.351	110.88	0.17
Reactive FF (JPCC 2013)	2.301	111.24	0.70
ab initio	2.242	116.46	0.42
Bulk Si	**2.351**	**109.47**	**0.78**

Generating New Potential: Fitting Dispersion Curve



New Potential: Reproduce Silicene Structure

Potentials	Bond Length (Å)	Bond Angle (°)	Buckling (Å)
Tersoff (PRB1989, 5566)	2.304	120.00	0.00
Tersoff (PRB 1988, 9902)	2.305	120.00	0.00
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Reactive FF (JPCC 2013)	2.301	111.24	0.70
ab initio	2.242	116.46	0.42
Optimized SW 1	**2.242**	**116.46**	**0.42**
Optimized SW 2	**2.242**	**116.46**	**0.42**
Bulk Si	**2.351**	**109.47**	**0.78**

Simulation Methods

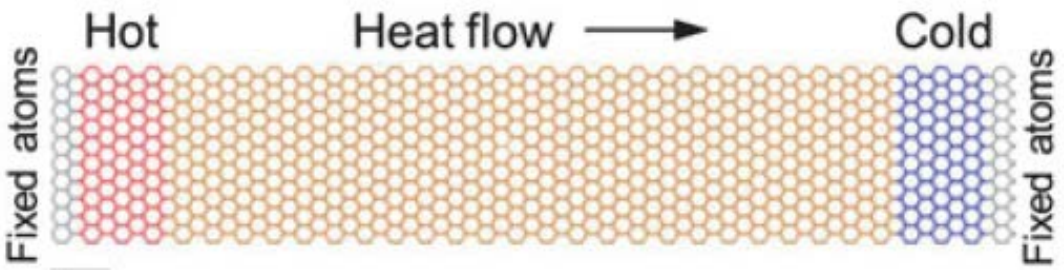
Two approaches:

(1) Equilibrium Molecular Dynamics (EMD)

$$\kappa_{MD} = \frac{V}{3k_B T^2}\int \left\langle \vec{J}(0)\cdot\vec{J}(t)\right\rangle dt \qquad \vec{J} = \frac{1}{V}\left[\sum_i E_i\vec{\upsilon}_i - \sum_i \vec{\vec{S}}_i\vec{\upsilon}_i\right]$$

(2) Non-Equilibrium Molecular Dynamics (NEMD)

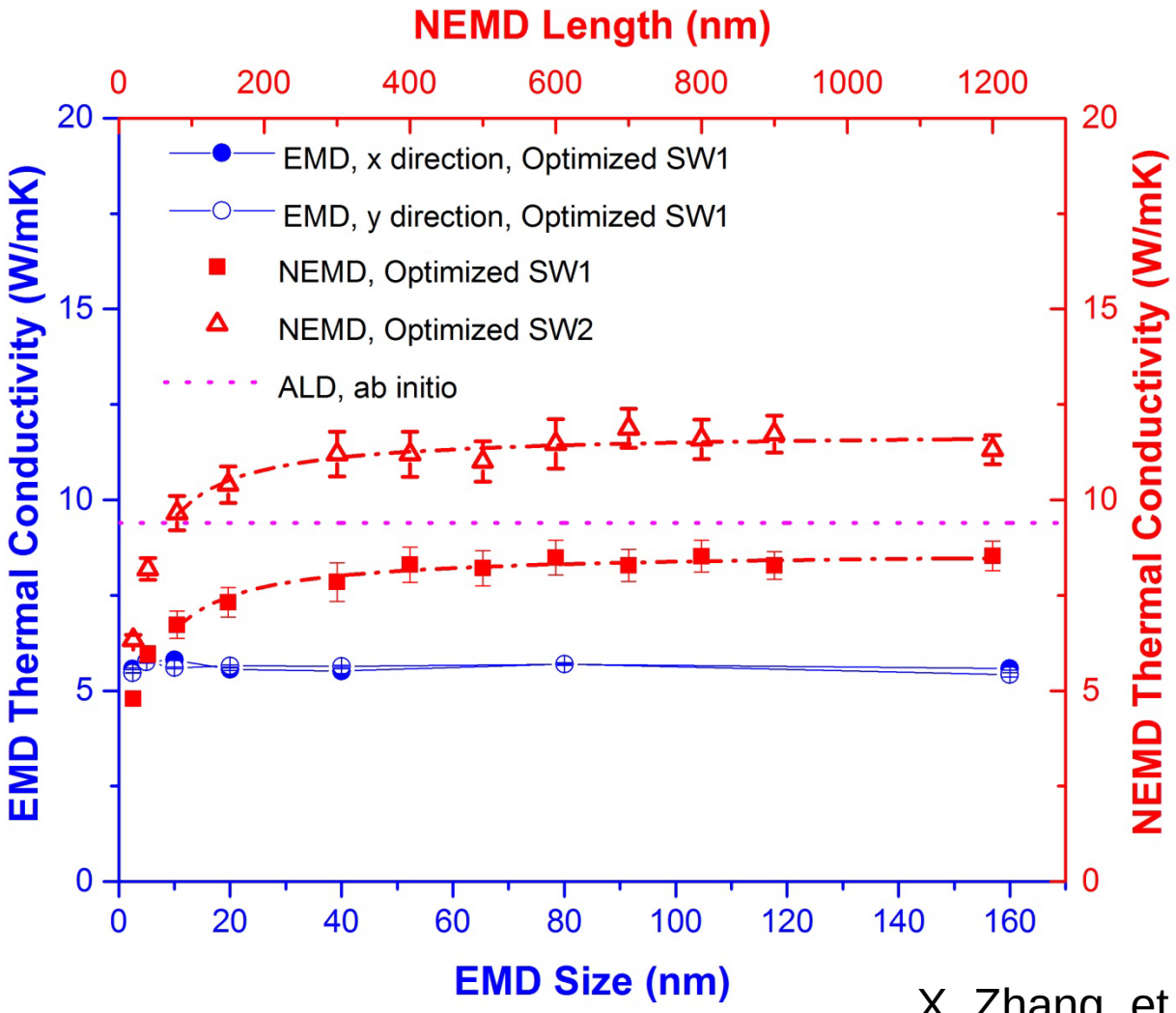
$$\kappa_{NEMD} = -\frac{J_L}{\partial T/\partial y}$$



Quantum correction:

$$T_{MD} = \frac{1}{k_B}\int_0^{\nu_{\max}} D(\nu)\left[\frac{1}{\exp(h\nu/k_B T_{qc})-1}+\frac{1}{2}\right]h\nu d\nu \qquad \kappa_{qc} = \kappa_{MD}\frac{\partial T_{MD}}{\partial T_{qc}}$$

Thermal Conductivity of Silicene



$$\frac{1}{\kappa_{qc}} = \frac{1}{\kappa_{\infty}}\left(\frac{l}{L_y}+1\right)$$

Phonon mean free path

$l \sim 20$ nm

Bulk Si:

