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Thermal conductivity of graphene oxide: A molecular dynamics study

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Graphene is a particularly unique form of carbon that can possess a number of desirable properties [1, 2]. The atomic structure of graphene enables it to conduct heat and electricity with great efficiency [3, 4]. In effect, graphene can dissipate heat more efficiently than copper or aluminum [5, 6]. The introduction of graphene oxide into both metals and polymers has yielded materials with enhanced thermal properties [7, 8]. However, the potential has not been fully exploited [9, 10]. Recent efforts have shown promise for enhancing thermal conductivity [11, 12]. The success has been driven by continuing technical advances in the surface chemistry of graphene [13] and a fundamental understanding the role of defects and grain-boundaries in thermal conductivity [14]. Chemical functionalization has especially great potential for improvements in composite thermal properties [15], thus stimulating intense research effort in this area [16].

The thermal conductivity of graphene oxide is much lower than that of pristine graphene due to enhanced phonon-boundary scattering resulting from surface functional groups [17, 18]. However, graphene oxide is dispersible in water, organic solvents, and different matrixes [19, 20], making it particularly desirable for certain applications. Previous theoretical studies have developed molecular dynamics models in which functional groups are substantially homogeneously distributed on the whole edge or surface of graphene oxide [21, 22]. However, this assumption is not necessarily completely correct, especially for chemically derived graphene oxide. It is therefore necessary to develop a molecular dynamics model in which functional groups are present in nonuniform distribution on the whole edge or surface of chemically functionalized graphene oxide.

This study relates to the mechanism of phonon transport in graphene oxide containing hydroxyl and epoxy functional groups. The thermal properties of graphene oxide are studied using non-equilibrium molecular dynamics to understand the thermal transport phenomena involved and the structure factors limiting heat conduction. Estimates are given in terms of phonon mean free paths for the reduction in thermal conductivity by interior defects due to scattering. The mechanism of phonon transport in the graphene oxide is discussed. The objective is to evaluate the effect of the degree of oxidation on the thermal properties of graphene oxide in order to understand the nanoscale thermal transport phenomena involved. Particular focus is placed on how sensitive the thermal conductivity of graphene oxide is to the concentration of oxygen-containing functional groups.

The graphene oxide modeled in this study contains hydroxyl and epoxy functional groups in the basal plane. Oxygen is present in the form of the above oxygen-containing functional groups with a molar ratio of 3 : 2. These functional groups are present in nonuniform distribution on the two sides of the graphene oxide sheet. The degree of oxidation ranges from 0 to 0.35. The graphene oxide sheet is 2.4 nm in width and varies in length from 5 to 40 nm. Atomistic simulations are carried out using reverse non-equilibrium molecular dynamics. The Müller-Plathe algorithm [23] is used to exchange kinetic energy, which is implemented in LAMMPS [24]. The atomistic interactions in the graphene oxide are treated with the reactive force-field interatomic potential. The carbon atoms that are chemically bonded thereto hydroxyl and epoxy functional groups in the graphene oxide are treated as interior defects. The effective mean free path for phonon scattering can be determined.

The results indicated that the degree of oxidation can significantly affect the thermal conductivity of graphene oxide. Oxygen-containing functional groups reduces the efficiency of phonon transport in graphene oxide, and they can adversely affect the thermal performance due to the mean free path of phonons limited mainly by interior defects. The effect of scattering from interior defects on the thermal conductivity

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becomes more pronounced with increasing the sheet length.

The thermal performance can be enhanced with low degrees of oxidation by effectively eliminating or reducing phonon-defect scattering within graphene oxide, and can be improved by increasing the sheet length due to the reduced probability of phonon-boundary scattering.

The thermal properties of the graphene oxide sheet with different lengths and with different degrees of oxidation are investigated. The calculated intrinsic thermal conductivity of single layer pristine graphene is around $2480\,W/m\cdot K$ at room temperature, which has good consistency with that determined by experiments [25]. Consequently, graphene nanoribbons, by their very nature, can conduct heat efficiently. This unique feature makes graphene particularly desirable for certain applications [26]. The intrinsic thermal conductivity of graphene oxide is around $72\,W/m\cdot K$ at room temperature with an oxidation degree of 0.35 and around $670\,W/m\cdot K$ with an oxidation degree of 0.05.

The effect of the degree of oxidation on the phonon mean free path due to internal scattering processes is evaluated. Oxygen-containing functional groups cause a sharp decrease in thermal conductivity due to the significantly reduced mean free path of phonons. With a high degree of oxidation, the structure of graphene oxide is ineffective to reduce the probability of phonon-defect scattering and enhance the capacity of phonon transport in graphene oxide, making the carbon-based material a poor conductor of heat in comparison with pristine graphene.

A high degree of oxidation causes a decrease in phonon mean free path due to enhanced phonon-defect scattering. A low degree of oxidation enhances the phonon transport properties and reduces the probability of phonon-defect scattering. Phonon transport in graphene oxide with a high degree of oxidation is governed by the phonon-defect scattering mean free path.

With respect to the thermal conductivity, the effective phonon mean free path is more important than the specific heat, especially in the case of high degrees of oxidation or high concentrations of oxygen-containing functional groups.

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