Failure Mechanisms of Graphene under Tension

C. A. Marianetti\textsuperscript{1} and H. G. Yevick\textsuperscript{2}

\textsuperscript{1}Department of Applied Physics and Applied Mathematics, Columbia University, New York, New York 10027, USA
\textsuperscript{2}Department of Physics, Columbia University, New York, New York 10027, USA

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Recent experiments established pure graphene as the strongest material known to mankind, further invigorating the question of how graphene fails. Using density functional theory, we reveal the mechanisms of mechanical failure of pure graphene under a generic state of tension at zero temperature. One failure mechanism is a novel soft-mode phonon instability of the \( K_1 \) mode, whereby the graphene sheet undergoes a phase transition and is driven towards isolated hexagonal rings resulting in a reduction of strength. The other is the usual elastic instability corresponding to a maximum in the stress-strain curve. Our results indicate that finite wave vector soft modes can be the key factor in limiting the strength of monolayer materials.

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The mechanical failure of materials is usually a complex process which may involve defects at a variety of length scales, such as dislocations, grain boundaries, cracks, etc. The complexity and statistical nature of these defects cause mechanical failure to be extremely dependent on not only the type of material but also on the manner in which the material was synthesized. To the contrary, ideal strength, which can be defined as the maximum attainable stress under a uniform strain field in the absence of any instabilities, is an intrinsic property of a material [1]. Recently, the measurement of ideal strength has been achieved in the case of graphene [2], a monolayer of carbon. Using nanoindentation, Lee et al. strained graphene until failure under conditions which appear to be very nearly ideal [3]. This experiment reinvigorates the fundamental question of how and why a material fails under ideal conditions. The answer lies within the forces which bond a material together. Computing these forces from the first principles of quantum mechanics is made possible by intelligent approximations to the quantum many-body problem, such as the local density approximation (LDA) of density functional theory (DFT) [4], in addition to plentiful computational resources. While LDA may qualitatively break down in certain situations where the electronic correlations are strong [5], it works reliably in materials with relatively large electronic bands such as graphene. Although quantitative errors are still to be expected, in the vicinity of 10\% for certain phonons of graphene [6,7], one can reliably explore the mechanical properties of graphene from first principles. In this study, we use DFT to determine the mechanism of mechanical failure for an arbitrary state of tension at zero temperature.

Perhaps the simplest instability is the so-called elastic instability, whereby a maximum in the stress-strain relation is achieved while retaining the symmetry of strained lattice. To determine the elastic instability of a material, DFT can be used to generate the forces as a function of strain, and such studies were performed once sufficient computational power was available (see Ref. [8] and references therein). However, there is no guarantee that the structure will remain stable with respect to inhomogeneous deformations under strain. In order to determine if a structure is mechanically stable, one needs to confirm that all of the phonon energies are real and positive [9]. Phonon modes with zero or very small energies, excluding the acoustic phonons for \( k \rightarrow 0 \), are usually termed “soft modes” [10]. There are numerous structural phase transitions in which the two phases are directly connected by a soft mode, and the concept of the soft mode gained prominence in the context of elucidating the ferroelectric transition in BaTiO\(_3\) [11,12]. In this work, we demonstrate that a soft mode is responsible for a phase transition and the resulting mechanical failure of graphene in certain states of tension. Previous DFT studies of bulk systems such as Al [13] and Si [14] have demonstrated that nontrivial acoustic phonon instabilities may precede the usual elastic instability for certain states of strain and therefore limit the ideal strength of the material. However, these scenarios are extremely difficult to decipher experimentally, even indirectly, due to defects and plastic deformation, while our predictions in graphene may be directly tested experimentally. Furthermore, our results on graphene yield an optical phonon instability, as opposed to the acoustic instability observed previously in bulk systems.

In the case of graphene, previous phonon calculations have determined that the elastic instability is the mechanism of failure for uniaxial strain in the armchair or zigzag directions [15] [i.e., \( x \) and \( y \) directions in Figs. 2(b) and 2(c), respectively]. Another study fit third order elastic constants to empirical tight-binding calculations [16], but this elastic parametrization cannot account for inhomogeneous instabilities revealed by the phonons. Therefore, the mode of failure in a general state of tension has never been considered.

We compute the phonons using the displacement method [17], where the forces are generated using DFT within the
lattice translations. Below we show the positive
modes form a twofold representation when including the
structure has become unstable and will undergo a
become imaginary resulting in a soft mode. This implies
identify the
à gives two distinct real distortions [21] (see Figs. 2(b)
and 2(c)). These modes can be classified as the
phonons is observed, which is to be expected given that
strain was constructed by applying the nominal strain
the strain is increased, the mode continually becomes
energy in the two dimensional space of the
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instability occurs at a strain of \( \epsilon_A = (\epsilon_x + \epsilon_y)/\sqrt{2} = 0.307 \). However, the primitive unit cell does not have the freedom to distort along the \( K_1 \) mode as the primitive translational symmetry is enforced in the calculation. The same curve can now be analyzed for the \( K \) cell. The phonon instability is clearly illustrated by a discontinuity in the curve at \( \epsilon_A = 0.213 \) (see inset of Fig. 3), in excellent agreement with our preceding two calculations. Upon activation of the \( K_1 \) mode, the force rapidly drops, and is subsequently nearly flat until decreasing. Therefore, this new phase which forms is essentially mechanically unstable, and there is no need to recompute the phonons for this new phase. As a result, the soft \( K_1 \) mode can be seen not only as the precursor to a phase transition as in soft-mode theory, but also as a soft-mode which leads directly to mechanical failure.