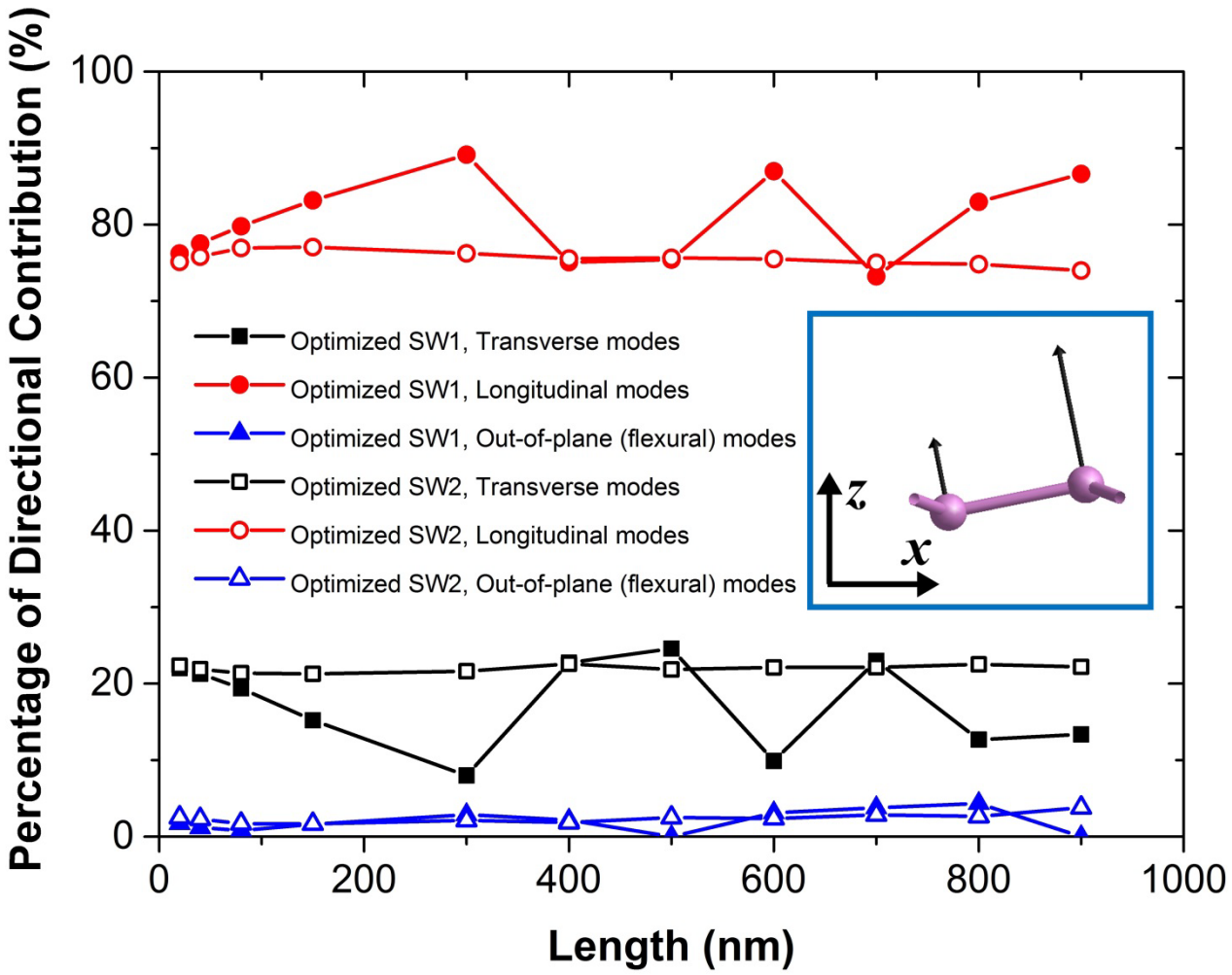
~ 200 nm – 1 µm

Graphene:

~ 600 nm – > µm

X. Zhang, et al. *Phys. Rev. B* (2014)

Relative Directional Contribution to Overall Phonon Transport

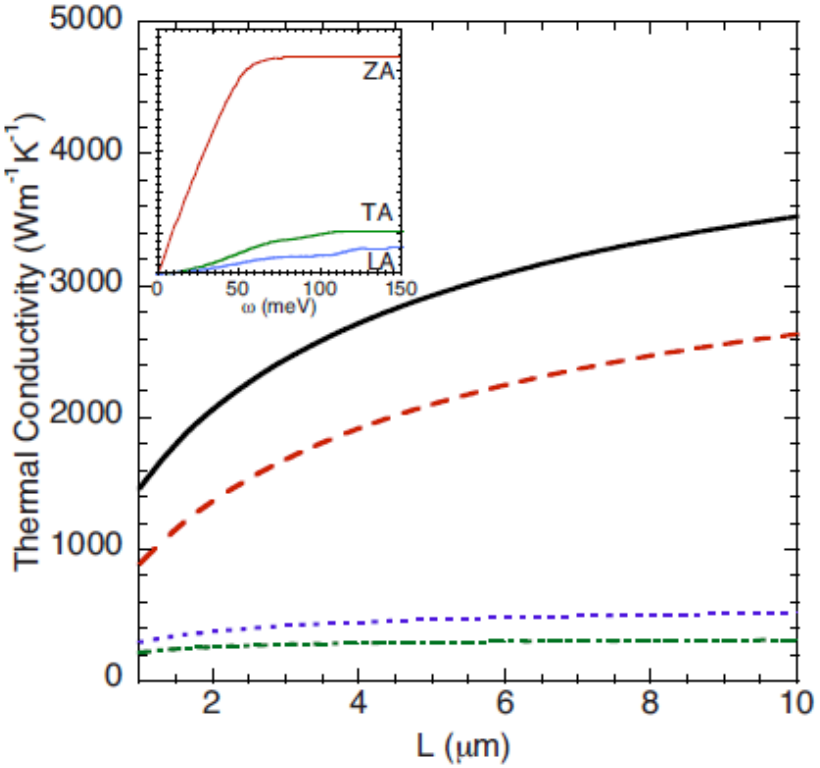


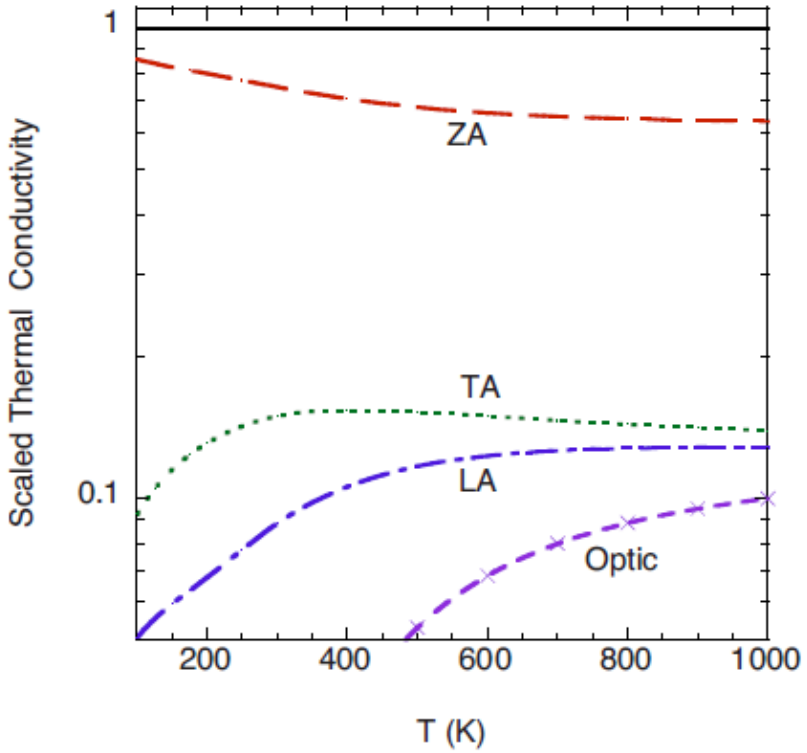
- Vibrations in longitudinal direction (in-plane modes) contribute almost 80% of total heat conduction, while flexural out-of-plane (ZA) modes has minor contribution.
- ZA modes are strongly coupled with other modes.

M. Hu, et al. *Phys. Rev. B* (2013); *J. Appl. Phys.* (2013)

Opposing to Graphene

Due to symmetry constrains, ZA mode in graphene can hardly scattering with LA and TA phonons and thus results in a long relaxation time.





L. Lindsay, et al. *Phys. Rev. B* (2010)

Outline

- Thermal conductivity of free standing silicene
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- Thermal conductivity of supported silicene

