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# Size-dependent deformation behavior of nanocrystalline graphene sheets

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ABSTRACT

Molecular dynamics (MD) simulation is conducted to study the deformation behavior of nanocrystalline graphene sheets. It is found that the graphene sheets have almost constant fracture stress and strain, but decreased elastic modulus with grain size. The results are different from the size-dependent strength observed in nanocrystalline metals. Structurally, the grain boundaries (GBs) become a principal component in two-dimensional materials with nano-grains and the bond length in GBs tends to be homogeneously distributed. This is almost the same for all the samples. Hence, the fracture stress and strain are almost size independent. As a low-elastic-modulus component, the GBs increase with reducing grain size and the elastic modulus decreases accordingly. A composite model is proposed to elucidate the deformation behavior.



## 1. Introduction

Since the discovery of graphene, two-dimensional systems have rapidly become one of the research focuses in chemistry, physics and materials science due to their exciting and unique electronic [1], optoelectronic [2], as well as magnetic [3] properties. Particularly, the highest strength over 100 GPa [4,5], the excellent flexibility with an ultimate strain higher than 20% [1,6] and the exceptionally high electron mobility of $10^5$ $cm^2$ $V^{-1}$ $s^{-1}$ [7] of pristine graphene stimulate the interests in applying graphene in flexible devices. Stress is often exerted on graphene sheets to engineer the band structure and phonon spectrum as well as the device performances [8,9]. Hence, it is of great scientific and technological significance to study the deformation behavior and mechanical properties of graphene sheets. Chemical vapor deposition (CVD) on metals [10,11] is one of the common techniques to fabricate large-area and high-quality graphene sheets and they are usually polycrystalline [12–15] as a result of the uncontrollable nucleation processes [16]. Undoubtedly, the grain boundaries (GBs) are considered a critical factor in determining the mechanical behavior of such a monolayer system [17–20].

Experimentally, nanoindentation based on atomic force microscopy (AFM) has been used to characterize the mechanical properties of graphene membranes [21–23]. But it is very difficult to observe the microstructure evolution in situ. Moreover, the stress field induced by AFM is inhomogeneous. This makes it difficult to study and fathom the intrinsic deformation mechanism. Recently, two-point and four-point bending approaches [24] are exploited to uniaxially stretch the graphene deposited on a flexible substrate or a tunable biaxial strain is exerted on the graphene deposited on a piezoelectric substrate due to piezoelectric effect [25]. For example, Garza et al. [26] demonstrated a reversible uniaxial strain >10% by pulling graphene sheets via a microelectromechanical system (MEMS). However, the applied strain is still smaller than the ultimate strain and it is difficult to elucidate the deformation mechanism experimentally. Molecular dynamics (MD) simulation enables researchers to examine the intrinsic mechanical behavior of graphene sheets [27]. It was found that the mechanical strength of graphene sheets depends on both grain misorientation and GB rotation [28]. Large-angle tilt boundaries are able to better accommodate the strained rings and are much stronger than low-angle boundaries having fewer defects [27]. Jhon et al. [29] further verified the effects of misorientation angle

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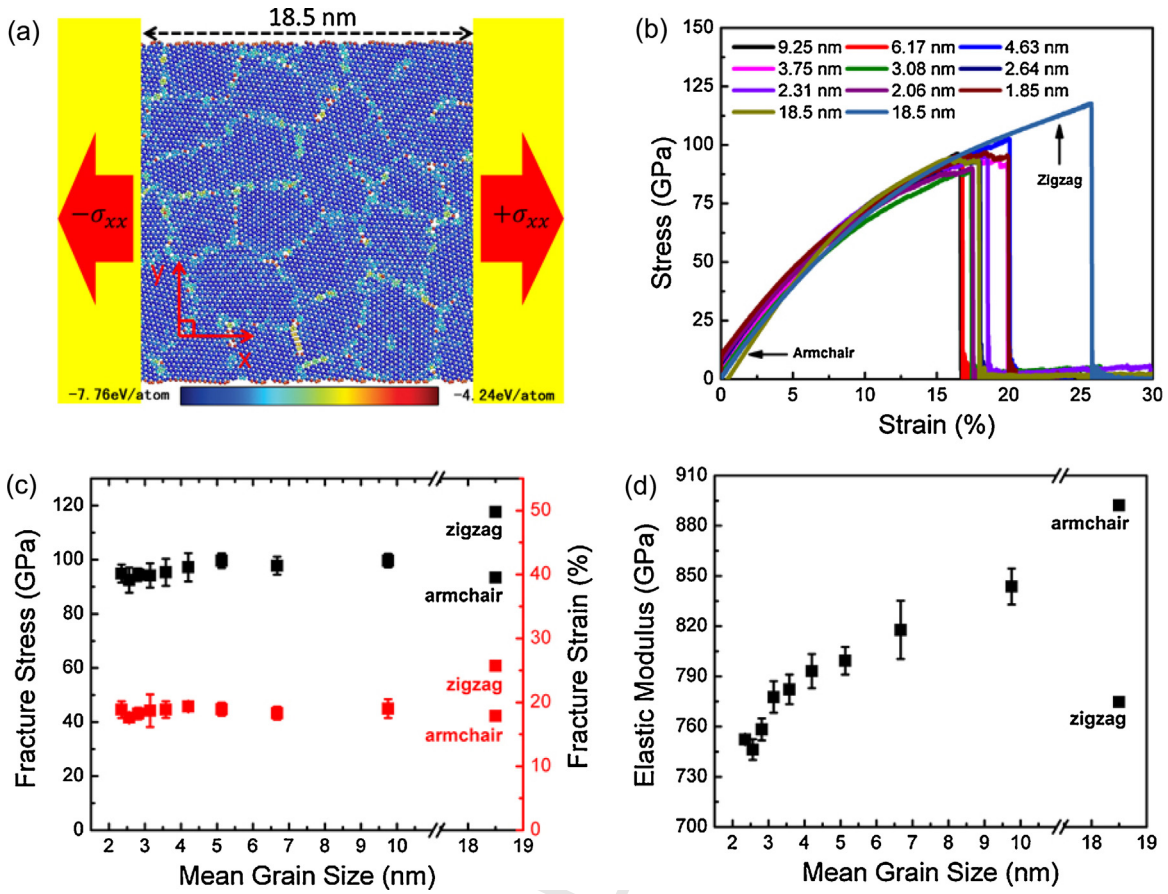


