

From Order to Disorder: Assessing Thermal Properties in Amorphous Graphene with Machine Learning-Driven Simulations

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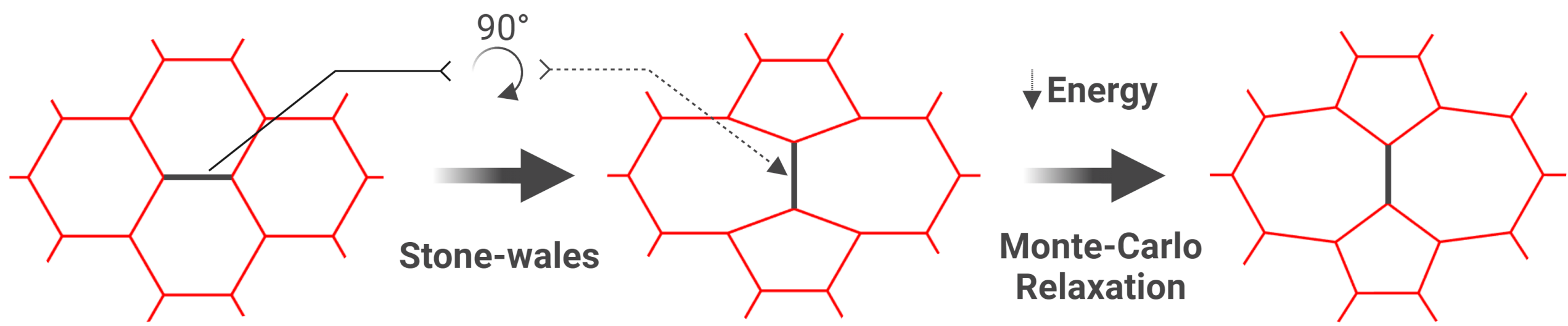
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Abstract

The study of thermal properties in amorphous graphene presents unique challenges and opportunities for advancing materials science and engineering. Accurately and efficiently representing the potential energy surface (PES) of amorphous materials is crucial for precise thermal transport calculations but remains a significant challenge. Our work addresses this gap by leveraging the Neuroevolution potential (NEP4), a high-fidelity machine learning interatomic potential (MLIP) specifically trained on amorphous graphene, which benefits from GPU acceleration [1]. We generated amorphous graphene structures incorporating Stone-Wales defects via a Monte Carlo algorithm, enabling controlled exploration of disorder in carbon-based materials. Using the homogeneous non-equilibrium molecular dynamics (HNEMD) method, we determined the thermal conductivity tensor and decomposed the thermal conductivity κ into contributions from in-plane and out-of-plane vibrational modes. The HNEMD simulations provided spectrally decomposed thermal conductivity using the virial-velocity correlation function [2]. We also evaluated the dispersion relation for amorphous graphene through current correlation functions over q points, utilizing spherical q-point sampling and averaging techniques [3]. Additionally, Density of States (DOS) and Phonon Participation Ratio (PPR) plots were generated to elucidate the role of disorder in 2D amorphous graphene. By adopting this approach, our study not only adeptly navigates the computational hurdles associated with the intricate nature of amorphous graphene but also sets a new precedent for the accurate, efficient investigation of thermal properties in disordered carbon materials.

Formation of Amorphous Graphene via KMC Simulation



Kinetic Monte Carlo (KMC) algorithm was employed to generate amorphous graphene structures, beginning with a perfect hexagonal lattice. In each simulation step, a random atom and a neighboring atom, within a cutoff distance of 1.85 Å, were selected. These atoms underwent a Stone-Wales (SW) transformation, involving a 90° rotation of the bond between them. The acceptance of the SW transformation was determined by two criteria:

■ **Topological Constraint:** The resulting structure must retain threefold coordination for all atoms. Failure to meet this condition resulted in the rejection of the transformation.

■ **Energetic Criteria:** When the coordination condition was satisfied, the transformation was accepted with a probability defined by the Boltzmann factor,

$$w = \begin{cases} 1, & \text{if } \Delta E \leq 0 \\ \exp(-\beta \Delta E), & \text{if } \Delta E > 0 \end{cases} \quad (1)$$

here $\beta = (k_B T)^{-1}$ and $\Delta E = E_{\text{new}} - E_{\text{old}}$. For cases where $\Delta E > 0$, a random number $z \in [0, 1)$ was generated, and the transformation was accepted if w exceeded z ; otherwise, the system retained its previous configuration. Post-transformation, the structures were relaxed using a Monte Carlo relaxation algorithm to minimize their energy.

