Theoretical prediction of stress-induced phase transformations of the second kind in graphene

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Simulations of planar graphene undergoing in-plane deformations are found to develop crystal structures different from the usual hexagonal configuration—either monoclinic or nearly orthorhombic—through two different types of solid phase transitions of the second kind. They are achieved through a concerted C2 rotation similar in appearance to the onset of the Stone-Wales transformation. The key result is the observation of the early rotation in even the smallest primitive cell. In connection to earlier findings on reversibility, the thermodynamic or kinetic character of the rearrangement is found to depend on the macroscopic straining direction.

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Since their discovery,\textsuperscript{1,2} intense interest has focused on the engineering of materials and devices from various forms of elemental carbon. The readily encountered single-crystal form of single-wall carbon nanotubes, in particular, continues to be explored for its myriad uses\textsuperscript{3,4} and seemingly unlimited engineering potential.\textsuperscript{5,6} It is therefore exceedingly important from a practical application standpoint and for the engineering of nanotube-based devices to understand the mechanical behavior and, in general, its mechanics, outside of the standard linear elastic regime. Significant progresses have been made in recent years in this regard by examining the mechanical limits of nanotubes and graphene. Of heightened interest has been the identification and simulation of the so-called Stone-Wales (SW) transformation,\textsuperscript{7} a mechanism recognized for its critical role in the mechanical deformation under tension near the yield point.\textsuperscript{8–19}

The SW mechanism is a C2 rotation that changes the local coordination of the carbon atoms, which is tantamount to a local phase transformation of the material. The rotation is accompanied by a local relaxation of the lattice in the neighborhood of the C2. It has been shown that either at zero or finite temperature, under uniform bulk stretching, the local lattice rearrangement is energetically more favorable and relieves the amount of strain energy the system sustains.\textsuperscript{10} This is usually signified in the literature by a lower energy than found in the homogeneously strained case. Studies to date have shown the significance of this transformation and the unique consequence it has on the mechanical behavior of nanotubes. Its influence on other physical properties have also been studied in detail.\textsuperscript{13,18,20–22} Its particularly interesting feature is that it is a multiaxial stress-induced effect, unlike the hydrostatic pressure or temperature-induced behavior historically known for carbon forms,\textsuperscript{23,24} such as pressure-induced transformation from graphite into diamond.

In essence, the dislocation dipole created by the bond rotation “unlocks” the plasticity mechanism and serves as the core from which dislocations can emanate\textsuperscript{11} which can then ultimately lead to nanotube failure.\textsuperscript{10–12,14,25,26} In axial nanotube tension and at high temperatures, the formation of the defect has been shown to be reversible\textsuperscript{10} and substantially influenced by the curvature of the nanotube.\textsuperscript{9} Additional important mechanical parameters, particularly for the connection to experimentally realistic conditions, are the temperature and loading rate.\textsuperscript{27,28}

In a typical kinetic simulation of strains in a large lattice, the SW defect spontaneously forms at random locations, with some preferable orientation according to the zigzag (ZZ) or armchair (AC) configurations of the basal plane.\textsuperscript{20–22} Generally, the theoretical investigations thus far have considered relatively large supercells of atoms in graphene and nanotubes or formation studies of molecular fullerenes. This necessarily presumes that the localized SW defect will form somewhere in the system upon mechanically loading the perfect crystal, or in the case of fullerenes, upon changing environmental conditions such as pressure or temperature. In contrast to this, we currently assume that the motion of the atoms can occur everywhere in the system in a concerted fashion. The point of departure, therefore, is in the selection of a periodic primitive cell to perform our calculations using mechanical uniaxial loading conditions. This effectively isolates the bond-rotation effect from other parametric dependencies so that we can examine the mechanics separately and decouple the longitudinal and transverse directions to study the anisotropy of the material.