**Fig. 1.** (a) Typical model of nanocrystalline graphene sheets 18.5 nm × 18.5 nm in size under uniaxial tensile loading, (b) tensile stress-strain curves, (c) fracture stress and strain of the nanocrystalline graphene sheets as a function of grain size, and (d) elastic modulus.

and critical bond length on the tensile strength of polycrystalline graphene. However, based on an ideal GB model consisting of pentagon-heptagon pairs, Cao et al. [30] found that the mechanical strength deceases slightly with the misorientation angle and they ascribed the difference to the stress gradient around the crack tips. Hence, the mechanical strength of polycrystalline graphene can be either enhanced or weakened dependent on the detailed arrangement of the defects, but not just the defect density [31].

Although the deformation behavior and mechanical properties of graphene have been extensively studied, the single-crystal, bi-crystal or hexagonal grain configurations as ideal models have usually been considered [27,32]. The influence of GBs on the deformation may be addressed to a certain degree, but it is different from the polycrystalline case with randomly distributed grain orientation and grain sizes. The mechanical deformation of nanocrystalline graphene sheets can be quite complicate depending on the grain size, morphology, orientation, and so on [33,18]. Particularly, when the grain size is reduced down to nanometer scale, the effects of the grain size and GBs may be appreciable. For example, Li et al. [34] found that the fracture strength are significantly reduced owing to the combined weakening effect of pre-straining in highly defective GBs and $sp^3$ hybridization of hydrogenated carbons there, moreover, the smaller the grain size is, the larger the reduction in fracture strength is.

In this work, MD simulation is performed to systematically investigate the deformation behavior and mechanical properties of nanocrystalline graphene in more realistic sense. Unexpectedly, they have almost the constant fracture strain and stress, nearly independent on the grain size, but the elastic modulus decreases sharply with the grain size. The results are completely different from the deformation behaviors exhibited in nanocrystalline metals in which size-dependent strength is generally observed. A composite model with grain domains and GBs as two components is proposed to understand the size-dependent elastic modulus and size-independent fracture strength.

## 2. Models and simulation methods

More realistic simulation models of nanocrystalline graphene with randomly distributed grain size and orientation are constructed by Voronoi tessellation [35]. A Voronoi tessellation represents a collection of convex polygons isolated by planar cell walls perpendicular to lines connecting neighboring points. Each cell is filled with randomly oriented graphene domains and the atomic layers adjacent to the planar cell walls are defined as GBs. The initial carbon–carbon bond length is set as 1.42 Å that is the same as the experimental value. If two atoms in GBs have too small separation (<1.41 Å) from each other, one of them will be removed, while an atom will be added if there is a large void in GBs. Fig. 1a displays one of the typical atomic models 18.5 nm × 18.5 nm in size. The colors of the atoms are mapped according to the potential energy (PE), and GBs with higher PE are clearly evident. A set of Voronoi tessellations with N × N (N takes 2, 3,. . ., 10) grains are adopted to represent the nanocrystalline graphene sheets with average grain sizes of 9.25, 6.17, 4.63, 3.75, 3.08, 2.64, 2.31, 2.06, and 1.85 nm, respectively. The misorientation angles of the grain boundaries are randomly distributed in the range of 0–60°. For each average grain size, five models are built to avoid the accidental errors.

The MD simulation is carried out using LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulator) package. The 3D visualization software AtomEye is used for post-pocessing

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