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Geometry and temperature effects of the interfacial thermal conductance in copper– and nickel–graphene nanocomposites

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Abstract

Graphene has excellent mechanical, electrical and thermal properties. Recently, graphene–metal composites have been proposed as a means to combine the properties of metals with those of graphene, leading to mechanically, electrically and thermally functional materials. The understanding of metal–graphene nanocomposites is of critical importance in developing next-generation electrical, thermal and energy devices, but we currently lack a fundamental understanding of how their geometry and composition control their thermal properties. Here we report a series of atomistic simulations, aimed at assessing the geometry and temperature effects of the thermal interface conductance for copper– and nickel–graphene nanocomposites. We find that copper–graphene and nickel–graphene nanocomposites have similar thermal interface conductances, but that both cases show a strong performance dependence on the number of graphene layers between metal phases. Single-graphene-layer nanocomposites have the highest thermal interface conductance, approaching $\sim 500 \text{ MW m}^{-2}\text{K}^{-1}$. The thermal interface conductance reduces to half this value in metal–bilayer graphene nanocomposites, and for more than three layers of graphene the thermal interface conductances further reduces to $\sim 100 \text{ MW m}^{-2}\text{K}^{-1}$ and becomes independent with respect to the number of layers of graphene. This dependence is attributed to the relatively stronger bonding between the metal and graphene layer, and relatively weaker bonding between graphene layers. Our results suggest that designs combining metal with single graphene layers provide the best thermal properties.

(Some figures may appear in colour only in the online journal)

1. Introduction

Recent advances in the fabrication of ultrathin graphene layers have attracted a great deal of attention to study size effects of multilayer graphene films \cite{1–3}. Due to its remarkable physical properties such as high mechanical strength, and electrical and thermal conductivity, many studies have been devoted to the electronic structure of $n$-layer
Figure 1. Illustration of the Müllner-Plathe approach and geometry of the metal–graphene nanocomposite. (a) Temperature distribution of a metal–graphene nanocomposite and illustration of copper/cross-plane multilayer graphene nanocomposite. (b) Copper/in-plane multilayer graphene nanocomposite.

Graphene systems [4, 5] and their vibrational properties [6–8]. Graphene nanocomposite materials have been recently studied with the aim of creating new materials with bulk quantities of graphene. However, most of the earlier studies have primarily been focused on polymer matrices [9–11] and few have been concerned with metal matrices, albeit some recent studies have focused on the synthesis and assessment of the mechanical properties of this class of materials [12–14].

Graphene–metal materials are high performance thermal interface materials [15, 16] and the understanding of thermal interface conductance between metal and graphene is crucial for the design of next-generation electronic or energy devices. However, there is limited amount of data for thermal interface conductance at the metal–graphene interface [17]. Previous studies have measured the thermal interface conductance at SiO$_2$–graphene [18] and Au–graphene interfaces [8]. Schmidt et al have reported that the thermal interface conductances between c-axis-oriented highly ordered pyrolytic graphite and several metals, including Al, Au, Cr and Ti, in the temperature range of 87–300 K are found to be similar to those of metal–diamond interfaces in the range of 40–100 MW m$^{-2}$ K$^{-1}$.

Here, a series of atomistic simulations, aimed at assessing the geometry and temperature effects, are performed to systematically study the thermal interface conductance between n-layer graphene (n = 1, 2, 3, 4, 8 and 12) and copper and nickel interfaces. We calculate and compare the thermal interface conductance of different orientations of graphene layers (metal and in-plane graphene and metal and cross-plane graphene interfaces). Furthermore, the temperature effects on the thermal interface conductance in the temperature range of 230–430 K and the size effects on the thermal interface conductance are investigated to provide overall studies of the thermal interface conductance of metal–graphene nanocomposites.