Through simulations, we offer an alternate mechanical interpretation of previously observed results, i.e., that the defect formation is related, in part, to a zero temperature limiting behavior of a stress-induced solid-solid phase transformation. The conclusion stems from a hypothesis that the concerted rotation of many C2 pairs, under conditions of uniform strain and periodicity, may be energetically more favorable than the isolated rotation of one. We compute the entire strain energy landscape for a periodic primitive cell undergoing large deformations and examine differences in the results as they depend on the orientation of the basal plane. To contrast this with earlier works, the key result here is therefore that an early rotation event not only occurs but is observable even in the smallest primitive cell, interacting with its images at relatively low energies. Our calculations focus primarily on the first 45° rotation of the C2 pair, one-half of the 90° to reach the Stone-Wales configuration.

This subsequently suggests a phase change of the second kind occurs in the sense of a space-filling crystal,\textsuperscript{29} which is taken here to mean that unlike SW where one localized defect is considered the present consideration is of a defect in a periodic image with supercell boundaries not permitting any vacuum space in the plane of the lattice. Here we are using the additional terminology of Landau and Lifshitz\textsuperscript{29} where...
kinetic processes involve an energy barrier with behavior that is discontinuous and where thermodynamic processes involve no energy barrier with behavior that is continuous. Though previously shown to be a kinetic process, we further show through constrained uniaxial deformations that bond rotations possess both kinetic and thermodynamic features, depending on the axis of loading, that helps explain earlier observations of the reversibility of the process.

We use the concepts of finite strain continuum mechanics for the definitions of deformations and strains. Points in the reference configuration are defined by \( \mathbf{X} \) and their corresponding points in the deformed configuration by \( \mathbf{x} \). The deformation gradient tensor is then defined as the gradient of \( \mathbf{x} \) with respect to the reference configuration, \( \mathbf{X} \), such that \( \mathbf{F} = \nabla_{\mathbf{X}} \mathbf{x} = \partial \mathbf{x} / \partial \mathbf{X} \). Consideration is presently limited to uniaxial stretching along either the principal ZZ or AC axes. In the following, the ZZ axis corresponds to the 11-component and the AC axis to the 22-component, respectively, of the deformation gradient tensor. This simplifies the tensor to a diagonal \( 3 \times 3 \) matrix whose components are \( (1+\alpha, 1+\beta, 1) \), where for all parametric variations of \( \alpha \), \( \beta \) is currently held fixed at zero and, likewise, for all \( \beta \) variations \( \alpha \) is set to zero. In a one-dimensional sense, \( \alpha \) and \( \beta \) are the so-called engineering strains that measure the uniaxial change in length relative to the reference length. Discussions henceforth interchangeably use deformation to refer to the relevant component of \( \mathbf{F} \) being used and strain to the respective engineering strain component, i.e., in the context of this paper deformation is \( 1+ \) (strain). Deformations are then applied in the conventional way by multiplying \( \mathbf{A}_i \) for \( i=1,2,3 \) by \( \mathbf{F} \) to give the deformed lattice vectors \( \mathbf{a}_i = \sum_{j=1,2,3} (\mathbf{F})_{ij} \mathbf{A}_j \). The strain energy is then determined by the difference between the energy in the configuration corresponding with \( \mathbf{a}_i \) with that in configuration \( \mathbf{A}_i \).

The calculations proceed by taking the periodic cell of single-crystal graphene containing two atoms in the primitive basis as shown in Fig. 1. The procedure to determine the strain energy landscape is as follows. One atom is held fixed while the position of the other atom is varied in the plane. At each deformation state where \( \mathbf{a}_i \) is held fixed, the strain energy of the system is determined at 2200 alternate locations of the second atom (grid points) using density functional theory (DFT) \(^{30} \) from the plane-wave ABINIT code, \(^{31} \) in which the exchange and correlation term is treated through the generalized gradient approximation (GGA) according to the Perdew-Burke-Ernzerhof functional \(^{32} \) with the Hartwigsen-Goedecker-Hutter pseudopotential for carbon. A plane-wave energy cutoff of 1360 eV is used throughout. Each grid point represents a single self-consistent field (SCF) calculation and the points combine to generate a full energy landscape. It is noted that the simplicity of this approach is afforded by having a planar structure of graphene with only two atoms in the computational domain.

