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Atomistic modeling of mechanical properties of polycrystalline graphene

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Abstract

We performed molecular dynamics (MD) simulations to investigate the mechanical properties of polycrystalline graphene. By constructing molecular models of ultra-fine-grained graphene structures, we studied the effect of different grain sizes of 1–10 nm on the mechanical response of graphene. We found that the elastic modulus and tensile strength of polycrystalline graphene decrease with decreasing grain size. The calculated mechanical properties for pristine and polycrystalline graphene sheets are found to be in agreement with experimental results in the literature. Our MD results suggest that the ultra-fine-grained graphene structures can show ultrahigh tensile strength and elastic modulus values that are very close to those of pristine graphene sheets.

Keywords: polycrystalline graphene, molecular dynamics, mechanical properties

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

1. Introduction

Graphene [1], an \textit{sp}^2-bonded carbon atom sheet, is an exceptional material because of its extremely high crystal and electronic qualities [2–4]. Having exceptionally high thermal conductivity [5] and mechanical [6] and electrical properties [7], graphene has attracted a great deal of attention and ongoing demands for its use in a wide variety of applications from nanoelectronics to the aerospace industry. Atomic force microscope nanoindentation experiments [6] revealed that defect-free graphene sheets have a very high elastic modulus of 1±0.1 TPa and an exceptional tensile strength of 130±10 GPa. Graphene also has an extremely high thermal conductivity of 4100±500 W/m-K [5], which is greater than that of all other known materials. This unique combination of high thermal conductivity, elastic properties, and surface-to-volume ratio means that graphene is an excellent candidate for the reinforcement of thermal, mechanical, and electrical properties of polymeric materials [7–11]. As with other known materials, the extraordinary properties of graphene also are affected by the existence of defects in the graphene lattice. It is worth mentioning that the high stability of graphene sheets at temperatures below its melting point does not allow the formation of any detectable concentration of defects [12]. Accordingly, defects in the graphene lattice are formed primarily during the fabrication of graphene sheets. Currently, the chemical vapor deposition (CVD) technique is the only way to produce industry-scale graphene sheets [13]. Crystal growth during the CVD process results in the development of grain boundaries at places where the grains meet, leading to the formation of polycrystalline graphene structures. It should be noted that the reported high thermal, mechanical, and electrical properties of graphene belong to defect-free, monocrystalline and single-layer graphene samples. Therefore, it is to be expected that the grain boundaries in polycrystalline graphene sheets grown by the CVD technique not only may result in decreased electrical and thermal conductivity [4] but also may cause decreased structural stability of the graphene under mechanical loading [14]. Accordingly, a fundamental understanding of the mechanical, thermal, and electrical properties of CVD-grown polycrystalline graphene sheets is of great importance.
The first experimental studies on the mechanical properties of polycrystalline graphene samples were carried out in 2011 [15, 16]. As a result of these experiments, the elastic modulus and tensile strength of polycrystalline graphene sheets were reported to be 160 and 35 GPa, respectively. The mechanical properties of graphene shown in this early experimental work [15, 16] are very different from recent experimental results reported by Lee et al [17] who found that polycrystalline graphene sheets with grain sizes of 1–5 μm had an elastic modulus of around 965 GPa and a tensile strength of around 100 GPa. This considerable discrepancy with earlier experimental results [15, 16] was found to be due to an inaccurate processing technique that weakened the grain boundaries [17]. Because of the complexities, uncertainties, and cost of nanoscale experimental studies, numerical simulations are offered as an alternative. Theoretically, it has been reported that the grain boundaries in graphene consist of a series of pentagon-heptagon pairs [18, 19] that act as dislocation cores. These theoretical observations prompted a number of studies investigating the effects of pentagon-heptagon grain boundaries on the mechanical strength of graphene using molecular dynamics (MD) simulations [20–23]. Nonetheless, in all the MD models developed in these studies [20–23], periodic boundary conditions were applied along the width of the graphene sheet, meaning that the results correspond to infinite grain boundaries. Therefore, such studies fail to achieve accurate modeling of grain boundary junctions that play an important role in the weakening of polycrystalline graphene sheets. Moreover, because the models produce infinite grain boundaries, it would be inaccurate to correlate the reported results with those of bulk polycrystalline graphene sheets. Recently, Song et al [14] developed an MD model of polycrystalline graphene sheets with hexagonal grains for the investigation of mechanical response. The assumption that all the grains have equal hexagonal shapes in the work of Song et al [14] is very different from the result seen in experimentally fabricated polycrystalline graphene sheets, where the grains have unsystematic geometries with complex grain boundary junctions. To the best of our knowledge, the most accurate MD modeling of the mechanical properties of polycrystalline graphene sheets has been achieved by Kotakoski and Meyer [24]. In their work, a methodology is proposed for the construction of polycrystalline graphene sheets with random grain distributions and geometries with realistic grain boundaries. Thus the model constructed by Kotakoski and Meyer [24] was used to determine the mechanical response of graphene with grain sizes ranging from 4 to 16 nm. However, modeling of a limited number of grains resulted in considerable variation in the reported results. The objective of this study is to perform MD simulations for evaluation of the mechanical response of ultra-fine-grained graphene sheets. We note that the accuracy of the MD results strongly depends on the accuracy of the potential functions used to introduce the atomic interactions as well as the applied loading conditions. The validity of the MD modeling developed in this work is confirmed by the strong agreement seen for elastic modulus, tensile strength, and strain-at-failure values with experimental results [6] of defect-free graphene sheets. In this study, we used a methodology that is similar that used by Kotakoski and Meyer [24] for the construction of relatively large polycrystalline graphene samples including 25 up to 400 grains and equivalent average grain sizes ranging from 1 to 10 nm. Next, our MD models were subjected to uniaxial tensile loading conditions to study the mechanical response of the polycrystalline graphene sheets. Our results were found to be in excellent agreement with the recent experimental results of Lee et al [17].

