Interflake thermal conductance of edge-passivated graphene

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Based on the quantum-junction transmission/Green’s function formalism and the dynamical matrix/DF, we find the phonon wave features result in bimodal resonant transmission in the interflake conductance of H or O edge-passivated graphene. The low-frequency resonant transport mode is due to the weak interaction between the flakes, while the high-frequency resonant transport mode depends on the passivated species and brings the temperature dependence. The phonon transport polarized in the transport directions is dominant because of the asymmetric charge distribution of $\ldots$C–O–H–C$\ldots$ and this contributes to the conductance. Thermal conductance decreases due to the passivation junctions, and the electronic thermal conductance becomes negligible except for the O–H junction at high temperatures.

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I. INTRODUCTION

The bottleneck in the electronic and phonon transport of graphene-based composites,\textsuperscript{1} promising for their superior electrical and thermal transport properties,\textsuperscript{2–4} is in the interflake resistance. This is due to the very weak interflake interactions compared to the strong covalent bonds in the graphene flakes. Here, we examine the interflake thermal energy transport using the quantum thermal energy transport treatments, while considering that applications of graphene may include its inevitable passivated form. The graphene flakes are commonly edge (and side) passivated with various atomic groups,\textsuperscript{5,6} and these edge passivations influence the graphene properties.\textsuperscript{7} We consider those O or H passivations of graphene edge-passivated graphene. The low-frequency resonant transport mode is due to the weak interaction between the flakes, while the high-frequency resonant transport mode depends on the passivated species and brings the temperature dependence. The phonon transport polarized in the transport directions is dominant because of the asymmetric charge distribution of $\ldots$C–O–H–C$\ldots$ and this contributes to the conductance. Thermal conductance decreases due to the passivation junctions, and the electronic thermal conductance becomes negligible except for the O–H junction at high temperatures.

II. PHONON THERMAL TRANSPORT

A. NEGF formalism

In analogy to the NEGF for the electronic transport,\textsuperscript{19} we calculate the Green’s functions using the Hessian matrix with elements $\partial^2 E/\partial x_i x_j$ ($E$ is the energy and $x_i$ and $x_j$ are the $i$th and $j$th degree of freedom).\textsuperscript{20} These matrices are calculated using the density functional theory (DFT) calculation with finite differences (0.015 Å) provided in the Vienna \textit{ab initio} simulation package (VASP).\textsuperscript{21} The equilibrium structures for the Hessian matrix calculations are obtained by the relaxation of the considered structure with the conjugate gradient (CG) method, and all the atoms are relaxed until the maximum absolute force is less than 0.01 eV/Å. The DFT calculation in VASP employs the Perdew-Burke-Ernzerhof (PBE) parametrization of the generalized gradient approximation (GGA) for exchange and correlation\textsuperscript{22} with the projector augmented wave method.\textsuperscript{23,24}

The relaxed structures of the joined, passivated graphene flakes (zigzag edges) show restructuring within the first four C atoms from the edge (and negligible difference from the bulk, within less than 0.01 Å, beyond that). In the Green’s function formalism, we consider a central region connected to two semi-infinite regions representing the bulk graphene, as shown in Fig. 1. The central region is divided into two “contact cells or electrodes” on each side with four carbon atoms and a “scattering region or junction” with four carbon atoms on each side of the passivated atoms, also shown in Fig. 1. We consider the interaction of the nearest-neighbor cells only and the energy flow from the left to the right with the temperatures $T_L$ and $T_R$ prescribed. The interatomic distance ($d$) is 1.42 Å from the DFT relaxation and the width ($a$) and the height ($b$) of the periodic bulk cell is $3d$ and $3^{1/2}d$. Since the interflake contact is 1D (in the $y$ direction), in addition to the carriers with the transport direction ($\kappa_y^* = 0$, where $\kappa_y^* = \kappa_y b$ and $\kappa_y$ is the wave number in the $y$ direction), we include other transport directions ($\kappa_y^* \neq 0$). So, we sample for $\kappa_y^*$ considering the upper and lower neighboring cells in the $y$ direction. From the orthogonalized dynamical matrix with elements $-1/(m_i m_j)^{1/2} (\partial^2 E/x_i x_j)$ ($m_i$ and $m_j$ are the mass of atoms),\textsuperscript{10} we extract the matrix of the central region with $\kappa_y^*$ given as\textsuperscript{25}