2. Materials and methods

We consider metal and n-layer graphene (n = 1, 2, 3, 4, 8 and 12) nanocomposite materials as shown in figure 1. We calculate the interfacial thermal conductances at the metal–graphene interface for different orientations of graphene, temperatures, metal and the thickness of the multilayer graphene. Copper and nickel are the two metals investigated in this study. As shown in figure 1, two orientations, in-plane and cross-plane, of the graphene are studied. We fix the thickness of the metal to 20 nm and vary the number of the layers of graphene n to study the size effects of the thermal interface conductance.

Embedded-atom-method (EAM) interatomic potentials [19], which include electron density contributions of atoms, are used for describing interactions between metal atoms. The interatomic interactions in graphene sheets are
shown that the thermal interface conductance between an
metal and graphene sheets. The choice of the pair
potential is motivated by previous results that have indicated
that the LJ potential with parameters derived from quantum
level simulations provides a reasonable approximation to
the behavior of metal–carbon interactions [21]. The LJ
potential used here is suitable for this study since bonding
between metal and graphene are van der Waals bonds and we
only focus on the vibrational properties of metal–graphene
nanocomposites at equilibrium configurations. We use the
parameters that have been developed, tested and used in
earlier studies to describe copper–graphene [22] and

LAMMPS is used to calculate the thermal interface
conductance of metal–graphene nanocomposites [24]. For
each model of the metal–graphene nanocomposites, an
NPT ensemble is used to obtain the equilibrium structure.
After NPT simulation, the Müller-Plathe approach [25] is
used to calculate the thermal interface conductance. In
the Müller-Plathe approach, a constant-energy molecular
dynamics simulation (NVE) is performed and additional
control is made through exchanging the momentum of
atoms between the ‘heat zone’ and ‘cool zone’ every
1.3 ps as illustrated in figure 1. After achieving a steady
state of the system, the temperature jump $\Delta T$ at the
metal–graphene interface is computed and then the thermal
interface conductance is calculated by

$$\kappa = \frac{J}{A \Delta T}$$

in which $J$ is the heat flux and $A$ is the cross-section area of
the nanocomposites.

### 3. Results and discussion

We first compute the thermal interface conductance for copper
and in-plane graphene and copper and cross-plane graphene
interfaces as illustrated in figure 1. We find that the copper
and cross-plane multilayer graphene ($n = 8$) nanocomposite
has a thermal interface conductance of 84 MW m$^{-2}$ K$^{-1}$
while the copper and in-plane multilayer graphene ($n = 8$)
nanocomposite has a larger thermal interface conductance of
230 MW m$^{-2}$ K$^{-1}$. We note that Gao et al have reported
that interface thermal conductance between a metallic carbon
nanotube and a Cu substrate is 296 MW m$^{-2}$ K$^{-1}$ [26],
which is close to our predicted value for the copper and
in-plane graphene case. Our results show that the interface
between the face-centered cubic (fcc) metal (111) surface
and the in-plane multilayer graphene has a larger thermal
interface conductance. The result is reasonable as the phonon
group velocity is much higher for in-plane graphite compared
to out-of-plane graphite. In agreement with our finding, an
extension of the diffuse mismatch model has also predicted
the same trend [27]. Experimental studies, which have
shown that the thermal interface conductance between an
individual carbon nanotube (CNT) and a Au surface for
$a$-axis orientation is larger than for its $c$-axis orientation [28],
also support the same trend as identified in our calculations.
Although the in-plane multilayer graphene has a larger
thermal interface conductance, the adhesion of the cross-plane
graphene on fcc metal (111) is more stable, and we thus
focus on the metal and cross-plane graphene case for studying
the temperature and size effects of the thermal interface
conductances.

We vary the temperature and calculate the thermal
interface conductance for a copper–four-layer-graphene
nanocomposite. We find that in the temperature range
230–430 K the thermal interface conductance of the
copper–graphene interface is about 120 MW m$^{-2}$ K$^{-1}$
(figure 2) and there is no strong dependence between
the thermal interface conductance and the temperature.
It is worth noting that our results are consistent with
theoretical models [27] and experimental data [29] which have
shown that the thermal interface conductance is essentially
independent of temperature at temperatures above 200 K.

