Graphene as a model system for 2D fracture behavior of perfect and defective solids

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ABSTRACT. A 2D bond-breaking model is presented that allows the extraction of the intrinsic line or edge energy, fracture toughness, and strain energy release rate of graphene from measured and calculated 2D Young's moduli and 2D pristine strengths. The ideal fracture stress of perfect graphene is compared with the critical fracture stresses of defective graphene sheets containing different types of imperfections. This includes (multiple) vacancies in the subnanometer range, grain boundaries, slits in the nanometer region, and artificial pre-cracks with sizes of 30 nm to 1 μm. Independent of the type of defect, a common dependence of the critical fracture strength on the square root of half defect size is observed. Furthermore, the results suggest the applicability of the Griffith relation at length scales of several nanometers. This observation is not consistent with simulations pointing to the existence of a flaw tolerance for defects with nanometer size. According to simulations for quasi-static growth of pre-existing cracks, the atomic mechanism may also consist of an alternating sequence of bond-breaking and bond-rotation steps with a straight extension of the crack path. Independent of the exact atomic failure mechanism brittle fracture of graphene is generally assumed at low temperatures.

KEYWORDS. Graphene; 2D bond-breaking model; 2D mechanical properties; Fracture mechanism; Fracture toughness; Strain energy release rate.

INTRODUCTION

Characterization of the elastic and fracture properties of covalent graphene monolayers is of fundamental scientific interest, because they define the upper limits of mechanical behavior [1]. Since perfect samples with an area sufficient for nanoindentation experiments can be prepared, the intrinsic mechanical properties of the class of two-dimensional (2D) solids can be measured directly by nanoindentation with an atomic force microscope, as first realized for graphene [2]. It is important to note that this opens up the unique possibility of studying fracture mechanics of perfect crystals experimentally, a possibility not available for three-dimensional (3D) solids. Furthermore, many theoretical approaches used in dynamic failure analysis are based on 2D models and thus can be applied directly to 2D solids without simplification. Accordingly, the role played by dimensionality is an important issue in advanced fracture analysis. In addition, graphene sheets are of enormous practical importance owing to promising technological applications of larger samples, which, however, may be more or less defective. Therefore, the influence of structural defects such as vacancies, dislocations, microcracks, grain boundaries, and pre-cracks on crack nucleation and propagation must be studied in engineering devices and compared with the behavior of the corresponding perfect solids to judge the mechanical quality and reliability of real materials.

Graphene is the paragon of the new class of 2D covalently bonded solids with unsurpassed intrinsic strength and strong in-plane but very weak out-of-plane stiffness. Together with h-BN monolayers (boronitrene) the one-atom-thick sp^2-bonded hexagonal graphene structure is one of the thinnest known materials, however, without the partially ionic character of boronitrene, which makes the isolation of boronitrene monolayers more difficult. Compared to these single-atom layer crystals, the presently actively studied transition-metal dichalcogenide (TMD) monolayers consist of several atomic layers, similar to the most widely studied MoS_2 sheets, which contain a central hexagonal plane of Mo sandwiched between two hexagonal S planes. For these multilayer materials the exact layer thickness still is a controversial issue with differences in the assumed thickness of a factor of two and the failure behavior is considerably less understood than for the single-atom monolayers.

Graphene is an ideal model system for studying the limitations of continuum mechanics, where the 2D crystal can no longer be characterized by the usual macroscopic mechanical properties. This is of interest for the application of the Griffith criterion, which is the most important basic relationship for investigating the role played by defects in engineering materials [3]. Therefore, an estimate of the critical size, where the model breaks down at the nanoscale, is of paramount importance for practical applications. Restrictions comparable to those for the Griffith relation may not be expected in the case of the 2D bond-breaking model introduced below, which contains the same mechanical quantities, however, a different meaning of the length scale. Presently, no contributions from experiments can be expected to solve this fundamental question concerning the range of validity of these basic models in applications to nanoobjects. Molecular dynamics (MD) simulations, which allow the treatment of fracture at the atomic scale, are strongly limited by the feature size. However, since a graphene monolayer is only one atom thick, larger sample areas may be investigated at reasonable computational cost, where size effects should be negligible.

