

Thermal Conductivity of Nanoperforated Graphene Monolayers: An Atomistic Study

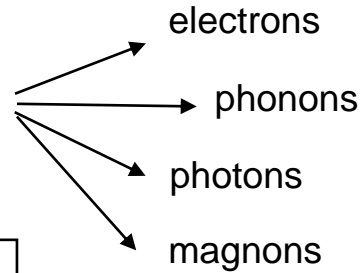
Markos POULOS

Supervisor: DR-CNRS Konstantinos TERMENTZIDIS

10/05/2023

Microscopic Theory of Heat Transport

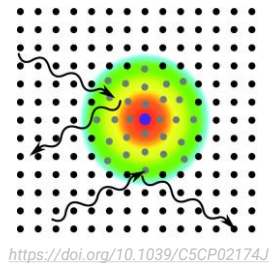
Heat Flux: Flow of **energy** + **momentum** by



+ resonances
(polaritons, polarons, etc.)

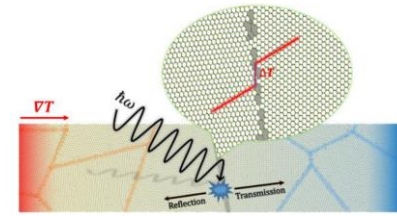
Thermal resistance is due to **scattering** processes that destroy the **total momentum** of the heat carriers

- **Phonon – Defect**
 - Isotope
 - Impurity
 - Dislocations
- **Phonon – Boundary**
 - Free surface
 - Grain Boundary
 - Substrate scattering
- **Phonon – Phonon**
 - U-processes: $\Delta\mathbf{q} = \mathbf{Q}$
 - N-processes: $\Delta\mathbf{q} = \mathbf{0}$

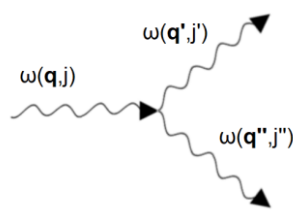


<https://doi.org/10.1039/C5CP02174J>

$\Gamma_{\text{boundary}} \sim 1/L$



<https://doi.org/10.1021/acsami.9b06196>



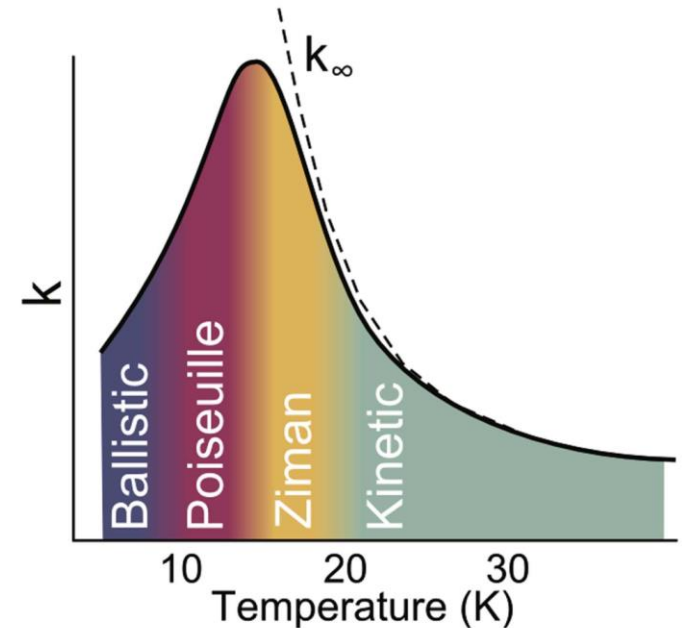
P-destroying

P-preserving

Microscopic Theory of Heat Transport

Transport Regimes:

	Dominant Mechanism	Diffusion Mechanism
Ballistic	Boundary	Boundary
Poiseuille	N-scattering	Boundary
Ziman	N-scattering	Umklapp + Defect
Kinetic	Umklapp + Defect	Umklapp + Defect



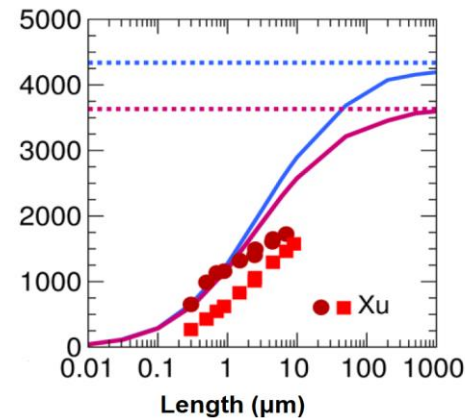
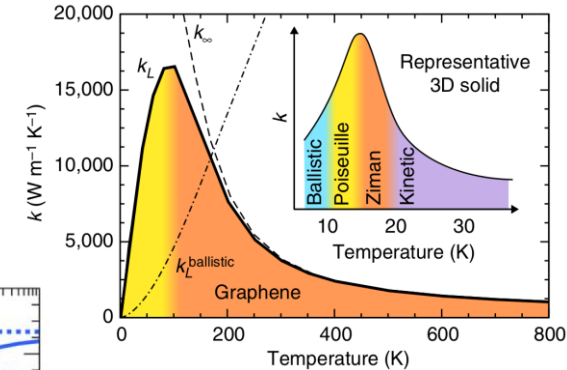
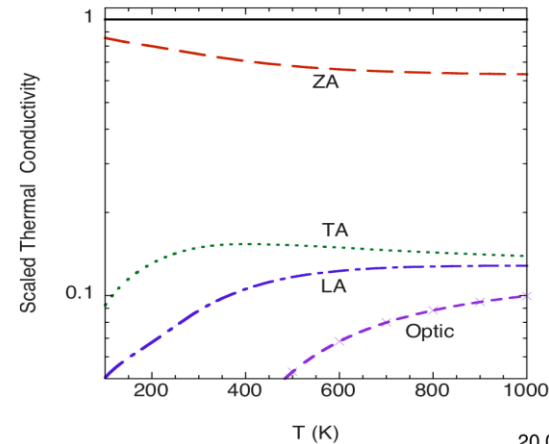
- **Ballistic:** Scattering only by the 'walls' ('ball-hitting-wall' model). Phonon $l_{\text{MFP}} \sim L$
- **Poiseuille:** Phonons \rightarrow hard balls bouncing from each other but 'feel the walls'
- **Ziman:** Phonons still 'feel the walls' but dissipation by resistive processes (U+defect)
- **Kinetic (Diffusive):** Classical Fourier regime. No size dependence

} **'Hydrodynamic'**

Microscopic Theory of Heat Transport

The special case of graphene:

- Light C atoms with strong sp^2 bonds and low dimensionality: high-energy phonons with restricted scattering phase space
- Although semimetal, $\kappa_{el} \ll \kappa_{ph}$ (~1%)
- Selection rules due to symmetry further restrict scattering paths of ZA phonons
→ ZA dominate Thermal Transport? [2]
- N-processes dominant at all temperatures
→ Ballistic/Hydrodynamic Transport [3]
- Thermal conductivity highly size-dependent: ballistic/hydrodynamic regime reaches orders of ~mm !! [4]