$$K_{CC}(\kappa_y^*) = \begin{bmatrix} K_{ll}(\kappa_y^*) & K_{lw}(\kappa_y^*) & 0 \\ K_{wl}(\kappa_y^*) & K_{ww}(\kappa_y^*) & K_{wv}(\kappa_y^*) \\ 0 & K_{rv}(\kappa_y^*) & K_{rr}(\kappa_y^*) \end{bmatrix}.$$
where for each element $K_{ij}(\kappa_y^\pm) = K_{M,U}\ e^{-i\kappa_y^\pm} + K_{M,M_i} + K_{M,L}\ e^{i\kappa_y^\pm}$. Here, $i$ and $j$ can be $l$, $c$, or $r$ (for the left electrode, the scattering region, or the right electrode). The subscripts, $U$, $M$, and $L$ represent upper, middle, and lower cells in the vertical ($y$) direction. $K_{M,M_i}$ is the dynamical matrix for the interaction between the $i$ and $j$ cells that are in the middle strip, and $K_{M,U}$ (or $K_{M,L}$) is the matrix for the interaction between the $i$ cell in the middle strip and the $j$ cell in the upper (or lower) strip. To represent the interaction of semi-infinite bulk graphenes, we calculate the self-energy ($\Sigma_y^P$ or $\Sigma_y^R$) employing the decimation technique suggested by Lopez-Sancho et al.\textsuperscript{26} The phonon-retarded Green’s function of the central region is given by\textsuperscript{27}

$$G^R(\kappa_y^\pm, \omega_p) = \left[(\omega_p + i\eta)^2 \mathcal{I} - K_{CC}(\kappa_y^\pm) - \Sigma^L(\kappa_y^\pm, \omega_p) - \Sigma^R(\kappa_y^\pm, \omega_p)\right],$$

(2)

where $\omega_p$ is the phonon frequency and $\eta$ is an infinitesimal number corresponding to the phonon energy dissipation.\textsuperscript{16} The phonon transmission across the central region is written as\textsuperscript{19,28}

$$\tau_p(\kappa_y^\pm, \omega_p) = \text{Tr}[\Gamma_L(\kappa_y^\pm, \omega_p)G^R(\kappa_y^\pm, \omega_p)\Gamma_R(\kappa_y^\pm, \omega_p)]G^A(\kappa_y^\pm, \omega_p)],$$

(3)

where $G^A$ is the phonon advanced Green’s function equivalent to $(G^R)^\dagger$ and $\Gamma_L$ ($\Gamma_R$) is the energy-level broadening function caused by the left (right) electrode and described by

$$\Gamma_{L/R}(\kappa_y^\pm, \omega_p) = i\left[\Sigma^L_{L/R}(\kappa_y^\pm, \omega_p) - \Sigma^A_{L/R}(\kappa_y^\pm, \omega_p)\right].$$

(4)

With these Green’s functions the phonon density of states is\textsuperscript{27}

$$D_p(\kappa_y^\pm, \omega_p) = \frac{2\omega_p}{\pi} \text{Im}[\text{Tr}[G^R(\kappa_y^\pm, \omega_p)]].$$

(5)

**B. Transmission**

For calculations of the self-energy and the bulk graphene properties, the scattering region is replaced with the same structure as the left and right electrodes. The graphene phonon dispersion is obtained using the dynamical matrix from the DFT calculations with the lattice dynamics relation with the

![Diagram](image-url)
Born-von Karman boundary condition\textsuperscript{30}
\[ \omega_p^2 (\kappa_x^*, \kappa_y^*, \alpha) = \mathbf{K}_{cc} (\kappa_x^*) - \mathbf{K}_{cl} (\kappa_x^*) e^{-i \kappa_y^*} = 0, \]
where \( \kappa_x^* \) is the dimensionless wave number in the transport direction (\( \kappa_x^* = \kappa_x a \) and \( \kappa_x \) is the wave number in the \( x \) direction), \( \alpha \) is the polarization (four atoms in each unit cell and three degrees of freedom per each atom and the number of total branches (\( \alpha \)) is 12], \( s \) is the eigenvector, and \( \mathbf{K}_{cc} \) (\( \mathbf{K}_{cl} \)) is the dynamical matrix for the interaction between the left (right) electrode and the scattering region. The phonon dispersion found from Eq. (6) is unfolded to show it for the primitive cell of graphene composed of two C atoms. The dispersion curve from \( \Gamma \) to \( M \) (\( \kappa_u = 0 \)) is in good agreement with the experiments,\textsuperscript{29} as demonstrated in Fig. 2(a). Because the passivated atoms are linearly aligned and the transport with the \( \kappa \) vector (wave vector) propagating in the transport direction is expected to dominate (when expanding to the longer functional groups, it would be more dominant), we, first, focus on the dominant transport direction (\( \kappa_x^* = 0 \)). In the ideal ballistic transport, when all modes are transmitted without scattering, the phonon transmission is the number of modes at frequency \( \omega_p \)\textsuperscript{30} and the NEGF transmission for graphene is similar to this ballistic limit with a small \( \eta \), as shown in Fig. 2(b). Phonons incident from the graphene are transported through the passivated edges in the three junctions with significantly suppressed transmissions. The \( \tau_p \) for the O–H junction is the largest among the three, and in all three the phonons with the low energy (less than 30 meV) and some high energies have relatively high transmissions.

