



# Molecular junctions for thermal transport between graphene nanoribbons: Covalent bonding vs. interdigitated chains



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## ABSTRACT

Proper design and manufacturing thermal bridges based on molecular junctions at the contact between graphene platelets or other thermally conductive nanoparticles would provide a fascinating way to produce efficient heat transport networks for the exploitation in heat management applications. In this work, using Non Equilibrium Molecular Dynamics, we calculated thermal conductance of alkyl chains used as molecular junctions between two graphene nanoribbons, both as covalently bound and as Van der Waals interdigitated chains. Effect of chain length, grafting density, temperature and chain interdigitation were systematically studied. A clear reduction of conductivity was found with increasing chain length and decreasing grafting density, while lower conductivity was observed for Van der Waals interdigitated chains compared to covalently bound ones. The importance of molecular junctions in enhancing thermal conductance at graphene nanoribbons contacts was further evidenced by calculating the conductance equivalence between a single chain and an overlapping of un-functionalized graphene sheets. As an example, one single pentyl covalently bound chain was found to have a conductance equivalent to the overlapping of an area corresponding to about 152 carbon atoms. These results contribute to the understanding of thermal phenomena occurring within networks of thermally conductive nanoparticles, including graphene nanopapers and graphene-based polymer nanocomposites, which are of high interest for the heat management application in electronics and generally in low-temperature heat exchange and recovery.

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## 1. Introduction

In the last decade, a great deal of research interest has been devoted to graphene [1,2], owing to its amazing characteristics: electrical properties [3,4], thermal conductivity [5–7], mechanical stiffness and strength [8] which are on the top of the known materials. Since its discover, significant effort has also been devoted to exploring graphene and graphene-related materials [9] for various applications, such as in energy storage [2], nanoelectronics [2], sensors and functional materials [1,2]. In several of these fields, thermal conductivity of graphene may play an important role whenever dissipation of heat is crucial. In particular, in high-performance electronics, heat removal has become a critical issue [7]. Owing to their ultrahigh thermal conductivity, graphene and graphene-related materials have been suggested as candidates in nanomaterials for efficient thermal management.

Significant efforts have been devoted to the preparation of nanocomposite materials embedding graphene and graphene-

related materials. However, graphene properties are only partially reflected in nanocomposites [10], where thermal transport is not limited by the thermal conduction of graphene itself but rather by the high thermal resistance at the contact between nanoplatelets [11–13]. In fact, the reach of a percolation threshold, a value over which the particles inside a composite material get physically in contact, is not enough to improve radically the overall thermal conductivity [14]. Indeed, for every single contact, physical limitations in phonon transfer have to be taken into account, leading to a highly inefficient heat transfer across the nanoparticles network that characterize nanocomposites materials [15]. Compatibilization between nanoparticles or between nanoparticles and matrix have been suggested by various authors [16–18] as a possible solution to decrease interfacial resistance. A chemical compatibilization is typically obtained by the functionalization of nanoplatelets with molecules able to build chemical bridges towards the matrix. Different functionalization methods are possible for graphene, either through covalent or non-covalent surface modifications [19]. Covalent functionalization leads to rehybridization of a fraction of the carbon atoms in graphene, thus introducing defects in the  $sp^2$  graphene bidimensional lattice [20], creating an

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alteration of the pristine phonon scatter modes and therefore reducing the conductivity of the nanoplatelets [19]. On the other hand, the non-covalent interactions between the platelets and suitable molecules [19] does not damage the atomic structure, so the thermal properties of the graphene layers are preserved. However, the weak forces involved between the molecules can still be a remarkable bottleneck in thermal conductivity [15].

Computational tools, including first principle quantum calculations and Molecular Dynamics (MD), have been crucial to study and evaluate the interfacial properties between graphene platelets as well as between graphene and the matrix in a nanocomposite. In an experimental and computational work, Han et al. [10] exploited silane functionalization to reduce thermal resistance between substrate and supported graphene nanoflakes. Both computational and experimental results agree that the bridging molecule density tuned the thermal conductivity leading to an heat conduction enhancement. A Reverse Non-Equilibrium MD (RNEMD) approach was proposed from Gao and Müller-Plathe [21] using bonded fragments of Polyamide 6,6 backbone molecule between graphene sheets. The interfacial and planar thermal boundary conductance (TBC) were evaluated as a function of grafting density and molecule length effect, finding an optimum density value. These results were used in EMA (Effective Medium Approach) to develop a predictive model to extrapolate the macroscopic conductivity of a massive nanocomposite. Liu et al. [22] used  $C_2H_4$  linkers to joint two partially overlapping graphene nanoribbons. Thermal conductance and thermal jump were related to the position and amount of linkers used in the simulations. An inversely proportional relation was found between the thermal jump across the junction and the number of cross-linkers. The related phonon spectra were described as effective mainly on the out of plane vibrational modes due to a mismatch between the in-plane vibrational modes of the linkers and the graphene ones. Chen et al. [23] simulated the use of external force and chemical functionalization through  $CH_2$  linkers across stacked nanotubes to investigate thermal transport, the conductance going through a maximum at the optimal concentration of linkers. A single molecular junction analysis was studied by first-principles full quantum calculations by Li et al. [24] to evaluate the thermal conductance in short alkanes between two graphene nanoplatelets. The thermal conductance as a function of the molecule stretching state was evaluated, determining that an extended junction almost doubles the thermal conductance compared to the compressed form. In a more recent paper, the same group addressed the comparison between covalently bound molecular junction vs. non-covalently bonded  $\pi$ -stacked systems, showing strong suppression of phonon transport, leading to about 95% reduction in thermal conductance for  $\pi$ -stacked junctions, compared to the covalent one [25]. In this work, we investigate the effect of edge grafted short  $(CH_2)_n$  alkyl chains as a thermal bridge between two adjacent graphene nanosheets, by the calculation in interfacial conductance via classic Non Equilibrium Molecular Dynamics simulations (NEMD). In particular, the effect of chain length and grafting densities were systematically studied for alkyl chains covalently bound on both graphene nanoribbons. Furthermore, comparisons were done between covalently bonded molecules and interdigitated ones (chains covalently grafted on one graphene sheet and interacting with opposite chains via van der Waals forces), as well as with non-functionalized partially overlapped graphene nanoribbons.