Ab initio Based ALD/BTE

Single mode relaxation time model for Boltzmann Transport Equation (BTE)

$$\kappa = \sum_{p} c_p \upsilon_{g,p}^2 \tau_p$$

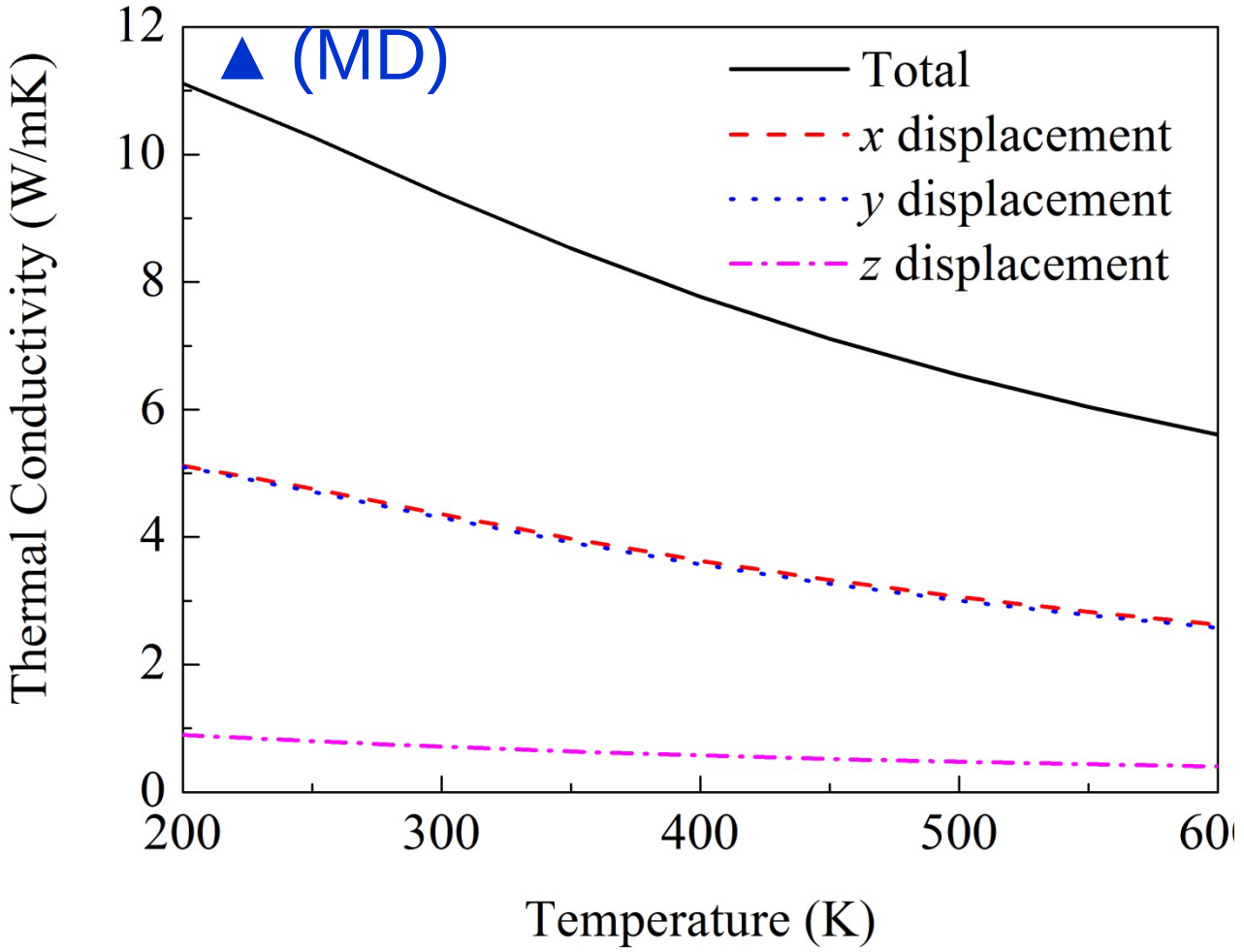
- The group velocities of phonons are calculated using a central difference method
- phonon relaxation time are obtained using anharmonic lattice dynamics (ALD)
- The ALD method calculates the scattering rates of all the three-phonon processes from the anharmonic force constants, which are obtained from *ab initio* calculation

Conductivity from ALD/BTE

Mode specific thermal conductivity

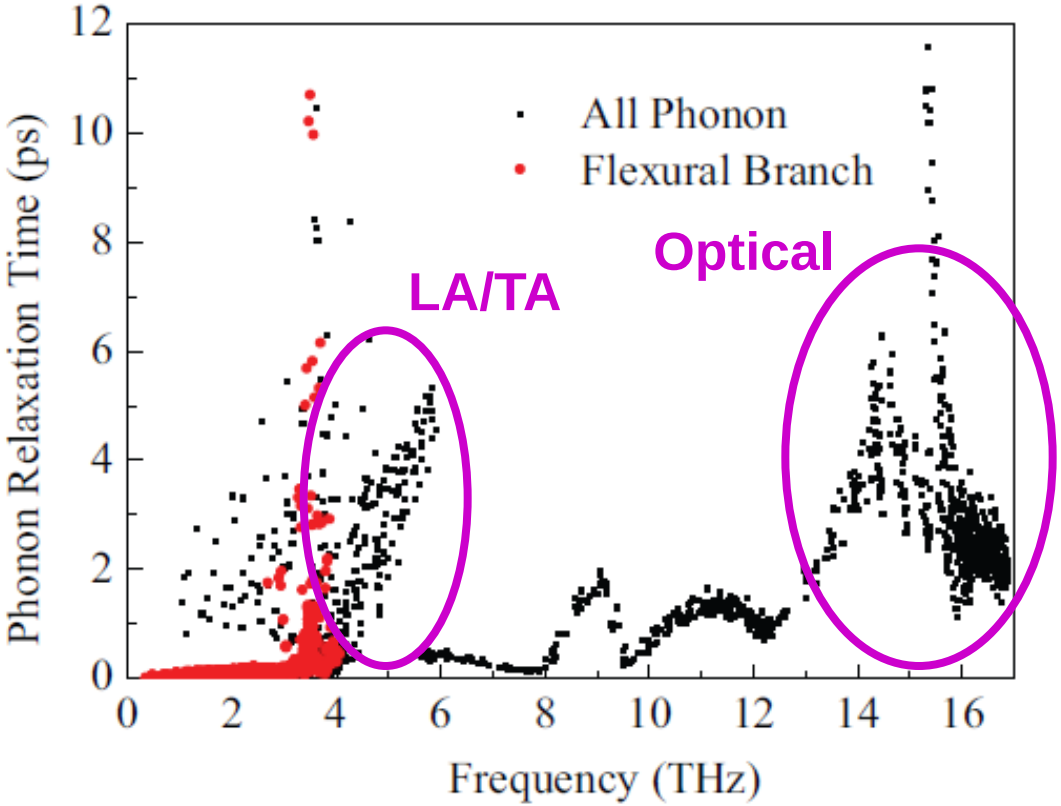
$$k^{\alpha} = \sum_{\kappa,\nu,b} (e_{\kappa\nu}^{b\alpha})^2 c_p u_g^2 \tau$$

vibrational component along *z* (out-of-plane) direction contributes less than **10%** of the thermal conductivity, while the in-plane vibrational components contribute more than **90%**.



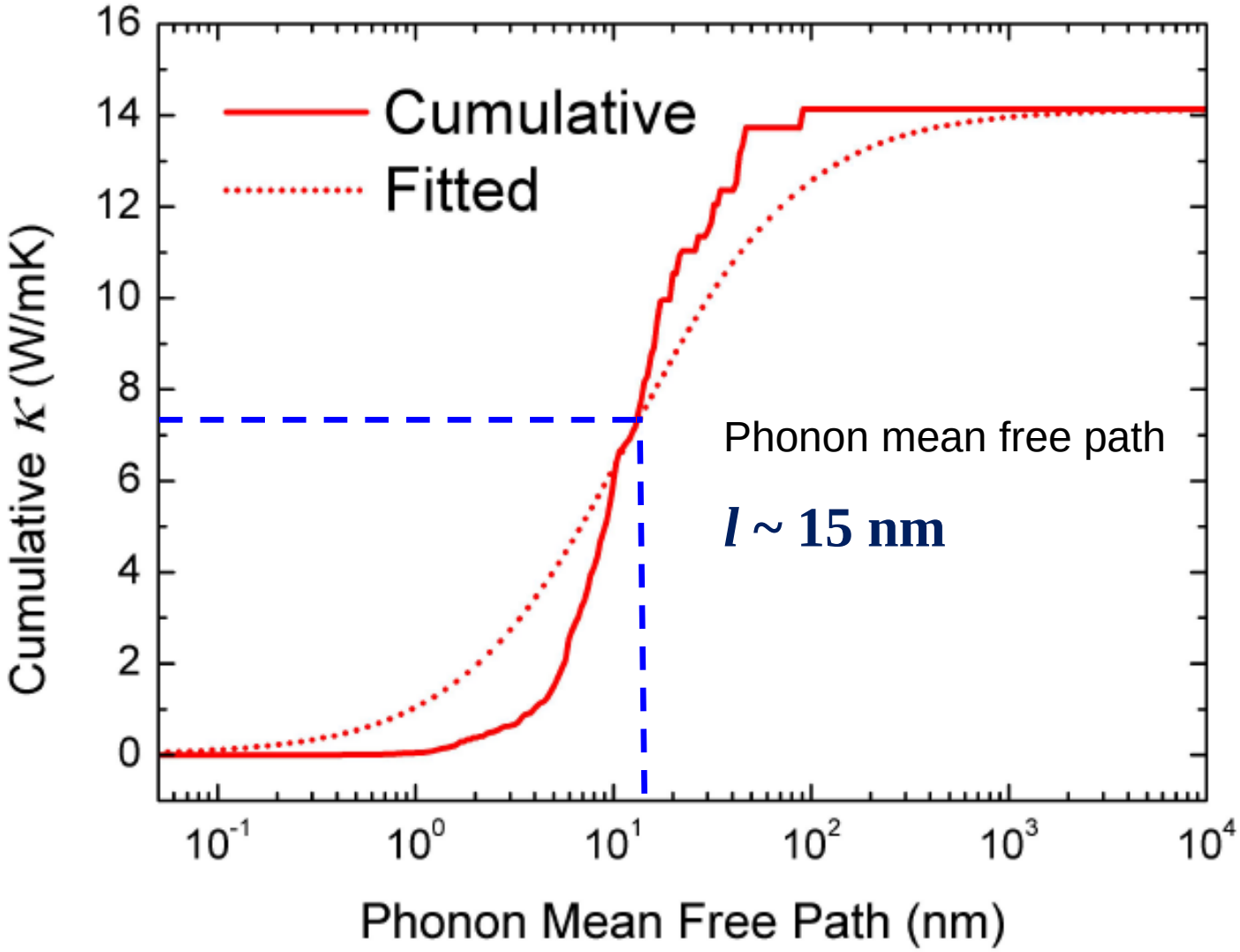
M. Hu, et al. *Appl. Phys. Lett.* (2014)