### C. Polarization

Since the dynamical matrices demonstrate that the couplings between the different polarizations are weak, we consider the three polarizations separately, which are the longitudinal (L or the transport direction), transverse in plane (T), and out-of-plane (Z) directions. Figures 3(a)–3(c) show the phonon density of states and transmissions, as a function of phonon energy, for the three polarizations of wave vectors with the transport direction for the O–H interflakes. The \( D_p \) for the carbon atoms near the flake edges are distorted compared to the bulk \( D_p \), due to the restructuring in the edges and the interaction with the passivated atoms.\textsuperscript{31} The \( D_p \) for the edge atoms have sharp peaks due to the asymmetric coupling and the nonperiodicity, and their frequencies mostly depend on the interaction with the nearest C atoms [\( \sim (\Gamma_{ij}/m_{ij})^{1/2} \), where \( \Gamma_{ij} \) is the force constant and \( m_{ij} \) is the reduced mass].\textsuperscript{32} Because

![Graphene thermal conductance](image-url)
of the much smaller mass of the H atom compared to O, H acquires high frequencies in spite of the stronger interaction of O with the nearest C atom.

The asymmetric charge distribution in the O–H is shown from the Bader charge analysis as Fig. 3(d), which shows the isosurface of the charge density \( \rho_e^* \) for the right region, and \( \rho_e^* = 0.02 \), the charge associated with each atom according to Bader partitioning \( \rho_e^* \), and the net charge \( \bar{\delta} \) which is the difference from the valence charges. This induces the Coulomb interaction between the two flakes, and the interaction with the transport direction enhances the phonon transport polarized with the L direction. Thus, in the O–H junction, the phonon transmission in the L polarization is much larger than the other polarizations (T and Z), and most of the phonon energy is transported by the phonons polarized in the L direction. Differing from the O–H junction, the O–O and H–H junctions cause much weaker coupling between the two flakes and do not show the dominance of the phonons with a particular polarization (because the transport in the L polarization is suppressed as much as the other directions).

The transmission in the L polarization in the O–H junction is bimodal showing the broad peak at the low frequency and the sharp peak at the high frequency for the O-resonant vibration. Only phonons with the energies available in the graphene reservoirs can contribute to the phonon transport and the frequencies for H are over the cutoff of the graphene (L) or are in the phonon bandgaps (in the T and Z polarizations), so the phonons with the H-resonant frequencies cannot contribute to the transport for wave vectors vectors with the transport direction. Despite the absence of the phonon energy states in the H atom, the phonons with the resonant frequency of O can be transmitted through the tunneling. This resonant tunneling is enhanced by the strong interaction of the passivated atoms with the opposite flake, so the L-polarized phonon has a higher \( \tau_p \) at the resonance of the passivated atom. The long-wave phonons with the low energy (resonant with the weak couplings between two flakes) are less scattered and dominate in the phonon transport. This bimodal transport leads to different channels depending on the temperature (high-energy phonons have higher population at high temperature).