The MD simulations give access to microscopic details of the fracture process in graphene such as the difference between uniaxial and biaxial tension, the role played by chirality, e.g., the difference of strength in the zigzag and the armchair directions, and the temperature dependence of failure. Unfortunately, the uncertainties involved in these simulations are still large and in fact may be larger than the difference between the specific types of tension or the effect of chirality. For these reasons, it is useful to consider mean values of mechanical properties to extract the main characteristic behavior, such as the decrease of the critical fracture stress with the actual size of defects. To date contradictory results have been obtained by MD simulations at the nanoscale, yielding, for example, on one hand flaw tolerance in the nanometer range and on the other hand the applicability of continuum models at the nanometer length scale.

THEORY

2D fracture model of 2D mechanical properties of graphene

The 2D bond-breaking model can be derived [4] from the corresponding 3D cleavage model [5] that combines the basic elastic and fracture properties with a subnanometer length. The analytical 2D bond-breaking model connects the relevant in-plane mechanical quantities of 2D solids belonging to continuum mechanics with a subnanometer length scale, describing the atomistic fracture behavior of chemical bonds by introducing a Morse-type interaction function

$$\sigma^{2D} = [(\gamma^{1D} E^{2D})/(4r_0)]^{1/2} \qquad (1)$$

Here σ^{2D} is the 2D intrinsic strength or critical stress in (N/m), E^{2D} the 2D Young's modulus in (N/m), γ^{1D} the breaking force in (N) or line (edge) energy or (J/m), and r_0 the nanoscopic length scale representing the equilibrium bond length of the covalent monolayer. This parameter-free 2D fracture model provides a versatile tool to determine any missing intrinsic mechanical property if the other two and the length scale are known.

The so-called 2D solids are not really 2D in the strict mathematical sense but possess a finite thickness and volume determined in the single-atom layers by the size of the constituent atoms. For this reason bulk mechanical properties can be assigned to this particular atomic volume, despite the subnanometer thickness of the monolayer. The thickness of the building blocks in the layered graphite material agrees well with a definition of the active nanoscopic volume in such a way that the average electron density of the isolated monolayer matches that in the parent bulk material [6]. As expected, this general definition provides layer thicknesses in very close agreement with those known for the building blocks in the layered structure of the corresponding bulk crystals, however, takes into consideration the real shape of the nanoobject.

The 2D Young's modulus and 2D intrinsic strength of perfect graphene have been measured by nanoindentation under biaxial tension and have also been studied by density-functional theory (DFT) calculations and MD simulations, considering fracture by uniaxial tension. From this information the breaking force and line or edge energy can be obtained by using Eq. (1). Furthermore, the fracture toughness and critical strain energy release rate can be determined. Owing to the large scatter of published experimental and theoretical data on graphene, which is larger than the differences due to chirality and the type of tension, the following mean 2D values were used in the present analysis: $E^{2D} = 333$ N/m, $\sigma^{2D} = 34.6$ N/m, and $\gamma^{1D} = 2.0$ nJ/m, using $r_0 = 0.142$ nm as bond length in graphene [4]. In addition, the values of the fracture toughness and critical strain energy release rate were estimated from these quantities: $K_{IC}^{2D} = \sigma^{2D}(8r_0)^{1/2} = 1.2\times10^{-3}$ N/m$^{1/2}$ and $G_{IC}^{2D} = 2\gamma^{1D} = 4.0$ nJ/m. For comparison with literature data, bulk properties were calculated by dividing these properties by the thickness of the graphene monolayer of $h = 0.334$ nm, extracted from the interlayer thickness of the covalent layers in bulk graphite [7]. The layer thickness is generally employed to connect the 2D monolayer properties with the corresponding bulk properties of the 3D solid. These formal bulk properties are: $E^{3D} = 997$ N/m², $\sigma^{3D} = 104$ N/m², $\gamma^{2D} = 6.0$ J/m², $K_{IC} = 3.5$ MPa m$^{1/2}$, and $G_{IC} = 12$ J/m².