Phonon Relaxation Time of Silicene



Phonon relaxation time of the flexural branch is not evidently longer than other phonon modes, which is quite different from the case of graphene!

Cumulative thermal conductivity of silicene



Outline

- Thermal conductivity of free standing silicene
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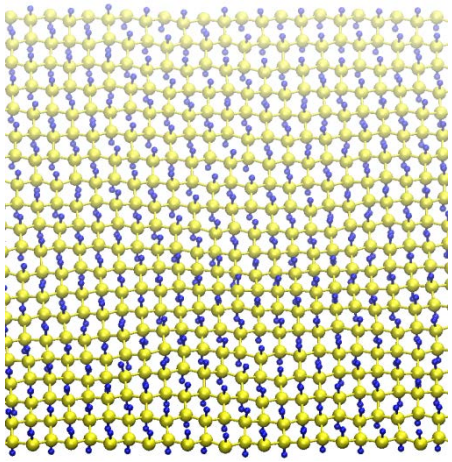
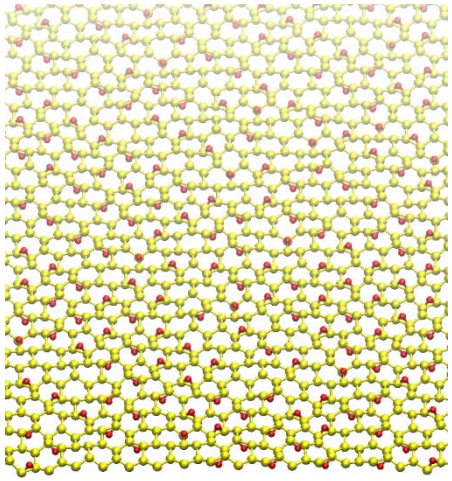
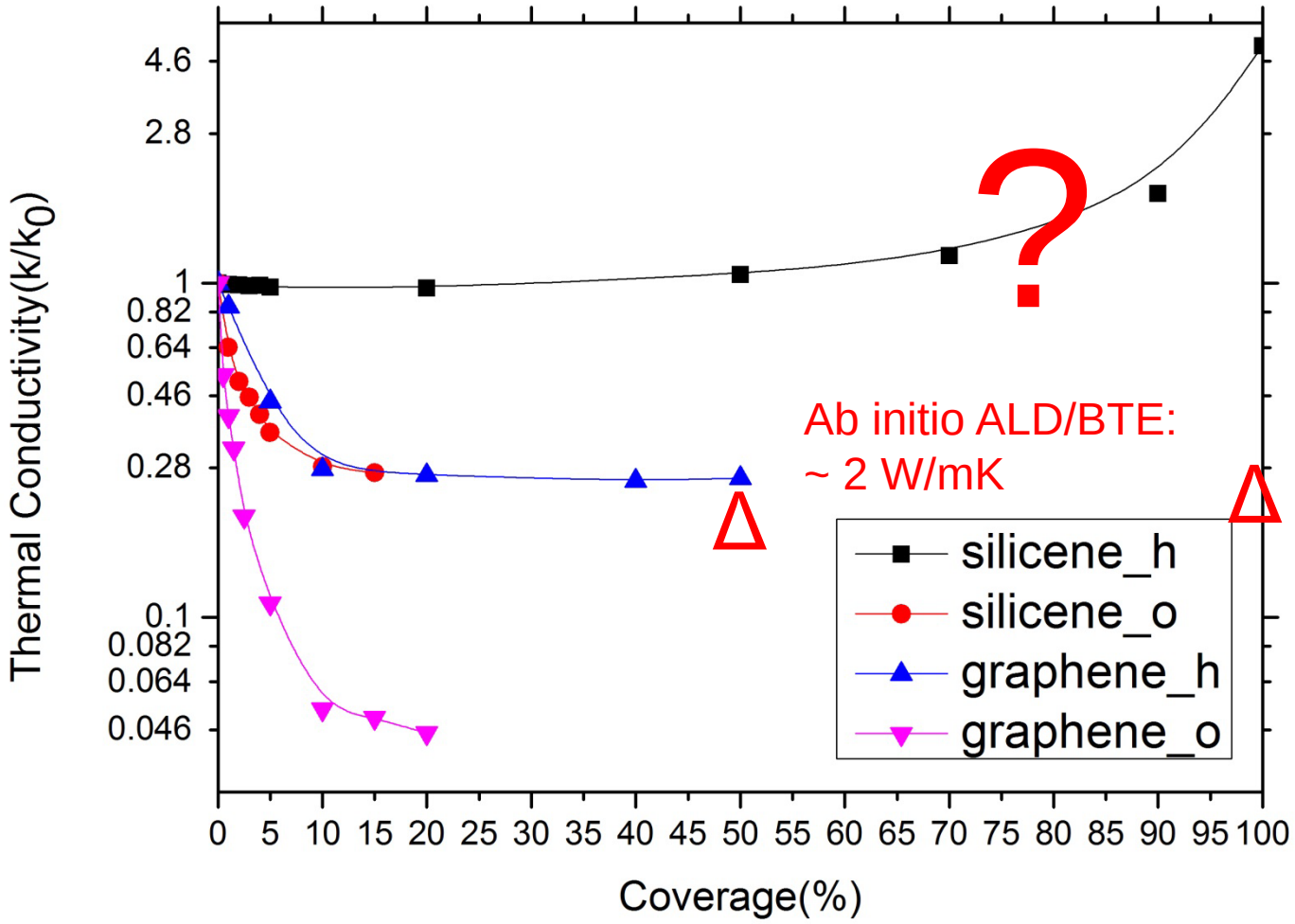
Effect of Surface Functionalization



Silicene + H



Silicene + O



Outline

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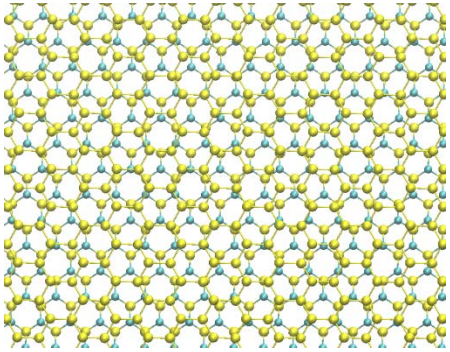
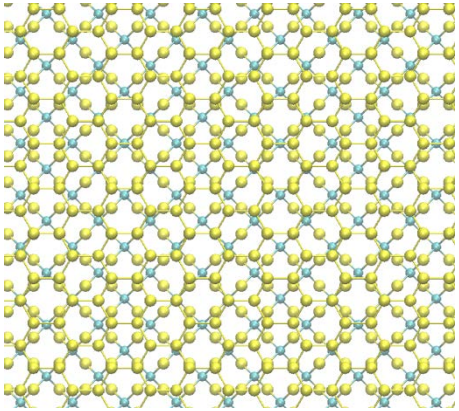
- **Thermal conductivity of supported silicene**

