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# Mechanical properties of wrinkled graphene generated by topological defects

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ABSTRACT

In a free standing graphene with topological defects, e.g. heptagons and pentagons, the out-of-plane wrinkles are generated to release in-plane deformation energy. In this work, different aspect ratios (amplitude over wavelength) of the wrinkled graphene sheet are obtained by adjusting the topological defects in the graphene sheet. Due to the geometrical locking effect, the interlayer shear mechanical properties are significantly increased by increasing the aspect ratio of the wrinkled graphene sheet. For example, the shear modulus and strength for aspect ratio $\xi = 0.177$ are 1106.79 MPa and 612.06 MPa, which are 13.5 and 31.1 times larger than the values of the flat graphene system, respectively. On the other hand, the in-plane tensile modulus and strength of the wrinkled graphene sheet are weakened caused by the decreasing of the tensile stiffness for wrinkled surface and large residual stress at the topological defects. Benefiting from the high interlayer shear modulus and strength, the assembling of the wrinkled graphene sheet can construct a graphene membrane with tensile strength up to 12.57 GPa. This work has proposed a new mechanism to enhance the interlayer load transfer capacity of graphene sheet which is helpful to the design of high performance graphene nanocomposites.



## 1. Introduction

Graphene is consisted of honeycomb packed $sp^2$ carbon atoms which has excellent in-plane mechanical properties. The in-plane tensile modulus and strength of graphene sheet are on the order of 1 TPa and 100 GPa, and the fracture strain can be larger than 0.2 [1,2]. However, due to the weak van der Waals interaction, the interlayer shear modulus and strength are much smaller than those of the in-plane tensile modulus and strength [3–5]. Because of the extremely anisotropic mechanical properties, some of the anomalous mechanical behaviors are observed in the multi-walled carbon nanotube or multilayer graphene systems, examples such as the bending rippling of the multi-walled carbon nanotube, interlayer shear effect on the multilayer graphene resonator, and high speed superlubricity of graphene slider [2,6–9].

Recently, the graphene-derived materials, e.g. graphene oxide paper [10–12], graphene membrane [13–15] and graphene foam [16,17], have attracted great research interest. Owing to their excellent mechanical, electrical properties, lightweight and sub-nanometer channel, these type of materials hold great potential applications in aerospace, flexible electrodes and sensors, desalination, gas separation, etc. For the aforementioned graphene-derived materials, the graphene sheets are assembled in a layer-by-layer manner. Due to the discontinuity of graphene sheet, the in-plane tensile load in one graphene sheet is transferred to another graphene sheet through interlayer shearing, based on which a deformable tension-shear model (DTS) has been proposed in previous literatures to describe the mechanical properties of the graphene-derived layer-by-layer materials [18,19]. So, both of the in-plane tensile and interlayer shear mechanical properties play important roles in determining the mechanical properties of the graphene-derived layer-by-layer materials. Indeed, in order to improve the mechanical properties of graphene oxide paper, different interlayer crosslink mechanisms have been introduced, examples such as hydrogen bonding [8,20], coordinative cross-linking [21,22] and covalent bonding through small molecular adhesives [8,23]. However, there should be a lot of functional groups in the graphene sheet to form the interlayer crosslinks. Due to the functional groups, the mechanical and electrical properties of the

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graphene sheet are significantly weakened which is a disadvantage for the most applications of the graphene-derived materials [24,25].

Topological defects, such as disclinations (heptagons or pentagons) and dislocations (heptagon-pentagon dipoles), have been widely observed in polycrystalline graphene [26–28]. Due to the atomic scale thickness, the out-of-plane wrinkles are generated in a free standing graphene with topological defects to release the in-plane deformation energy and different three dimensional configurations are obtained through specifically distributing the topological defects [29,30]. Zhang et al. have proposed a continuum model based on the generalized von Karman equation to describe the configuration of the wrinkled graphene sheet which agrees well with the atomic simulation results [31]. Though the topological defects have significant influence to the mechanical properties of the graphene sheet, the previous studies mainly focused on the in-plane mechanical properties, mostly the in-plane tensile strength and fracture toughness [32–35]. Indeed, the interlayer shear modulus and strength of the wrinkled graphene sheet should be significantly enhanced due to the geometrical locking effect. Besides, the wrinkled morphology of graphene sheet can also be generated by rough substrate, nanoparticle on substrate or initial stress, as illustrated in the previous literatures [36–39]. However, the introducing of rough substrate or initial stress may be impossible for some applications of graphene sheet in nanodevices and nanocomposites. Therefore, in this work we mainly focus on the enhancement of the interlayer shear mechanical properties of the wrinkled graphene sheet generated by topological defects. First, the wrinkled graphene sheets with different amplitudes of the wrinkling wave are generated through properly arranging the topological defects in the graphene sheet. Then, the interlayer shear and in-plane tensile mechanical properties of the wrinkled graphene sheet were studied via molecular dynamic (MD) simulation. Furthermore, a type of graphene membrane is proposed which is consisted of the wrinkled graphene sheet in a layer-by-layer manner. The mechanical properties and optimization of the graphene membrane are further discussed.