2. Molecular dynamics modeling

In the fabrication of graphene sheets using the CVD method, the growth of graphene along arbitrary crystal orientations is initiated at several nucleation sites simultaneously. To simulate such a growth mechanism, we developed a program that creates a preselected number of randomly placed nucleation sites on a plane with predefined dimensions. The initial nucleation sites were randomly and uniformly distributed in the plane. By assuming a square geometry for an equivalent average grain size in a polycrystalline graphene sheet, the grain size in this study is defined as $\sqrt{L/N}$, where $L$ is the plane length and $N$ is the number of grains in the plane. Therefore, for a plane with a length of 50 nm containing 25 grains, the equivalent grain size would be 10 nm. Then a random angle was assigned for each nucleation site that defines the crystal growth orientation with respect to the armchair direction. In the next step, the nucleation sites were grown using an iterative process in which any of the missing neighbors of a boundary atom can appear with the same probability. The further growth of a grain from a boundary atom is terminated when it meets with another atom from a neighboring grain at a distance of less than 0.1 nm. The growth of the polycrystalline graphene sheet is complete when all the grains meet with their neighbors and there is no possibility for any atom to be added to the lattice. In order to eliminate the effects of edge atoms on the reported properties of the graphene sheet, the MD models were developed by taking into account the periodicity criterion along planar directions. This means that if one puts two samples side by side, no mismatch in the lattices will be observed. In this way, the reported results can be considered to be the mechanical response of the graphene sheets and not graphene nanoribbons. Moreover, in order to achieve perfect uniaxial loading conditions, the structure must be periodic so as to be able to accurately apply the periodic boundary conditions. This is so because any kind of fixing of atomic positions could result in a local two-dimensional (2D) stress condition that would cause a stress concentration.

