

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/DFT, 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 $\dots\text{C}-\text{O}-\text{H}-\text{C}\dots$ 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,¹ promising for their superior electrical and thermal transport properties,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,^{5,6} and these edge passivations influence the graphene properties.⁷ We consider those O or H passivations of graphene flake edges which do not corrugate the graphene plane, so there are three interflake junction arrangements, O-H, O-O, and H-H. The carrier scattering then is concentrated in the interflakes junction when considering the long intragraphene mean free path for the energy carriers compared with the flake dimension.^{4,8} The nanoscale thermal transport addresses the quantum features and the carrier wave effects,⁹ and within that the nonequilibrium Green's function (NEGF) formalism is the treatment we use.¹⁰ Also, for phonon transport in heterostructures, the semiclassical acoustic mismatch model (AMM)¹¹ or diffuse mismatch model (DMM)¹² and molecular dynamics (MD)¹³ can provide limited, but more intuitive, insights into the phonon transport. However, MD based on the classical Newtonian mechanics has the limitation whereby the quantum effects must be considered even though it can easily include the anharmonic effects, and the conventional semiclassical AMM and DMM do not include the atomic details of the interfaces and the quantum and wave natures of the phonon transport.¹⁴⁻¹⁶ In this work, we employ both the NEGF formalism and the AMM treatment for the interflake phonon transport across the edge-passivated graphene and, although the electronic thermal transport is expected to be small in this system,^{17,18} we include it for insight into the force fields and to complete treatment of the thermal transport.

II. PHONON THERMAL TRANSPORT

A. NEGF formalism

In analogy to the NEGF for the electronic transport,¹⁹ we calculate the Green's functions using the Hessian matrix with

elements $\partial^2 E / \partial x_i \partial x_j$ (E is the energy and x_i and x_j are the i th and j th degree of freedom).²⁰ These matrices are calculated using the density functional theory (DFT) calculation with finite differences (0.015 Å) provided in the Vienna *ab initio* simulation package (VASP).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 correlation²² with the projector augmented wave method.^{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 κ_y is the wave number in the y direction), we include other transport directions ($\kappa_y^* \neq 0$). So, we sample for κ_y^* considering the upper and lower neighboring cells in the y direction. From the orthogonalized dynamical matrix with elements, $-1/(m_i m_j)^{1/2} (\partial^2 E / \partial x_i \partial x_j)$ (m_i and m_j are the mass of atoms),¹⁰ we extract the matrix of the central region with κ_y^* given as²⁵

$$\mathbf{K}_{CC}(\kappa_y^*) = \begin{bmatrix} \mathbf{K}_{ll}(\kappa_y^*) & \mathbf{K}_{lc}(\kappa_y^*) & 0 \\ \mathbf{K}_{cl}(\kappa_y^*) & \mathbf{K}_{cc}(\kappa_y^*) & \mathbf{K}_{cr}(\kappa_y^*) \\ 0 & \mathbf{K}_{rc}(\kappa_y^*) & \mathbf{K}_{rr}(\kappa_y^*) \end{bmatrix}, \quad (1)$$

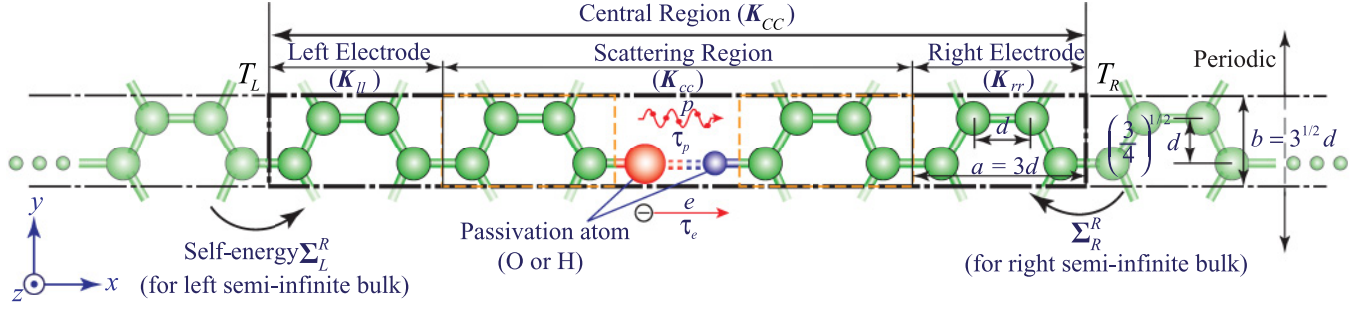


FIG. 1. (Color online) The edge-passivated graphene-flake junction used for the thermal transport calculations. The entire domain is divided into a central and two semi-infinite regions, and the central region is divided into a scattering and two electrode regions. The temperatures T_L and T_R are prescribed. d is the interatomic distance, and a and b is the width and height of the periodic bulk cell.