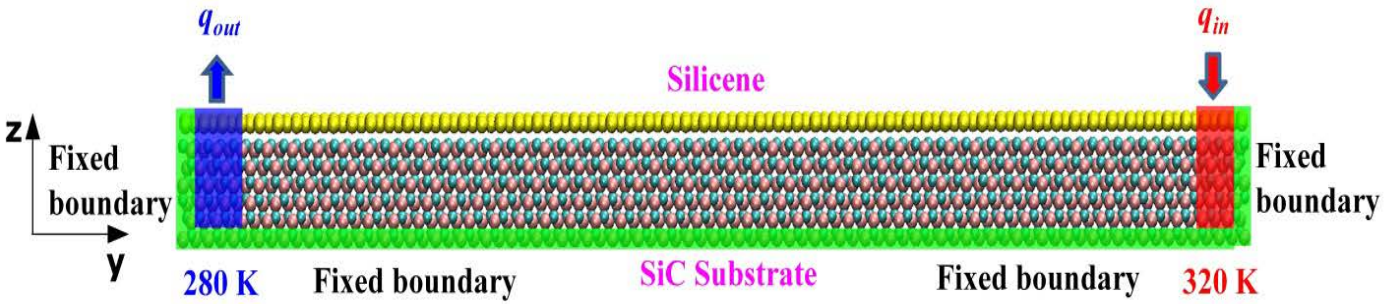
Silicene on SiC Substrates

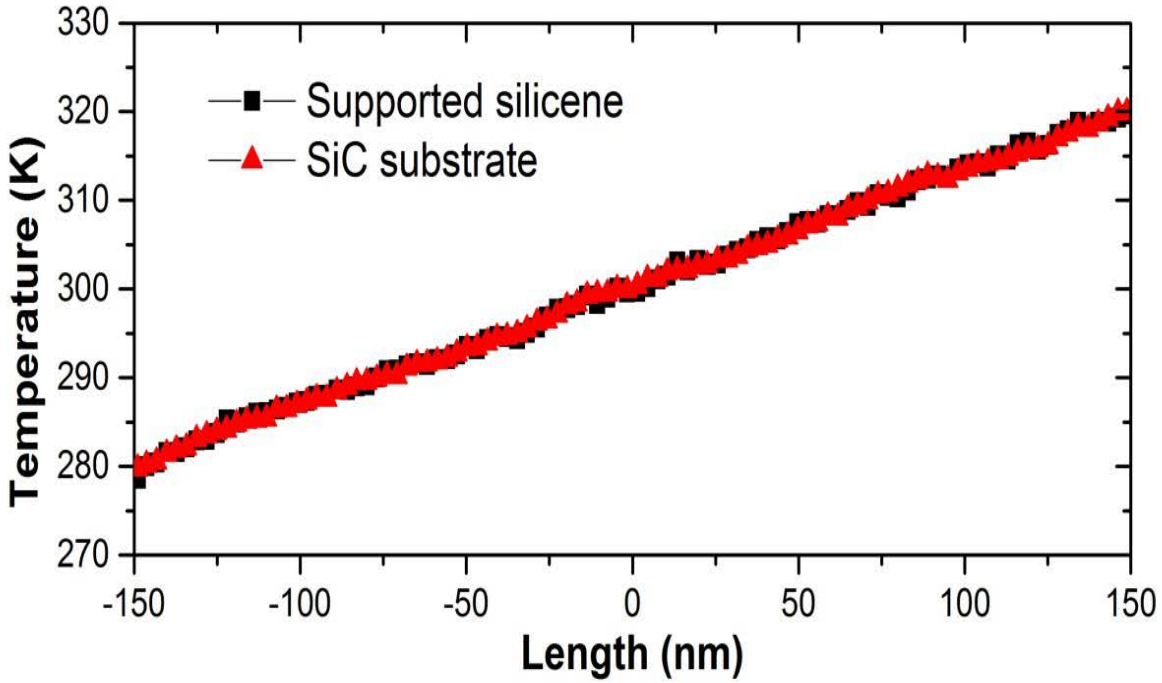


Silicene on 6H-SiC

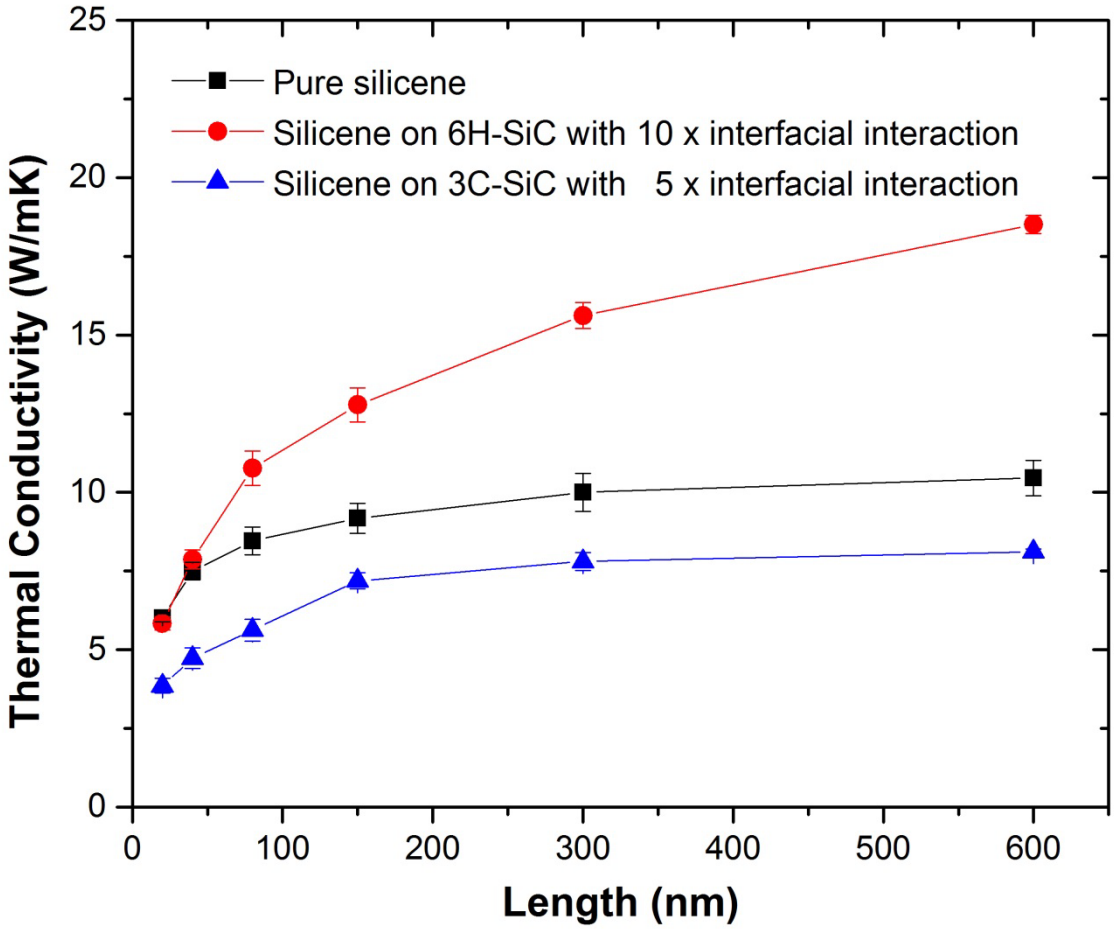


Silicene on 3C-SiC





Size Effect:
6H-SiC (WZ) vs. 3C-SiC (ZB) Substrate

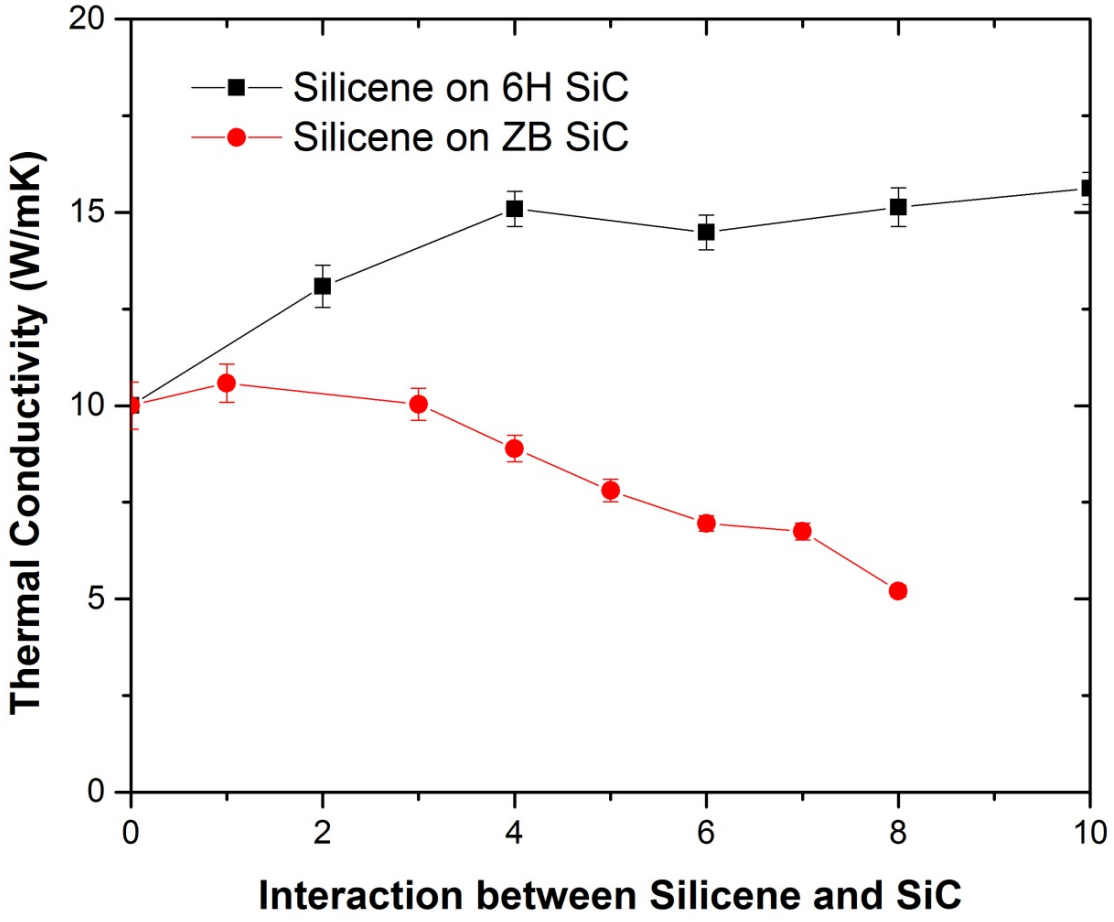


Silicene on 6H-SiC > FS silicene

Silicene on 3C-SiC < FS silicene

M. Hu, et al. *(submitted)*

Effect of Interfacial Interaction Strength



