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Pressure effects on the thermal resistance of few-layer graphene

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ABSTRACT

The non-equilibrium Green's function method was employed to investigate the pressure effects on the interfacial thermal resistance of few-layer graphene. It is found that a compressive pressure of 10 GPa along the cross-plane direction can reduce the interfacial resistance by approximately 4 times, when compared with no applied pressure. As pressure is applied along both in-plane and cross-plane directions, the effects of the in-plane direction pressure on the cross-plane thermal transport are much weaker than those of the cross-plane pressure. Our results indicate that the interlayer interfacial thermal resistance of graphite can be modulated to a large extent by external pressure.

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1. Introduction

Graphene, the two-dimensional monoatomic layer of sp^2 carbon atoms, was first mechanically exfoliated from graphite in 2004 [1]. During the past decade, it has attracted great interest in fundamental physics and for engineering applications due to its extremely high in-plane thermal conductivity k [2–4], great room-temperature carrier mobility [5,6] and mechanical strength [7]. These outstanding properties stem from the strong sp^2 carbon–carbon bonds and the two-dimensional planar structure. In 2008, Balandin et al. [2] measured the thermal conductivity of suspended single-layer graphene to be as high as 5300 W/m K at room temperature, which qualifies graphene to be a potential material for heat removal in thermal management. Compared with the single-layer graphene, few-layer graphene (FLG) is more promising because k is less suppressed by extrinsic influences, such as substrate and impurity scattering [8–10]. For example, by using a heat spreader method, Jang et al. [8] measured the thermal conductivity of SiO$_2$-encased few-layer graphene (FLG). They found that k increases from ∼50 W/m K to ∼1000 W/m K as the thickness of FLG increases from 2 to 21 layers.

It is well known that graphite is an anisotropic material, and the cross-plane thermal conductivity is approximately two orders of magnitude lower than the corresponding in the basal plane [11]. This is attributed to the robust in-plane bond strength and the

weak interfacial interaction. Both graphite and FLG can be viewed as layer-by-layer stacks of graphene. Therefore, the cross-plane k of FLG could be quite small. Recent experimental results [12] have indicated that the cross-plane thermal conductivity of FLG is approximately 0.7 W/m K at room temperature with a thickness of approximately 35 nm. Thus, there is a need to further increase the cross-plane k of FLG for applications in heat dissipation.

Strain engineering is a widely used method to modulate the physical properties of graphene. For example, the thermal conductivity of suspended single-layer graphene can be reduced by loading strain [13]. Above 110 K, compressive strain can decrease the specific heat of graphene [14]. Bu et al. [15] have shown that the Young's modulus of graphene nanoribbons increases as the strain exceeds 18%. Using molecular dynamics, it has been found that strain can improve the thermal rectification in graphene nanoribbons [16]. However, in these works, only the in-plane strain and its effect on the in-plane physical properties have been taken into consideration. Only a few works [17] have investigated the influence of strain/pressure on the cross-plane properties of FLG and graphite. In this paper, we systematically investigated the thermal resistance of FLG under pressure, applied in-plane and cross-plane directions, to increase the interfacial thermal conductance, which can help increase the efficiency of FLG-based heat dissipation devices.

There are two widely used models to illustrate phonon transmission at an interface: the acoustic mismatch model and the diffusive mismatch model [18]. Both models neglect the atomic level detail of an interface and are usually applied under the assumption of a linear phonon dispersion relation. Moreover, both

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models assume a perfectly welded contact (strong bond) at the interface. They are therefore clearly not applicable to the cases of graphite and FLG. Beyond these two models are atomic level methods, such as lattice dynamics [19], molecular dynamics (MD) [20–23] and nonequilibrium Green's functions (NEGF) [24–26], that have been used to study interfacial thermal resistance. Recently, some works [21,22] have been reported regarding the cross-plane k of FLG that were obtained through MD simulations. Here, we use the NEGF method to systematically investigate the effects of cross-plane and in-plane pressure on the interfacial thermal resistance of FLG. The phonon transmission across an interface can be calculated for different loading conditions, which can help to better explain the phonon transport through an interface. The phonon density of states is also calculated to explain the variations in phonon transmission that are caused by pressure. Our results provide guidance to future experiments and to designing practical applications for the modulation of interfacial thermal resistance of graphite and FLG by the loading of an external pressure.