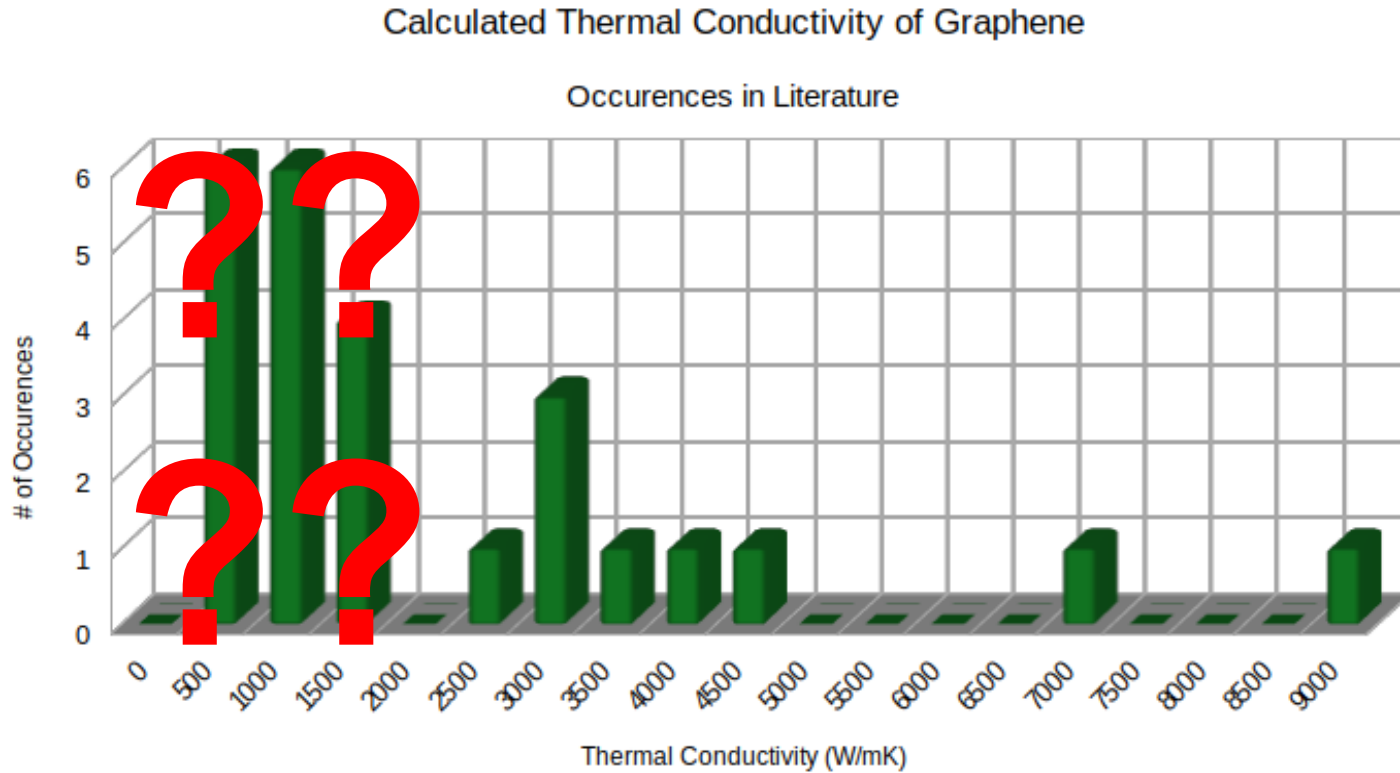
[2] Lindsay et al (2010), *Phys. Rev. B* **82**, 115427

[3] Cepellotti et al (2015), *Nat. Commun.* **6**, 6400

[4] Fugallo et al (2014), *Nano Lett.* **14** (11) 6109

Thermal Conductivity of Pure Graphene

An open debate:



No converging value?

Heat Transport Calculations in Graphene

Influencing factors:

1. Computational Method (*NEMD, GK, BTE, etc.*)
2. Definition of Heat Flux operator (*Even in QM non unique definition!*)
3. Type of Interatomic Potential (*Tersoff, AIREBO, LCBOP, GGA, LDA*)
4. Choice of Boundary Conditions (*Periodic BC vs Free BC*)
5. Temperature
6. Size
7. Substrate (*or freestanding*)
8. Chemical Purity (*dopants, natural isotopes, etc.*)
9. Divergence from Pristine Structure (*grain boundaries, vacancies, dislocations, pores etc.*)

Computational

Physical

Heat Transport in Graphene

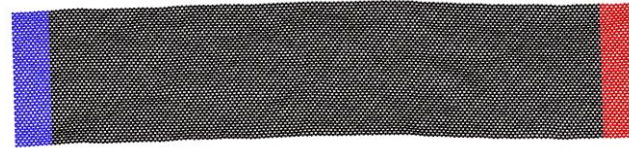
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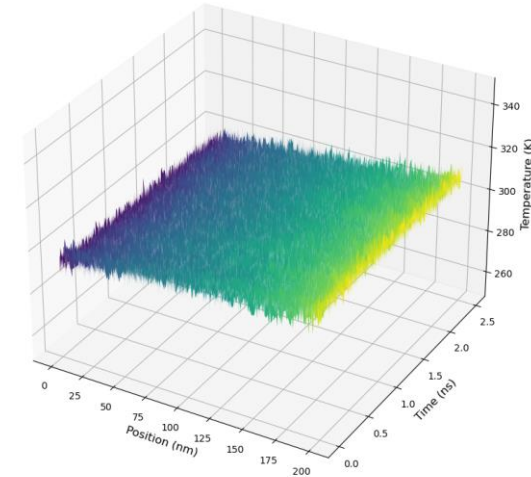
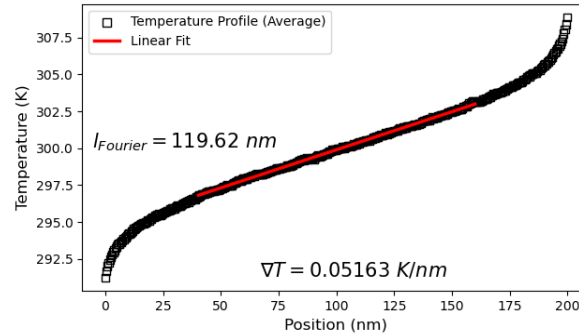
Thermal Conductivity: Non-Equilibrium MD

Methodology:

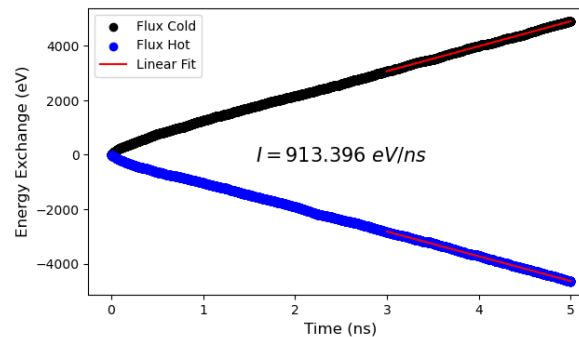
❖ Impose a Bias (ΔT or J)



❖ Reach steady state



❖ Measure response (J or ΔT)

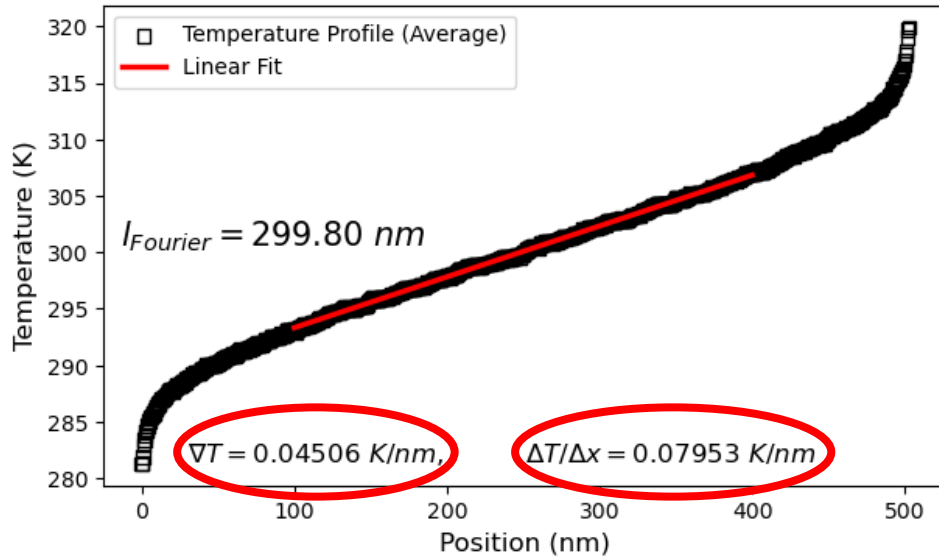


$$\kappa = \left(\frac{I}{A} \right) \cdot \frac{1}{\nabla T}$$

Thermal Conductivity: Non-Equilibrium Method

Variations:

How to define **thermal gradient** ?
(linear regime gradient vs external bias)

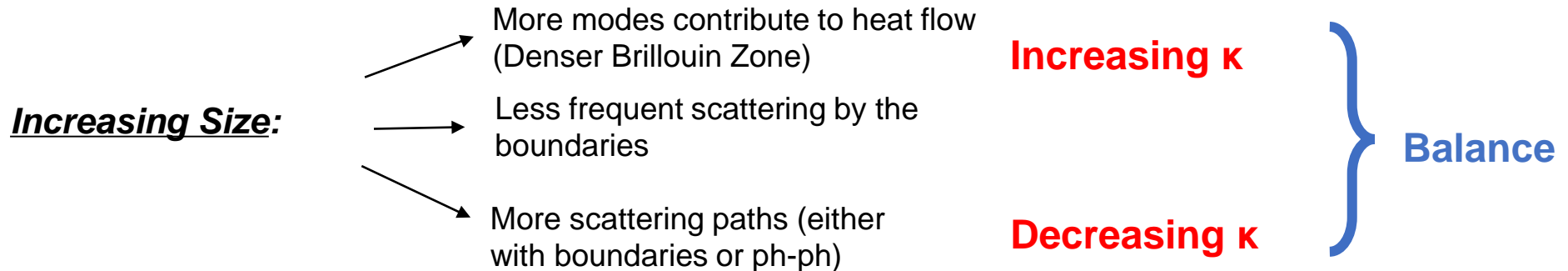


- Linear regime gradient is theoretically correct according to Fourier's law
- Bias is experimentally measured