### D. Semiclassical transmission

In relating the semiclassical treatment to the NEGF, we calculate the \( \tau_p \) in the AMM employing the specular scattering as an analogy to the electromagnetic waves. In the AMM \(^{17}\), the phonon transmission is obtained with the acoustic impedance \( Z_p \) as

\[
\tau_{p,L/R,\text{AMM}} = \frac{4Z_{p,L}Z_{p,R}}{(Z_{p,L} + Z_{p,R})^2},
\]

where \( \tau_{p,L/R,\text{AMM}} \) is the phonon transmission from the left to right region, \( Z_{p,L} \) is the impedance for the left and \( Z_{p,R} \) is for the right region, and \( Z_p \) is commonly used as \( \rho u_p \), where \( \rho \) is the density and \( u_p \) is the phonon speed \( u_p \) is proportional to \( D_p^{-1} \) in 1D systems. Here, scattering is due to the mismatch in the phonon spectra (phonon speed, density, etc.). (The maximum transmission is unity with the same phonon properties for both sides, as in the bulk.) Because \( D_p \) in the central region is heterogeneous, due to the restructuring as confirmed in Fig. 3, we consider the phonon scattering at the interface of neighboring atoms \( (\tau_{p,i/i+1,\text{AMM}}) \), using the local \( \rho_{up} \propto D_p^{-1} \) and combine all interfacial \( \tau_{p,i/i+1,\text{AMM}} \) in the central region to find the overall transmission \( \tau_{p,\text{AMM}} \),

\[
\tau_{p,\text{AMM}} = \tau_{p,1/2,\text{AMM}}\tau_{p,2/3,\text{AMM}}...\tau_{p,17/18,\text{AMM}}
\]

Since the semiclassical treatments, e.g., the AMM applied here, assume a quasiparticle carrier, the wave natures (e.g., interference) are not addressed. In spite of that, we observe that \( \tau_{p,\text{AMM}} \) is in good agreement with the NEGF results as in Fig. 4, except for the high-frequency transmission by treating the atomic details with \( D_p \) at every atomic location in the scattering region. Small disagreement is ascribed to the omitted wave natures in the AMM and the simple combination that only counts the nearest-neighbor interactions, thus excluding the interference, the tunneling, and the multiple reflections and transmissions.

### E. Phonon conductance

In 1D transport with a given \( \kappa_y^* \), the phonon conductance is evaluated using the Landauer formula \(^{34,35}\),

\[
G_{p,1D}(\kappa_y^*) \text{ [W/K]} = \int_0^\infty \frac{d\omega_p}{2\pi} \text{Re} \rho_{up} \tau_p(\kappa_y^*,\omega_p) \left[ \frac{\partial f_{p}(\omega_p,T)}{\partial T} \right],
\]

where \( T \) is the temperature, \( \hbar \) is the the reduced Planck constant, the equilibrium Bose-Einstein distribution function is \( f_{p}(\omega_p,T) = \exp(\hbar \omega_p/k_B T) - 1 \)^{-1}, and \( k_B \) is the Boltzmann constant. To include contributions from all wave vectors (as well as \( \kappa_y^* = 0 \)), we sample \( \kappa_y^* \) values (200 points in the first
FIG. 5. (Color online) Phonon transmissions as functions of the component $\kappa^*_{y}$ in the wave vector space and the phonon energy for (a) bulk graphene, (b) O−H, (c) O−O, and (d) H−H junctions. The transmissions are symmetric and larger near the transport direction ($\kappa^*_{y} = 0$).

The phonon conductance per unit width ($G_{p,2D}$, W/m K) is calculated by use of Eqs. (9) and (10) with the transmission in Fig. 5 and, using the layer separation distance (0.335 nm) in the graphite as the thickness, we find the phonon conductance per unit area ($G_{p,3D}$, W/m² K), which is shown in Fig. 6(a). $G_{p,3D}$’s for the edge-passivated graphene junctions are largely suppressed to less than 1% of bulk graphene $G_{p,3D,Bulk}$ at 300 K (4.76 GW/m² K from this work) because only phonons with the low energy or the tunneled resonant energy can be transmitted through the interflakes, as shown in Fig. 6(b). Figure 6(c) shows the contribution of wave vectors to thermal conductance [$G_{p}(\kappa^*_{y}) = G_{p,1D}(\kappa^*_{y})/(bG_{p,2D})$ satisfying $\int_{-\pi}^{\pi} d\kappa^*_{y} G_{p}(\kappa^*_{y}) = 1$] and it confirms that the phonons with the transport direction are dominant. This is further clear for the passivated graphene junctions at lower temperature.