## 2. Simulation model and methodology

In this section, the wrinkled graphene sheets with different amplitudes of wrinkling wave from 2.1 Å to 5.3 Å have been generated using an in-house FORTRAN code. The method is similar with those presented in the previous literatures [31,40] and the minimum energy configuration of a triangular lattice sheet on a curved surface is obtained. Note that in the previous literatures, the particles are assumed to have the same charge, so that the inter-particle interaction is described by the repulsive Yukawa potential [40]. However, in this work we have modified the inter-particle interaction with van der Waals interaction and replace the Yukawa potential with the Lennard-Jones potential, i.e. $U = 4\varepsilon[(r_0/r)^{12}-(r_0/r)^6]$ where $r_0 = \sqrt{3}r_{C-C}/2^{1/6}$ and $r_{C\text{-}C} = 1.42$ Å is the carbon-carbon bond length in graphene sheet and $\varepsilon$ is the depth of the potential well. This is because the Lennard-Jones potential has both the repulsive and attractive terms which is more robust to predict the equilibrium state of the triangular lattice sheet with different amplitudes of wrinkling wave.

Here, the motion of the particles of the triangular lattice is constrained on the given curved surface and periodic boundary conditions are applied in the in-plane directions. At the beginning, the system temperature is gradually increased, so that the particles can overcome the local energy barrier to find the global energy minimum configuration, and then the wrinkled triangular lattice sheet is obtained by decreasing the system temperature. After obtaining the wrinkled triangular lattice sheet, the wrinkled graphene sheet is defined as the reciprocal lattice of the triangular lattice, i.e. every carbon atom locates at the center of a triangle, as shown in Fig. 1. Due to the curved surface, the particles of the triangular lattice have five, six or seven nearest neighbors which correspond to the five, six and seven carbon rings in the graphene sheet, respectively, as indicated by red and blue colours in Fig. 2. As the equilibrium distance of the Lennard-Jones potential is $\sqrt{3}r_{C-C}$, the bond length of the triangular lattice is also about $\sqrt{3}r_{C-C}$ which gives the bond length in the graphene sheet is $r_{C\text{-}C}$. The wrinkled graphene sheet is first annealed at 400 K for 80 ps and the in-plane dimensions are also rescaled so that the in-plane stresses are zero, and then it is quenched to 0.1 K to get the relaxed configuration of the wrinkled graphene sheet. Besides the wrinkled graphene sheet, the method presented herein is also suitable for generating other types of graphene morphology.

In this work, we aim to study the interlayer shear and in-plane tensile mechanical properties of the wrinkled graphene sheet with different aspect ratios (amplitude over wavelength). The curved surface is simplified as the sinusoidal surface

$$z = h \sin\left(\frac{2\pi x}{l}\right)\sin\left(\frac{2\pi y}{l}\right), \tag{1}$$

where $h$ is the amplitude ranging from 0 Å to 6 Å and $l = 3$ nm is the wave length. Following the aforementioned procedure the wrinkled graphene sheet with different amplitudes is obtained. The relaxed configurations of the wrinkled graphene sheet are shown in Fig. 2 and the heptagonal and pentagonal defects are marked in red and blue colours, respectively. As the distribution of the topological defects is constrained by the graphene lattice and the number of the topological defect is also integer, it is almost impossible to exactly find the graphene sheet with arbitrary curved surface.

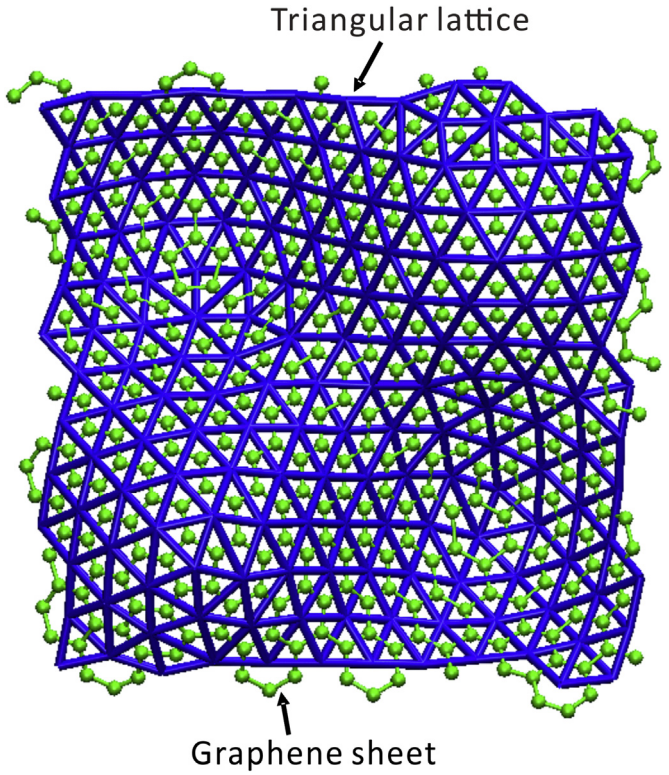


**Fig. 1.** Illustrations of the wrinkled triangular lattice sheet (represented by blue bond) and graphene sheet (represented by green dot and line). (A colour version of this figure can be viewed online.)