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Thermal Transport in Graphene-Polymer Nanocomposites

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ABSTRACT

Graphene-polymer nanocomposites have attracted considerable attention due to their unique properties, such as high thermal conductivity ($\sim 3000 \text{ W mK}^{-1}$), mechanical stiffness ($\sim 1 \text{ TPa}$) and electronic transport properties. Relatively, the thermal performance of graphene-polymer composites has not been well investigated. The major technical challenge is to understand the interfacial thermal transport between graphene nanofiller and polymer matrix at small material length scale. To this end, we conducted molecular dynamics simulations to investigate the thermal transport in graphene-polyethylene nanocomposite. The influence of functionalization with hydrocarbon chains on the interfacial thermal conductivity was studied, taking into account of the effects of model size and thermal conductivity of graphene. The results are considered to contribute to development of new graphene-polymer nanocomposites with tailored thermal properties.

Keywords: Graphene, functionalization, nanocomposite, interface, thermal transport

1. INTRODUCTION

Graphene possesses exceptional electrical, mechanical and thermal properties,¹⁻³ which make it an ideal candidate as filler for making composite materials. For instance, the reported value of thermal conductivity of graphene is about 3000 W/mK ,³ while most of the polymers have thermal conductivity less than 0.5 Wm/K . Adding a small percentage of graphene to the polymer matrix can greatly enhance its thermal conductivity. Recent studies have indicated that significant improvements in thermal conductivity have been achieved in these nanocomposite systems ($3\sim 6 \text{ Wm/K}$).⁴⁻⁶

It has been found that interfacial thermal conductivity between fillers and polymer matrix is crucial to the thermal transport in composites. Recently, Huxtable et al.⁷ reported that the exceptionally small interfacial thermal conductivity ($\sim 12 \text{ MW/m}^2\text{K}$) restricts the heat transport in a carbon nanotube composite. For graphene-polymer nanocomposites, Hu et al.⁸ has reported an effective interfacial thermal conductivity of $30 \text{ MW/m}^2\text{K}$ between graphene and phenolic resin. Chemical functionalization serves as an effective routine to enhance the thermal conductivity graphene-polymer nanocomposites.^{4,9} Since phonons are the primary mode of thermal transport in polymers, covalent bond between the matrix and filler can reduce phonon scattering at graphene-polymer interface, resulting in higher thermal conductivity of nanocomposite. However, the influence of chemical functionalization on interfacial thermal conductivity in graphene-polymer nanocomposites has not been well understood. Due to the nano-sized structure, it is still a technical challenge to conduct experiment across the graphene polymer interface. Numerical simulation such as molecular dynamics (MD) modelling provides an alternative approach to study the interfacial thermal transport. In this study, we have conducted non-equilibrium molecular dynamics (NEMD) simulations to study the thermal transport across graphene-polymer interface. The effect of functionalization, i.e., grafting hydrocarbon chains to graphene layer with covalent bonds, on the interfacial thermal conductivity was also investigated. The effect of model size and thermal conductivity of graphene was taken into account.

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2. MODEL AND METHODOLOGY

Due to structural simplicity, polyethylene (PE) was selected in the simulation, whose molecule ($\text{CH}_3-(\text{CH}_2-\text{CH}_2)_{29}-\text{CH}_3$) is composed of 30 monomers. Two models were built using Material Studio (Accelrys Inc) to simulate PE and graphene-PE nanocomposite. The PE model was prepared with the dimensions of $30 \text{ \AA} \times 30 \text{ \AA} \times 77 \text{ \AA}$, with an initial density of 0.8 g/cc . To build the graphene-PE nanocomposite model, a sandwich structure with graphene placed in the middle of PE matrix was prepared firstly, with dimensions of $25 \text{ \AA} \times 25 \text{ \AA} \times 200 \text{ \AA}$. Then, the model was duplicated along the stacking direction for later simulations, as shown in **Figure 1**. Graphene layers grafted with short linear hydrocarbon chains ($-\text{C}_n\text{H}_{2n+1}$, $n=15$) were established in order to explore the effect of functionalization on interfacial thermal conductivity, **Figure 2**. Such covalent end-grafting with a range of grafting densities $\sigma=0.0032, 0.0064, 0.0096, 0.0144 \text{ \AA}^{-2}$ corresponds to 2, 4, 6, 9 linear hydrocarbon chains grafted on graphene layers. The interatomic interactions were described by an *ab initio* force field (polymer consistent force field, PCFF)¹⁰. All MD simulations were performed with the large-scale atomic/molecular massively parallel simulator (LAMMPS) package.¹¹ In general, the total potential energy of a simulation system contains the following terms:

$$E_{total} = E_{bond} + E_{over} + E_{val} + E_{tors} + E_{vdW} + E_{Coulomb} \quad (1)$$

where E_{bond} , E_{over} , E_{val} , E_{tors} , E_{vdW} and $E_{Coulomb}$ are the energies corresponding to bond, over coordination, angle, torsion, Van der Waals (vdW) and Coulomb interactions, respectively. The detailed expression for each component of the total potential energy can be found anywhere else.¹²