where for each element $K_{ij}(\kappa_y^*) = K_{M_i U_j} e^{-i\kappa_y^*} + K_{M_i M_j} + K_{M_i L_j} e^{i\kappa_y^*}$. 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. $K_{M_i M_j}$ is the dynamical matrix for the interaction between the i and j cells that are in the middle strip, and $K_{M_i U_j}$ (or $K_{M_i L_j}$) 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 (Σ_L^R or Σ_R^R) employing the decimation technique suggested by Lopez-Sancho *et al.*²⁶ The phonon-retarded Green's function of the central region is given by²⁷

$$\mathbf{G}^R(\kappa_y^*, \omega_p) = [(\omega_p + i\eta)^2 \mathbf{I} - \mathbf{K}_{CC}(\kappa_y^*) - \Sigma_L^R(\kappa_y^*, \omega_p) - \Sigma_R^R(\kappa_y^*, \omega_p)], \quad (2)$$

where ω_p is the phonon frequency and η is an infinitesimal number corresponding to the phonon energy dissipation.¹⁶ The phonon transmission across the central region is written as^{19,28}

$$\tau_p(\kappa_y^*, \omega_p) = \text{Tr}[\Gamma_L(\kappa_y^*, \omega_p) \mathbf{G}^R(\kappa_y^*, \omega_p) \Gamma_R(\kappa_y^*, \omega_p) \mathbf{G}^A(\kappa_y^*, \omega_p)], \quad (3)$$

where $\mathbf{G}^A$ is the phonon advanced Green's function equivalent to $(\mathbf{G}^R)^\dagger$ and Γ_L (Γ_R) is the energy-level broadening function caused by the left (right) electrode and described by

$$\Gamma_{L/R}(\kappa_y^*, \omega_p) = i[\Sigma_{L/R}^R(\kappa_y^*, \omega_p) - \Sigma_{L/R}^A(\kappa_y^*, \omega_p)]. \quad (4)$$

With these Green's functions the phonon density of states is²⁷

$$D_p(\kappa_y^*, \omega_p) = -\frac{2\omega_p}{\pi} \text{Im}\{\text{Tr}[\mathbf{G}^R(\kappa_y^*, \omega_p)]\}. \quad (5)$$