Structure Characterization

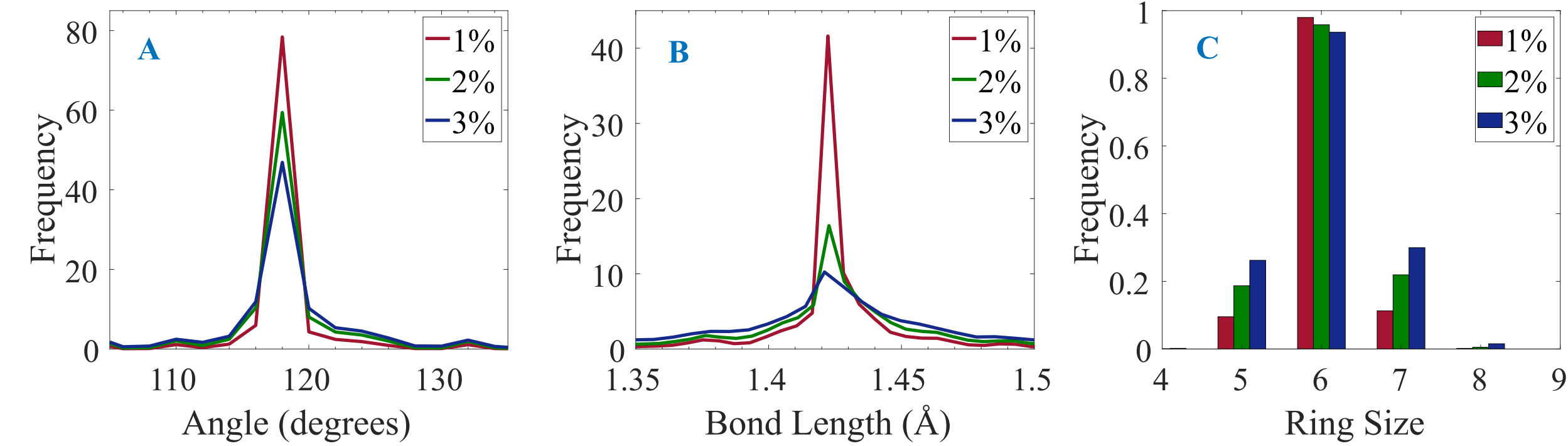


Fig 1: (A) statistical distribution of bond angles; (B) statistical distribution of the C-C bond length; (C) Ring statistical distribution in a-G samples;

Four structures were created for each defect concentration. These structures were then characterized, and subsequent calculations were performed. The resultant characterization and heat transport calculations for each defect concentration were obtained by averaging the data from the four structures.

Heat transport calculations

The homogeneous non-equilibrium molecular dynamics (HNEMD) method for heat transport was utilized to determine the thermal conductivity tensor and enabled κ to be decomposed into contributions from in-plane and out-of-plane vibrational modes. In this method, an external force of the form is added to each atom i , driving the system out of equilibrium. The driving force will induce a non-equilibrium heat current $\langle \mathbf{J} \rangle_{\text{ne}}$ linearly related to F_e :

$$\frac{\langle \mathbf{J}^{\mu}(t) \rangle_{\text{ne}}}{TV} = \sum_v \kappa^{\mu\nu} F_e^{\nu}, \quad (2)$$

where $\kappa^{\mu\nu}$ is the thermal conductivity tensor, T is the system temperature, and V is the system volume. In the framework of the HNEMD method, one can also calculate spectrally decomposed thermal conductivity (or conductance). One first calculates the following virial-velocity correlation function and its fourier transform pair.

$$K(t) = \sum_i \langle \mathbf{W}_i(0) \cdot \mathbf{v}_i(t) \rangle, \tilde{K}(\omega) = \int_{-\infty}^{\infty} dt e^{i\omega t} K(t) \quad (3)$$

