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# Engineering of thermal transport in graphene using grain size, strain, nitrogen and boron doping; a multiscale modeling

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ABSTRACT

Large scale graphene sheets and other two-dimensional (2D) materials are commonly fabricated via chemical vapor deposition (CVD) technique which produces polycrystalline samples wherein Kapitza conductance along grain boundaries may substantially affect thermal transport. In this work, thermal conductivity of polycrystalline graphene (PG) was explored with grain sizes ranging from 2 nm to 10 nm employing non-equilibrium molecular dynamics (NEMD) simulations. Kapitza conductance at grain boundaries was estimated by fitting continuum models to the NEMD results. By calculating 2D temperature profile, both NEMD and continuum models show that Kapitza resistance is the dominant factor in thermal transport within PG with small grain sizes. Effects of nitrogen and boron doping and compressive and tensile strain on effective thermal conductivity of PG nanomembranes were further investigated. The results showed that, doping affects neither the Kapitza conductance nor the thermal conductivity of PG with nano-sized grains. Moreover, applying strain to PG in two directions, namely parallel and normal to the heat flow direction, suppress the thermal conductivity by increasing the grain size. The obtained results can provide useful understanding about heat transport not only in the polycrystalline graphene, but also in other CVD-grown 2D materials.



## 1. Introduction

Synthesized graphene sheets usually come with various types of defects that may substantially affect thermal, mechanical, electrical and other properties of graphene [1–5]. Currently, the most promising method for synthesizing graphene sheets in large-scale is chemical vapor deposition (CVD) [6]. Crystal growth during the CVD process usually generates polycrystalline graphene sheets wherein grain boundaries can intensely affect properties of final product [7–12]. As the grain size decreases, the number of carbon atoms along the grain boundaries increases, eventually concentrating the structural defects. The polycrystalline graphene sheets synthesized by CVD method are expected to suppress thermal properties; as a result, fundamental understanding of the impact of grain boundaries on the thermal conductivity is very important [13–16].

Engineering of thermal conduction properties of 2D materials in order to use them under special conditions or prepare them for particular applications is an interesting topic which has attracted great deals of attention during the last decade. Decreasing the material size to the order of heat carriers' characteristic lengths, scattering effects of carriers at boundaries, interfaces and grain boundaries become more dominant, necessitating detailed discussions on thermal transport control in nanostructures by configuring grain boundaries, doping, strain, etc. The fact that grain boundaries can affect heat transfer has comprised a topic for many research works employing atomistic simulations [17–21]. Bagri et al. measured the effect of grain boundaries on thermal conductivity of graphene by equilibrium molecular dynamics (EMD) simulations. They obtained the interfacial thermal resistance at grain boundaries as a function of the angle between orientations of the grains [20]. Kotakoski and Meyer developed a method to model PG sheets in atomic scale in accordance to what has been observed in experiments [22]. The obtained model then was used to study mechanical [22] and electrical [23] properties of PG samples. Mortazavi et al. investigated thermal conduction in PG sheets following a multiscale approach. They utilized equilibrium MD simulations to examine the effects of grain size on heat transport in polycrystalline graphene. Their results indicated that, thermal conductivity of fine-grained graphene is lower than pristine graphene by one order of magnitude [24]. Hahn et al. calculated thermal conductivity of PG sheets employing approach-to-equilibrium molecular dynamics simulations. They estimated thermal conductivity of a PG sample of 1 nm in grain size as just 3% of that of single crystalline graphene [25]. Yasaei et al. showed that, in coarse-grained

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PG, Kapitza conductance at grain boundaries has a bimodal behavior depending on the grain structure [26]. More recently, Fan et al. showed that, in large-scale PG samples, variation of thermal conductivity with grain size exhibits a bimodal behavior due to the different contribution of in-plane and out-of-plane phonons to the Kapitza conductance [27]. According to Azizi et al., Kapitza resistance was strongly dependent on the tilt angle between two grains; they calculated a mode-by-mode quantum correction on Kapitza conductance obtained via MD [28].

Most of the nanostructures investigated in experiments are under residual strain with values greater than those in bulk structures. Considering the kinetic theory and according to anharmonic effect in crystals, strain can largely influence thermal properties of crystals by affecting their stiffness and consequently phonon group velocities [29]. However, most of the studies have been performed on the effect of strain on thermal properties of LJ crystals [30–34], with only a few studies reporting thermal conductivity of graphene under strain. Li et al. explored thermal conductivity of graphene under tensile and compressive strains using EMD simulations. They showed that, graphene has its thermal conductivity maximized at a specific compressive strain [29]. Guo et al. calculated thermal conductivity of 12 nm long graphene using NEMD simulations and concluded that, thermal conductivity of graphene decreases with increasing tensile strain due to decreasing the stiffness and increasing anharmonic effects in the lattice. They also reported that, in contrast to other crystalline structures under the same conditions, thermal conductivity of a compressed graphene decreases with increasing tensile strain. They attributed this phenomenon to the unique structure of graphene in which the structural wrinkles and phonon scattering increases in the presence of compressive strain [35]. Bonini et al. employed first-principle calculations to show that, strain is a key factor in engineering thermal conductivity of graphene [36]. Pereira and Donadio used EMD and Kuang et al. utilized quantum mechanics equations and Peierls-Boltzmann transport equations to find that, one could impose some strain to eliminate out-of-plane modes in graphene and obtain perfect 2D structures which could diverge thermal conductivity values according to the system dimensions [34,37,38]. Wu et al. examined the effect of strain on thermal conductivity of polycrystalline graphene with 12–25 nm grain sizes using NEMD simulations considering AIREBO potential function to describe atomic interactions. Accordingly, they showed that, compared to the pristine graphene, polycrystalline graphene had its thermal conductivity less sensitive to the imposed strain, and this sensitivity decreased by decreasing the grain size [30]. Bazrafshan and Rajabpour explored the effect of strain on thermal conductivity of defected amorphous graphene and examined the effect of strain on heat transfer engineering by NEMD simulations [31].

