On the hyperelastic softening and elastic instabilities in graphene

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Elastic material instabilities are precursors to failure in defect-free graphene single crystals. Elastic instabilities originate from softening in the material response (decay of tangent moduli) induced by dilatant mechanical deformation. Here, we characterize the softening in the constitutive response of graphene within the framework of hyperelasticity based on symmetry-invariants of the two-dimensional logarithmic strain tensor $\mathbf{E}^{(0)}$. The use of symmetry-invariants provides significant functional simplification in representation of the strain energy function of graphene; ab initio calculations of deformation energy are well-fit using half the number of elastic constants of previous formulations. For a set of large homogeneous deformations comprising uniaxial stretch/stress along the armchair and the zigzag directions, and equi-biaxial tension, stress values predicted by the model compare well with those directly calculated from ab initio solutions. Using acoustic tensor analysis, we show that the constitutive model accurately captures elastic stability limits for a number of biaxial deformation modes, providing results that compare well with independent phonon calculations carried out using linear response density functional perturbation theory. In the case of equi-biaxial deformation, an elastic shearing instability is identified which occurs prior to the configuration of maximum true stress. Potential implications of the present results on the interpretation of limiting deformations achieved in nanoindentation experiments are briefly noted.

1. Introduction

Graphene is an atomic monolayer comprising a hexagonal network of $sp^2$-bonded C-atoms. Nanoindentation experiments on suspended graphene sheets suggest...
that defect-free, single-crystalline graphene can sustain near-ideal-strength stresses while remaining within the reversible regime of deformation [1–3]. These studies also indicate that graphene is intrinsically brittle and exhibits hyperelastic softening. The experimentation involves instrumented indentation of a suspended graphene sheet by a nanometre-sized diamond indenter. The nanoscale size of the indenter ensures that only a submicrometre region of the graphene sheet is probed to the largest deformation levels, and this region often comprises a single defect-free grain. Unfortunately, the stress and strain beneath the indenter are not directly measurable in such nanoindentation experiments; instead, the indentation load (\(F\)) as a function of indentation depth (\(d\)) during the course of indentation is recorded. Continuum-level finite-element analysis (FEA) is then used to estimate the stress and strain beneath the indenter, especially values corresponding to the measured fracture load and indentation depth [1,3,4].

For this purpose, a constitutive function for graphene appropriately describing the stress–strain response over the entire range of deformation up to failure is desired.

One approach to crystal hyperelasticity is based on Cauchy–Born lattice kinematics and tailored interatomic potentials. In applications near dislocations or crack tips, the use of interatomic potentials is generally required, as first principles calculations prove prohibitively costly. But continuum crystal hyperelasticity can be directly calibrated on the energetics of deformed but fully relaxed first principles models of small unit cells, bypassing approximations inherent in the definition of interatomic potentials.

Previously, numerous constitutive models of graphene have been proposed. Within the framework of hyperelasticity, constitutive response is characterized by the dependence of the strain energy density, or free energy per unit reference area, \(\psi\), on the measure of imposed elastic strain, with all symmetries belonging to the material symmetry group duly incorporated [5]. Cadelano et al. [6] developed a nonlinear hyperelastic constitutive model of monolayer graphene by expressing \(\psi\) as a cubic polynomial in components of the Green–Lagrange strain measure, and then imposing the symmetry to reduce the number of independent fitting coefficients [7]. Wei et al. [1,8] noted that the model of Cadelano et al. failed to reproduce with sufficient fidelity the response at both infinitesimal and finite strains. They proposed a fifth-order series expansion for \(\psi\), again based on components of the Green–Lagrange strain measure, to model the in-plane elastic properties of graphene. Their symmetry-reduced expression contained fourteen independent elastic constants. Xu et al. [9] modelled the constitutive response in terms of polynomials based on isotopic invariants of Green–Lagrange strain and accounted for the anisotropy evidenced at larger deformations by means of cumbersome switch-functions. Certain of these constitutive models offer better numerical accuracy than the others; however, owing to the polynomial nature of the representations, the underlying material physics has been—to some degree—obscured in all of these models. This obscurity is a by-product of the common modelling paradigm based on reduction-by-symmetry. The reduction-by-symmetry approach incorporates material symmetry into the constitutive modelling by extrinsically imposing symmetry constraints to reduce the number of independent fitting coefficients [7]. A major limitation, in this context, arises from the fact that the reduction-by-symmetry method is \textit{a priori} restricted to the use of polynomials in the components of strain as the basis of representation—with no scope for including arbitrary non-polynomial functions in the representation.