The spectrally decomposed thermal conductivity in the HNEMD method can then be obtained by the following relation, where F_e is the magnitude of the driving force parameter :

$$\kappa(\omega) = \frac{2\tilde{K}(\omega)}{VTF_e} \quad (4)$$

Thermal conductivity

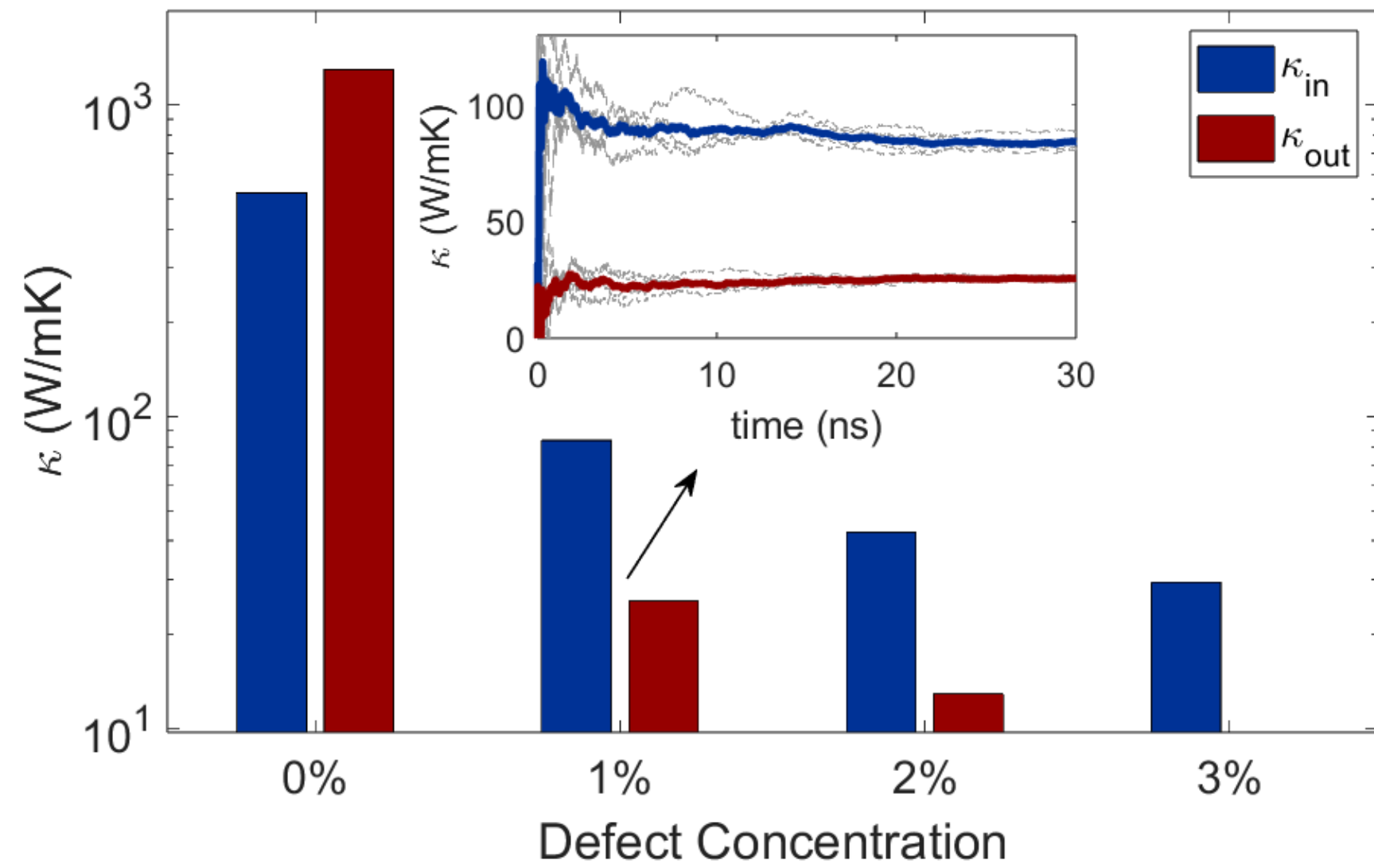


Fig 2: In-plane and Out-of-plane thermal conductivity contributions as a function of disorder (calculated from the last 10ns of the HNEMD simulations); Inset: HNEMD simulations (the red and blue lines are averaged across 4 separate runs signified by the Grey lines)

In amorphous graphene, the dominant contribution to thermal conductivity comes from the in-plane vibrational modes, rather than the out-of-plane modes, which is a notable contrast to the behavior observed in pristine graphene. This distinction is significant because the structural disorder in amorphous graphene disrupts the coherence of out-of-plane phonons, leading to reduced thermal transport in that direction. Meanwhile, the in-plane vibrational modes, which are less affected by this disorder, continue to contribute significantly to thermal conductivity.