## 2. Theory and computational methods/MD modeling

Classical Molecular Dynamics (MD) calculations was used on LAMMPS (Large-scale Atomistic Molecular Massively parallel Simulator) package code which uses Velocity Verlet integration algo-

rithm to recalculate velocities and positions of the atoms. The 2<sup>nd</sup> generation of the AIREBO (Adaptive Intermolecular Reactive Empirical Bond Order) [26] force field was employed due to its thermal transport capability as described from a wide literature on carbon and graphene family structures [27–29] and hydrocarbons [30].

The model topology was composed by two  $\approx 100$  Å graphene nanoribbons in zigzag configuration joint from alkyl chains chemically grafted between the two graphene sheets, as shown in Fig. 1C. The width (Y axis) was set to  $\approx 50$  Å, while the total length of simulation box (X axis) varied from 193 Å to 200 Å, depending on the length of the chains, in a stretched configuration, among the sheets. The thickness of the sheet (Z axis) was assumed 3.45 Å from the Van der Waals (VdW) diameter of the carbon atom and the C–C is 1.41 Å as average value, very close to which reported from Diao et al. [29].

NEMD calculations were performed by the application of Nosé-Hoover thermostats at the two ends of the simulation box, which coincides with the graphene sheets ends. The Hot (310 K) and the cold bath (290 K) of the thermostats regions (last 10 Å) are set as NVT canonical ensemble (constant Number of atoms, Volume and Temperature) while the slabs among the two thermostats ran under NVE (constant Number of atoms, Volume and Energy) condition. All the simulations were carried out for 5 ns using a 0.25 fs timestep. An initial 500 ps of thermal equilibrium at 300 K was set as previously reported by Mortazavi et al. [31,32]. A second 500 ps stage of transient non-equilibrium heating, followed with the purpose to reach a constant heat flux. After those initial stages, the constant energy flowing through the thermostats [33] started recording. The thermal flow inside NVE regions is derived from the slope of energy versus time plots [31]. Additional investigations involved different equilibrium and run temperatures: 200 K; 400 K; and 500 K while the  $\Delta T$  at the thermostats was kept constant to  $\pm 10$  K as previously described. In this range the temperature quantum correction suggested at lower temperatures by classic Molecular Dynamic simulation is considered negligible [34].

To evaluate the temperature variation inside the sample along the thermal flow, the simulation box length was virtually split transversally into 22 thermal layers. The temperature of each thermal layer was then computed using the relation in Eq. (1),

$$T_i(\text{slab}) = \frac{2}{3N_i k_B} \sum_j \frac{p_j^2}{2m_j} \quad (1)$$

In Eq. (1),  $T_i(\text{slab})$  is the temperature of  $i^{\text{th}}$  slab,  $N_i$  is the number of atoms in  $i^{\text{th}}$  slab,  $k_B$  is the Boltzmann's constant,  $m_j$  and  $p_j$  are atomic mass and momentum of atom  $j$ , respectively. All the slabs temperatures were then time-averaged to the simulation runtime excluding the non-linear regions at the nanoribbon boundary, i.e. the ones close to the thermostats and the ones coupled to the junction. The thermal boundary conductance (TBC) of the model,  $G$ , expressed in pW/K, was evaluated using the Eq. (2).

$$G = \frac{q_x}{\Delta T} \quad (2)$$

Here  $q_x$  is the thermal flow derived from the energy versus time plot slope and  $\Delta T$  is the thermal difference across the jump, as projection of the two linear fit of the temperature-length plot in the junction middle point.

The single chain thermal conductance,  $G_{\text{chain}}$ , expressed in pW/K was calculated through the Eq. (3).

$$G_{\text{chain}} = \frac{q_x}{n \cdot \Delta T} \quad (3)$$

where  $n$  is the number of molecules bridging the two adjacent graphene nanoribbons.

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