One objective of this work is to present, and to illustrate with the example of graphene, the idea that an adequate elucidation of the underlying physics requires an appropriate choice of representation of the material response. To this end, we present a constitutive modelling scheme for crystal hyperelasticity based on symmetry-invariants of the logarithmic measure of strain \(E^{(0)}\). The \textit{symmetry-invariants} are scalar-valued functions of the tensor agency (here, strain) that satisfy all the symmetry constraints of the crystal’s material symmetry group [10,11]. Compared to reduction-by-symmetry, the symmetry-invariants-based approach offers substantial advantages. First, the resulting description of material response automatically satisfies the material symmetry requirements without further constraints. Secondly, in terms of the symmetry-invariants, \(\psi\) is expressed in a fashion independent of any particular choice of coordinate frame. Lastly, and most importantly, the approach does not restrict the representation to be only in terms of polynomials.
but allows for usage of more general functions. Using symmetry-invariants of $E^{(0)}$ for the $C_{6v}$ symmetry of graphene, we obtain a constitutive model for deformations involving both large area-change and shape-change. The proposed representation, involving both polynomial and more general functions, not only results in a functional simplification with fewer coefficients in the representation, but also introduces a certain transparency that affords clearer insights into the deformation physics of the material.

The other major objective of this work is to develop a predictive capability—using the obtained hyperelastic constitutive response—which allows the identification of elastic material instabilities in graphene. Elastic instabilities are the major mechanisms governing the elastic-to-inelastic transition in defect-free single crystals [12–14]. Such instabilities are precursors to incipient plasticity or the initiation of fracture in these crystals and originate from hyperelastic softening in the material response (decay of tangent moduli) induced by mechanical deformation. Provided this softening is well captured in the hyperelastic model, acoustic-tensor analysis enables identification of such instabilities. However, construction of the acoustic tensor can be a challenging task unless a convenient representation is employed. The present approach enables straightforward evaluation of the acoustic tensor in a frame-independent form. By evaluating elastic-stability limits for a number of deformation modes, results of which compare well with phonon-calculations carried out using density functional perturbation theory (DFPT), we demonstrate that the acoustic-tensor analysis constitutes a rigorous and effective means of predicting deformation-induced elastic instabilities in graphene.

In §2, we briefly discuss the kinematics of a two-dimensional deformable body and introduce relevant field variables and notations used in the formulation. In §3, we outline the general framework of hyperelasticity, Boehler’s principle of isotropy of space based on the structure tensor [15,16], and invariant-based representation theory [10,11]. The structure tensor and symmetry-invariants of $E^{(0)}$ are explicitly derived for graphene in §4. Form-invariant tensors are obtained as derivatives of the symmetry-invariants with respect to $E^{(0)}$. In §4d, we propose a representation for $\psi$ in the basis of the symmetry-invariants. The expression for work-conjugate stress in terms of the form-invariants and the conversion from the work-conjugate stress measure to Cauchy stress is presented in §4b. We obtain expressions for the work-conjugate tangent modulus tensor in §4c, and for the acoustic tensor in §4d. The model is validated in §5 by computing the stress for a set of finite deformations comprising uniaxial stretch/stress along the armchair and the zigzag directions; and equi-biaxial tension. The predictive capability of the model is demonstrated by obtaining elastic stability limits—based on acoustic tensor analysis—for a number of biaxial deformation modes in §6. We conclude in §7 by summarizing our results and considering certain of its implications.

2. Kinematics

We consider graphene as a two-dimensional deformable body denoted by unstressed reference configuration $B$. The kinematics of this deformable body is described by time-varying vector and tensor fields belonging to the two-dimensional Euclidian space $\mathbb{R}^2$. We denote by $X$ an arbitrary material point of $B$. As the body is deformed, the material point $X$ moves to another point in the two-dimensional space, characterized by its deformed coordinate $x$ at current time $t$. The convection of material points under deformation is described by a smooth, injective (one-to-one) function $\chi(X,t)$ called the motion. The non-translational part of the motion can be equivalently defined by the positive-definite second-order deformation gradient tensor, $F = \nabla_\chi(X,t)$. Notationally suppressing this functional dependence for convenience, the polar decomposition theorem provides the following factorizations of $F$ [17,18].