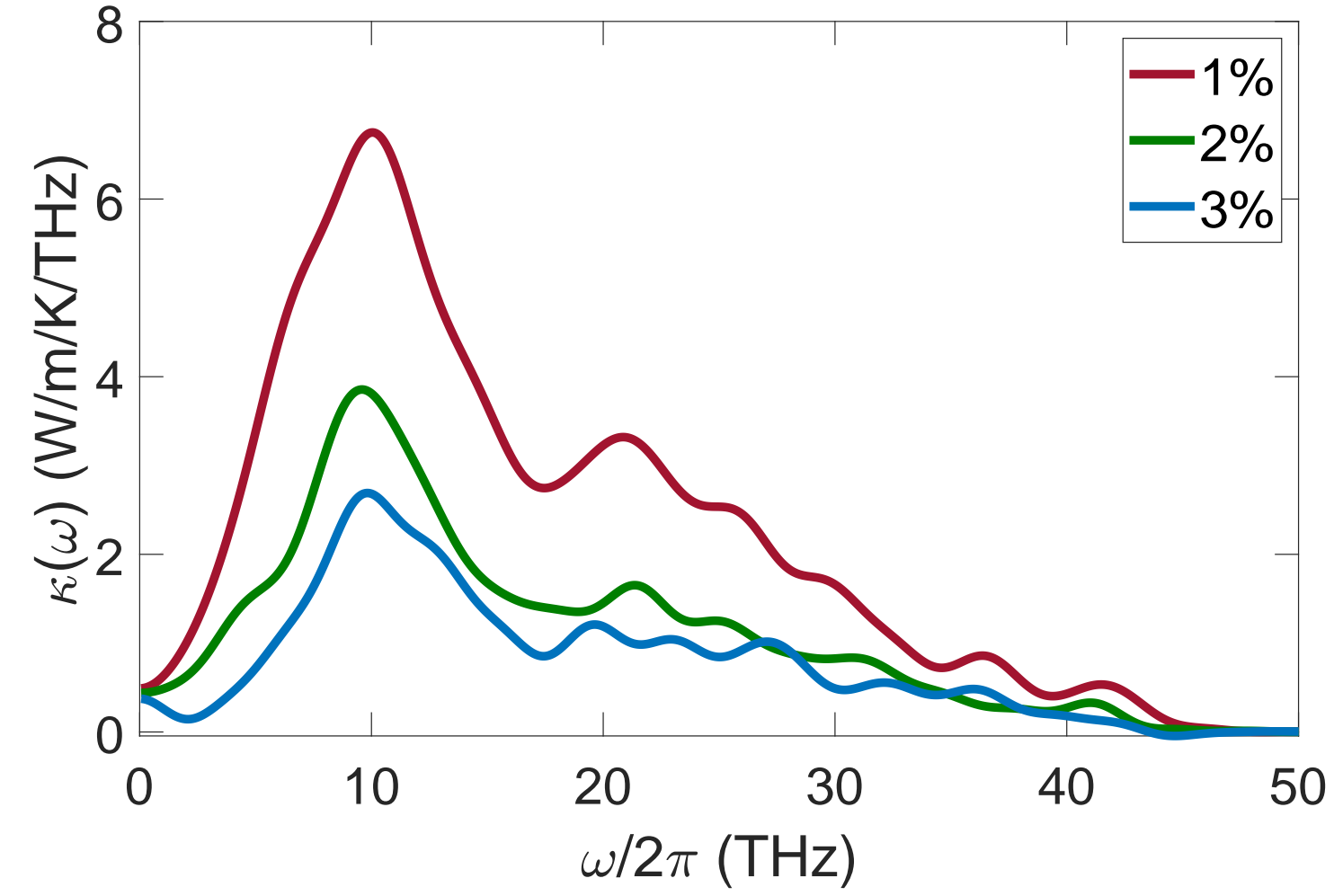


Fig 3: Spectral thermal conductivity $\kappa(\omega)$; Each line represents an average of 4 runs

Dispersion relation

Unlike pristine graphene, where low-frequency modes, dominated by out-of-plane vibrations, substantially contribute to thermal conductivity due to a higher density of states, amorphous graphene shows minimal contribution from these modes.