Usually, $\nabla T < \frac{\Delta T}{\Delta x}$, therefore $\kappa_{\text{Bias}} < \kappa_{\text{Gradient}}$

Thermal Conductivity: Length-Dependence

Size-dependence of κ for Graphene:



Theoretical Approaches

Converging:

- ❑ Phonon Gas Kinetic Model
- ❑ Averaged phonon properties
- ❑ $\frac{1}{\kappa} = \frac{a^3}{4k_B\bar{v}} \left(\frac{1}{l_\infty} + \frac{2}{L} \right)$ → $\frac{1}{\kappa} = a + \frac{b}{L}$
- ❑ Converges for $L \gg l_\infty$

$$\frac{1}{\kappa} = a + \frac{b}{L}$$

Diverging:

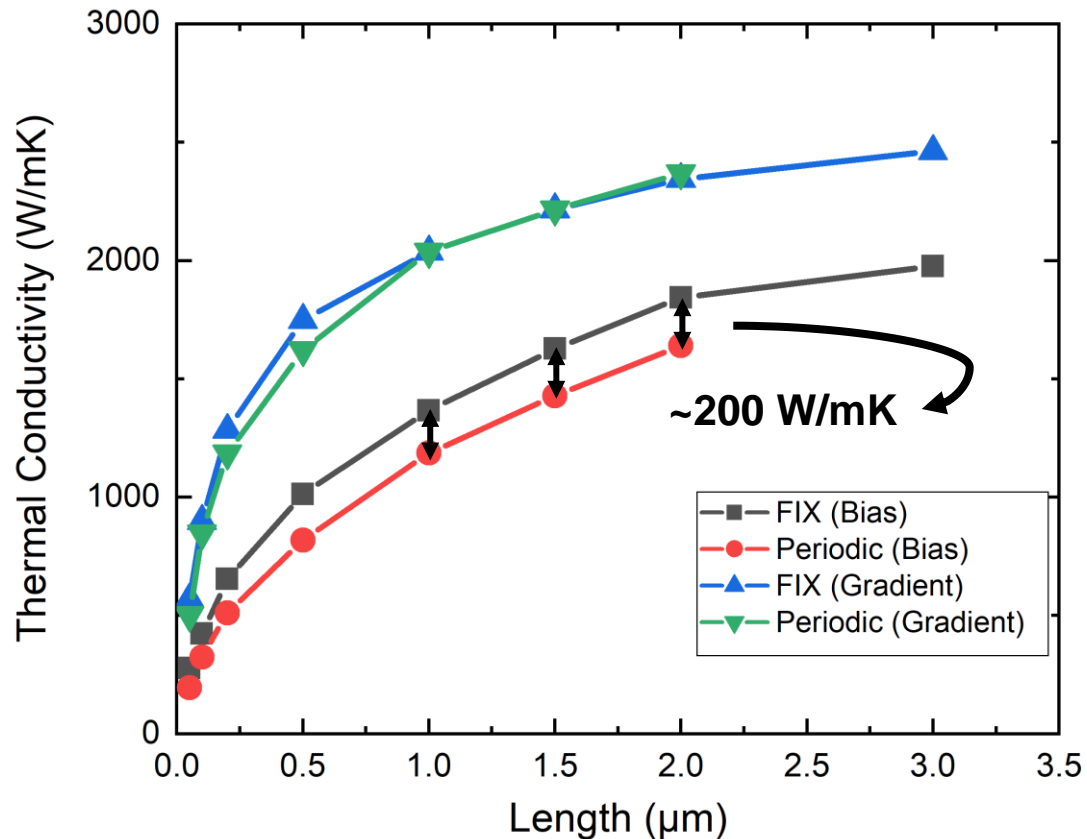
- ❑ $\kappa \sim \log(L)$ [5,6]
- ❑ Strictly 2D (no out-of plane movement)
- ❑ Basic Principle: Non-ergodicity and non-thermalization due to restricted scattering phase-space (Fermi-Pasta-Ulam systems)

[5] Wang et al (2012) Phys. Rev. E, **86** 040101(R)

[6] Lippi (2000) J. Stat. Phys, **100** 1147-1172

Thermal Conductivity: Length-Dependence

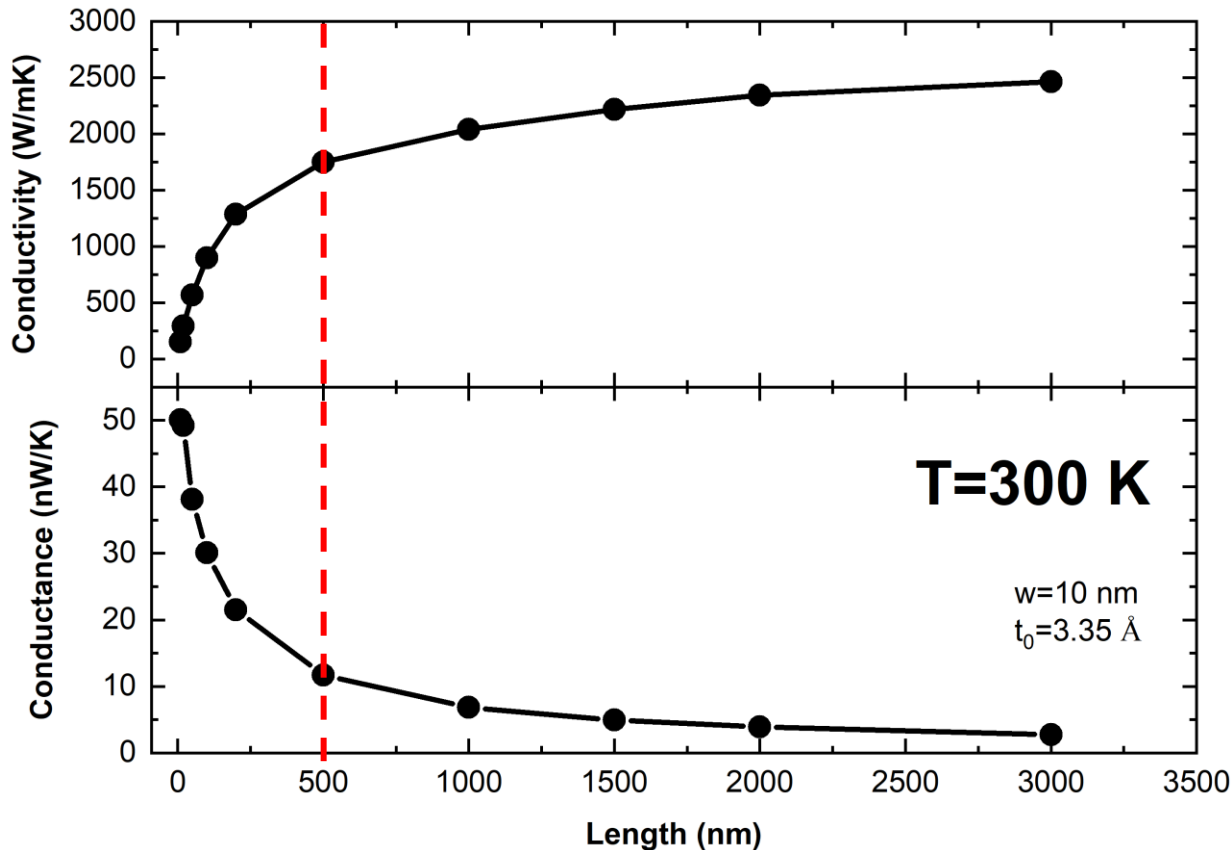
Results:



- ❑ Fix has larger values for smaller sizes because the thermostats need to inject more energy to keep T constant against the fixed ends.
- ❑ For larger sizes, this effect becomes negligible.
- ❑ **Bias:** $J/\Delta T$ (Experimentally measured).
Gradient: $J/\nabla T$ (Theoretically accurate)
- ❑ For the Bias definition, almost constant difference of **~ 200 W/mK** between pNEMD and fNEMD results for $l > 500$ nm.