We then used MD simulations to form grain boundaries in the polycrystalline graphene sheets. Molecular dynamics calculations in this study were performed using the Large-Scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) package [25]. In all MD calculations, periodic boundary conditions were applied in planar directions, and
the time increment of simulations was fixed at 1 fs. We used second-generation reactive empirical bond-order (REBO) potential [26] for the formation of grain boundaries. The initial structures were equilibrated at room temperature (300 K) for 50 ps using the Nosé-Hoover thermostat method (NVT). Then the structures were uniformly heated to 3000 K, below the melting point of graphene, using the NVT method for 50 ps. The high mobility of carbon atoms at 3000 K allows them to rearrange their positions to reach the minimum-energy state. Next, the samples were cooled from 3000 K to room temperature for 50 ps. Then the structures were equilibrated at 300 K for another 50 ps using the NVT method. The structures were finally relaxed to zero stress at room temperature using the Nosé-Hoover barostat and thermostat method (NPT) for 10 ps. At this stage, the structure is accurately prepared for the evaluation of mechanical properties.

For the modeling of mechanical properties, interaction between carbon atoms was modeled using the optimized Tersoff potential developed by Lindsay and Broido [27]. The optimized Tersoff potential predicts the phonon dispersion curves of graphite in closer agreement with experiments than the original Tersoff potential [28, 29]. It is worth noting that because of the limited reactivity of Tersoff potentials, we could not use this potential for the formation of grain boundaries. In the MD modeling of the uniaxial tensile test of polycrystalline graphene sheets at room temperature, periodic boundary conditions were applied in planar directions (x- and y-directions in this work) to remove the finite-length effect. Prior to applying the loading conditions, all systems were relaxed to zero stress at room temperature using the NPT method. For the loading conditions, the periodic simulation box size along the loading direction (x-direction in this study) was increased by a constant engineering strain rate of $1 \times 10^8$ s$^{-1}$ at every simulation time step. Because we are dealing with single-layer graphene sheets, the stress in the sheet thickness is zero (z-direction). Therefore, in order to guarantee uniaxial stress conditions, the periodic simulation box along the sample width (y-direction) was altered to achieve zero stress in this direction using the NPT method. Virial stresses were calculated at each strain level to obtain an engineering stress-strain response assuming a thickness of 0.335 nm for the graphene membranes. Engineering strain $\epsilon$ at each time step was calculated by multiplying the total time of loading by the applied engineering strain rate. The true strain $\epsilon_t$ was then obtained by calculating $\ln(1 + \epsilon)$. In this work, the elastic modulus is reported by calculating the slope of the linear part of the stress–true strain response.

3. Results and discussion

Because our objective is to evaluate the tensile response of polycrystalline graphene sheets in which the grains have random orientations, first we studied the intensity of the loading-direction effect on the mechanical properties of defect-free graphene sheets. We note that a graphene structure has a symmetry angle of 30° and chirality angles of 0 and 30°, which are commonly called armchair and zigzag directions, respectively. Thus we calculated the stress-strain curves of the graphene sheets subjected to uniaxial loading conditions along four different loading chirality directions, as illustrated in figure 1. The results shown in the figure suggest that graphene sheets have a slightly higher elastic modulus and tensile strength along the zigzag direction than along the armchair direction. For defect-free graphene, our MD model based on the optimized Tersoff potential yields an elastic modulus of 0.96–0.98 TPa and a tensile strength of 154–161 GPa at a failure strain of 0.24 to 0.26, all depending on the loading direction. The calculated results for elastic modulus and strain at failure are in considerable agreement with the experimental measurements by Lee et al [6] in which the mechanical properties of defect-free graphene sheets were reported as follows: an elastic modulus of $1 \pm 0.1$ TPa and a tensile strength of $130 \pm 10$ GPa at an ultimate strain of 0.25. However, our result for tensile strength is by around 20% higher than the experimental measurements. Nevertheless, using the REBO potential, Kotakoski and Meyer [24] reported an intrinsic strength of 90–100 GPa at a failure strain of 0.15 to 0.20 and an elastic modulus of around 0.6 TPa for pristine graphene. In an MD study conducted by Pei et al [30] with the adaptive intermolecular reactive empirical bond-order (AIREBO) potential [31], the mechanical properties of pristine graphene were reported as follows: elastic modulus of $0.860 \pm 0.03$ TPa and tensile strength of $121 \pm 16$ GPa at a failure strain of 0.22 $\pm 0.05$. Using the original Tersoff potential, Ni et al [32] reported an elastic modulus of 1.05–1.13 TPa and a tensile strength of 180–210 GPa at a failure strain of 0.3–0.45 for defect-free graphene. This comparison confirms the suitability and accuracy of the optimized Tersoff potential for modeling of the mechanical response of graphene.