As heterostructure systems experience large decrease in the transport by the Kapitza resistance at the interfaces, the reduction in thermal conductance of the graphene junctions with the edge passivation drastically reduce the effective thermal conductivity of the graphene composite. The total thermal resistance of the linear chain of graphene flakes ($1/G_{p,3D,Chain}$) is the sum over the resistances for the graphene flakes and the interflakes junctions, i.e.,

$$\frac{1}{G_{p,3D,Chain}} = n_{j} \left( \frac{1}{G_{p,3D,GF}} + \frac{1}{G_{p,3D,j}} \right) + \frac{1}{G_{p,3D,GF}},$$

where $n_{j}$ is the number of the interflakes junctions in the chain and $G_{p,3D,GF}$ and $G_{p,3D,j}$ are the thermal conductance of the...
graphene flake and the interflake junction. With uniform length for the graphene flakes \( l_{GF} \), the effective thermal conductivity of the chain with sufficiently long length, \( L_c = (n_j + 1) l_{GF} \), is

\[
(k_{p,\text{Chain}}) = G_{p,\text{3D,Chain}} L_c = \frac{G_{p,\text{3D,GF}} G_{p,\text{3D,j}}}{G_{p,\text{3D,GF}} + G_{p,\text{3D,j}}} l_{GF}. \tag{12}
\]

Since the conductance calculated in this work is based on the ballistic transport, the thermal conductivity of graphene flakes depends on \( l_{GF} \) and the phonon mean free path \( \lambda_p \), i.e.,

\[
k_{p,\text{GF}} = G_{p,\text{3D,GF}} l_{GF} = G_{p,\text{3D,Bulk}} \frac{l_{GF} \lambda_p}{l_{GF} + \lambda_p}. \tag{13}
\]

The phonon thermal conductivity of undisrupted graphene \( k_{p,\text{Bulk}} \) (i.e., \( l_{GF} \rightarrow \infty \)) is

\[
G_{p,\text{3D,Bulk}} k_p = 4756 \text{ W/m K} \quad \text{with} \quad \lambda_p = 1.0 \mu \text{m} \quad \text{and} \quad 3567 \text{ W/m K} \quad \text{with} \quad \lambda_p = 0.75 \mu \text{m}.
\]

Using the phonon conductance of interflake junction and the graphene flake, we find the effective thermal conductivity of the linear chain composed of graphene flakes with uniform length. Figure 6(d) shows variation of the effective thermal conductivity as a function of the flake length \( (k_{p,\text{Chain}}) \) increases with \( l_{GF} \).

Here we confirm the large reduction of the effective thermal conductivity compared to the undisrupted graphene.

III. ELECTRONIC THERMAL TRANSPORT

The electronic thermal conductance is calculated using the NEGF and the TranSIESTA module within the SIESTA code (with the GGA-PBE exchange correlation, the CG relaxation, and a single \( \zeta \)-plus-polarization basis set)\(^{36} \) and the same configuration shown in Fig. 1. For infinitesimal voltage and temperature differences, the electronic thermal conductance is\(^{37} \)

\[
G_{e,\text{2D}} \text{ [W/m K]} = \frac{1}{\hbar \beta T} \left( K_e - K_0^2 \right), \tag{14}
\]

where \( K_e \) is defined as \( K_e = (1/\pi \hbar) \int dE_e (E_e - E_F) \delta f_{\epsilon_e}(E_e, T) \delta E_e \), \( E_F \) is the Fermi-level defined by the external electrode, \( \tilde{\tau} \) is the average electron transmission over the sampled \( k \) vectors (200 points in the \( \kappa \) direction) with regard to the
We examined the interflake electronic and phonon thermal conductances of the edge-passivated graphene flakes. We found a bimodal phonon transmission at the low and high frequencies caused by the weak coupling between two flakes and the tunneling resonant peaks of the passivated atoms with the NEGF, whereas the AMM treatment with the multiple interfaces predicts only the low-frequency transmission. This transmission also explains the different phonon transport mechanisms at low and high temperatures. The relatively strong interaction between O- and H-passivated graphene flakes leads to a high conductance and the dominance of the phonon polarized in the transport direction. We suggest that the mode or frequency dependence of the phonon transport is controlled by the edge passivation, and this provides a tool for the phonon engineering of the graphene compounds. Thermal conductance noticeably decreases due to the edge-passivated graphene junctions and the phonon transport dominates over the electronic except for the asymmetric junction at high temperatures. Since the bottleneck of the effective phonon transport in the graphene composites is the conductance between the flakes (or fibers), our findings can benefit the design of such high-effective-thermal-conductivity composites.

IV. CONCLUSIONS

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