Thermal Conductivity: Length-Dependence

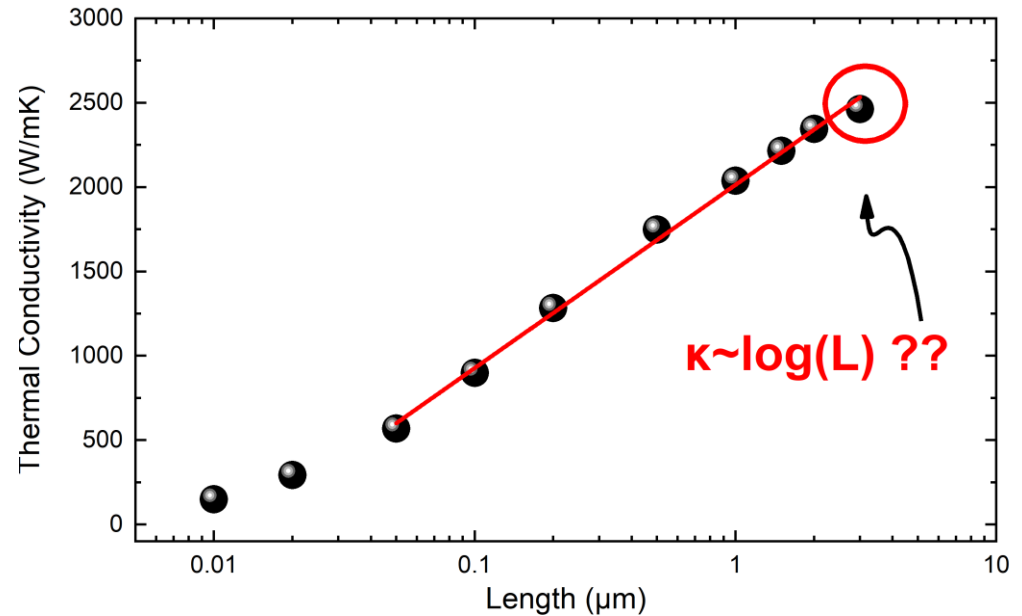
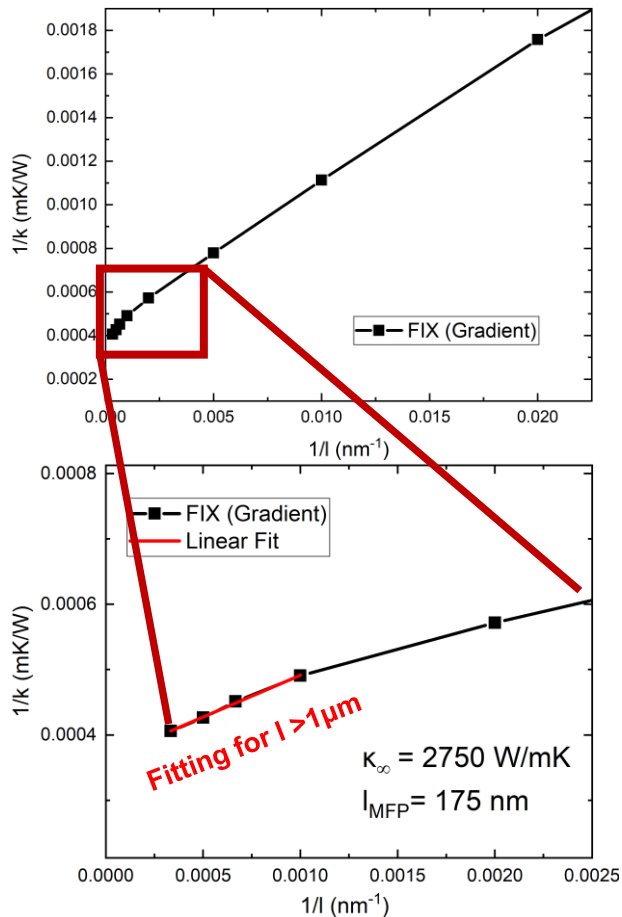
Ballistic-Diffusive limit:



- ❑ **Ziman vs Poiseuille**
- ❑ At the ballistic regime, $\kappa \propto L$
- ❑ However, down to $\sim 10\text{ nm}$ no linear relation!
- ❑ Therefore, the simple formula $\left(\frac{1}{l_\infty} + \frac{2}{L}\right)$ is not valid at small lengths
- ❑ For $L > 500\text{ nm}$ we have sort of a plateau

Thermal Conductivity: Length-Dependence

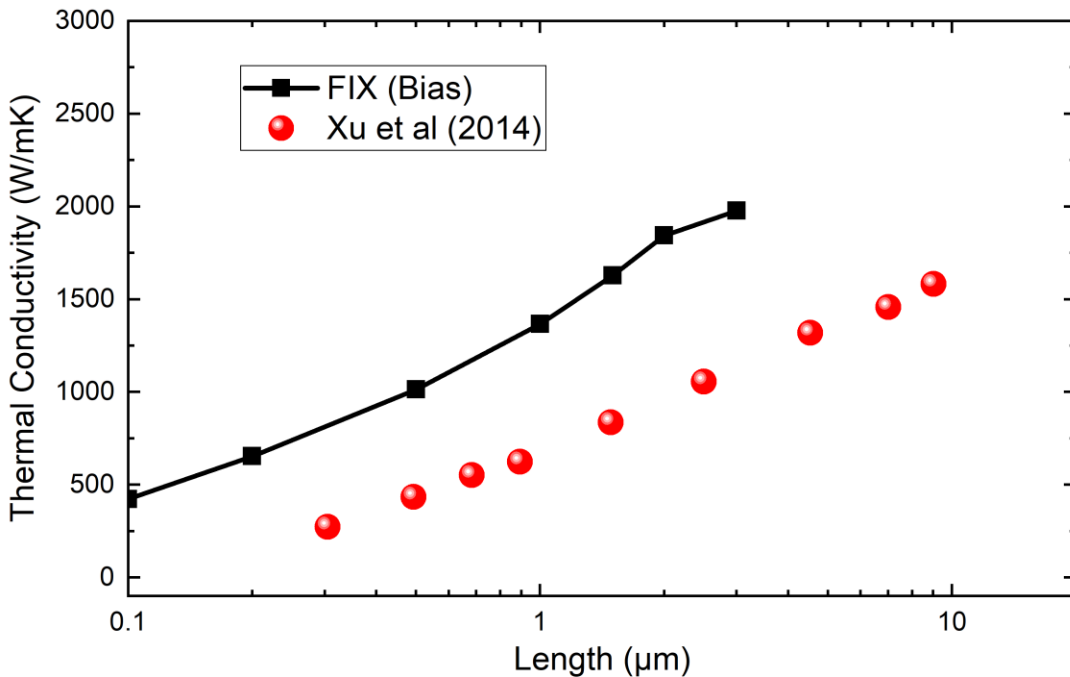
Fitting with Models:



- Below $\sim 500 \text{ nm}$ we have different slope
- Both models fit well the calculated points
- Does the log divergence still persist at larger lengths?

Thermal Conductivity: Length-Dependence

Comparison with Experiment:



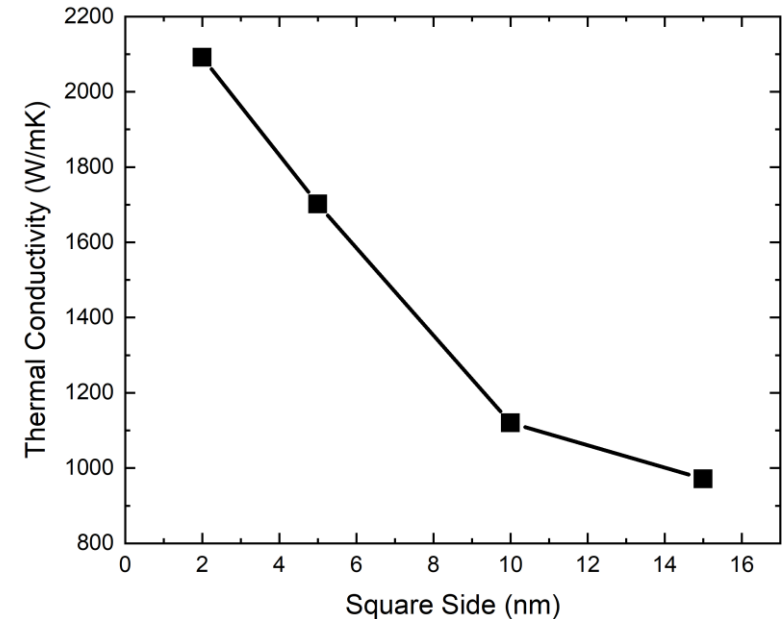
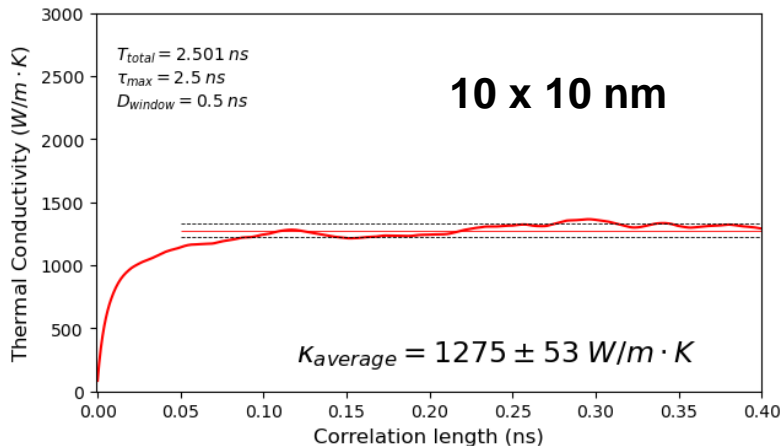
- ❑ Experimentally, divergence at least up to 10 μm [7]
- ❑ BTE calculations have implied convergence at much larger scales (~1 μm) [4]
- ❑ Computationally prohibitive for MD (~ 10^9 atoms)
- ❑ But BTE assumes molecular chaos (no correlation between scattering events)