In this study, we developed relatively large polycrystalline graphene structures with 15 000–100 000 atoms consisting of 25 up to 400 grains. Two samples of polycrystalline graphene sheets with an average grain size of 10 nm with 25
grains and an average grain size of 1 nm with 400 grains are illustrated in figure 2. As can be seen, the grain boundaries and grain boundary junctions are accurately formed. The resulting polycrystalline structures are also similar to those reported by Kotakoski and Meyer [24]. As can be seen in the side views of the structures (figures 2(b)–(d)), considerable deformation and deviation from planarity in the graphene samples is observed as grain size decreases. Figure 3 compares the instantaneous angle distribution of equilibrated pristine graphene and polycrystalline graphene sheets. In a honeycomb planar structure, the angle between two linked bonds is 120°. Accordingly, in an ideally planar graphene structure, one would expect the angle distribution to present only one peak at 120°. Thus it can be seen that broadening the angle distribution peak results in waviness of the structure and deviation from an ideal planar structure. Based on the results shown in figure 3, it is apparent that the angle distribution peak broadens as grain size decreases. This means that as the grain size in polycrystalline graphene sheets decreases, the structure deviates more from the planar structure seen in defect-free graphene sheets. As shown in figure 3, the angle distribution for a polycrystalline graphene sheet with an average grain size of 10 nm is very close to that of a pristine graphene. These results suggest that differences in the angle distributions between pristine and polycrystalline graphene become conspicuous for grain sizes smaller than 3 nm.

Figure 4 shows the typical stress-strain responses of polycrystalline graphene sheets with average grain sizes of 1 and 5 nm. In this study, calculations for a particular grain size were performed for four different samples with different initial grain configurations. As is apparent, the two grain sizes studied show distinctly different results. We also found that decreasing grain size increased the variations in the stress-strain responses. For the case of polycrystalline graphene sheets with a grain size of 5 nm, the linear parts of the stress-strain response, which are used to evaluate elastic modulus, are the same, and only the tensile strength and failure strain are different for various samples. For polycrystalline graphene sheets with a grain size of 1 nm, there was more variation in the acquired stress-strain curves.

Figure 5 shows the calculated elastic modulus, tensile strength, and ultimate strain for polycrystalline graphene sheets as a function of grain size. As an overall trend, we found that decreasing the grain size in polycrystalline graphene structures decreases the elastic modulus and tensile strength.
strength and increases the strain at failure. Our results show a clearly decreasing trend for the elastic modulus as the grain size in the polycrystalline graphene is decreased. The calculated elastic modulus of the polycrystalline graphene sample with a grain size of 10 nm is lower than that of the defect-free graphene sheet by about 8%. The decreasing trend in elastic modulus becomes more pronounced as grain size is decreased. In particular, for a grain size of 1 nm, we found an approximately 50% reduction in elastic modulus compared with pristine graphene. These observations suggest a limited dependence of polycrystalline graphene elastic properties for grain sizes larger than 10 nm. We note that the experimental results show that the mean elastic modulus of polycrystalline graphene sheets with grain sizes of 1–5 μm decreases only slightly by around 3% compared with defect-free graphene. This reported reduction in elastic modulus is indeed within the range of reported error for the elastic modulus of pristine graphene (±10%, as reported by Lee et al [6]).