Calculations of strain energies are shown in Fig. 2 in the unloaded reference state and at the critical value of 29% strain. To be able to compare the results as they change with
deformation, we normalize the cell dimensions so that (0,0) signifies the origin of the local coordinate frame in the lower left corner of the cell, (1,0) the lower right corner, etc. In the undeformed case with the fixed position of the first atom at the reduced coordinate of (1/3, 1/3), the equilibrium position of the second atom is clearly at (2/3, 2/3). The additional minima at (1,0), (1,1), and (0,1) represent the crystal symmetries.

At the critical value of 29% strain there is a clear change from hexagonal to monoclinic structure—two additional local minima appear in the cell. Figure 2(b) shows these to be at (1/3, 5/6) and (5/6, 5/6) at an energy of 1.32 eV per atom. The new configuration may be interpreted as one-half of the turn to reach the Stone-Wales configuration.

It is important to note that in the SW formation, the energy depends critically on the local strain fields in the region and the present disabling of this relaxation through the use of periodicity conditions makes a direct quantitative comparison difficult with other published results. Having stated this, however, the values can still be useful by computing energies on a per cell basis, which takes into consideration those atoms participating in the rotation much like the defect energies computed elsewhere. Thus, the energy of the “defect” in Fig. 2(b) is 2.64 eV.

Consistent with earlier results, we observe two energetically equivalent kinetic pathways, or direct exchange channels, created by the deformation, thus indicating there is no preference between the clockwise and counterclockwise bond rotations. This result was shown in earlier investigations. The reverse barrier is approximately 50 meV per atom at this strain suggesting a total activation of 2.74 eV. The resulting two variants of the crystals are distinct by a mirror reflection across a plane transverse to the strain direction. The barrier height is very high due to the assumption of a space-filling crystal which does not allow for relaxation in the vicinity of the defect. The key observation is that the minima actually appear for such a small system, expedited by the applied mechanical loads, and the character is kinetic as evident by a nonzero reverse barrier.

The activation corresponds to a transformation stress of 24.9 GPa, assuming a graphite layer thickness of 3.35 Å while neglecting interlayer interactions. The transformation occurs at approximately 29% engineering strain under the zero temperature presumption. These values are in reasonable agreement with earlier calculations that show nanotube yield strains of 5–30 % (Ref. 25) and Stone-Wales defect activation energies of 3–8 eV via theory and 4–10 eV via experiments. Experimental tensile strengths are in the range 10–150 GPa.

The strain energy surface for uniaxial tension along the AC axis is considerably different. The second minimum that appears in Fig. 2(c) is from the minimum originally at (1,0), i.e., the point corresponding to the 60° crystal invariant, that travels upward with increasing deformation. The result is a reduction in the symmetry of the crystal without the creation of new minima, contrary to the case of ZZ loading in Fig. 2(b) where new minima spontaneously appear. The two minima remain distinct at 29% strain but continue to grow closer in location with increasing strain. The midpoint along the line connecting them corresponds to the orthorhombic structure. These observations appear to be consistent with general findings that the SW defect appearance depends on nanotube chirality under tension. However, it is noteworthy that it is a gradual closing of the minima, suggesting a thermodynamic behavior. Discontinuous motion, if any were to occur, would be evident by a crystal “flipping” about the plane perpendicular to the basal plane as the second atom alternates between the two minima. The thermodynamic behavior for this loading mode may partly explain the reversibility observed previously.

The kinetic and thermodynamic properties of the deformations are made more evident in Fig. 3 in which the energy levels along the lines ABC and A'B'C' are shown in Fig. 2(a). At the 29% ZZ strain, a new minimum appears at B which becomes the preferred configuration with subsequently increasing strain. Up to 29% and high AC strains,
the minima that were originally at A’ and C’ grow closer to B’. But their equilibrium locations remain qualitatively the same throughout deformation.

Using the space-filling crystal concept, two alternate crystal configurations can be proposed. In the ZZ direction, the crystal takes a monoclinic form, and in the AC direction, the form is “nearly” orthorhombic. The latter is made conditional because of the thermodynamic feature of the C$_2$ rotation described earlier. The strain energies of the hypothetically deforming crystals in Fig. 4 demonstrate the lowest energy paths follow these alternate structures. In the case of AC straining, however, the crystal finds a lower energy configuration in a small neighborhood around the C$_2$ bond in the SW mechanism.

