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# Molecular dynamics study of oxygen functionalization effects on graphene thermal conductivity: Roles of C/O ratio and functional-group chemistry

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**Abstract.** Graphene has been widely explored as a thermally conductive filler in nanocomposites and interface materials, yet its performance is highly sensitive to surface functionalization introduced during processing. Oxygen functional groups including epoxy (-O-), hydroxyl (OH), and carboxyl (COOH) are beneficial to composite matrices formation but simultaneously disrupt phonon transport by breaking the  $sp^2$  carbon network. A systematic non-equilibrium molecular dynamics study was conducted to elucidate how oxygen content and functional-group chemistry influence the thermal properties of graphene. Pristine graphene (2-12 nm lateral size) was first simulated to validate the methodology. Thereafter, the overall C/O ratio was varied from 300 to 4 while keeping the relative proportions of COOH, -O-, and OH groups constant; a steady decline in the relative thermal conductivity from 0.76 to 0.10 was observed as oxygen coverage increased. Finally, at a fixed C/O ratio of 7, the loading of each functional group was independently increased from 12 % to 65 %, and their respective impacts on thermal conductivity were quantified. COOH was found to yield the mildest thermal conductivity reduction due to the edge functionalization, whereas -O-functionalization caused the steepest decline (up to  $\approx 0.15$  at 65 % loading) because of the stronger interruption on the  $sp^2$  domain. The OH groups produced an intermediate, nonmonotonic response. These findings provide molecular-level design rules for balancing dispersion stability against thermal performance in graphene-based composites and thermal interface materials.

## 1. Introduction

Graphene family materials have attracted extensive attention in materials science owing to their extraordinary electrical, mechanical, and optical properties, along with their outstanding in-plane thermal conductivity [1]. When incorporated as a filler into composite materials, graphene can dramatically enhance their thermal conductivity. For instance, 10 wt% addition of graphene oxide (GO) or reduced graphene oxide (rGO) was reported to improve the thermal conductivity of epoxy resin and polyamide by 11-fold and 2.1-fold, respectively [2, 3]. Consequently, graphene-based composites show great promise in fields involving thermal sensors, energy storage, and thermal management where improved thermal conductivity is essential [4, 5].



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However, graphene typically retains a certain amount of oxygen functional groups to improve hydrophilic interactions and provide sites for covalent bond functionalization in composite matrices formation [6]. These functional groups disrupt the  $sp^2$ -hybridized carbon network and increase phonon scattering, thereby significantly reducing thermal conductivity [7]. Mu et al. reported that an oxygen content of 5 % on graphene reduces the thermal conductivity by nearly 90 % [8]. Thus, minimizing the detrimental impact of functional groups on thermal conductivity, while maintaining sufficient dispersion, represents a critical design challenge for graphene-based composites.

Theoretical calculations offer unique advantages in elucidating the molecular-level mechanisms by which functional groups affect thermal conductivity. Equilibrium molecular dynamics (EMD) and non-equilibrium molecular dynamics (NEMD) are the two primary simulation methods used for this purpose [9, 10]. However, the EMD method suffers from phase cancellation of the heat flux autocorrelation function at boundaries, making it less suitable for calculating the thermal conductivity of nanomaterials [11]. In contrast, NEMD simulates actual heat transfer by imposing a thermal gradient, effectively avoiding artificial phonon scattering, and thus has been widely applied in graphene thermal conductivity studies. Notably, existing NEMD studies have largely focused on size-dependent effects or the macroscopic influence on the C/O ratio [12, 13], while the role of functional group types and proportions has received limited attention.

In this work, NEMD simulations were employed to calculate the thermal conductivity of pristine graphene (pG) with 2-12 nm lateral size to validate the reliability of our models by comparing them with reported data. Based on this, we investigate the effect of oxygen content on thermal conductivity while keeping the ratio of the three major functional groups constant. Finally, at a fixed C/O ratio, we vary the relative proportions of hydroxyl, carboxyl, and epoxy groups to analyze their contributions to thermal conductivity. The results of this work aim to provide a molecular-level understanding of the optimal design of graphene-based composites where dispersion and thermal conductivity must be balanced.

## 2. Methodology

### 2.1. Molecular modeling

The molecular modeling process was carried out using Matlab. We constructed graphene models in two stages. First, pG sheets ranging from 2-12 nm in lateral size were generated by adding rows of aromatic carbon rings until the target dimensions were reached. We then selected the 12 nm sheet that is large enough to support more stable heat fluxes with less ballistic transport for the study of functional groups' influence on thermal conductivity.