2. Theoretical model

In a linear system, three- or higher-order terms are ignored, while the vibrational normal modes of the system satisfy the following dynamical matrix equation [25]:

$$\left(\omega^2 \mathbf{I} - \mathbf{K}\right)\mathbf{\Psi} = \mathbf{I} \tag{1}$$

where ω is the angular frequency ($\omega = 2\pi f$, f is the phonon frequency), $\mathbf{\Psi}$ is the amplitude of the normal modes and $\mathbf{I}$ is the identity matrix. The force constant matrix $\mathbf{K}$ of the system is defined as:

$$K_{ij} = \frac{1}{\sqrt{m_i m_j}} \begin{cases} \frac{\partial^2 E}{\partial u_i u_j} & i \neq j \\ -\sum_{i \neq j} \frac{\partial^2 E}{\partial u_i u_j} & i = j \end{cases} \tag{2}$$

where i and j ($i, j = x, y, z$) represent the coordinate directions, m is the atom mass, u is the displacement from the equilibrium and E is the total energy of the system.

Generally, it is difficult to solve equation (1), and the atomistic Green's function is a powerful tool to obtain the dynamic response of the system under small perturbations [25]:

$$\left[(\omega + i\eta)^2 \mathbf{I} - \mathbf{K}\right]\mathbf{G} = \mathbf{I} \tag{3}$$

where η is a small positive number and $\mathbf{G}$ is Green's function matrix [27–29].

The system in this paper is infinitely large in the x- and y-directions and is, therefore, infinite in the atom number. As a result, the harmonic force constant matrix $\mathbf{K}$, defined in equation (2), is infinite. Considering the translational invariance of the basal plane, the harmonic matrix $\mathbf{K}$ can be described using the wave vector representation based on $\boldsymbol{k}_\parallel$ [24]. Thus, the FLG system is divided into discrete layers along the cross-plane direction, where one unit cell in each layer can represent the vibration of the whole layer. In this work, two monolayer graphene sheets are treated as one discrete layer; thus, there are four atoms in one unit cell. Because each atom can vibrate in the x, y and z directions, a 12×12 harmonic matrix $\mathbf{K}_l$ is used to represent the intralayer interactions in the l plane, and another harmonic matrix $\mathbf{K}_{l,m}$ is used to represent the interlayer interactions between layer l and the right layer m.

$$\mathbf{K}_l(\boldsymbol{k}_\parallel) = \sum_{n=0}^{p} \mathbf{K}_{t,n} e^{-i\boldsymbol{k}_\parallel \boldsymbol{R}_n} \tag{4}$$

$$\mathbf{K}_{l,m}(\boldsymbol{k}_\parallel) = \sum_{m=1}^{q} \mathbf{K}_{t,m} e^{-i\boldsymbol{k}_\parallel \boldsymbol{R}_m} \tag{5}$$

where t is an artificially selected unit cell in the l plane with p neighboring unit cells, $\boldsymbol{R}_n$ is the relative position from unit cell n to t, including itself. The summation index m loops from 1 to q, which is the number of the neighboring unit cells of t in the layer m. With the intralayer and interlayer matrices, the complete harmonic matrix of a system can be expressed. For instance, the force constant matrix to represent the vibration of l-layer central part is:

$$\mathbf{K}_C = \begin{bmatrix} \mathbf{K}_1 & \mathbf{K}_{12} & \mathbf{0} & \cdots & \mathbf{0} \\ \mathbf{K}_{21} & \mathbf{K}_2 & \mathbf{K}_{23} & \cdots & \mathbf{0} \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ \mathbf{0} & \cdots & \mathbf{0} & \mathbf{K}_{l,l-1} & \mathbf{K}_l \end{bmatrix} \tag{6}$$