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

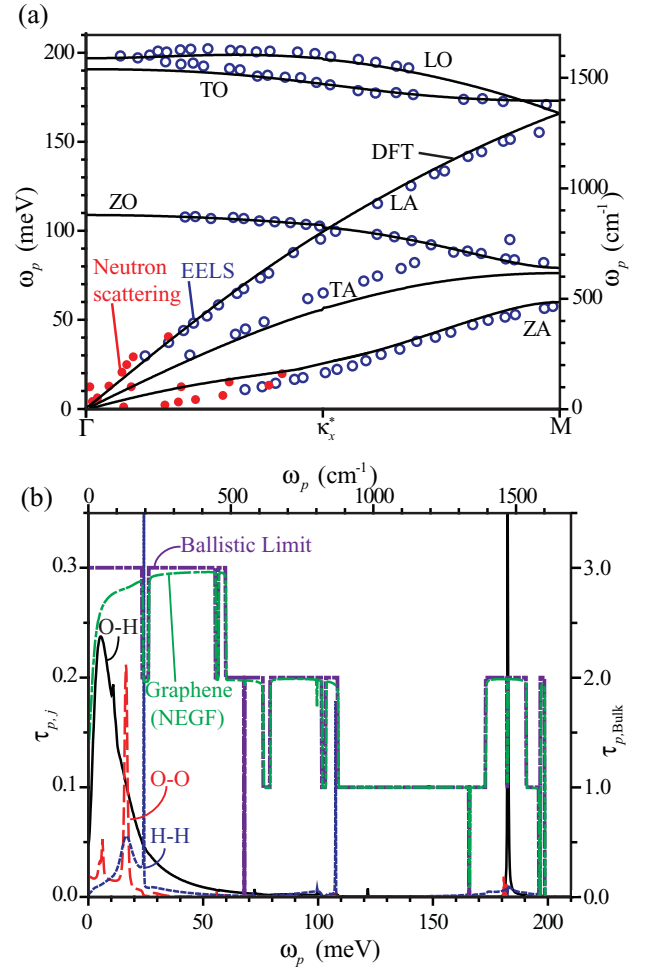


FIG. 2. (Color online) (a) The phonon dispersion from Γ to M for the bulk graphene. The solid line is from the DFT dynamical matrix calculations. The red solid circles are from the neutron scattering data and the blue open circles are from the electron energy loss spectroscopy (EELS) data.²⁹ (b) The variations of the phonon transmission with the transport direction ($\kappa_y^* = 0$) with respect to the phonon energy, for the bulk graphene and the passivated junctions. The transmissions for the passivated junctions are largely suppressed, while the O-H junction has the largest transmission.

Born-von Karman boundary condition³⁰

$$\begin{aligned} [\omega_p^2(\kappa_x^*, \kappa_y^*, \alpha) \mathbf{I} - \mathbf{K}_{cc}(\kappa_y^*) - \mathbf{K}_{cl}(\kappa_y^*) e^{i\kappa_x^*} \\ - \mathbf{K}_{cr}(\kappa_y^*) e^{-i\kappa_x^*}] \mathbf{s}(\kappa_x^*, \kappa_y^*, \alpha) = 0, \end{aligned} \quad (6)$$

where κ_x^* is the dimensionless wave number in the transport direction ($\kappa_x^* = \kappa_x a$ and κ_x is the wave number in the x direction), α is the polarization [four atoms in each unit cell and three degrees of freedom per each atom and the number of total branches (α) is 12], $\mathbf{s}$ is the eigenvector, and $\mathbf{K}_{cl}$ ($\mathbf{K}_{cr}$) 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 Γ to M ($\kappa_y^* = 0$) is in good agreement with the experiments,²⁹ as demonstrated in Fig. 2(a). Because the passivated atoms are linearly aligned and the transport with the κ 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 ($\kappa_y^* = 0$). In the ideal ballistic transport, when all modes are transmitted without scattering, the phonon transmission is the number of modes at frequency ω_p ,³⁰ and the NEGF transmission for graphene is similar to this ballistic limit with a small η ,

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 τ_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.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 [$\sim(\Gamma_{ij}/m_{ij})^{0.5}$, where Γ_{ij} is the force constant and m_{ij} is the reduced mass].³² Because