This difference explains the observed variation in thermal conductivity contributions between the in-plane and out-of-plane directions. Figures 3 and 4 illustrate these points, showing the varying defect concentrations and their effects, with 0% representing pristine graphene.

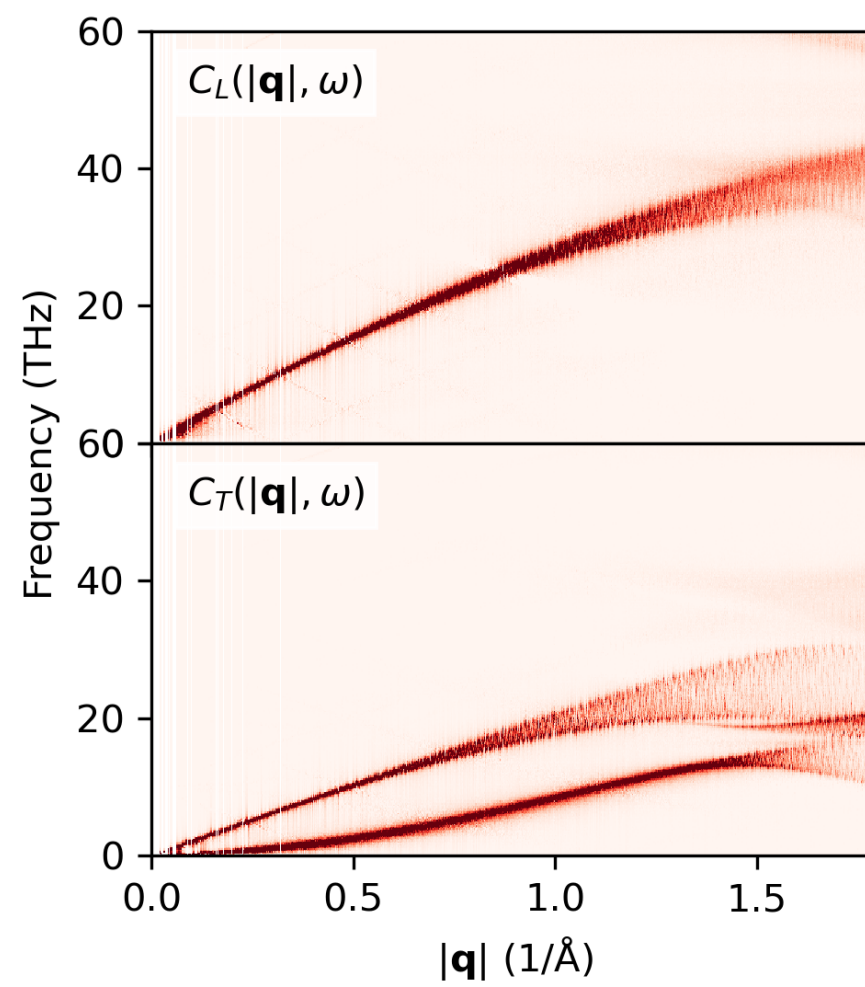


Fig 4: Longitudinal and transverse current correlation heatmaps

The Phonon Participation Ratio (PPR) is a measure used to understand the localization of phonon modes in materials. It is particularly useful in the study of disordered systems like amorphous materials. The PPR was calculated from the localized phonon density of states (DOS):

$$\text{PPR} = \frac{(\sum_{i=1}^N \text{DOS}_i^2)^2}{N \cdot \sum_{i=1}^N \text{DOS}_i^4} \quad (5)$$