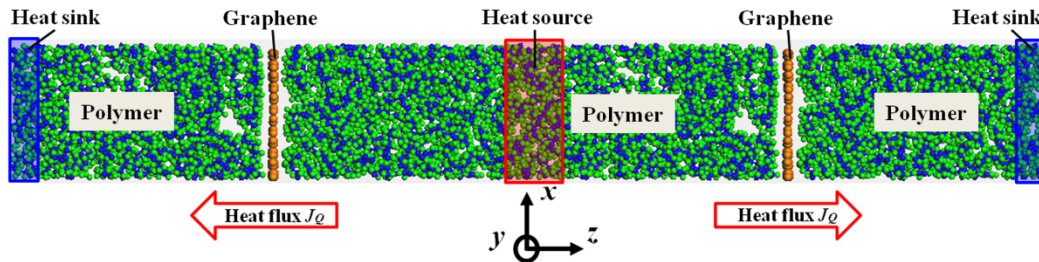


Figure 1. The model of graphene-polymer nanocomposite for non-equilibrium molecular dynamics simulations. The heat source is placed in the center and heat sink placed in each end to generate the heat flux J_Q .

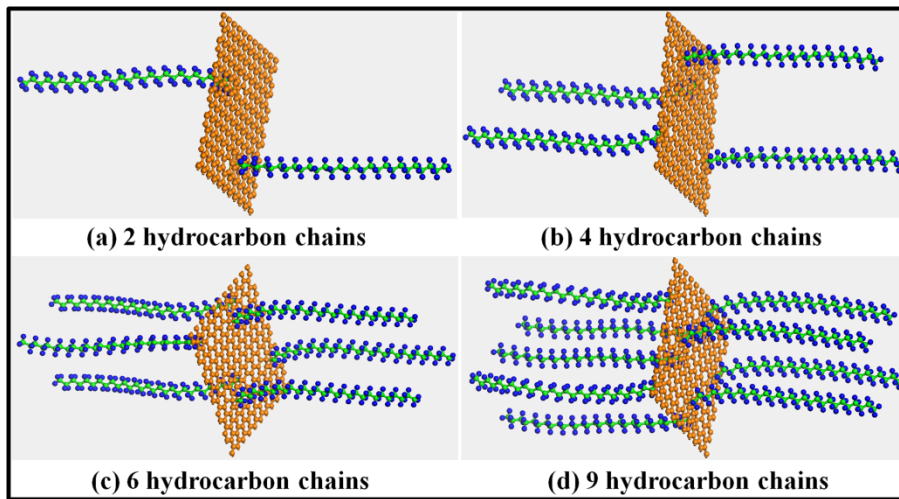


Figure 2. Monolayer graphene grafted with (a) 2, (b) 4, (c) 6 and (d) 9 linear hydrocarbon chains.

For all simulations, systems were firstly equilibrated at constant volume and constant temperature of 300 K for 0.25 ns with a time step of 0.25 fs. Then, they were equilibrated at constant temperature of 300 K and constant pressure of 1 atm for 0.5 ns with the same time step. The thermal conductivity is calculated on the basis of Fourier's law,

$$J_Q = -\kappa \frac{\Delta T}{\Delta z} \quad (2)$$

where J_Q is the heat flux; κ is the thermal conductivity; $\Delta T/\Delta z$ is the temperature gradient. As for the interfacial thermal conductivity, it is calculated using the expression

$$J_Q = -G_\kappa \Delta T \quad (3)$$

where J_Q is the heat flux across the interface; G_κ is the interfacial thermal conductivity; ΔT is the temperature variation across the interface. To calculate thermal conductivity of pure PE and interfacial thermal conductivity of nanocomposite, NEMD method is applied to both models of pure PE and graphene-PE nanocomposite in constant volume and constant energy ensemble. According to Muller-Plathe algorithm, heat source and sink are placed on the center and each end of simulation cells to generate constant heat flux. When simulation systems reach steady state after 2.5 ns simulation, the heat flux can be calculated as $J_Q = \Delta E/2A\Delta t$, where ΔE is the energy added into heat source; A is the cross-sectional area of simulation cell; Δt is the time step.

3. RESULTS AND DISCUSSION

3.1 Model validation

In order to validate the PCFF potential for thermal transport simulation in graphene-PE nanocomposite, the thermal conductivity of the PE was calculated using NEMD method. **Figure 3** shows the heat flux and the temperature profile. The temperature gradient is linear, indicating the regime of linear response in heat source/sink simulation. The thermal conductivity of the PE model is calculated as $\kappa_{PE}=0.3599$ W/mK. This value is in agreement with the previous simulations,^{13,14} validated the model and methodology used in this work.