Thermal Conductivity: Equilibrium MD

Green-Kubo Formalism:
$$\kappa = \frac{V}{3k_B T^2} \int_0^\infty \langle \mathbf{J}(t)\mathbf{J}(t + \tau) \rangle d\tau$$

Fluctuation Dissipation Theorem + Linear Response:

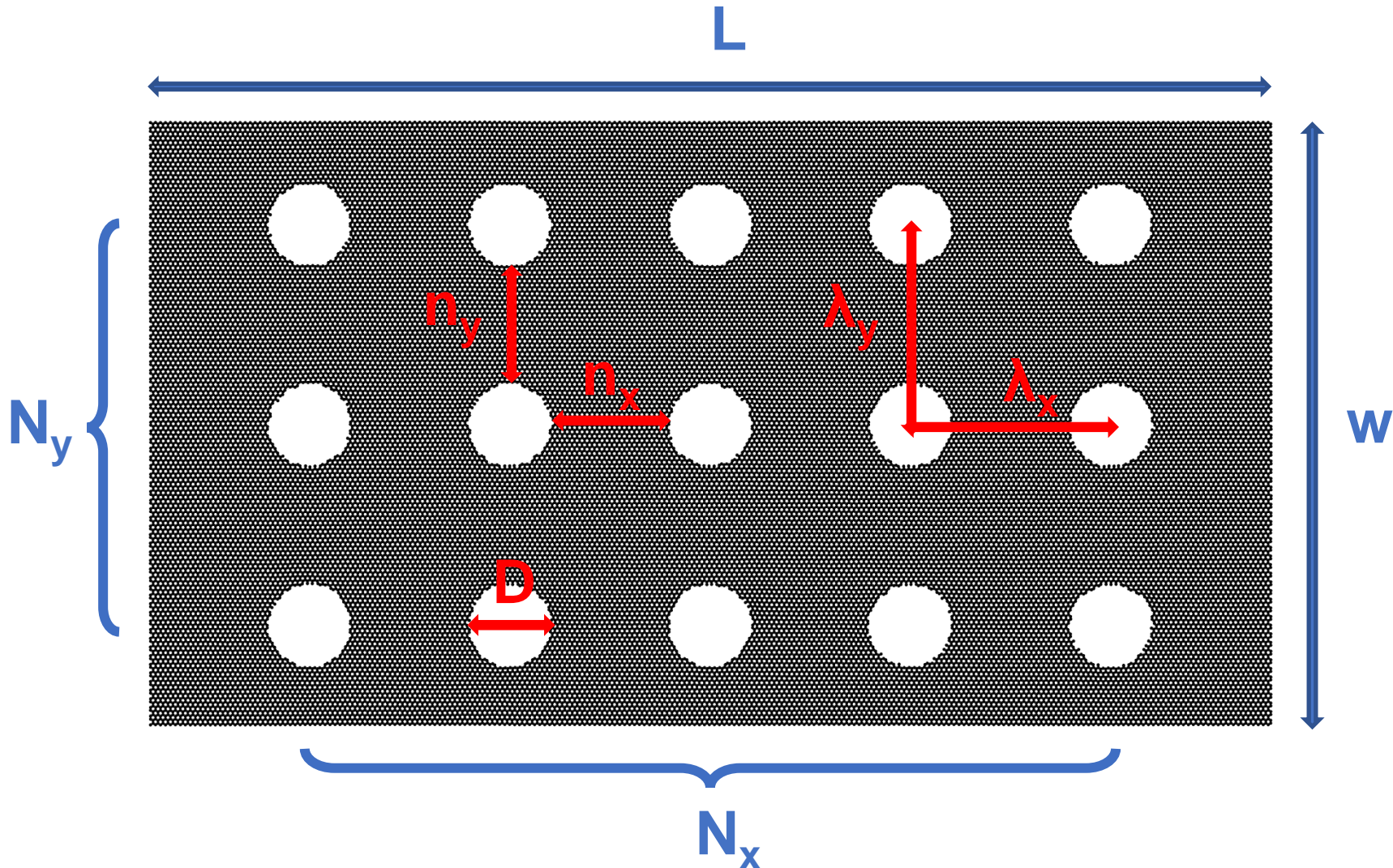
- Naturally occurring fluctuations of heat flux (zero average in equilibrium)
- Mechanism that restores these *fluctuations* are the same that *dissipate* the energy that those fluctuations carry



- ❑ For small sizes κ is overestimated due to “*memory effect*” in Periodic Boundary Conditions
- ❑ Large underestimation: the heat flux formulation of LAMMPS doesn’t consider many-body potentials!

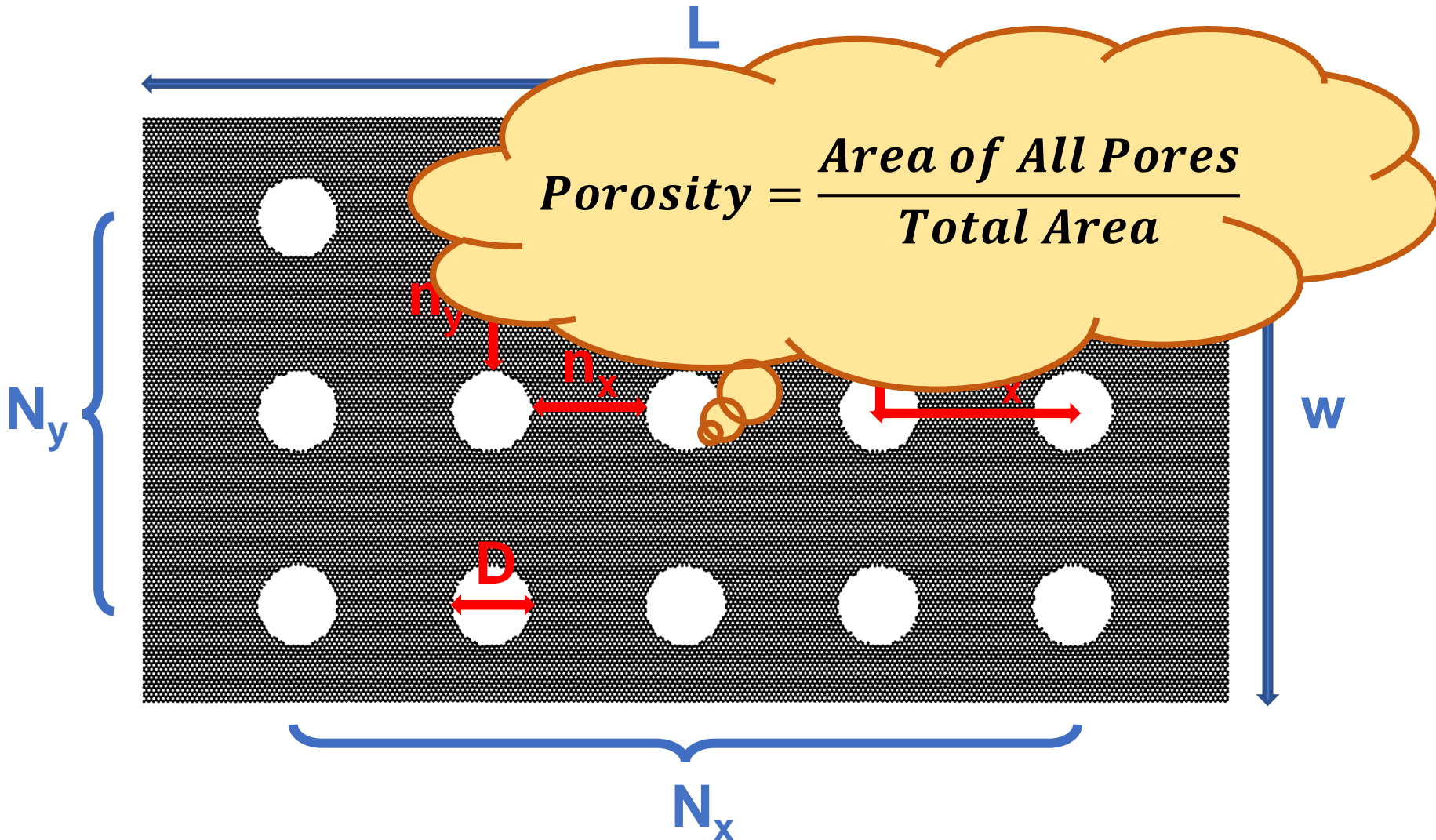
Thermal Conductivity: Nanoporous Graphene

Perforation Parameters:



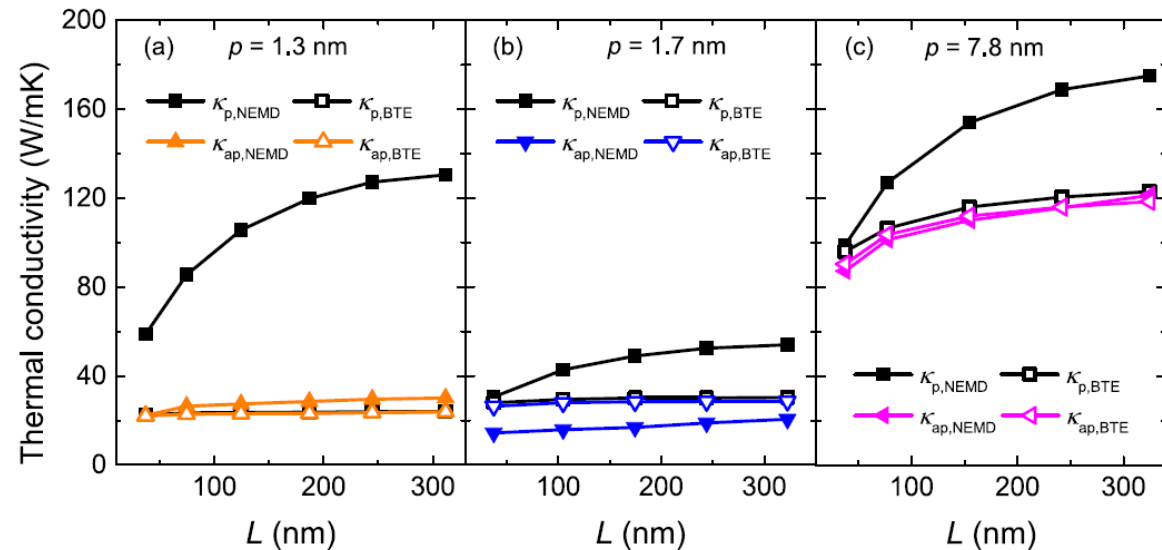
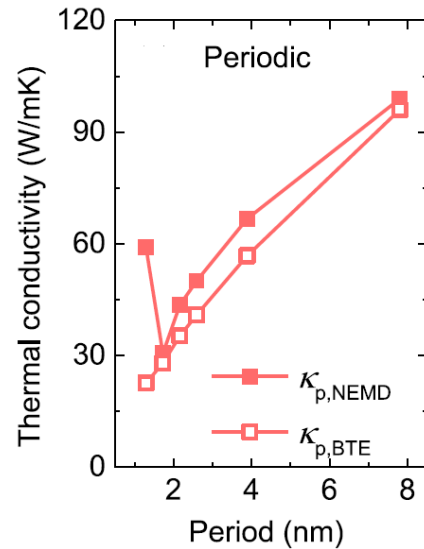
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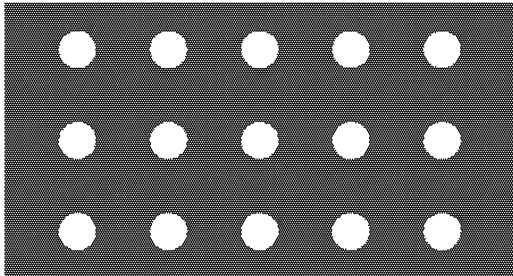
Previous Work:



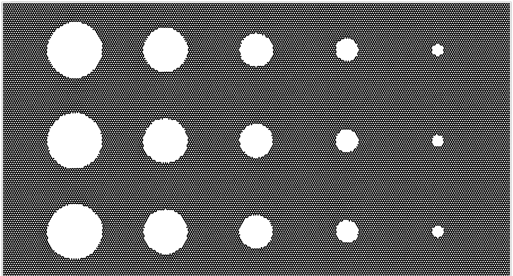
- ❑ NEMD-BTE
- ❑ Periodically Perforated Graphene
- ❑ Studying the effect of:
 - Perforation Period
 - Sample length
- ❑ Comparison between MD-BTE: at small periods *phonon interference enhances* conductivity
- ❑ At larger lengths, κ quickly saturates

Thermal Conductivity: Nanoporous Graphene

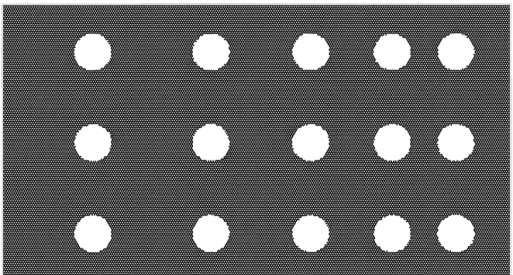
Perforation Parameters:



Periodic (n, d constant):

$$\left\{ \begin{array}{l} w = 10 \text{ nm} \\ d_0 = 4 \text{ nm} \\ l_0 = 6 \text{ nm} \end{array} \right.$$


Diameter-Modulated:

$$d_i = \left(\frac{d_0 - N_x}{N_x} \right)$$


Neck-Modulated:

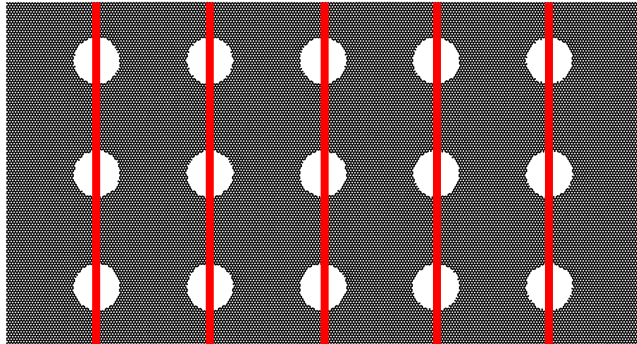
$$l_i = \left(\frac{l_0 - N_x}{N_x} \right)$$

p = 12.6 %

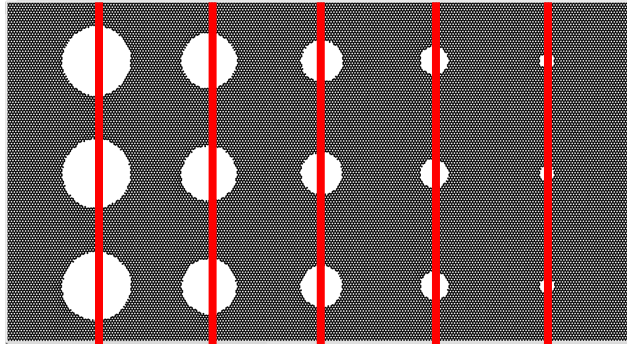
Thermal Conductivity: Nanoporous Graphene

Results: Temperature Profiles

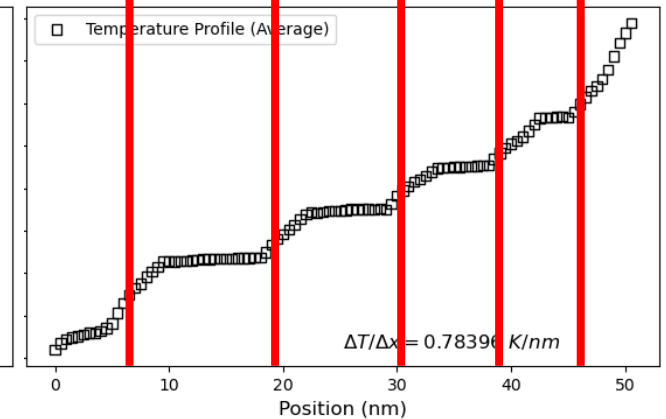
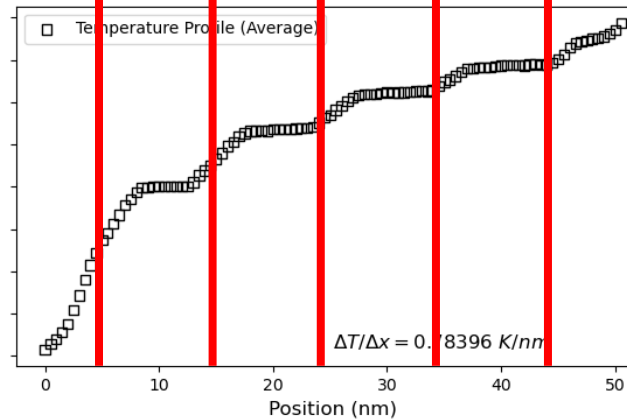
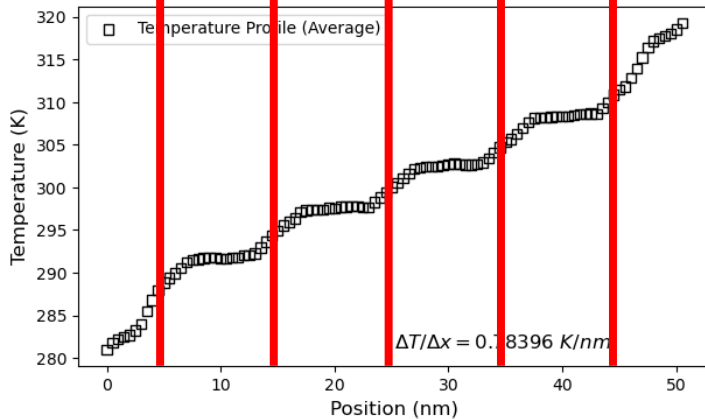
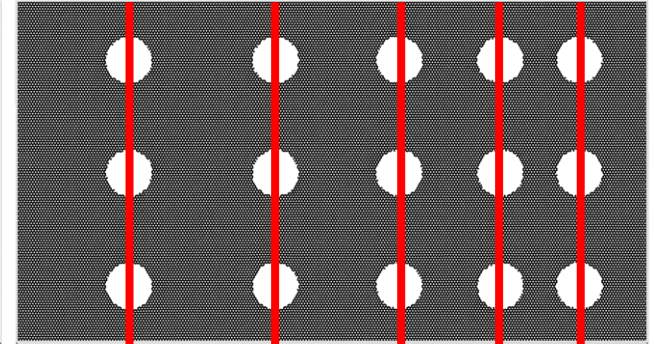
Periodic