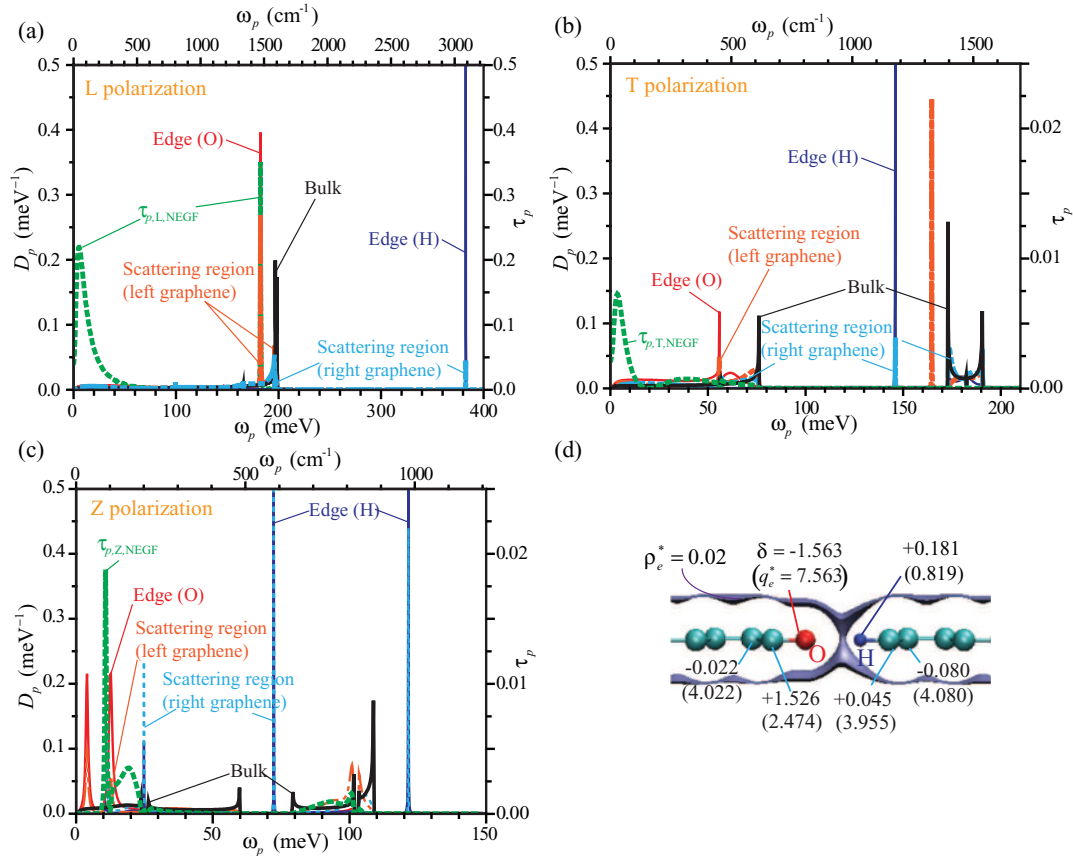


FIG. 3. (Color online) Variations of the phonon density of states and transmissions (at $\kappa_y^* = 0$) with respect to the phonon energy for (a) the longitudinal (L), (b) transverse (T), and (c) out-of-plane (Z) directions, for the O–H passivated junction. Due to the interaction with the junction atoms and the atomic restructuring, D_p is distorted in the interfacial regions. The isosurface of the charge density ($\rho_e^* = 0.02$), the charge (q_e^*) associated with each atom, and the difference from the valence charges (δ) are shown in (d). Note that τ_p is the largest in the L direction and is bimodal with the wide peaks at low and the sharp peaks at the edge-resonant frequencies.

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 analysis³³ as Fig. 3(d), which shows the isosurface of the charge density ($\rho_e^* = 0.02$), the charge associated with each atom according to Bader partitioning (q_e^*), and the net charge (δ) 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 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 τ_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 τ_p in the AMM employing the specular scattering as an analogy to the electromagnetic waves. In the AMM,¹¹ the phonon transmission is obtained with the acoustic impedance (Z_p) as

$$\tau_{p,L/R,AMM} = \frac{4Z_{p,L}Z_{p,R}}{(Z_{p,L} + Z_{p,R})^2}, \quad (7)$$

where $\tau_{p,L/R,AMM}$ 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 ρu_p , where ρ 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

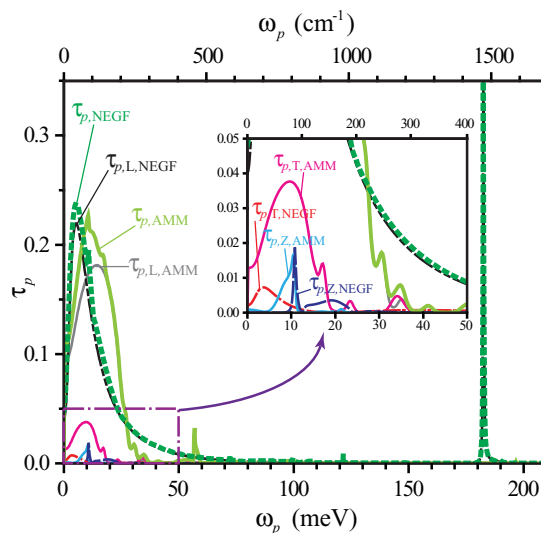


FIG. 4. (Color online) Comparison of the phonon transmission (at $\kappa_y^* = 0$) from the AMM treatment with the NEGF. The AMM transmission is in good agreement with the NEGF at low frequencies but does not show the high-frequency transmission.