The above analysis has revealed that for equibiaxial strain the mode of failure of graphene is radically different than the usual elastic instability which is observed for uniaxial strain in the zigzag or armchair directions. Therefore, the question arises as to when the elastic instability is the failure mode versus the \( K_1 \)-mode instability for a generic state of tension. In order to resolve this we have computed the strain at maximum stress for both the primitive unit cell and the \( K \) cell, as above, for all possible linear combinations of tensile strain in the zigzag and armchair uniaxial strain tensors. A given direction of strain corresponds to an angle \( \theta = 0^\circ \) to \( 90^\circ \). (b) The nominal stress in the \( x \) and \( y \) directions for all points along the \( K \)-cell curve in (a). (c) The same as (a), except uniaxial strains are applied in the \( x' \) and \( y' \) directions, which correspond to a \( 15^\circ \) rotation of the coordinate system.

This analysis is not yet exhaustive due to the fact that graphene is anisotropic, and therefore shear strain would have to be included in the present coordinate system to enumerate every possible state of tension. Alternatively, one could repeat the above analysis for every possible rotation of the coordinate system which is not generated by a member of the point group of graphene. This corresponds to generating Fig. 4(a) for every possible rotation of the coordinate system between \( 0^\circ \) and \( 15^\circ \). We have repeated the coordinate system in \( 3^\circ \) increments and regenerat-ed Fig. 4(a) at each increment (see Fig. 4(c) for \( 15^\circ \) rotation). Conveniently, all of the results for the different rotations are bounded by the envelope curves created by superimposing the original result and the \( 15^\circ \) rotation. All rotation curves progress monotonically with rotation between the limits of the envelope. It should be noted that Fig. 4(c) is symmetric about \( \theta = 45^\circ \) due to a mirror line which maps \( x' \leftrightarrow y' \). In summary, shear strain does not
introduce any qualitative changes, and even the quantitative changes are very small for the onset of the $K_1$-mode instability.

Our prediction of the soft $K_1$ mode may be directly verified experimentally by measuring the phonon dispersion as a function of strain. Electrons have been used to measure the surface phonons of graphite, using both reflection electron-energy-loss spectroscopy [22] and high-resolution electron-energy-loss spectroscopy [23]. Therefore, the phonons could potentially be measured directly for graphene. The challenge in this particular case would be the fact that the graphene would have to be strained in situ. Another more indirect probe would be Raman spectroscopy [21], which has already been performed for graphene under uniaxial tension [24] in the regime of small strains.

It is instructive to compare our results to the nanoindentation experiments of Lee et al. [3]. They estimated a Lagrangian breaking strain of $\varepsilon_x = \varepsilon_y = 0.250$, which corresponds to a nominal strain of $\varepsilon_x = \varepsilon_y = 0.225$. Unexpectedly, this far exceeds the breaking strain as dictated by the $K_1$ mode of $\varepsilon_x = \varepsilon_y = 0.151$. Therefore, it is clear that theory and experiment are not operating under identical conditions, and it is necessary to detail all significant differences. First, our calculations are performed at zero temperature, while the experiments are performed at room temperature. Second, the experiment could be influenced by the presence of the nanoindenter tip or other elements which may react with the graphene layer. Finally, the experiment is assumed to be in a state of equibiaxial strain while our calculations are by construction. Any and all of these differences may be linked to the difference between theory and experiment. Naively, one would expect theory to overpredict the maximum strain given that impurities may be present in the experiment or defects may be nucleated via thermal fluctuations which are not included in our simulations. However, we have shown the exact opposite to be true, and therefore this discrepancy is an anomaly. Given that LDA overpredicts the energy of the $K_1$ mode in the unstrained case [6,7], the exact result is likely to yield an even smaller breaking strain even farther from the experimental value. Interestingly, the results of Lee et al. are in much better agreement with our results for the elastic instability of equibiaxial strain (i.e., $\varepsilon_x = \varepsilon_y = 0.216$). This is suggestive that perhaps somehow the $K_1$ mode is being stabilized in the nanoindentation experiment due to one of the differences outlined above. This issue can be resolved by bridging theory and experiment in future work. Nanoindentation experiments may be performed at low temperatures, and molecular dynamics simulations may be performed at high temperature and in a geometry similar to experiment.

In conclusion, we have determined the failure mechanisms of pure graphene in a generic state of tension at zero temperature. The usual elastic instability causes failure for strains near uniaxial while a novel soft-mode phonon instability of the $K_1$ mode causes failure for strains near equibiaxial. Further experiments have been suggested to directly test our prediction of the softening of the $K_1$ mode.

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