Atomic-scale mechanisms of fracture pathways in graphene

Elucidation of the elementary steps of graphene fracture by first-principles calculations and experimental investigations employing high-resolution imaging are largely lacking. For this reason, atomistic simulations have been performed to investigate the fracture pathways in graphene. For example, an analytical bond-order potential has been used to describe the interaction of the covalent C–C bonds in graphene [8]. With this model two competing atomic failure processes have been identified, namely bond breaking at the crack-tip and C–C bond rotation by 90°, leading to the formation of two pentagon/heptagon Stone–Wales (SW) defects. Usually, brittle fracture via bond breaking is expected to prevail at low temperatures, whereas plastic deformation based on dislocations and the nucleation and motion of SW defects should dominate at high temperatures. Simulations of the minimum energy paths indicate that bond rotation may be energetically and kinetically more favorable with a 1–2 eV lower energy barrier. However, the generation of the SW defect changes the local environment at the crack tip, leading to a crossover point, where symmetric and asymmetric bond breaking may dominate kinetically. Crack extension is expected to remain straight according to the condition of quasi-static growth on the plane of maximum normal stress. Consequently, the model suggests a mixed mechanism involving an alternating sequence of bond breaking and bond rotation under quasi-static loading conditions near the energetic limit of fracture [8]. The non-uniform bond deformation and rupture processes with highly localized stresses at the tip may create a variety of edge morphologies including reconstructed edges, which influence the electronic properties of graphene [8]. Thus, alternatively to a simple bond-breaking process as the atomic-scale fracture pathway in the presence of pre-existing cracks in graphene, an alternating bond-breaking and bond-rotation mechanism may occur.

Besides the temperature, the fracture mechanism depends also on the loading rate. In the case of fast strong loading, crack kinking and branching will take place in graphene. Atomistic MD simulations on the dynamics of rapid fracture show that under pure opening load (mode I) the crack moves straight along the zigzag direction with atomically smooth edges at a speed of up to 8.2 km/s, which corresponds to 65% of the Rayleigh wave phase velocity that is 12.56 km/s in graphene [9]. Above this critical speed, kinking and instability with the formation of rough and irregular edges involving pentagons and heptagons is observed, owing to the strong energy input.

RESULTS AND DISCUSSION

Theoretical analysis of the influence of defects in graphene

As mentioned before, structural defects such as vacancies may play an important role in deteriorating the structural integrity and mechanical performance, especially of large graphene layers. In the subnanometer length scale range the effects of (multiple) vacancies on the fracture strength have been studied by MD simulations [10,11]. Fig. 1 shows the critical fracture strength of $n = 1$, 2, and 3 vacancy units with a crack length of $l = na$, where a is the lattice spacing $a = \sqrt{3}\, r_0 = 0.246$ nm, normalized to the mean intrinsic strength of $\sigma^{2D} = 34.6$ N/m [10] as a function of the square root of half defect length. These values are for tensile load at 300 K, where graphene is expected to fail by brittle fracture either by bond breaking or combined bond-rupture and bond-rotation processes.

Larger slits in the range of 0.7–4 nm have been studied by a quantum mechanical/molecular mechanical/continuum mechanical (QM/MM/CM) model and compared with the Griffith formula [12]. Quantum mechanics was used to describe a small region around the slit and the coupled continuum-atomistic model was applied elsewhere. The electronic structure calculations agree with continuum fracture mechanics within 10% for the longest crack investigated. The Griffith relation, assuming linear behavior of the stress–strain relationship and neglecting lattice trapping, allows a reasonable description of graphene fracture initiated by crack-like defects as small as 1 nm in size. In fact, DFT calculations of the energy release rate exceeded the lower bound value of $G_{IC} = 2\gamma^{2D}$ by only 10%, indicating modest lattice trapping [12]. Fig. 1 presents the normalized critical fracture strengths of the nanometer slits obtained by the QM/MM/CM calculations versus the square root of half defect lengths. The decrease of the critical strength values is nearly paralel to the main correlation, however, with higher fracture strengths. As stated by the authors, the shape of such slits bears little relationship to sharp cracks assumed in the Griffith model. This could be a simple explanation for the higher strength values.