$$F = RU = VR, \quad (2.1)$$

where the orthogonal tensor $R \in SO_2$ characterizes rigid-body rotation, whereas $U$ (or $V = RUR^T$), termed the right (left) Cauchy–Green tensor, characterizes shape- and area-change. Physically, deformation in the neighbourhood of a material point in the body can be kinematically considered
as stretching followed by a superimposed rigid-body rotation, or vice-versa. \( U \) is a symmetric tensor having two real positive eigenvalues, the principal stretches \( \lambda_1 \) and \( \lambda_2 \). Using spectral decomposition, \( U \) can be expressed as

\[
U = \lambda_1 r_1 \otimes r_1 + \lambda_2 r_2 \otimes r_2,
\]

where \( r_1 \) and \( r_2 \) are orthogonal principal unit vectors in the plane. The deformation of a material point can be kinematically factored as the product of a purely dilatational (or shape-preserving, but area-changing) deformation \( U^a \), with \( \det U^a = \det U \), and a purely isochoric (or shape-changing, but area-preserving) deformation \( \tilde{U} \), with \( \det \tilde{U} \equiv 1 \). Accordingly, the stretch tensor can be product-decomposed as

\[
U = U^a \tilde{U} = \tilde{U} U^a,
\]

where

\[
U^a \equiv J^{1/2} I
\]

and

\[
\tilde{U} \equiv \lambda r_1 \otimes r_1 + \lambda^{-1} r_2 \otimes r_2;
\]

here \( J = \det U = \lambda_1 \lambda_2, \lambda = \sqrt{\lambda_1/\lambda_2} \geq 1 \), and \( I \) is the two-dimensional identity tensor.

The spectral representation of \( E^{(0)} \equiv \ln U = \ln U^a + \ln \tilde{U} \) is then given by

\[
E^{(0)} = \frac{1}{2} \ln J + 2 \ln \lambda \left( r_1 \otimes r_1 - r_2 \otimes r_2 \right)
\]

\[
= \frac{1}{2} \epsilon_a I + E_0^{(0)},
\]

where

\[
\epsilon_a = \text{tr} E^{(0)} = \ln J = \ln(\det U)
\]

gives the areal logarithmic strain, and

\[
E_0^{(0)} = \ln \tilde{U} = \ln \lambda (r_1 \otimes r_1 - r_2 \otimes r_2)
\]

denotes the deviatoric part of \( E^{(0)} \).

3. Invariant-theoretic approach to constitutive modelling

In a hyperelastic modelling framework, the strain energy density \( \psi \) is formally expressed as a scalar-valued function of deformation gradient \( F \). Material frame indifference requires that this function should remain invariant under superimposed rigid body motion; i.e.

\[
\psi = \hat{\psi}(F) = \hat{\psi}(QF),
\]

where arbitrary \( Q \in \text{SO}_2 \) denotes a rigid-body rotation. Such objectivity is automatically satisfied if \( \psi \) is functionally dependent on one of the Seth–Hill strain measures — \( E^{(m)} \equiv (\text{tr}(F^T F)^m/2 - I)/m \), for real \( m \). In particular, for \( m = 0 \), the corresponding strain measure is the logarithmic strain \( E^{(0)} = \ln U \) [19,20].

The use of any particular strain measure is, in principle, arbitrary. However, different strain measures can lead to differing levels of complexity or simplification in accurately describing material response. For example, Anand [21] explored the extension of the classical quadratic strain energy function of isotropic linear elasticity based on two small-strain Lamé constants, replacing invariants of the infinitesimal strain tensor with corresponding invariants of various of the Seth–Hill strain measures. The formulation based on invariants of \( E^{(0)} \) (Hencky’s strain energy function) most accurately captured the initial constitutive nonlinearities at moderate deformations, with results clearly superior to those obtained by using invariants of the Green–Lagrange strain measure \( E^{(2)} \).
Here, for reasons further described in §4a, we adopt the logarithmic strain tensor $E^{(0)}$ to construct a hyperelastic constitutive response of graphene, i.e.

$$\psi = \hat{\psi}(F) = \tilde{\psi}(E^{(0)}).$$

(3.2)

The restrictions on $\psi$ due to material symmetry are expressed as

$$\tilde{\psi}(E^{(0)}) = \hat{\psi}(Q^T E^{(0)} Q) \forall Q \in \mathcal{G},$$

(3.3)

where $\mathcal{G}$ denotes the material symmetry group. A scalar function, such as $\psi$, that remains invariant under a material symmetry group $\mathcal{G}$, is called a $\mathcal{G}$-invariant scalar function. Obtaining a representation for a generic $\mathcal{G}$-invariant function involves using the isotropicization theorem and symmetry invariants.