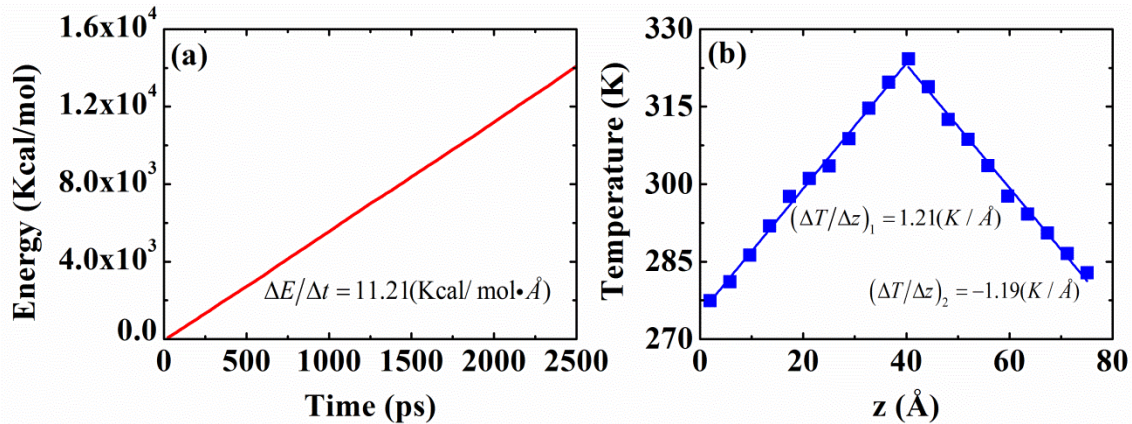


Figure 3. (a) Heat energy in PE system versus time. (b) Steady-state temperature profile along the entire length of the PE model.

3.2 Effect of length and functionalization on the thermal conductivity of graphene

In NEMD simulations, the model size is finite and can influence the calculated interfacial thermal conductivity. Recent research has demonstrated that there is no obvious dependence of matrix thickness (block size L along the stacking direction) on the interfacial thermal conductivity of graphene-polymer nanocomposite. Therefore, only one value of matrix thickness ($L=35$ Å) is chosen in this work.¹⁴ Such matrix-size independence might be owing to the fact that the propagating vibration modes in polymer matrix have the propagation lengths on the order of a few bond lengths, and the block size of 35 Å is large enough to involve all the significant vibration modes in PE matrix. However, the length of

graphene is crucial to its thermal conductivity. Small model size can omit some significant modes of long wavelengths. We thus discuss the effect of the length and functionalization on the thermal conductivity of graphene. As shown in Figure 4(a), the thermal conductivity of monolayer graphene κ is deteriorated by functionalization with grafted hydrocarbon chains. Functionalization at a very small grafting density of 0.0032 surprisingly leads to the drop of κ around 69%. With the increase of grafting density, the drop of κ becomes slower and gets saturated at a value of 80%. Moreover, κ also enhances with the increase of simulation cell in Figure 4(b). This can be attributed to the ballistic nature of thermal transport, which is also observed in pure graphene.

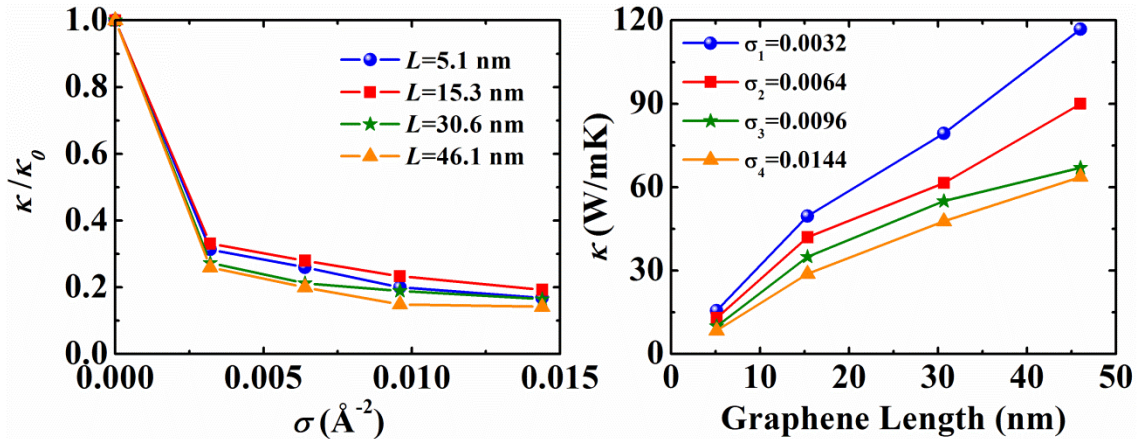


Figure 4. (a) Normalized thermal conductivity of functionalized graphene κ/κ_0 versus grafting density σ . κ_0 represents the thermal conductivity of pure graphene. (b) Thermal conductivity of functionalized graphene versus graphene length L .