Phonon participation ratio

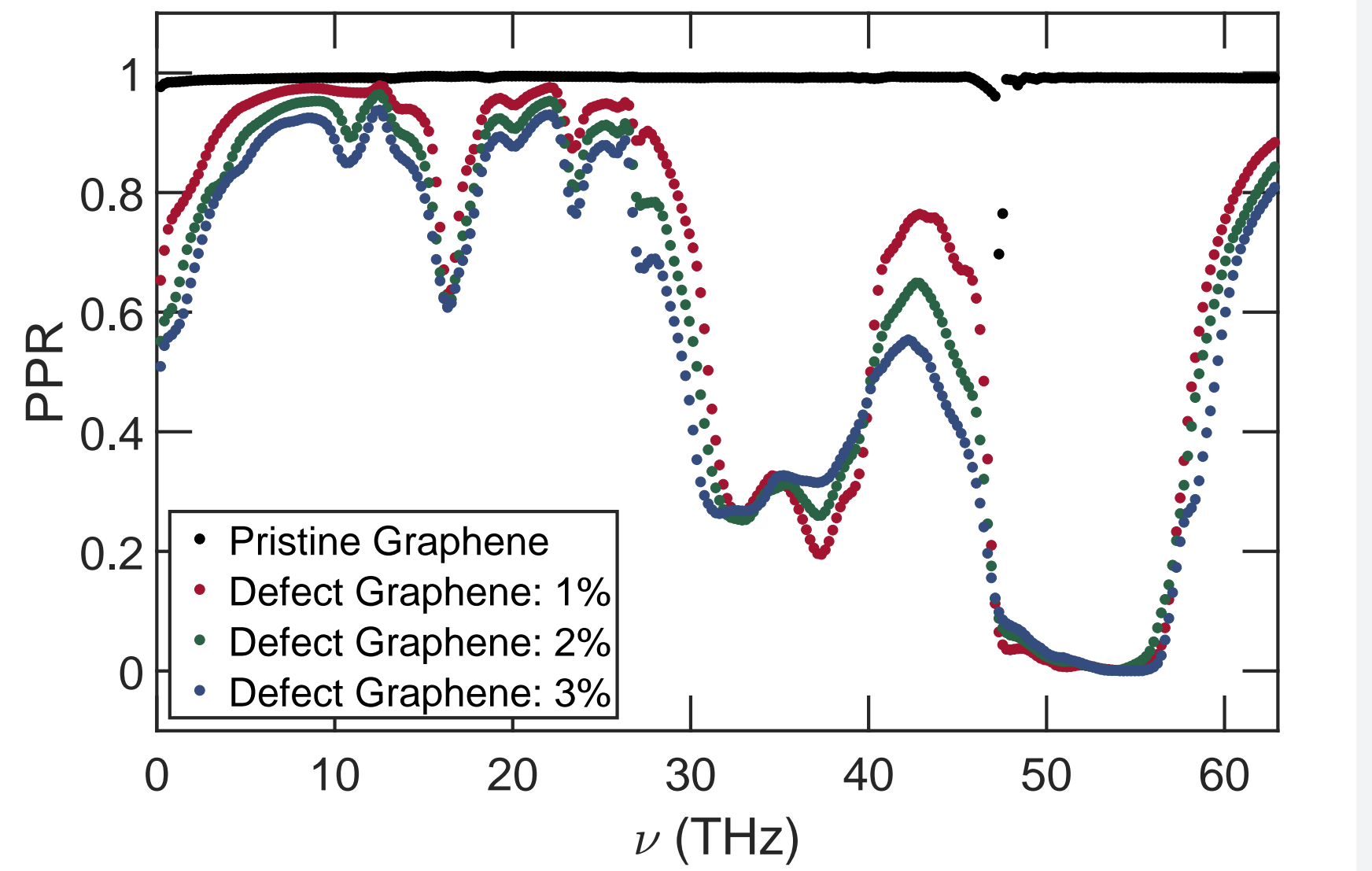


Fig 5: Phonon participation ratio as a function of frequency

The differences in thermal conductivity between amorphous and pristine graphene can be attributed to the Phonon Participation Ratio (PPR). The attached PPR graph shows that amorphous graphene has a low PPR at low frequencies, indicating localization of phonon modes, particularly out-of-plane vibrations. This localization reduces the contribution of these low-frequency modes to thermal conductivity, in contrast to pristine graphene, where these modes play a more significant role.

References

- [1] Fan et al, Journal of Chemical Physics **157**, 114801 (2022)
- [2] Gabourie et al, Phys. Rev. B **103**, 205421 (2021)
- [3] Fransson et al, Advanced Theory and Simulations **4**, 2000240 (2021)