restructuring as confirmed in Fig. 3, we consider the phonon scattering at the interface of neighboring atoms ($\tau_{p,i/i+1,AMM}$) using the local Z_p proportional to the D_p^{-1} and combine all interfacial $\tau_{p,i/i+1,AMM}$ in the central region to find the overall transmission $\tau_{p,AMM}$,

$$\begin{aligned} \tau_{p,AMM} &= \tau_{p,1/2,AMM} \tau_{p,2/3,AMM} \cdots \tau_{p,17/18,AMM} \\ &= \prod_{i=1}^{17} \tau_{p,i/i+1,AMM}. \end{aligned} \quad (8)$$

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 $\tau_{p,AMM}$ 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 κ_y^* , the phonon conductance is evaluated using the Landauer formula,^{34,35}

$$G_{p,1D}(\kappa_y^*) [W/K] = \int_0^\infty \frac{d\omega_p}{2\pi} \hbar \omega_p \tau_p(\kappa_y^*, \omega_p) \left[\frac{\partial f_p^o(\omega_p, T)}{\partial T} \right], \quad (9)$$

where T is the temperature, $\hbar$ is the reduced Planck constant, the equilibrium Bose-Einstein distribution function is $f_p^o(\omega_p, T) = [\exp(\hbar \omega_p / k_B T) - 1]^{-1}$, and k_B is the Boltzmann constant. To include contributions from all wave vectors (as well as $\kappa_y^* = 0$), we sample κ_y^* values (200 points in the first