3.3 Interfacial thermal conductivity of graphene-PE nanocomposite

Both heat flux and temperature profile in graphene-polymer nanocomposite are determined using NEMD method. Then, the corresponding interfacial thermal conductivity can be calculated in terms of Eq. (3). Figure 4(a) shows obvious temperature drop at graphene-PE interface, which dominates the overall temperature across whole model. This temperature drop leads to the value of interfacial thermal conductivity to be $G_k=76.5$ $\text{MW/m}^2\text{K}$, which is close to the value obtained in previous work.¹⁴ Figure 4(b) shows a plot of G_k as a function of grafting density for linear hydrocarbon chains. It is observed that after grafting linear hydrocarbon chains to monolayer graphene, the interfacial thermal conductivity are surprisingly enhanced. Grafting only two chains ($\sigma=0.0032$ \AA^{-2}) on each side of graphene raises G_k by 33.3%. When grafting up to 6 chains ($\sigma=0.0096$ \AA^{-2}), G_k is remarkably enhanced by 196%, which is higher than the enhancement by increasing layer number of graphene. At higher grafting density, the increase of G_k becomes much smaller, showing a saturation trend of interfacial thermal conductivity. As for the influence of graphene length on G_k , previous work¹⁴ indicated that increasing graphene length can enhance G_k . However, such enhancement will be saturated when graphene size is larger than about 79 \AA .

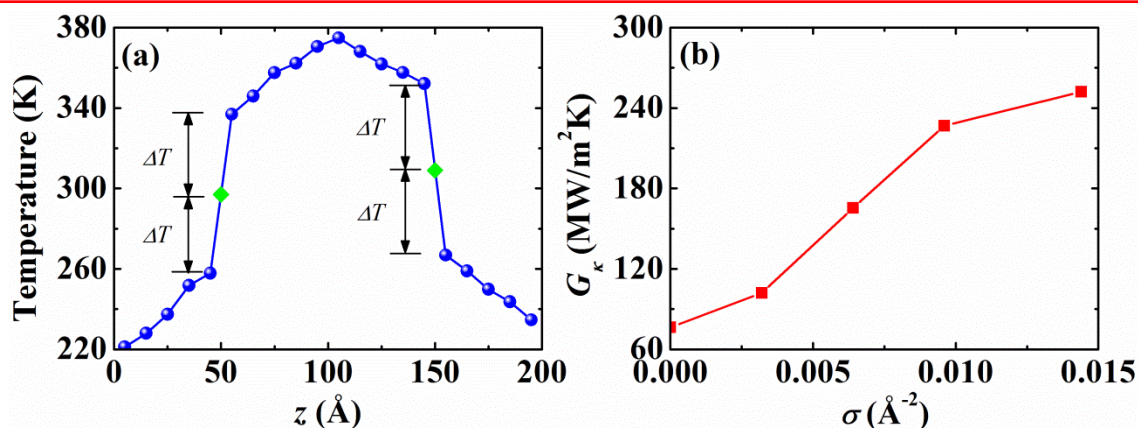


Figure 5. (a) Steady-state temperature profile in the case of monolayer graphene without functionalization. (b) Interfacial thermal conductivity G_k versus grafting density σ .

In order to explore the underlying mechanism of improvement of G_k , Hu et al.¹⁵ demonstrated that the heat transport between graphene and polymer matrix is dominated by their low-frequency vibration modes. Grafted hydrocarbon chains can widen the overlap in low-frequency vibration modes and consequently enhance the interfacial thermal conductivity. Our results are also consistent with previous study of interfacial thermal conductivity of CNT-polymer nanocomposite.¹⁶ Therefore, functionalization of graphene by grafting hydrocarbon chains is an effective approach to improve the interfacial thermal conductivity of graphene-polymer nanocomposite.

4. CONCLUSIONS

In this work, we have conducted MD simulations to investigate the thermal transport in graphene-polymer nanocomposite. The effects of functionalization on both thermal conductivity of graphene and interfacial thermal conductivity of graphene-polymer nanocomposite were systematically investigated. Our simulation results indicate that functionalization with grafted hydrocarbon chains can reduce the thermal conductivity of graphene. On the other hand, it can strengthen the coupling between graphene and polymer, and increase the corresponding interfacial thermal conductivity. Our studies provide an effective approach to enhance the thermal transport in graphene-polymer nanocomposite.

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