Nitrogen and boron-doping of graphene has attracted many attentions compared to other atomic dopings, because of the fact that, nitrogen and boron atoms have similar atomic sizes to carbon atom and the number of electrons in their valance orbital make them appropriate candidates for $sp^2$ hybridization and formation of strong covalence bonding structures [32], and more notably, nitrogen and boron doping can be used to turn electronic character of graphene to those of a semiconductor, which is very appealing for nanoelectronic applications. Chien et al. investigated the effect of nitrogen-doping on thermal conductivity of carbon nanotubes utilizing NEMD simulations. According to their report, thermal rectification was observable by axisymmetric doping in carbon nanotubes [33]. Goharshadi and Mahdizadeh studied the effect of nitrogen-doping on relaxation time and mean free path of phonons in graphene using EMD simulations. They observed that, compared to pristine graphene, nitrogen-doped graphene had its thermal conductivity less sensitive to temperature changes [39]. Lotfi and Neek-Amal examined the effect of nitrogen-doping on the thermal conductivity of graphene in the presence of grain boundaries. They found that, nitrogen atoms tend to increase graphene ripples, consequently decreasing the thermal conductivity of the whole system [40]. Yang et al. investigated thermal rectification of nitrogen-doped graphene with various distributions of nitrogen atoms employing molecular dynamics simulations [41]. Mortazavi et al. utilized MD simulations to show that, nitrogen-doping could greatly diminish thermal conductivity of graphene due to phonon scattering [42]. Izadifar et al. studied the effects of boron and nitrogen-doping on mechanical properties of PG and found that, tensile strength and failure strain exhibit different behaviors in doped PGs of different grain sizes [43]. Recently, 2D structures like carbon nitride have shown the importance of applying nitrogen in modification of electronic and thermal properties of graphene [44,45].

In the current study, thermal transport in polycrystalline graphene was explored for different grain sizes, nitrogen and boron-doping concentrations, and strains using NEMD simulations along with the optimized Tersoff potential function. All of the studied PG samples were constructed with grain sizes ranging from 2 nm to 10 nm. A two-dimensional temperature profile was introduced to probe the variation of temperature inside grains and across grain boundaries. Kapitza conductance at grain boundaries was estimated by fitting two continuum models (1D thermal resistance and 2D heat conduction equation) into NEMD results. In order to investigate the effects of nitrogen and boron-doping and strain on the thermal conductivity, pristine and polycrystalline graphene samples were subjected to −0.02 to 0.1 strain levels in two directions, namely parallel and normal to the heat flux direction, and with different concentrations of nitrogen/boron atoms ranging from 0.1% to 7%. Density of states analysis was also performed to examine how the influences of the presence of grain boundaries, nitrogen atoms and mechanical strain on vibrational behaviors of atoms.

## 2. Simulation method

Since the role of electrons in thermal transport of graphene is much less than phonons, classical MD simulation represents an appropriate technique for studying thermal conductivity of graphene [46–50]. In the present research, MD simulations were carried out by LAMMPS package [23]. Precision of predictions obtained from MD simulations is highly dependent on the employed potential functions. Previous studies have shown that, compared to original Tersoff potential function, phonon dispersion curves of graphene presented by its optimized version tend to give a better agreement with corresponding experimental data [51,52]. In this study, interactions of carbon atoms were described by the optimized Tersoff potential function developed by Lindsay and Brodio [53]. Nitrogen-carbon interactions were also described by Tersoff potential function parametrized to reproduce *ab initio* energetics of N-C bonds [54].

There are a few approaches to prepare polycrystalline graphene samples [22,55,56]. In this study, we utilized the method developed by Kotakoski and Meyer to model polycrystalline graphene samples in atomic scale in accordance to what has been observed in experiments[22]. Given that, the graphene growth initiates from various locations along random crystalline directions during the CVD graphene synthesis [22,57], developed computer programs that generate atomic positions of polycrystalline graphene were used by locating limited number of nucleation sites distributed randomly but uniformly across the sheet. Grain size was determined by $GS = \sqrt{A/n}$, where $GS$ is the grain size, $A$ is total area of the graphene sheet, and $n$ is the number of grains in polycrystalline graphene sheets. Thus, the size of each grain is represented by square root of its area. For example, in a 30 nm × 30 nm piece of