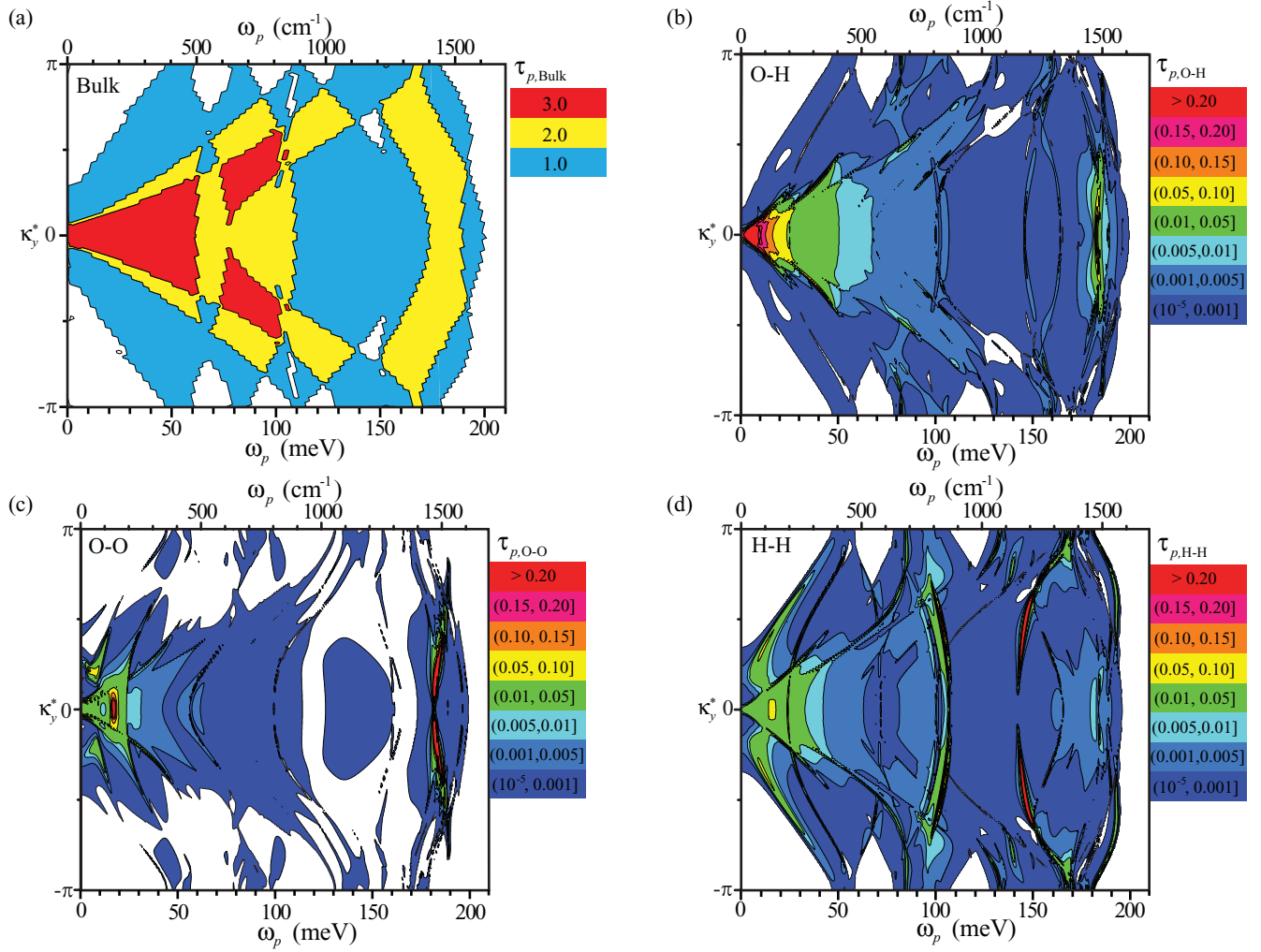


FIG. 5. (Color online) Phonon transmissions as functions of the component κ_y^* in the wave vector space and the phonon energy for (a) bulk graphene, (b) O–H, (c) O–O, and (d) H–H junctions. The transmissions are symmetric and larger near the transport direction ($\kappa_y^* = 0$).

Brillouin zone, $-\pi \leq \kappa_y^* < \pi$) and integrate 1D conductance for each direction for the 2D conductance as,²⁵

$$G_{p,2D} [\text{W/m K}] = \frac{1}{b} \int_{-\pi}^{\pi} d\kappa_y^* G_{p,1D}(\kappa_y^*). \quad (10)$$

Figures 5(a)–5(d) show the phonon transmissions as functions of the component κ_y^* in the κ vector space and the phonon energy for the graphene and passivated graphene junctions. The bulk graphene in the ballistic limit has integer transmission for all κ directions, and the phonon transmissions through interflake junctions are limited by the bulk graphene transmission. 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 $G_{p,3D,\text{Bulk}}$ 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 ($1/G_{p,3D,\text{Chain}}$) is the sum over the resistances for the graphene flakes and the interflakes junctions, i.e.,

$$\frac{1}{G_{p,3D,\text{Chain}}} = n_j \left(\frac{1}{G_{p,3D,\text{GF}}} + \frac{1}{G_{p,3D,j}} \right) + \frac{1}{G_{p,3D,\text{GF}}}, \quad (11)$$

where n_j is the number of the interflake junctions in the chain and $G_{p,3D,\text{GF}}$ and $G_{p,3D,j}$ are the thermal conductance of the

