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Geometrical effect 'stiffens' graphene membrane at finite vacancy concentrations

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ABSTRACT

The presence of defects not only modifies the stiffness and strength of materials, but also changes their morphologies. The latter effect is extremely significant for low-dimensional materials such as graphene. We show in this work that graphene swells while point defects such as mono-vacancies are created at finite concentrations. The distorted geometry resulted from this areal expansion, in combination with the in-plane softening effect, predicts an unusual defect concentration dependence of stiffness measured for supported graphene membrane in nanoindentation tests, which leads to a defect-induced stiffening phenomenon. The mechanism is elucidated through an analytical membrane model as well as numerical simulations at atomistic and continuum levels. In addition to elucidate the counter-intuitive observations in experiments and computer simulations, our findings also highlight the role of defect-modulated morphology engineering that can be applied to design nanoscale material and structural applications.

The presence of defects in solids modifies their mechanical response, which is an important subject in understanding the structure–properties relationship of materials for long time [1]. For example, point defects not only reduce the material stiffness and strength due to the local mass deficiency and stress concentration they create, but could also strengthen materials through mechanisms of solid solution and precipitate hardening [1]. The role of defects in defining material properties is even richer when the dimension of materials is reduced. A number of studies have demonstrated prominent geometrical effects of topological defects in two-dimensional (2D) materials in additional to the stress field they create [2–4]. Although these materials are often loaded in the basal plane in practical applications such as nanoelectromechanical devices and nanocomposites, their mechanical characterization is usually done through nanoindentation tests where concentrated load is applied towards a specific region of the material [5–10]. In this situation of local probes, the out-of-plane geometrical distortion could drastically change their mechanical response [4].

Recently there were two individual studies reporting that finite-concentration of vacancies in the graphene membrane leads to a remarkable stiffening effect under nanoindentation probes, which is contradicting to the conventional understanding that point defects in materials soften their mechanical performance. However, the underlying mechanism has not been well clarified. In the work conducted by Kvashnin and co-workers [11,12], molecular dynamics (MD) simulation results are reported, showing that the Young's modulus of the graphene membrane with the defects concentration up to $c = 1\%$ increases to 2.57 TPa. The further increasing of defects concentration ($c = 7\%$) leads to reduction in the stiffened value of Young's modulus to 1.08 TPa. The underlying mechanism is explained by a competition of two phenomena, which are the 'hardening' of the graphene membrane due to the shortening of bonds, and reduction in the density of graphene lattice due to the presence of vacancies.

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However, the shortening in bond lengths near the defects in graphene may not necessarily stiffen the local atomic structures compared to the perfectly hexagonal lattice of graphene, and the effect is contrastive with our previous calculations when graphene is loaded in its basal plane [11,13]. In their simulation setup, an indenter consisting of a few atoms are used to press the center of the supported graphene sheet. The 2D membrane stiffness E_{2D} is calculated by fitting the indentation force–depth relation through the Schwering type of solution

$$f(\delta) = \pi\sigma_0\delta + E_{2D}\delta^3/a^2 \quad (1)$$

where f is the indentation force, δ is the indentation depth, a is the radius of suspended graphene membrane, and σ_0 is the prestress. E_{2D} is the nominal two-dimensional stiffness defined through Eq. (1), which equals to the in-plane Young's modulus multiplied by membrane thickness if assumptions in the Schwering's model are fulfilled. The membrane is considered to be linear elastic, which is reasonable for graphene under strain lower than ∼0.05 and geometrical nonlinearity plays the dominant role [14–16]. It should be remarked here that this solution is based on the assumption that the graphene sheet is considered as a planar membrane experiencing small-deflection deformation. However, a prestrain could be introduced due to the fact that graphene swells as vacancies are created [17], and there will be an additional geometrical effect from this expansion—the graphene would buckle out of the plane. As a result, the membrane could suffer significant out-of-plane distortion under indentation, and the planar assumption could break down.