Molecular dynamics simulations indicate that tensile fracture in nanocrystalline graphene may become insensitive to a pre-existing hole or notch below a characteristic critical length of 30 nm [13,14]. Circular holes with 1–6 nm radius created in the center of a nanostrip of nanocrystalline graphene with 2 nm average grain size did not initiate crack nucleation by stress concentration at the flaw but nucleation of cracks started some distance away from the hole [14]. This increase of the characteristic length scale of flaw tolerance in nanocrystalline graphene was connected with a decrease in the elastic modulus, fracture strength, and the strain energy release rate to 8 J/m² compared to about 12 J/m² for single-crystalline graphene. As stated above, higher critical fracture strengths are expected for circular holes in comparison with atomically sharp tips due to reduced stress amplification.

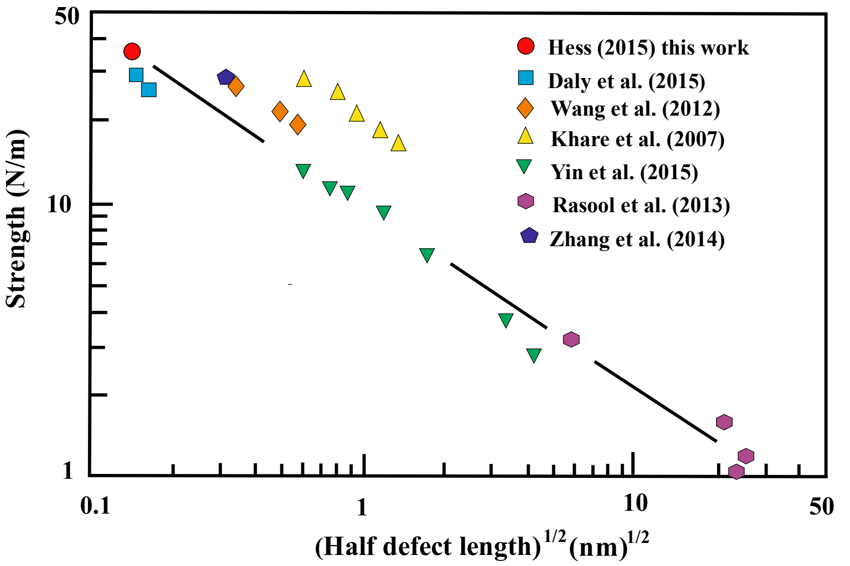

Figure 1: Intrinsic stress of perfect [4] and critical engineering stress of defective graphene containing vacancies [10,20], slits [12], grain boundaries [15], and pre-cracks studied theoretically by DFT and MD calculations [17] and experimentally by nanoindentation [16]. The straight line is a guide to the eye.

Experimental analysis of graphene with defects

Measurements of the intrinsic strength of crystalline and polycrystalline graphene membranes have been performed with a custom-fabricated diamond tip of 115 nm radius, to ensure a uniform stress distribution [15]. The strongest single-crystal membrane failed at 31.5 N/m, which is slightly lower than our mean value of 34.6 N/m presented in Fig. 1. For most large angle grain boundaries a strength of 80 GPa has been measured that corresponds to 26.8 N/m. Normalization of this value to the mean intrinsic strength considered here yields 29.4 N/m. By high-resolution transmission electron microscopy the atomic-scale strain field has been mapped showing bond lengths of up to 0.185 nm in comparison to the average bond length of 0.142 nm observed for the single-crystal material [15]. This maximum bond extension is used to display the reduction of the fracture strength by large angle grain boundaries in Fig. 1.