Diameter

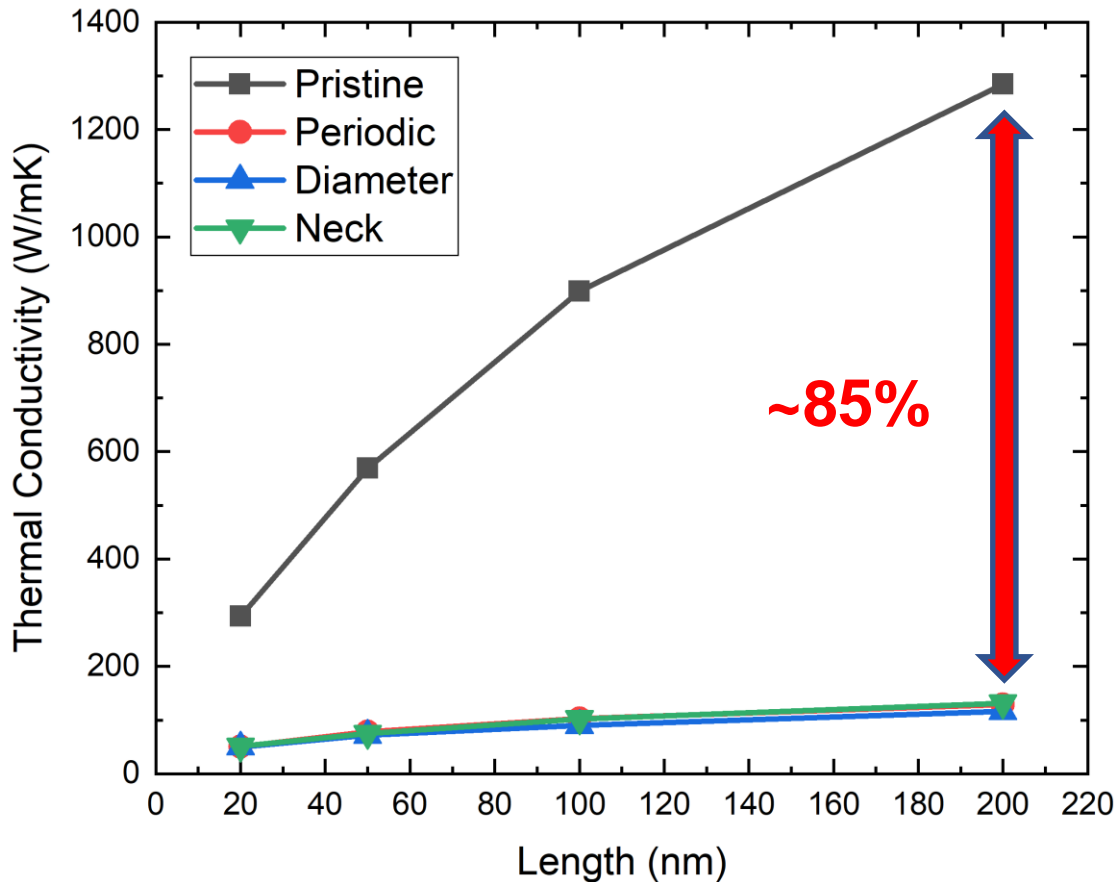


Neck



Thermal Conductivity: Nanoporous Graphene

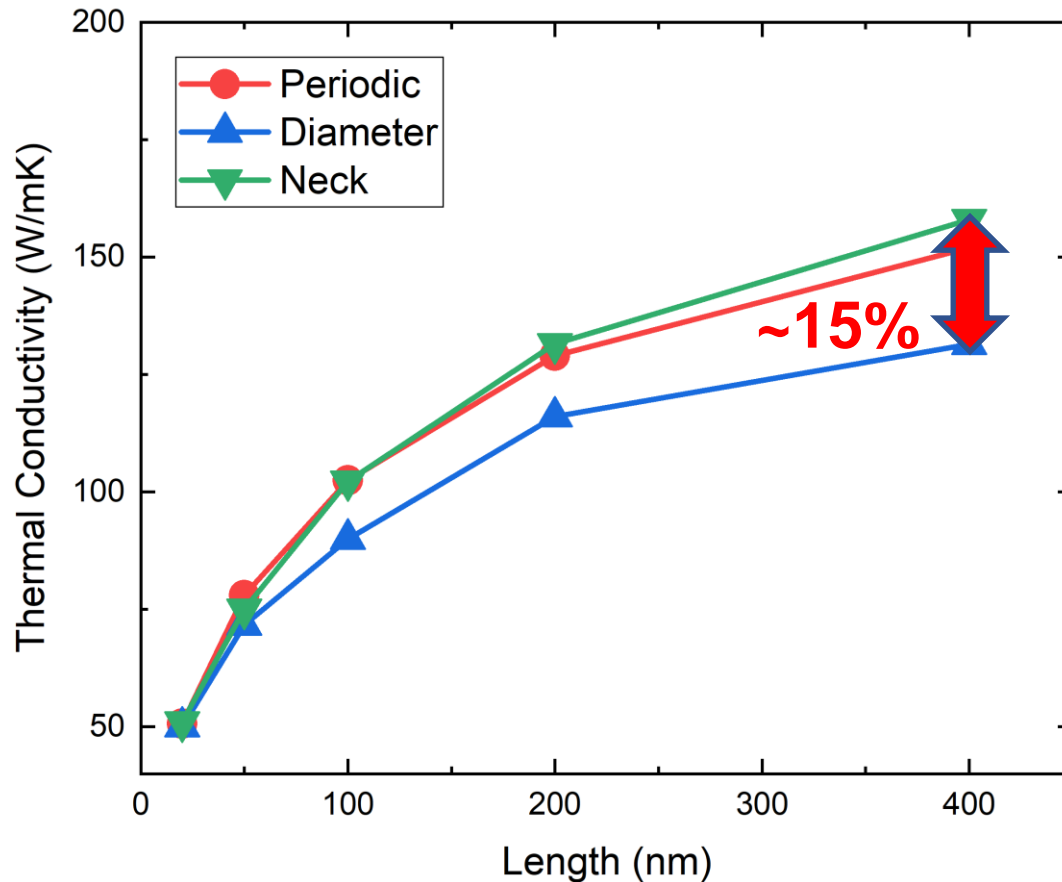
Results: κ -values



- ❑ Huge reduction with respect to pristine (**~85%**)
- ❑ Reaching a plateau at much lower lengths.
- ❑ Similar length-dependence for all perforation profiles.