In another recent report [5], results from nanoindentation experiments are presented, showing the same phenomenon of defect-induced stiffening, although the indentation strength is reduced that is in consistence with conventional understandings. The determination of elastic modulus is also achieved by fitting the experimental data from nanoindentation tests through Eq. (1). Similar results were also reported in Ref. [6]. The mechanism for the counter-intuitive defect-induced stiffening effect is discussed based on an argument of thermal-fluctuation-induced wrinkles in the graphene membrane, through the dependence of the elastic coefficients on the momentum of flexural modes of two-dimensional membranes [5]. The key idea is that with wrinkles the membrane is softened [9], while the introduction of vacancies will pin the long-wave fluctuations and thus effectively 'stiffen' the membrane compared with the membrane in absence of vacancies. However, this phenomenon-based reasoning is inconsistent with the abovementioned study using MD simulations if we assume these two similar results arise from the same origin. In the MD simulations [11], the formation of thermal wrinkles in graphene is negligible due to the limited lateral span of the supported membrane that is 3.8–14 nm, much smaller than the value of 0.5–3 μm in the nanoindentation experiments. Moreover, the argument of fluctuation renormalized tensile stiffness is valid only at thermal equilibrium [18,19], while by fitting the measured nanoindentation force–depth relation using Eq. (1), the second term, which is responsible for extracting E_{2D}, only dominates at the large-displacement regime, where the membrane is stretched significantly, and the wrinkled structures are reduced or even disappear. Actually previous experimental work using nanoindentation tests measured reasonable stiffness for monolayer graphene where defects such as grain boundaries are present [7–10]. That is to say, the thermal fluctuation induced stiffness renormalization picture may not apply in these measurements. This inconsistence and lack of understanding for the counter-intuitive phenomenon drives us to explore the physical mechanism behind the observed defect-induced stiffening effect. In the following text, we will first discuss the vacancy-induced in-plane softening and swelling behavior, and then elucidate the mechanism of stiffening effect of defective graphene membrane in response to nanoindentation loads, where we find a prominent geometrical effect that makes the key contribution.

In this work, we find that after mono-vacancies are introduced to the graphene membrane by exotic treatments such as irradiation, two major effects are introduced, which are critical for the subsequent mechanical characterization under nanoindentation. Firstly, the in-plane stiffness and strength are reduced upon defect creation [13]. Secondly, the defective lattice will expand that drives the membrane to buckle out of the plane due to the distortion of sp^2 bonding network, which stiffens the nanoindentation response due to a prominent geometrical effect as the membrane deforms significantly from a planar shape [4,20]. These two factors compete with each other in modifying the stiffness and will dominate at high and low concentrations of vacancies, respectively. As a result, there is a peak value of the two-dimensional elastic stiffness or the Young's modulus, which is extracted by fitting the nanoindentation results using Eq. (1).

To demonstrate this point, we firstly carry out full-atom MD simulations to probe the in-plane stiffness reduction and expansion upon the creation of mono-vacancies. In this work, MD simulations are performed using the large-scale atomic/molecular massively parallel simulator (LAMMPS) package [21]. The adaptive intermolecular reactive empirical bond-order (AIREBO) potential function is used to describe the interatomic interaction in graphene [22]. The monovacancy defects are created by randomly picking single carbon atoms with three bonded neighbors for removal in the graphene sheet. Although other types of defects such as divacancies and nanoholes could present in graphene under irradiation, we focus here on monovacancies that have been widely identified in experiments [23]. It should also be noted that at room temperature ∼300 K, the mobility of vacancies is prohibited and thus the spatial distribution of defects is fixed during the mechanical tests [23]. 2D periodic boundary conditions (PBCs) are applied with a simulation box size of 33.5 × 36.3 nm. Both atomic positions and the box size are optimized to obtain stress-free relaxed structures of graphene sheets with embedded defects, using the conjugated gradient algorithm. To quantify the in-plane elasticity of defective graphene, a planar graphene sheet is then stretched uniaxially in its basal plane, and the Young's modulus is calculated by fitting the small-deformation tensile stress–strain curve using a linear function $\sigma = Y\varepsilon$. The results are summarized in Fig. 1(a), which demonstrate