where $(\mathbf{K}_{12})^+ = \mathbf{K}_{21}$, and $\mathbf{K}_1 = \mathbf{K}_2 = \cdots = \mathbf{K}_l$. The wave vector $\boldsymbol{k}_\parallel$ can be expressed as $k_x \boldsymbol{b}_1 + k_y \boldsymbol{b}_2$, which represents the phonon vibration along some direction in a single, discrete layer. The structure of the discrete layer is two graphene sheets, so the first Brillouin zone (FBZ) is a regular hexagon. We discretize the FBZ into $N \times N$ parts, where each part can be represented by $\boldsymbol{k}_\parallel$. The transmission function and the heat flux of each part in the layer can be calculated independently. Therefore, the total heat flux can be obtained by adding all of the N^2 parts.

According to Ref. [24], the total heat flux, from left to right, is defined as an integral over the frequency ω and the wave vector $\boldsymbol{k}_\parallel$:

$$Q = \iint \frac{\hbar\omega}{2\pi} \left[f_L(\omega, T_L) - f_R(\omega, T_R)\right] \text{Tr}[\omega, \boldsymbol{k}_\parallel] \frac{d\boldsymbol{k}_\parallel}{(2\pi)^2} d\omega \tag{7}$$

where $\text{Tr}[\omega, \boldsymbol{k}_\parallel]$ is the transmission function, with frequency ω and wave vector $\boldsymbol{k}_\parallel$, of each phonon mode and is equal to $\text{Trace}[\mathbf{\Gamma}_L \mathbf{G} \mathbf{\Gamma}_R \mathbf{G}^+]$, which can be calculated by the method described in Ref. [24]. The Green function $\mathbf{G}$ in the calculation of the transmission function is obtained by equation (3) with the decimation technique [30]. The integral variable $\boldsymbol{k}_\parallel$ is limited in the first Brillouin zone, so discretizing the zone into $N \times N$ uniform parts serves to convert the integral over $\boldsymbol{k}_\parallel$ into the summation of over N^2 wave vectors $\boldsymbol{k}_\parallel$. Therefore, the equation (7) is equivalent to the following:

$$Q = \frac{1}{s} \int_0^\infty \frac{\hbar\omega}{2\pi} \left[f_L(\omega, T_L) - f_R(\omega, T_R)\right] \left[\frac{1}{N^2} \sum_{\boldsymbol{k}_\parallel} \text{Tr}[\omega, \boldsymbol{k}_\parallel]\right] d\omega \tag{8}$$

For equations (7) and (8), we used:

$$\int d\boldsymbol{k}_\parallel = \sum_{\boldsymbol{k}_\parallel} \frac{(2\pi)^2}{S} = \sum_{\boldsymbol{k}_\parallel} \frac{(2\pi)^2}{N^2 s} \tag{9}$$

where s is the area of the unit cell, and $f_L(\omega, T_L)$ and $f_R(\omega, T_R)$ are the phonon numbers of the left and right reservoir, respectively. The phonon number at the specified frequency ω and temperature T_α is calculated by the Bose–Einstein formula:

$$f_\alpha(\omega, T_\alpha) = \frac{1}{e^{\frac{\hbar\omega}{k_B T_\alpha}} - 1}, \quad \alpha = L, R \tag{10}$$

where k_B is the Boltzmann constant, and T_L and T_R stand for the temperatures of the two reservoirs. In the calculation, different temperatures, T_L and T_R, are applied to establish a heat flux through the central part. The thermal conductance can then be obtained by calculating the ratio of the total heat flux to the temperature difference:

$$\sigma = \frac{Q}{T_L - T_R} = \frac{Q}{\Delta T} \tag{11}$$