If defects are present, as is usually the case for large-area engineering graphene sheets, the concept of fracture toughness can be employed to characterize the real engineering strength of the material, using the Griffith relationship. For example, the Griffith relation has been employed for failure analysis in the case of artificial pre-cracks. The aim of this model is to explain the discrepancy between the theoretically predicted pristine strength and the actually observed real fracture strength. Griffith's brittle fracture model depends on the same mechanical properties as Eq. (1) and deviates only by a numerical factor and the meaning of the length scale involved in the brittle cleavage process between the weakest crystallographic cleavage planes [3]

$$\sigma_{cr} = [(2\gamma^{2D}E^{3D})/(\pi a_0)]^{1/2} \qquad (2)$$

Here σ_{cr} is the actual critical fracture strength of real crystals governed by the stress amplification effect generated by defects or flaws, E^{3D} the bulk Young' modulus, and γ^{2D} the surface energy. The length scale a_0 is connected with half the length of an internal failure-inducing microcrack or the depth of a surface-breaking crack responsible for inducing crack nucleation. Note that the intrinsic length scale occurs in Eqs. (1) and (2) for dimensionality reasons. For example, in Eq. (2) the Young's modulus has the dimension 'energy per volume' and the surface energy the dimension 'energy per surface area'.

Experimental values reported recently for the effective fracture stresses and corresponding crack lengths, observed for various artificial central cracks introduced with a focused ion beam, show for the first time the applicability of the Griffith relation to defective 2D crystals [16]. The extrapolation of the measured fracture strength values to the intrinsic value yields a surprisingly good agreement, as can be seen in Fig. 1. Thus, it is important to stress that the 2D bond-breaking model applied to the intrinsic fracture behavior of perfect graphene and the Griffith analysis of defective graphene deliver consistent results covering four decades of flaw size from the subnanometer to the micrometer range, despite the relatively large scatter in the data. This conclusion is supported by recent MD simulation indicating that the difference between the Griffith criterion and MD simulation is small for cracks propagating along the zigzag direction with the lowest critical fracture stress. For an energetically less favorable crack path, e.g., a kinked path approaching during propagation the zigzag direction from a different chirality, deviations of more than 15% may be observed for small crack sizes below 10 nm [17]. This conclusion has been obtained by comparing the apparent fracture resistance used as a fitting parameter in the relationship of the Griffith stress to crack length and the evaluation of the fracture resistance by MD calculations of the line or edge energy for different chiralities. Such an overestimation of the fracture strength in the nanometer region by the Griffith criterion is in agreement with the results observed in the previously discussed QM/MM calculations [12].

CONCLUSIONS

With the two 2D fracture models discussed above a complete and consistent set of mechanical properties of graphene has been derived that is in good agreement with the extensive published data. The pristine strength is consistent with most modeled and the measured critical fracture strengths of graphene containing crack-like defects, stretching from vacancies with subnanometer size to artificial pre-cracks extending to micrometer size. The observed correlation of defect size behavior in the nanometer range is in disagreement with a general flaw tolerance in the nanoscale, where essentially theoretical strengths should be observed in the presence of cracks of nanometer size [13,14]. The present findings clearly support the alternative point of view discussed in more detail in [18]. A further argument against general flaw tolerance is that the pathway and direction of crack propagation in graphene can be controlled under tensile load by the presence of atomistic defects in the form of vacancies placed deliberately in the monolayer. This has been demonstrated by applying a first-principles-based reactive force field potential (ReaxFF) that features specific patterns of vacancies to simulate the fracture paths in graphene [19]. In fact, it was possible to cut graphene monolayers along these selected patterns simply according to the spatial arrangement of vacancies.

The mechanical reliability and ability of defective covalent monolayers to resist failure is an important practical issue, because graphene and other 2D solids may play a crucial role in the post-silicon era. The critical strength–defect size dependence presented in Fig. 1 provides essential information on the degree of degradation of the engineering strength with the square root of half defect length taking into consideration very different structural imperfections. Furthermore, it confirms that the combination of the 2D bond-breaking model, describing the perfect monolayer, and the Griffith model, taking into account the specific defect size dependence postulated by the Griffith relation, grasps the main features of graphene fracture mechanics, however, neglecting detailed features such as the dependence of fracture on crystallographic direction and the nature of applied tension.

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