In contrast with the results for elastic modulus, considerable variation in the calculated tensile strength and ultimate strain values for polycrystalline graphene sheets was observed. This variation in tensile strength and corresponding ultimate strain can be explained by the stochastic nature of failure occurrence in polycrystalline and defective graphene structures. One way to decrease the variation in MD results is to study larger systems, which, unfortunately, would increase the computational cost of the calculations. In the case of tensile strength, we found an overall decreasing trend as grain size is decreased. We note that the grain boundaries in polycrystalline graphene sheets act as sources of stress concentration and crack nucleation as well, resulting in a reduction of tensile strength. The tensile strength of polycrystalline graphene was experimentally reported to be around 100 GPa [17], which is about 25% below the ultimate strength of pristine graphene. We found a tensile strength of around 93 ± 5 GPa for polycrystalline graphene sheets with a grain size of 10 nm, which is about 40% below our prediction for pristine graphene. However, because the trend in tensile strength is predicted to increase as grain size increases, we would expect higher predicted tensile strength values for samples with microscale grain sizes. On the other hand, in the MD work of Kotakoski and Meyer [24], the tensile strength of polycrystalline graphene samples was reported to be around 46 GPa, independent of grain size. Song et al [14] reported that the tensile strength of graphene increases from 36.62 to 53.67 GPa as grain size decreases from 5 to 2 nm, which contradicts our MD results.

For the case of ultimate strain, our results show that decreasing grain size results in a gradual increase in ultimate strain. We found that the ultimate strain of polycrystalline graphene samples with grain sizes of 5–10 nm is almost half that of pristine graphene. The ultimate strain of a sample with an average grain size of 1 nm is found to be around 20% higher than that of a sample with an average grain size of 10 nm. This increasing trend in ultimate strain for smaller grain sizes is in agreement with other recent MD study results [14–24]. This finding is interesting because one would expect a decreasing trend in ultimate strain given that the ultimate strain for samples with the largest grain sizes in our work and earlier studies [14–24] is lower than that of defect-free graphene. From an experimental point of view, the ultimate strain of polycrystalline graphene is reported to be around 0.2
approximately 20% below the reported ultimate strain of 0.25 for defect-free graphene [6]. We note that the grain boundaries, because of the stress concentration there, show weakened properties compared with atoms inside the grains. Therefore, in a polycrystalline sample, the material response is not uniform, and gradients in material response exist that depend on distance from the grain boundaries. However, as grain size decreases, the ratio of atoms along the grain boundaries to the total number of atoms increases, resulting in the extension of defective zones. In this way, by decreasing grain size (see figure 2), defective zones extend more uniformly throughout the sample, making the structure more homogeneous. In this case, the material is softened, and because of its homogeneous structure, it could flow more uniformly during loading conditions, resulting in a higher ultimate strain. It is worth mentioning that the ideal homogeneous structure belongs to defect-free graphene, which shows the maximum ultimate strain. In contrast with our results and the predictions of Song et al [14], Kotakoski and Meyer [24] predicted that polycrystalline graphene sheets would present higher ultimate strains than pristine graphene. Our MD results for ultra-fine-grained polycrystalline graphene sheets suggest that the graphene could keep its exceptional mechanical properties for equivalent grain sizes greater than 2 nm.