To quantify this, we use a modified elastic diffuse
mismatch model (DMM) originally described by Duda
et al for thermal contact between isotropic and anisotropic
materials [30]. The thermal interface conductance from a
metal film to a graphite substrate is given by

$$h_{BD} = \frac{1}{4} \sum_j \int_{\omega_0, j} h_{\omega} \nu_{1,j} D_{1,j} (\omega, \nu_{1,j}) \frac{\partial f}{\partial T} \sigma_{1-j}^{g,c} \omega d\omega.$$

Here $j$ is a particular polarization, $h$ is the Planck’s
constant divided by $2\pi$, $\omega$ is the phonon angular frequency,
$T$ is the temperature and $f$ is the Bose–Einstein distribution
function. The metal properties are denoted by a subscript.
...orsuperscript‘1’. The symbol ‘$g$’ represents graphite, ‘c’ denotes the direction along the $c$-axis of graphite, $\omega_{p,j}$ is the Debye cutoff and $\xi_{2,ij}^{1-p,c}$ is the transmission coefficient from the metal film to the $c$-axis graphite. Only the elastic processes are considered here and hence

$$\xi_{2,ij}^{1-p,c} = \frac{v_{f,j}}{v_{f,j} + \frac{v_{c,j}}{2}}$$  \hspace{1cm} (3)

where $d$ is the interlayer spacing in graphite and is taken as $d = 3.35$ Å. The parameter $v_{f,j}$ is the polarization-specific Debye phonon group velocity and we use the values reported in [31] for copper. For graphite, we use the same values as used by Duda et al., where $v_{a,l} = 23,600$ m s$^{-1}$, $v_{a,t} = 15,900$ m s$^{-1}$, $v_{c,l} = 1960$ m s$^{-1}$ and $v_{c,t} = 700$ m s$^{-1}$ [30].

The predicted thermal interface conductances are plotted in figure 2. In accordance with results from previous studies [29, 30, 32] the DMM qualitatively captures most of the temperature trend, but the DMM under-estimates the thermal interface conductance.

In order to study how the thermal interface conductance varies as the thickness of the graphene changes, we vary the number of layers of graphene $n$ and calculate the thermal interface conductance for copper–graphene and nickel–graphene nanocomposites at a temperature of 300 K. Without presuming the stacking between the interface of metal and graphene, for $n = 1$ we construct interface models with both topfcc and hcpfcc stacking between the interface of metal and graphene. The results show that after NPT simulations, no matter if the initial model is topfcc or hcpfcc stacking, the stacking between the metal and graphene interface changes into hcpfcc stacking at equilibrium, indicating that the hcpfcc stacking is more stable for metal–graphene nanocomposites.

In order to validate the predictions from our molecular simulations, we compute the interface stacking sequence for graphene–copper using density functional theory (DFT) for topfcc and hcpfcc cases. A fully periodic unit cell is used with the copper atoms oriented in the (111) direction with one layer of graphene at the interface of the copper–graphene composite. The periodic system is then relaxed to find the stable stacking sequence. We use the Quantum ESPRESSO package [35] for DFT calculations with Perdew–Zunger pseudopotential parameters [33]. Energy cutoffs of 30 and 300 Ryd are used for plane-wave basis sets and charge density grids with 32 Monkhorst–Pack sampling $k$-points for Brillouin zone integration and has been verified to achieve a total energy convergence less than 1 meV/atom. Geometric relaxations are carried out for both topfcc and hcpfcc cases such that the force on atoms converged below a threshold of 10 meV Å$^{-1}$. Our DFT results indicate that the hcpfcc case has a lower energy state compared to the topfcc case. This confirms the stacking sequence predicted by our molecular dynamics results and hence the hcpfcc stacking sequence obtained in the molecular simulations is not an artifact of the interatomic potential employed at the interface.