Silicene on 6H-SiC:

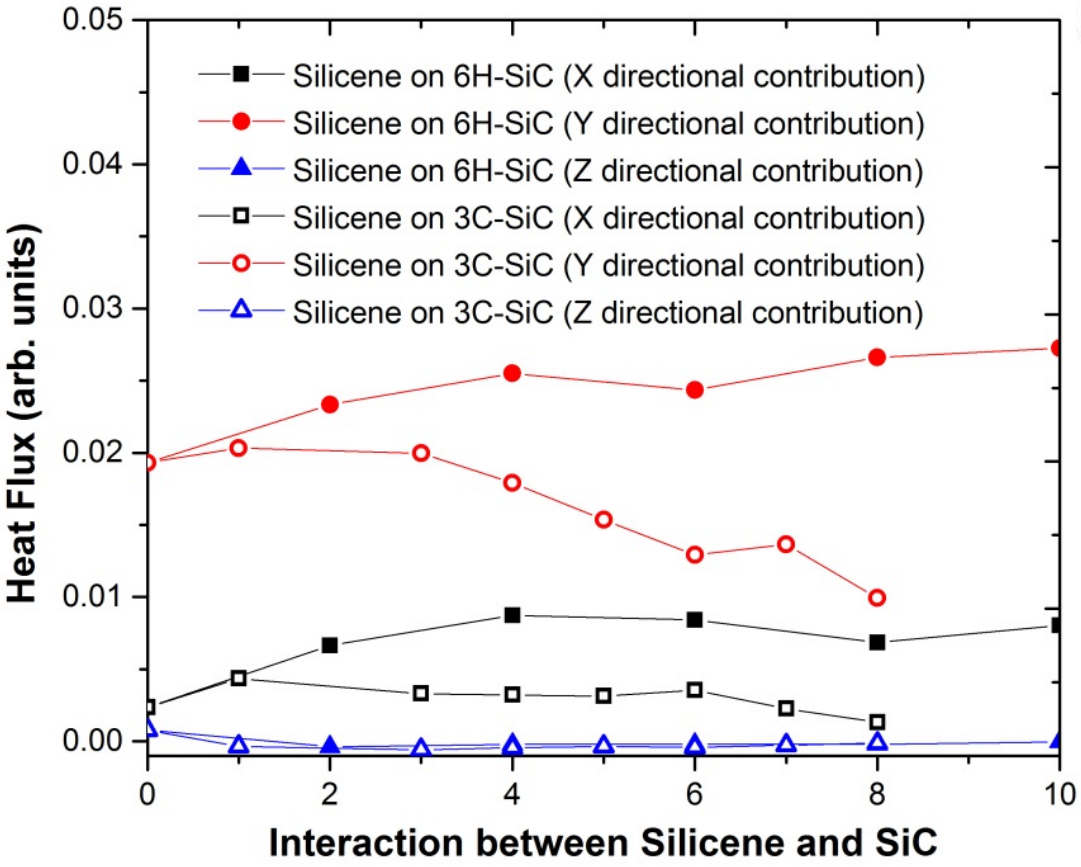
Thermal conductivity **increases** with the interfacial interaction

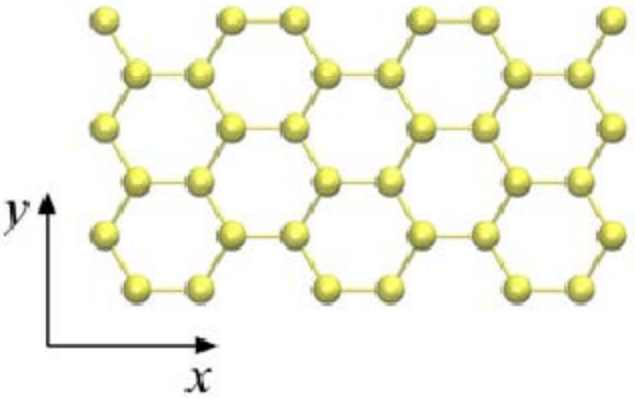
Silicene on 3C-SiC:

Thermal conductivity **decreases** with the interfacial interaction

Mechanism: Mode Polarization Analysis

$$J_{left\to right,\alpha} = -\frac{1}{2S}\sum_{i\in left}\sum_{j\in right} F_{ij\alpha}(\upsilon_{i\alpha}+\upsilon_{j\alpha})$$