For functionalized graphene, edge carboxylation and basal-plane oxygenation were introduced in a randomized manner. Edge carbons were randomly sampled and their terminating hydrogens were replaced with carboxyl (COOH) groups. Independently, interior carbons with three neighboring atoms were randomly chosen and decorated with either epoxide (-O-) or hydroxyl (OH) species. New atom coordinates were determined by projecting along the local surface normal to maintain realistic bonding geometries. A built-in sequencing and classification routine prevented multiple or adjacent substitutions on the same carbon site, ensuring a uniform distribution of functional groups across the sheet.

### 2.2. Molecular dynamics simulations

The molecular dynamics simulations were performed using LAMMPS. ReaxFF for hydrocarbon systems was utilized as the force field describing atom interactions in pG and GO models as it has been validated in previous studies [14, 15]. In the simulation, the pG and GO models underwent initial structural relaxation using the NVT ensemble to ensure system equilibration at room temperature. Subsequently, the system was prepared for the thermal conductivity calculation with the definition of the heat source and sink regions that contain atoms at two ends of the graphene model. The system was then equilibrated again under the NVE ensemble. After that, the thermal conductivity was calculated by applying a temperature gradient using the Langevin thermostat to the atomic groups involved in the heat source and sink regions, and the system was treated under the NVE ensemble using the NEMD method.

During this process, the temperature distribution across the system was sampled and recorded. The atomic temperature along the x-axis was then calculated for the generation of a temperature profile. The results were outputted to files for further analysis.

### 2.3. Thermal conductivity calculations

Thermal conductivity was calculated based on the sampling data of temperature profile along the x-axis ( $T$ ), the spatial coordinates of each bin along the x-axis ( $L$ ), the energy in heat ( $E_{hot}$ ) and sink region ( $E_{cold}$ ), and cross-sectional area ( $A$ ), all obtained from LAMMPS output. Thermal conductivity ( $\kappa$ ) is given by

$$\kappa = \frac{Q}{A} \times \frac{\Delta L}{\Delta T} \quad (1)$$

where  $\Delta L/\Delta T$  is the inverse temperature gradient, and the heat flux  $Q$  is described as

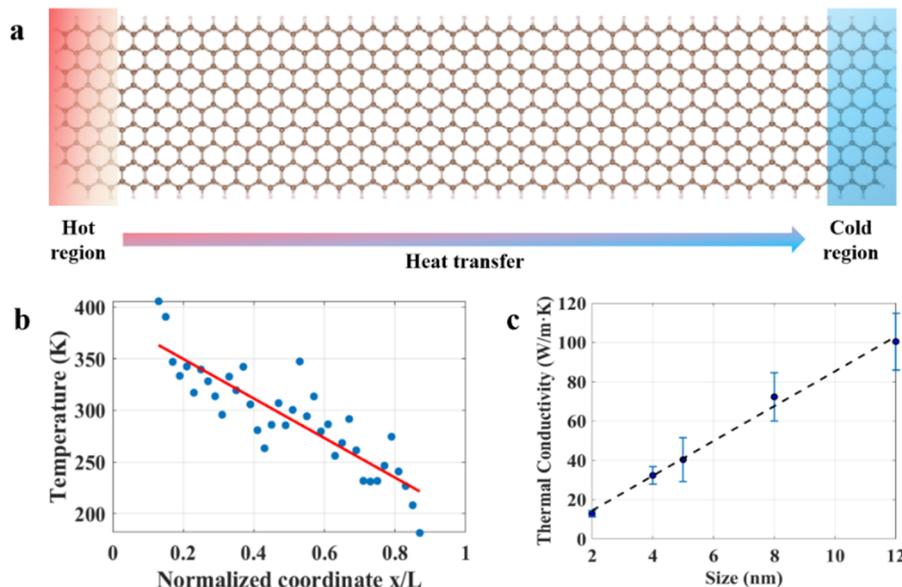
$$Q = \frac{\frac{\Delta E_{hot}}{\Delta t} + \frac{\Delta E_{cold}}{\Delta t}}{2} \quad (2)$$

where  $\Delta t$  denotes the sampling duration on simulation time over which energy exchange is measured.