As discussed in our recent work [33], in the case of defect-free graphene, the specimen extends uniformly and remains defect-free up to the tensile strength. The tensile strength is the point where the first debonding occurs between two adjacent carbon atoms, and the voids grow rapidly. The main characteristic of these voids is the formation of monoatomic carbon chains. In the case of defect-free graphene, the monoatomic carbon chains form mainly along the armchair direction [33]. The final rupture of the specimen occurs as the last connecting monoatomic carbon chain fails. Figure 6 shows the deformation process of a polycrystalline graphene sample with a grain size of 10 nm at various stages of loading. As shown in figure 6(a), at strain levels below the tensile strength, several voids form along the grain boundaries throughout the sample by debonding of C–C bonds. These voids occur primarily in parallel and consist of monoatomic carbon chains along the armchair direction. An increase in the strain level produces more voids in the sample. The tensile strength typically occurs at a point where a crack (see figure 6(b) inset) that has already formed at a grain boundary junction propagates (figure 6(c)) and results in a characteristic sharp decrease in the stress-strain response. Therefore, the characteristic sign of tensile strength is crack coalescence through the breaking of monoatomic carbon chains. As the defect concentration increases for samples with smaller grain size, crack coalescence becomes more probable, which results in lower tensile strength. At the ultimate strength point, one sees rapid growth of the crack perpendicular to the loading direction (figure 6(c)). This finding implies that in the polycrystalline graphene structures, the tensile strength and corresponding ultimate strain occur at an occasional point in which the initial debonding of neighboring carbon atoms forms a crack that propagates through the sample. Such a failure mechanism could explain the considerable variation in reported tensile strength and ultimate strain values in comparison with the elastic response, which is more deterministic in nature. Similar to what has been suggested experimentally [17–34] and in line with recent MD studies [24], the crack rapidly propagates through the bulk of the neighboring grains and also along the grain boundaries (figures 6(c) and (d)). This observation clearly suggests the comparable strength of grain boundaries in comparison with defect-free bulk material; otherwise, crack growth would only occur along grain boundaries. Similar to what occurs in defect-free graphene sheets, we observed the formation of long monoatomic carbon chains that tend to keep the sides of the forming crack connected together (figures 6(e) and (f)). Despite the evolution of the defective zone through the entire width of sample, the formation of monoatomic carbon chains helps the sample to endure higher strain levels. In this way, we observed a series of rises in the stress and drops in the stress-strain curve as a result of the elongation and breaking of these carbon chains (see figure 4). These monoatomic carbon chains induce complex stress conditions at the crack ends that cause crack growth along an irregular pathway that results in crack edges with rough geometries. This observation is in agreement with the latest experimental findings [17], in which the crack edges in ruptured polycrystalline sheets were found to be irregular.

4. Conclusion

We used classical MD simulations to provide a detailed image of the mechanical responses of ultra-fine-grained polycrystalline graphene sheets. First, we studied the mechanical properties of defect-free graphene sheets, where we found close agreement with experimental measurements [6], verifying the accuracy of our MD approach. Then we constructed a series of polycrystalline graphene samples with ultrafine grains with equivalent average grain sizes ranging from 1 to 10 nm. The resulting polycrystalline molecular models were subjected to uniaxial loading conditions to establish detailed information concerning the effect of grain size on the mechanical properties of graphene. As an overall trend, we found that decreasing the grain size in polycrystalline graphene structures decreased the elastic modulus and tensile strength and increased the strain at failure. Our results for ultra-fine-grained graphene structures with an average grain size of 10 nm show approximately 8 and 40% reductions in elastic modulus and tensile strength, respectively, compared with defect-free graphene. Our results also suggest that polycrystalline graphene sheets with average grain sizes greater than 2 nm present an ultrahigh tensile strength of around 85 GPa, which is two orders of magnitude higher than that of high-strength steels and titanium alloys. Taking into account the small grain sizes of the samples studied, we conclude that ultra-fine-grained graphene structures have ultrahigh tensile strength and elastic modulus values that are very close to those for defect-free graphene sheets. By plotting the deformation process, we found that at the tensile strength point, a crack forms at a grain boundary junction that rapidly propagates through the bulk of the neighboring grains perpendicular to the loading direction and along the grain boundaries. Formation of long monoatomic
carbon chains not only helps the graphene to maintain load-bearing ability long after the tensile strength but also leads to the formation of irregular crack edges in agreement with experimental observations [17]. Our results suggest that the ultra-fine-grained graphene structures can have extraordinarily high mechanical properties noticeably close to those of defect-free graphene sheets.

Figure 6. Deformation process of a polycrystalline graphene sheet with an average grain size of 10 nm at different strain levels $\varepsilon$ with respect to the failure strain $\varepsilon_f$.

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