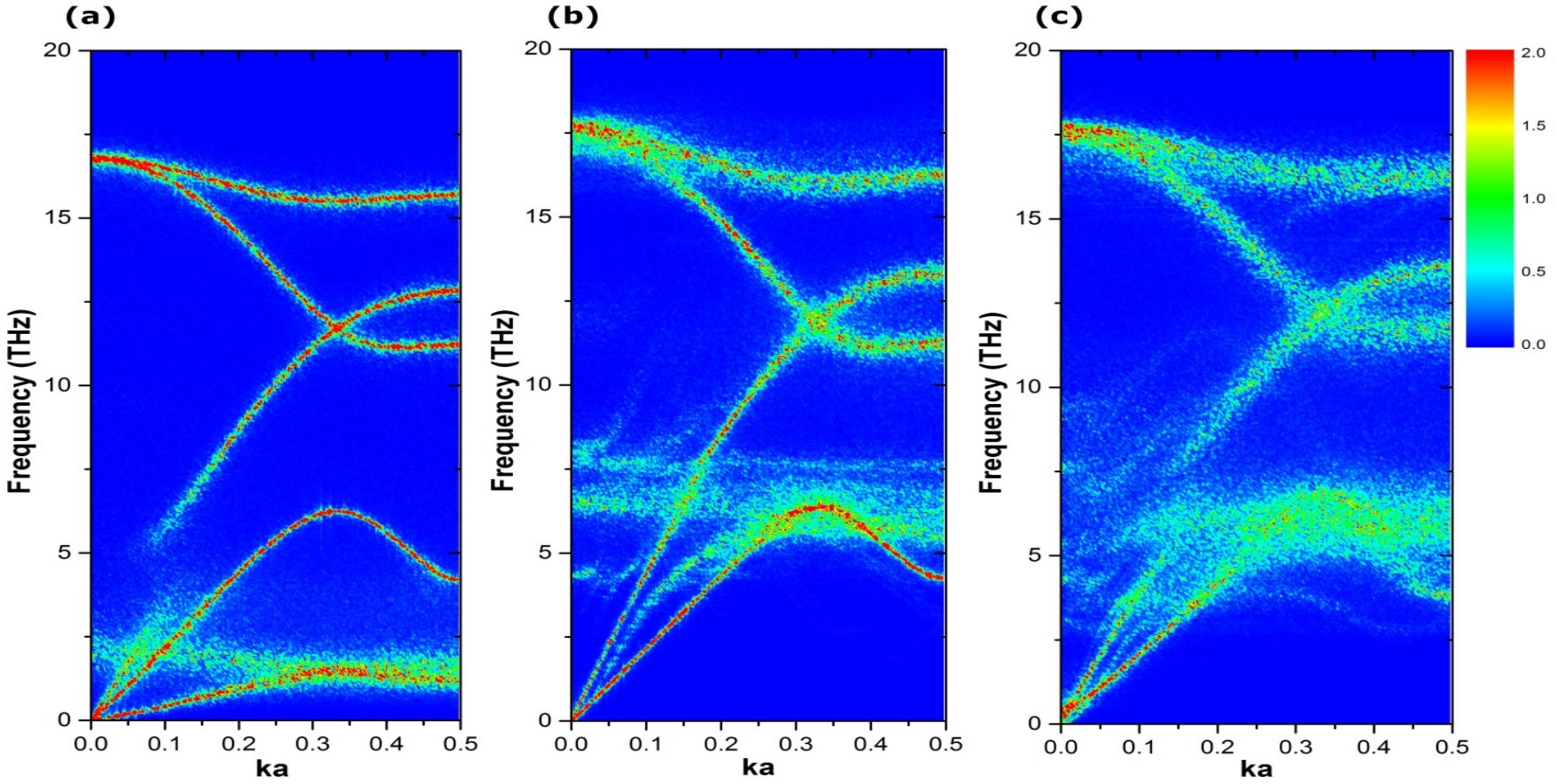




- Longitudinal > Transverse > Out-of-plane
- Substrate effects are mainly due to the modified in-plane phonon modes

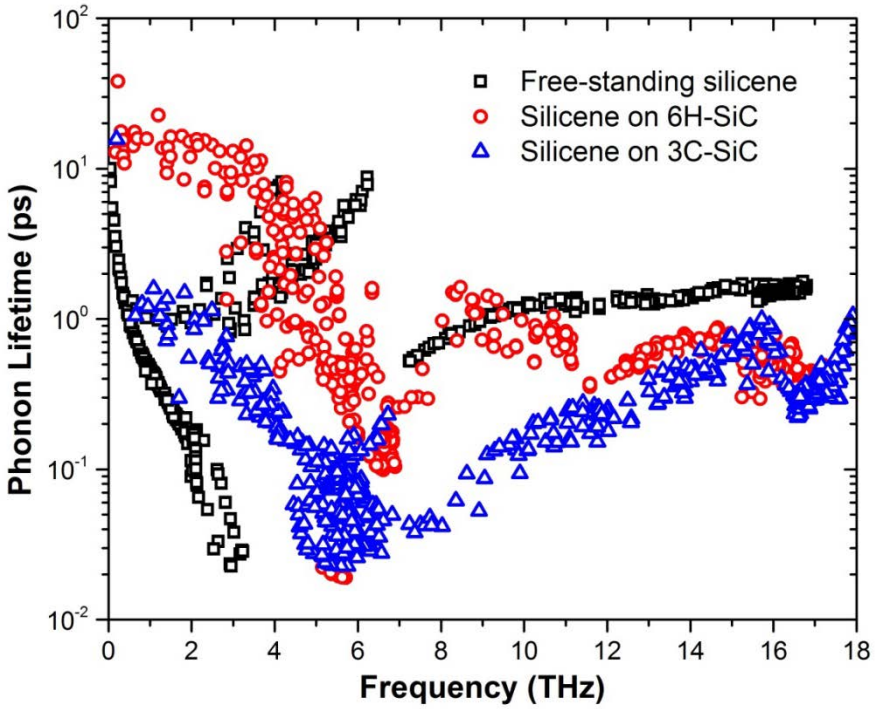
Mechanism: Phonon Spectral Energy Density (SED) Analysis

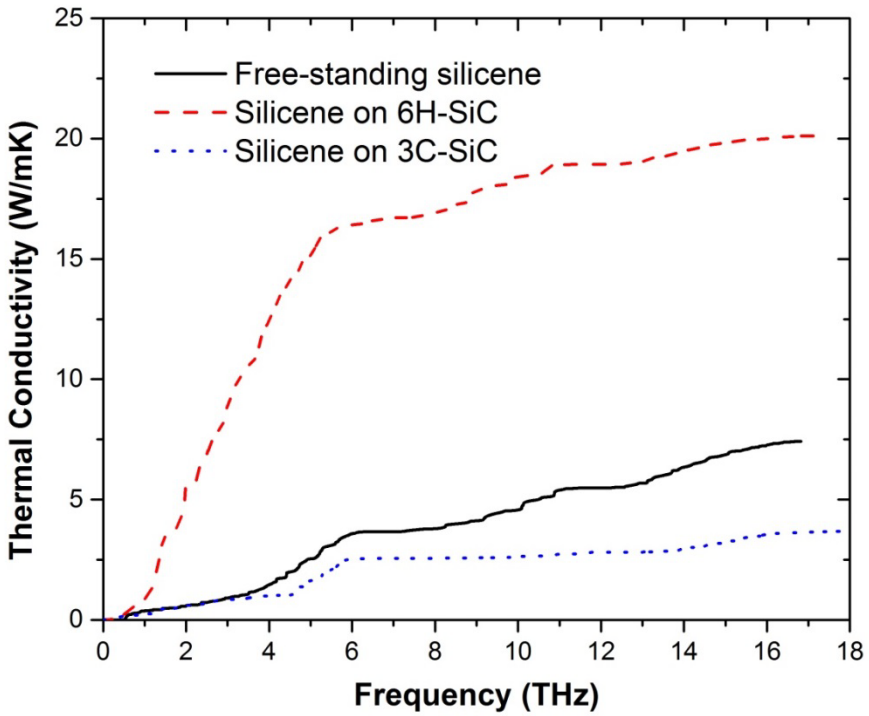
$$\dot{Q}(\vec{k},\nu,t)=\sum_{jl}\sqrt{\frac{m_j}{N}}\vec{\upsilon}_{jl}(t)\cdot\vec{e}_j^{*}(\vec{k},\nu)\exp(-2\pi i\vec{k}\cdot\vec{r}_l) \qquad \Phi(\vec{k},\nu,f)=\left|\int\dot{Q}(\vec{k},\nu,t)\exp(-2\pi ift)dt\right|^2$$



Free standing silicene | Silicene on 6H-SiC | Silicene on 3C-SiC

Mechanism: Phonon Spectral Energy Density (SED) Analysis





- For silicene supported on **6H-SiC** substrate the lifetime of phonons with frequency less than 5 THz is significantly enhanced as compared with free standing silicene, while the lifetime of high frequency phonons is slightly reduced.

- For silicene supported on **3C-SiC** substrate the phonon lifetime is reduced for almost the entire frequency range, especially for the phonons with frequency higher than 3 THz, i.e. the major affected phonons are optic.

Summary for 2-D Silicene

- ✓ The intrinsic lattice thermal conductivity of two-dimensional silicon (silicene) is around 10 W/mK at 300 K, which is substantially lower than its counterpart of graphene and bulk silicon.

Two-dimensional silicon ≠ graphene

- ✓ The out-of-plane vibration has minor contribution (less than 10%) to the overall phonon transport in silicene, which is opposed to graphene where heat conduction is dominated by the out-of-plane flexural modes.

from thermal transport point of view.