## 3. Results and Discussion

### 3.1. Thermal conductivity of pristine graphene

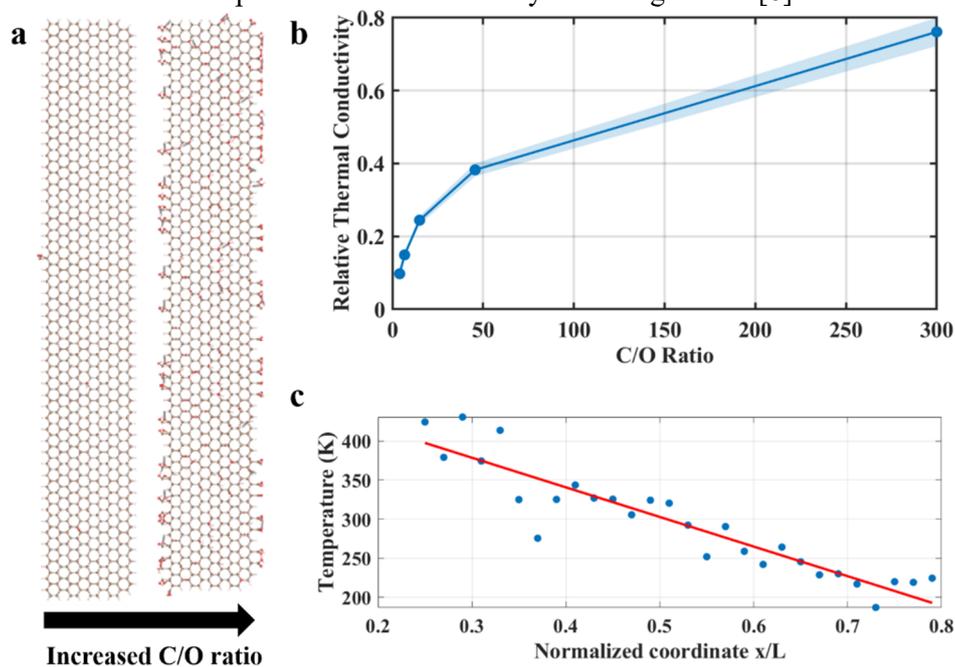
The thermal conductivity of pG sheets with lateral sizes ranging from 2-12 nm was first calculated both for comparison with functionalized models and to validate our calculations against previous literature. The schematic of the graphene model and the imposed heat flux is demonstrated in **Figure 1a**. The temperature gradient was then determined by sampling the atomic temperature distribution along the heat-flux direction. A clear temperature jump appears between the hot and cold regions and their adjacent zones (**Figure 1b**). This jump arises because graphene's extremely high thermal conductivity confines most of the temperature drop to the immediate source/sink interfaces, resulting in a nearly isothermal interior. **Figure 1c** presents the relationship between thermal conductivity and graphene sheet size: it increases from 12.8 to 100.4 W m<sup>-1</sup>K<sup>-1</sup> with a lateral dimension increase from 2 to 12 nm, reflecting graphene's unique phonon transport behavior and the non-equilibrium phonon population evolution under an applied heat flux, in agreement with earlier studies [12, 16].



**Figure 1.** Thermal conductivity of pG. (a) The schematic diagram of a specific heat flux applied on the pG sheet. (b) The temperature variation in the direction of the x-axis. (c) The thermal conductivity of pG increases as a function of sheet size (2 to 12 nm); the dashed line shows the linear regression fit.

### 3.2. Influence of carbon to oxygen ratio on thermal conductivity

The influence of the C/O ratio on thermal conductivity was investigated while keeping the proportions of COOH, O, and OH functional groups constant, with models ranging from C/O = 300 to C/O = 4 (**Figure 2a**). Relative thermal conductivity normalized to that of pG was extracted from nonequilibrium molecular dynamics simulations. With a decrease in the C/O ratio (increasing oxygen content), a sharp decrease in thermal conductivity is illustrated in **Figure 2b**. This continuous decline occurs because oxygen-containing groups involving OH, COOH, and O increasingly disrupt the  $sp^2$  carbon network and enhance phonon scattering. The temperature profiles in **Figure 2c** exhibit much steeper gradients than those of pG, further illustrating how functionalization impedes heat transfer. The most dramatic reduction appears at low C/O ratios below 15, indicating that once oxygen coverage exceeds a certain threshold, even small increases in functional groups cause disproportionately large decreases in thermal transport. These findings agree with earlier reports that only a few percent oxygen coverage can suppress graphene's thermal conductivity by more than 90 percent and that conductivity decays nonlinearly with the C/O ratio due to combined point defect and boundary scattering effects [8].



**Figure 2.** Influence of C/O ratio on thermal conductivity. (a) Molecular models of graphene sheets with C/O ratios that decrease from 300 to 4. (b) The relationship between relative thermal conductivity (normalized to pG) and C/O ratio. (c) Temperature variation profile in the direction of the heat-flux for the graphene sheet with C/O = 4.