Also, the results can be used to quantitatively compare observed kinematics with classical theories for deforming crystals such as the Cauchy-Born (CB) approximation. The computed order parameter $\eta = ||\mathbf{r} - \mathbf{r}_o||/||\mathbf{F}_\text{r}_o||$ is depicted in Fig. 5, where the changing magnitude of the position vector $\mathbf{r}$ connecting the atoms in the primitive cell normalized by the Cauchy-Born vector $\mathbf{F}_{\mathbf{r}_o}$ provides a measure of departure from the CB approximation. While $\eta$ makes no distinction of crystal invariants, the left axis values of $||\mathbf{r} - \mathbf{r}_o||/||\mathbf{F}_{\mathbf{r}_o}||$ make these distinctions clearer. The parameter $\eta$ follows the definition in the Landau theory.$^{29}$

In both loading conditions, the departure from the CB approximation, i.e., the closeness to the high symmetry phase where $\eta = 0$, occurs readily with increasing deformation, as expected. The main result is the quantifiable departure which is smooth and slow up to 15% strain in either uniaxial AC tension or compression, staying within 1% of CB. The departure is immediate under ZZ loading jumping to 2% difference from CB at less than 5% strain. This result also reiterates the earlier observation of the kinetic and thermodynamic nature of the deformations along the ZZ and AC axes, respectively, by the smoothly varying kinematics in AC (thermodynamic) and the discontinuous jumps in ZZ (kinetic).

Using the notation of Smith,$^{36}$ the graphene sheet in unstrained form belongs to the highest symmetry phase, the D$_{6h}$ crystal class, comprised of 24 unique symmetry operations that leave the lattice invariant. The group of symmetry operations is defined by $\mathcal{G} = \{I, C, S_i, R_i, D_i, C S_i, R_i S_i, D_i S_i\}$ for all combinations of indices $i = [1, 2, 3]$ and $j = [1, 2]$. For the deformed configurations in this discussion, the atom coordinates are rescaled by premultiplying by the inverse of the deformation gradient. That is, the symmetry observations are based on the coordinates $\mathbf{x}' = \mathbf{F}^{-1} \mathbf{x}$ where $\mathbf{x}$ are the coordinates in the deformed configuration. The alternate phases computed presently essentially retain eight of the 24 symmetry transformations. The $(1/3, 5/6)$ configuration has the symmetry group $\mathcal{G}'_{(1/3, 5/6)} = \{I, C, R_3, D_3, R_1 S_2, R_2 S_2, D_1 S_2, D_2 S_2\}$, and the $(5/6, 5/6)$ configuration has the group $\mathcal{G}'_{(5/6, 5/6)} = \{I, C, R_3, D_3, R_1 S_1, R_2 S_1, D_1 S_1, D_2 S_1\}$. Though the SW transformation involves the nucleation of an isolated defect,
and hence loses the Bravais translational symmetry, it is instructive to note that the symmetry group, to within a translation, is also comprised of eight elements, \(G_{SW} = \{I, C, R_1, R_2, R_3, D_1, D_2, D_3\}\). However, it is clear that the SW retains only mirror planes and inversions, while the presently computed phases also contain rotoinversions. Such observations hold significance in the constitutive behavior.

The results suggest an alternate interpretation of mechanically activated phase change in the phenomenology and structural behavior of graphene. Simulations of deformation reveal two types of behavior—one continuous and one discontinuous—in the change in order parameter with respect to the applied deformation. The two phases differ in the particular axis of loading applied to generate them. While the zigzag axis is more frequently studied in SW mechanisms with a commonly seen nontrivial kinetic transition barrier, loading in the transverse direction yields an unexpected response, a crystal rearrangement that is not accompanied by an energy barrier. This leads us to believe that graphene has both kinetic and thermodynamic (equilibrium) features that may be mechanically obtained. The computed associated energies also agree in magnitude with previous observations of the SW transformation. We hypothesize that the SW rearrangement may be a degenerate form of a concerted phase change that is reached through thermal fluctuations that make the SW configuration more accessible when atoms are perturbed from their zero temperature positions, allowing for the subsequent localization and inhomogeneous relaxation that leads to the full 90° turn of the C2 bond.

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