→ Calls for new force field

- ✓ Substrates can tune the thermal conductivity of silicene in a broad range (either increase or decrease the thermal conductivity), which is very important for the thermal management of electronic devices involving silicene.

- ✓ Despite the progress in thermal transport of free standing silicene using classical MD simulations, more accurate is needed for studying more complex silicene based structures, such as chemical functionalization, substrate effect, heterostructures, etc.

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Yanguang Zhou

PhD student:
Shengying Yue

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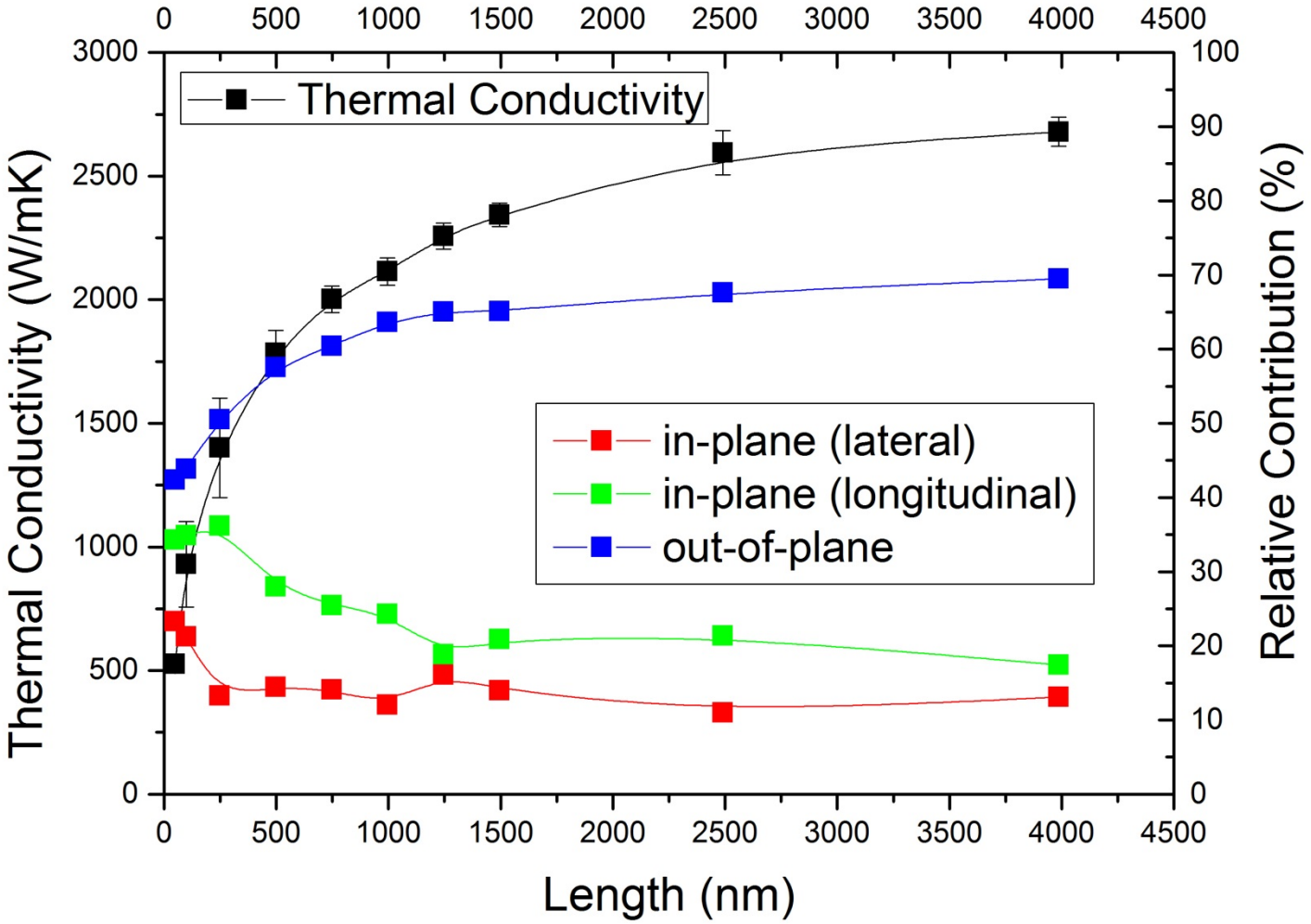
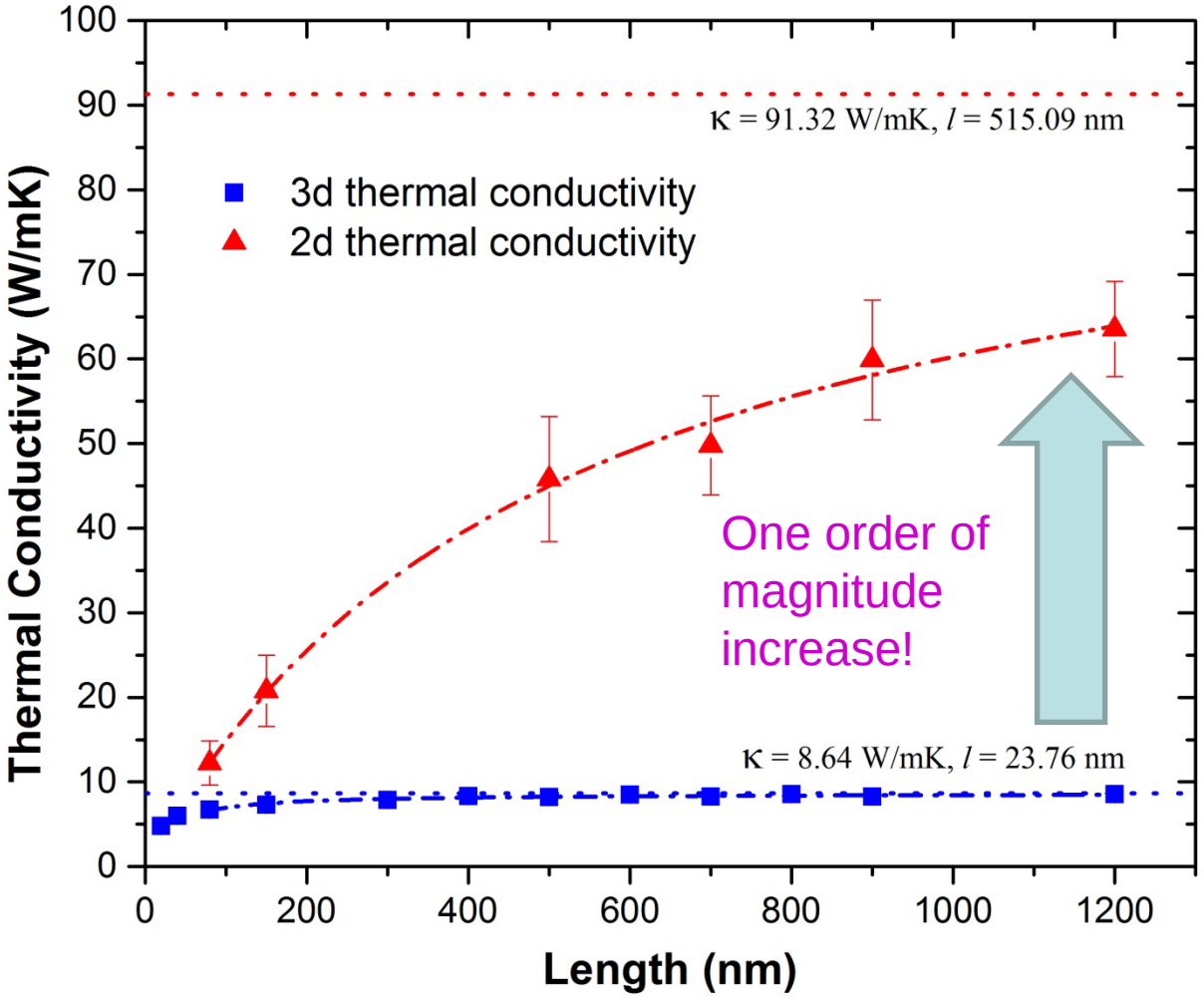
Thank you very much for your attention!

MD Result for Graphene



Numerical Experiments: How About Zero-out ZA Modes?



Graphene:

Length	With ZA	Without ZA
500 nm	1785	1232

How about longer length?