The results of thermal interface conductance for metal–graphene nanocomposites with different numbers of layers of graphene are shown in figure 3. We find that copper–graphene and nickel–graphene interfaces have similar thermal interfacial conductances. This finding is consistent with experimental results [34] that have shown that there is only a $\sim 5\%$ difference between the thermal boundary resistance between the CNT sheet and Cu, and between the CNT sheet and Ni, indicating that our results provide a reasonable qualitative model for studying the interface thermal conductance of metal–graphene nanocomposites.

Interestingly, we find that metal–single-layer graphene has excellent thermal interface conductance with a value of $\sim 500$ MW m$^{-2}$ K$^{-1}$. The thermal interface conductance of the metal–bilayer graphene interface is about half that of the metal–single-layer-graphene interface and when the number of layers of graphene is about 3 or more, the thermal interface conductance reduces to $\sim 100$ MW m$^{-2}$ K$^{-1}$ and there is no dependence between the number of layers of graphene and the thermal interface conductances. It is worth noting that Schmidt et al. have shown that the metal–graphite interface has a thermal interface conductance of 40–100 MW m$^{-2}$ K$^{-1}$ for Au–graphite, Al–graphite and Ti–graphite interfaces at 300 K [29]. Therefore, our results indicate that the value of the thermal interface conductance for the metal–multilayer ($n > 3$) graphene interface becomes close to the experimental data of metal–graphite interfaces. An important conclusion from this finding is that nanocomposites that consist of metal and single-layer graphene should have a much higher performance than metal–multilayer graphene nanocomposites.

The thermal interface conductance is mostly influenced by the interfacial bonding as both phonon flux and the...
vibrational mismatch are subject to the interfacial bond strength [32]. Hopkins et al have shown that the increase of the bond strength at the interface increases the graphene cross-plane velocities \(v_{c,t}\) and thus increases the thermal interface conductance [32]. We attribute the higher thermal interface conductance of metal–single-layer graphene to the increase of bond strength between the metal and single-layer graphene. Note that there is only metal–carbon bonds at the metal–single-layer graphene interface, while for the case of multilayer graphene, the weak interactions between graphene sheets has a significant effect at the interface. The spring constant of the metal–carbon bond, which is computed from parameters of the LJ potential (and originally derived from quantum simulations), is about 11 times larger than the spring constant between the c-axis graphene sheets. Since the velocity is proportional to the square root of the spring constant, this leads to a factor of 3.32 higher for the velocity. The factor coincides with the fact that the thermal interface conductance of the metal–single-layer graphene is 3.52 times larger than the metal and the multilayer-graphene interface. Therefore, we propose that the metal–single-layer-graphene nanocomposite has stronger bonding strength at the metal–graphene interface, which increases the graphene cross-plane velocities and thereby leads to a higher thermal interface conductance. Note that a similar mechanism has been reported by Hopkins et al [32] to explain the higher thermal interface conductance resulting from chemical functionalization of graphene layers. However, we anticipate that further fundamental studies are needed to fully understand the mechanisms by which heat transfers across this interface.

4. Conclusion

We studied the thermal interfacial conductance of copper–graphene and nickel–graphene nanocomposites for different geometries, including temperature effects. The analysis with respect to the effects of the number of layers of graphene on the thermal interface conductance revealed that metal–single-layer graphene has an excellent thermal interface conductance. However, the thermal interface conductance reduces by 80% as the number of layers of graphene increases to larger than trilayer graphene. We attribute the excellent thermal interface conductance of the metal–single-layer graphene to the stronger bonding strength at the metal and single-layer-graphene interface. Our results suggest that metal–single-layer-graphene nanocomposites would be potential candidate materials for the next-generation electronic or energy devices. On the other hand, since the nickel–graphene and copper–graphene interfaces have a similar thermal interface conductance—and considering nickel has better mechanical properties and nickel–graphene has a greater cohesive energy—we anticipate that the nickel–graphene nanocomposite is a better material for electronic, structural and energy applications.

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