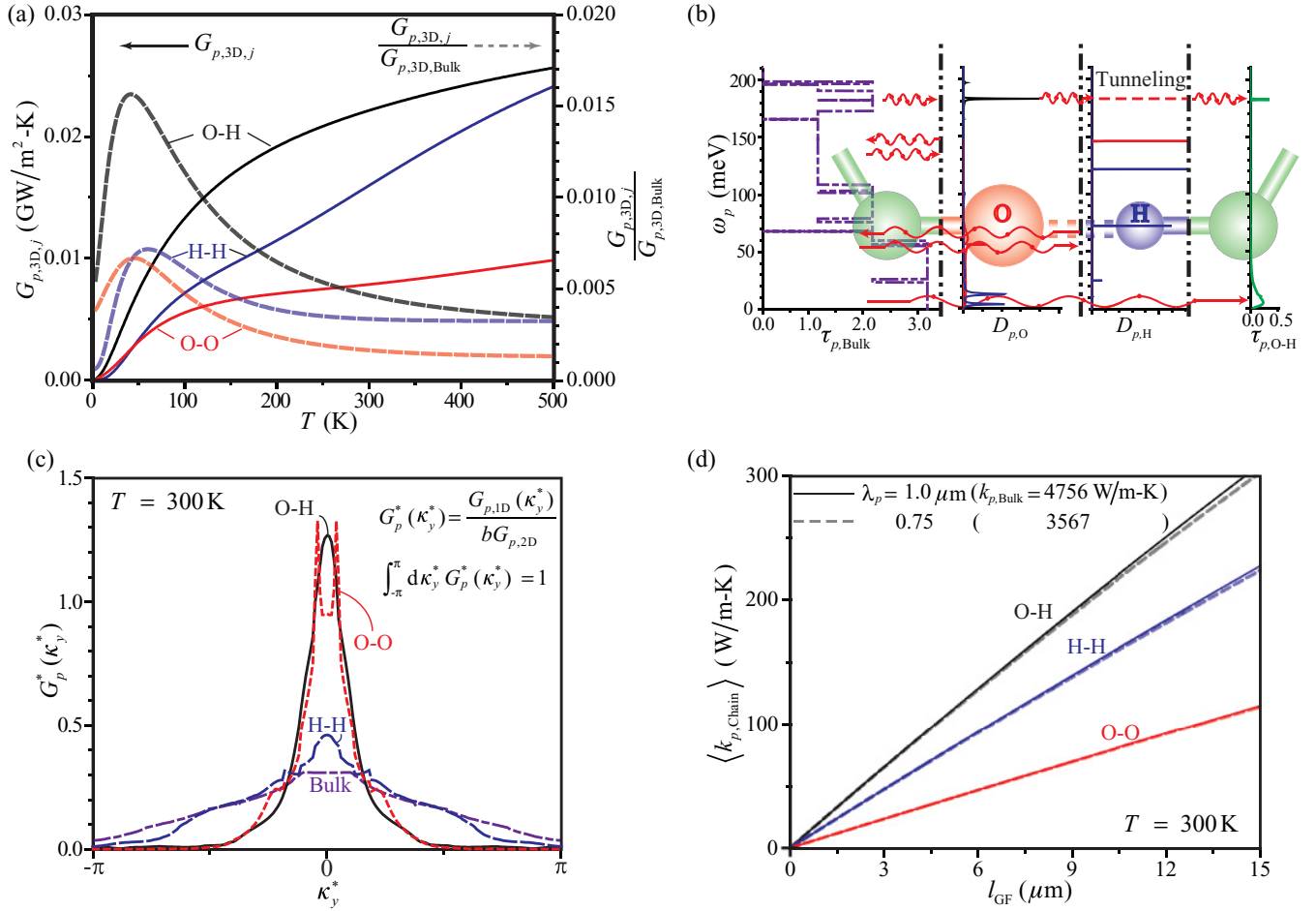


FIG. 6. (Color online) (a) Variations of the phonon conductance ($G_{p,3D,j}$, solid lines) of the three passivated flake junctions with respect to temperature, from the NEGF calculations, and comparison with the bulk behavior (dash lines). (b) Phonon transport channels and the mechanism of phonon transport suppression in the O–H passivated junction. (c) The contribution of wave vectors to thermal conductance [$G_p^*(\kappa_y^*)$] at $T = 300$ K. (d) The effective thermal conductivity of linear chains composed of graphene flakes with three cases of edge passivated junctions at $T = 300$ K as a function of the flake length. Two mean free paths, $\lambda_p = 1.0 \mu\text{m}$ ($k_{p,Bulk} = 4756$ W/m-K) and $\lambda_p = 0.75 \mu\text{m}$ ($k_{p,Bulk} = 3567$ W/m-K), are used.^{4,17}

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

$$\langle k_{p,Chain} \rangle = G_{p,3D,Chain} L_c = \frac{G_{p,3D,GF} G_{p,3D,j}}{G_{p,3D,GF} + G_{p,3D,j}} l_{GF}. \quad (12)$$

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 λ_p ,¹⁷ i.e.,

$$k_{p,GF} = G_{p,3D,GF} l_{GF} = G_{p,3D,Bulk} \frac{l_{GF} \lambda_p}{l_{GF} + \lambda_p}. \quad (13)$$

The phonon thermal conductivity of undisrupted graphene $k_{p,Bulk}$ (i.e., $l_{GF} \rightarrow \infty$) is $G_{p,3D,Bulk} \lambda_p$ (4756 W/m-K with $\lambda_p = 1.0 \mu\text{m}$ and 3567 W/m-K with $\lambda_p = 0.75 \mu\text{m}$). 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 ($\langle k_{p,Chain} \rangle$ 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 TransSIESTA module within the SIESTA code (with the GGA-PBE exchange correlation, the CG relaxation, and a single ζ -plus-polarization basis set)³⁶ and the same configuration shown in Fig. 1. For infinitesimal voltage and temperature differences, the electronic thermal conductance is³⁷

$$G_{e,2D} [\text{W/m K}] = \frac{1}{bT} \left(K_2 - \frac{K_1^2}{K_0} \right), \quad (14)$$

where K_n is defined as $K_n = (1/\pi \hbar) \int dE_e (E_e - E_F)^n \tilde{\tau}_e(E_e) [-\partial f_e^o(E_e, T)/\partial E_e]$, E_F is the Fermi-level defined by the external electrode, $\tilde{\tau}_e$ is the average electron transmission over the sampled κ vectors (200 points in the y direction) with regard to the