Thermal Conductivity: Nanoporous Graphene

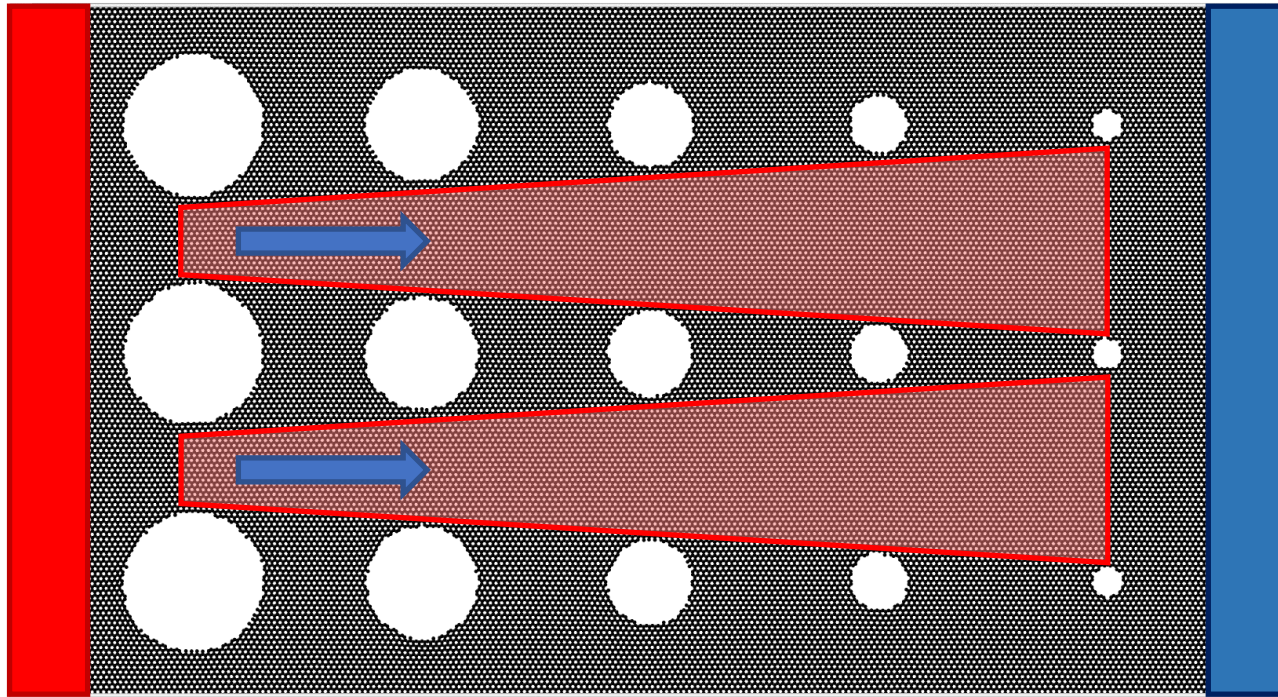
Results: κ -values



- ❑ Periodic and neck-modulated have similar trends
- ❑ Diameter-modulated is systematically lower (~15%)
- ❑ Despite **same porosity!**
- ❑ For larger sizes the neck - modulated is **mechanically unstable**.

Thermal Conductivity: Nanoporous Graphene

Results: κ -values



- Along the flow direction phonons are restricted in smaller “channels”, as the diameters increase (to keep porosity constant for larger lengths)

Conclusions:

- Large-length behaviour of κ of pristine 1L graphene is an open debate: **need ~mm orders of magnitude!**
- Perforation dramatically reduces κ even for small porosities
- Porosity is not the only influencing factor
- Modulation of the pore diameter affects more
- Restriction of phonon “pathways” along heat flow

Future Prospect:

➤ Thermal Rectification:

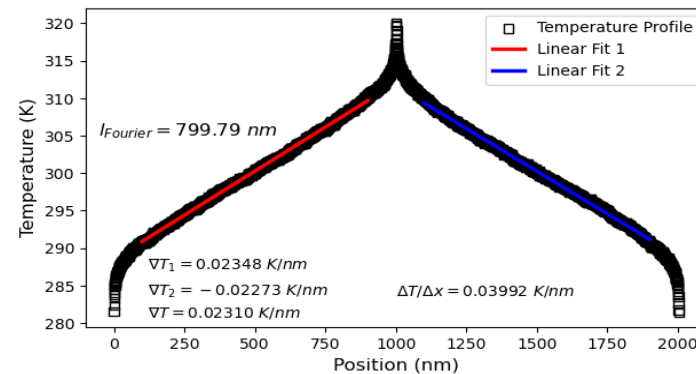
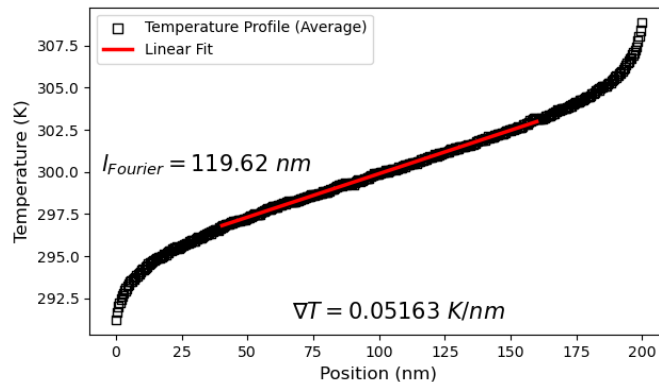
- Nanoperforated 2D structures
- Have found Rectification Ratio of **~6%**
- Extend study to more materials (hBN, TMDC's, multilayered, etc.)
- Possibly combine with experimental work

THANK YOU!!

Thermal Conductivity: Non-Equilibrium Method

Variations:

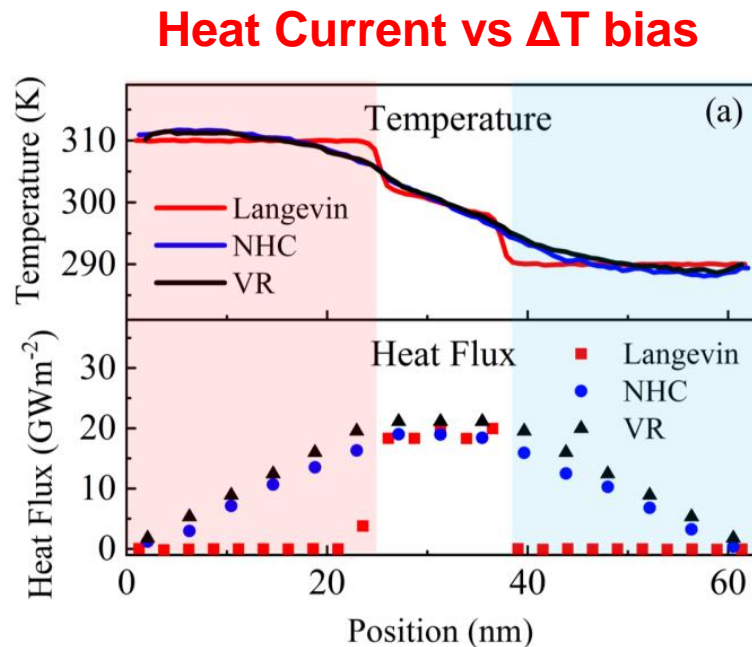
Fixed-ends NEMD (fNEMD) vs Periodic NEMD (pNEMD)



- The pNEMD method avoids possible artefacts caused by the clamped-ends, but x2 computational cost
- For larger characteristic sizes (e.g. lengths between thermostats), the influence of the fixed ends becomes negligible

Appendix: Thermal Conductivity: Non-Equilibrium Method

Variations:



Different temperature and heat flux profiles, but does it always give the same results?

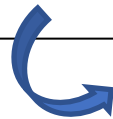
[Hu (2020) Phys. Rev. B, **101**, 155308]

Appendix: Microscopic Theory of Heat Transport

Thermal Conductivity:

$$J_h = \frac{1}{N\Omega_c} \sum_{\vec{q}j} \hbar\omega_{\vec{q}j} v_{\vec{q}j} n_{\vec{q}j}$$

Heat Flux (Harmonic Approximation)



Significant only for acoustic phonon branches (non-flat)

Acoustic Phonons carry most of the heat flux

Single Mode Approximation: Within steady state, each non-equilibrium phonon 'sees' the other phonons in equilibrium → no repopulation after scattering → heat is dissipated at each scattering event

$$\kappa^{SMA} = \frac{\hbar^2}{N\Omega_c} \sum_{\nu} C_{\nu,\nu} v_{\nu}^2 \tau_{\nu}^{SMA}$$

Not valid when momentum-preserving processes dominate

*In these cases, we solve the full Boltzmann Transport Equation!
Obtain a much higher thermal conductivity*

Appendix: Size Dependence of κ

Kinetic Model:

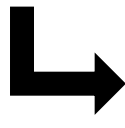
$$\Gamma_{\text{boundary}} \propto \frac{v_g}{L} \quad (\text{Ziman Model})$$

$$\frac{1}{\kappa} = \frac{a^3}{4k_B \bar{v}} \left(\frac{1}{l_\infty} + \frac{2}{L} \right)$$

l_∞ : Intrinsic Phonon MFP

L : Characteristic length (e.g. length between thermostats)

[Schelling et al, Phys. Rev. B 65 144306 (2002)]


$$\frac{1}{\kappa} = a + \frac{b}{L}$$

Assumptions:

□ Phonon gas kinetic model (Averaged phonon quantities)

□ $\Gamma_{\text{total}} = \Gamma_{\text{intrinsic}} + \Gamma_{\text{boundary}} \Rightarrow \frac{1}{l_{\text{eff}}} = \frac{1}{l_\infty} + \frac{2}{L}$

THANK YOU!