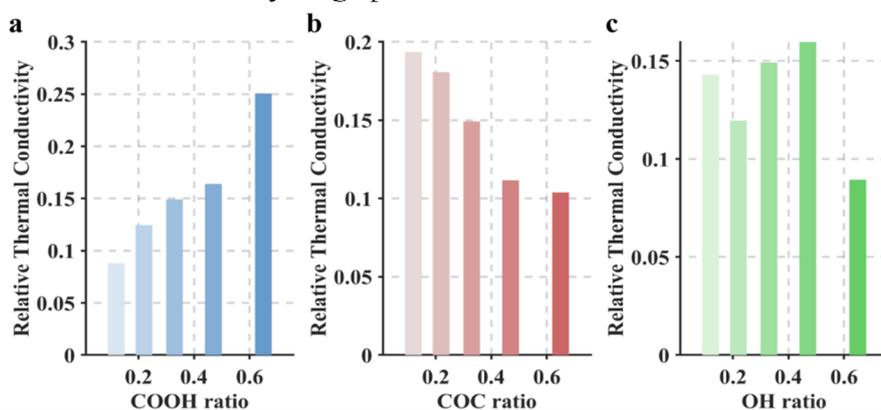
From an application perspective, these results highlight the trade-off between dispersion stability achieved by oxygen functionalities and thermal performance. To preserve at least half of the pristine thermal conductivity, our data suggest maintaining a C/O ratio above approximately 50. Such design criteria are critical for developing graphene-based thermal interface materials and nanocomposites that require both good polymer compatibility and efficient heat transport.

### 3.3. Influence of functional group types and proportion on thermal conductivity

The influence of COOH, epoxide ( $-O-$ ), and hydroxyl (OH) functional groups on thermal conductivity was examined at a fixed C/O ratio of 7, with the proportions of the two non-target groups held constant in each series. As shown in **Figure 3a**, when COOH loading was increased from 12 % to 65 %, the relative thermal conductivity rose steadily from 0.09 to 0.25. This increase occurs because COOH at edges induces less influence on  $sp^2$  bonds on graphene sheets than the equivalent removal of OH and epoxide groups, yielding a net reduction in phonon scattering.

In contrast, increasing the epoxide content produced a monotonic, pronounced drop in thermal conductivity as shown in **Figure 3b**. Each epoxide bridges two carbon atoms and disrupts up to five  $sp^2$  bonds, creating strong scattering centers and thereby reducing heat transport most severely among the three group types.

Hydroxyl functionalization showed a non-monotonic trend (**Figure 3c**): as OH content rose from 12 % to 22 %, thermal conductivity decreased; between 22 % and 47 % loading it increased; and beyond 47 % it declined again. Since each OH group affects only three adjacent  $sp^2$  bonds, which is fewer than epoxide but more than COOH. Hence, the impact of OH on thermal conductivity lies between the other two. These findings highlight the critical role of both the type and proportion of oxygen functional groups in optimizing the trade-off between the retention of oxygen contents that improve chemical interactions and thermal conductivity for graphene materials.



**Figure 3.** Influence of the types and proportion of oxygen functional groups on thermal conductivity. (a) Thermal conductivity variations with the proportion of COOH groups are adjusted, keeping the proportions of other functional groups constant. (b) Thermal conductivity variations by varying the content of -O- groups, with other functional groups fixed. (c) Thermal conductivity changes by modifying the amount of OH groups while maintaining the levels of other functional groups.

#### 4. Conclusion

Based on the results and discussions presented above, the following conclusions were drawn:

(1) pG sheets from 2 nm to 12 nm show increasing thermal conductivity with size, in agreement with the literature, confirming the reliability of our simulation framework.

(2) At fixed functional-group proportions, raising oxygen content (C/O from 300 to 4) induces a nearly tenfold reduction in thermal conductivity relative to pG, driven by progressive disruption of the  $sp^2$  network and enhanced phonon scattering.

(3) At a constant C/O ratio of 7, COOH has the mildest impact on heat transport (relative thermal conductivity rising from 0.09 to 0.25 as COOH increases), -O- functionalization is most detrimental (monotonic thermal conductivity decrease due to stronger disruption on  $sp^2$  network), and OH groups exhibit intermediate, nonmonotonic behavior.

(4) To preserve > 50 % of pristine thermal conductivity while maintaining functional groups, functionalization strategies should prioritize COOH or low-loading OH over -O-. These molecular-level rules enable the rational design of graphene-based thermal composite materials with optimized dispersion and thermal conducting performance.

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