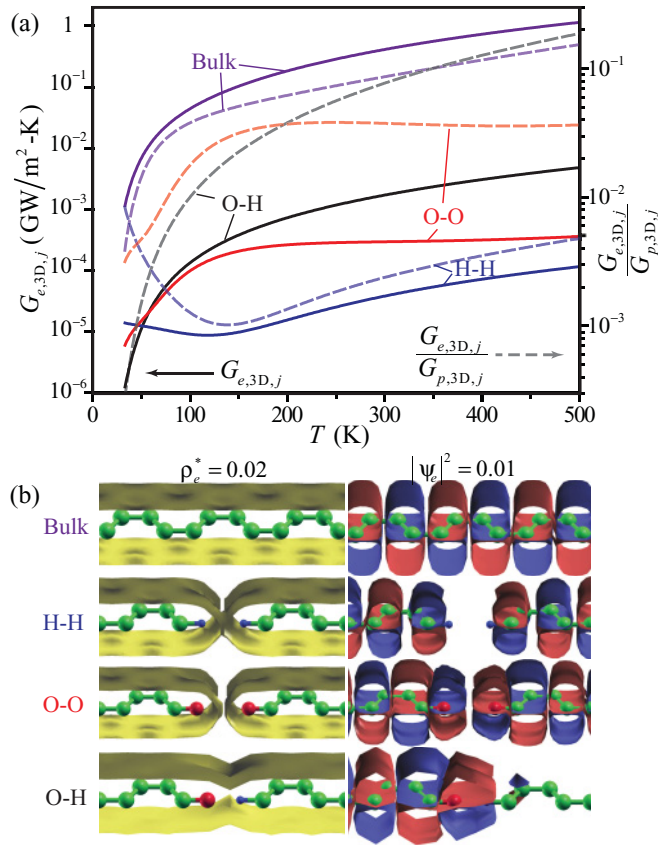


FIG. 7. (Color online) (a) Variations of the electronic thermal conductance ($G_{e,3D,j}$, solid lines) on the left and that scaled with $G_{p,3D,j}$ ($G_{e,3D,j}/G_{p,3D,j}$, dashed lines) on the right, without an external bias potential, with respect to temperature. (b) The charge-density isosurface ($\rho_e^* = 0.02$) on the left and the wave function ($|\psi_e|^2 = 0.01$) of the first eigenstate below the E_F (at the Γ point) on the right, for the bulk and the three junctions. Different colors (blue and red) in the wave functions correspond to the opposite signs.

electron energy, and f_e^o is for the equilibrium fermion, $f_e^o(E_e, T) = \{\exp[(E_e - E_F)/k_B T] + 1\}^{-1}$. $G_{e,3D}$ for bulk and three junctions are calculated with the layer separation distance as in $G_{p,3D}$ and compared with $G_{p,3D}$ in Fig. 7(a). The reduction of G_e from the bulk value is more pronounced than G_p , when no external-bias potential is applied. Figure 7(b) presents the charge-density isosurface ($\rho_e^* = 0.02$) and the

wave function of the first eigenstate below the E_F (at the Γ point). The low charge density presents between the flakes and the localized orbital exists near the passivated edge for the symmetric junctions differing from the chemical σ or π bond between the passivation atom and the nearest C^7 and the delocalized π bond in the bulk graphene. These lead to the large drop in the magnitude of G_e . For the asymmetric junction O–H, the G_e is less suppressed because of the delocalization in the molecular orbital due to the asymmetric charge distribution. As shown to right of Fig. 7(a), the G_e for all the three junctions is smaller than the G_p , especially at low temperatures, with the O–H junction suffering the least reduction.

IV. CONCLUSIONS

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 thermal 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.

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