The isotropicization theorem—based on the notion of a materially embedded structure tensor $\mathcal{H}$—allows the strain energy density of an anisotropic hyperelastic material to be expressed in terms of a list of special scalar functions—$J_1, J_2, \ldots, J_n$—which are joint isotropic functions of $E^{(0)}$ and $\mathcal{H}$ [15,16,22]; i.e.

$$\tilde{\psi}(E^{(0)}) = \hat{\psi}(J_1, J_2, \ldots, J_n),$$

(3.4)

where

$$J_i(E^{(0)}; \mathcal{H}) = J_i(Q^T E^{(0)} Q; \mathbb{P}_Q(\mathcal{H})) \forall Q \in \text{SO}_2.$$  

(3.5)

Here $\mathbb{P}_Q$ denotes the transformation of the structure tensor $\mathcal{H}$ under the orthogonal tensor $Q$. The functions $J_i$ are termed symmetry invariants since they satisfy all the symmetry constraints belonging to the material symmetry group of the crystal. Smith [10,11] showed that the finite set of mutually independent symmetry invariants serves as a complete and irreducible basis for the representation of scalar constitutive functions. In the following section, we explicitly derive a set of symmetry invariants of $E^{(0)}$ for the structure tensor characterizing the material symmetry group of graphene.

4. Hyperelastic constitutive response of graphene

Following the approach outlined in §3, we now systematically construct a hyperelastic strain energy function for arbitrary in-plane deformation of graphene. First, we explicitly obtain the structure tensor characterizing the material symmetry group of graphene. The structure tensor $\mathcal{H}$ corresponding to the $C_{2n_v}$ material symmetry group is obtained from a general expression given by [23,24]

$$\mathcal{H} = \text{Re}(M + iN)^{\otimes n},$$

(4.1)

where $\ldots^{\otimes n} = \ldots \otimes \ldots \otimes \ldots \otimes (n \text{ times})$, and $2n$ denotes the order of the principal rotation axis. $M$ and $N$ are dimensionless symmetric traceless tensors given by

$$M = \hat{x} \otimes \hat{x} - \hat{y} \otimes \hat{y} \quad \text{and} \quad N = \hat{x} \otimes \hat{y} + \hat{y} \otimes \hat{x},$$

(4.2)

where $\hat{x}$ and $\hat{y}$ denote orthogonal material unit vectors fixed in the frame of the reference crystal such that at least one of them is aligned with an axis of reflection symmetry (figure 1).

From equation (4.1), we obtain the sixth-order structure tensor characterizing $C_{6v}(n = 3)$, the material symmetry group of graphene, as

$$\mathcal{H} = M \otimes M \otimes M - (M \otimes N \otimes N + N \otimes M \otimes N + N \otimes N \otimes M).$$

(4.3)

The complete and irreducible set of polynomial joint invariants of $E^{(0)}$ and $\mathcal{H}$ constitute the symmetry invariants of $E^{(0)}$. Following the procedure of Zheng & Betten [24], we obtain three
independent scalar joint invariants of this two-dimensional system as

\[ J_1 \equiv \epsilon_a = \ln J \] (4.4)

and

\[ J_2 \equiv \left( \frac{\gamma_1}{2} \right)^2 = \frac{1}{2} E_0^0 : E_0^0 = (\ln \lambda)^2, \] (4.5)

where \( A : B = \text{tr}(A^T B) \) is the scalar tensor product, and

\[ J_3 \equiv \left( \frac{\gamma_3}{2} \right)^3 = \frac{1}{8} \left[ (M : E_0^0)^3 - 3(M : E_0^0)(N : E_0^0)^2 \right] \]

\[ = (\ln \lambda)^3 \cos 6\theta, \] (4.6)

where \( \cos \theta = \hat{r}_1 \cdot \hat{x} \) indicates the orientation of maximum principal stretch. The first two of these invariants, \( \epsilon_a \) and \( \gamma_1 \geq 0 \), are simply two isotropic invariants of \( E(0) \) alone. Thus, any material anisotropy in the constitutive response of graphene, evidenced only at large deformations, is captured solely by the third invariant \( \gamma_3 \).

In order to represent the second-order tensorial quantities, we need the following list of form-invariants:

\[ \frac{\partial \epsilon_a}{\partial E(0)} = I; \] (4.7)

\[ \frac{\partial (\gamma_1^2)}{\partial E(0)} = 4E_0^0 \] (4.8)

and

\[ \frac{\partial (\gamma_3^3)}{\partial E(0)} = 3 \left[ [(M : E_0^0)^2 - (N : E_0^0)^2]M - [2(M : E_0^0)(N : E_0^0)]N \right] = S_{E_0^0}. \] (4.9)

Figure 1. (a) Graphene lattice with orientations of the material unit vectors—\( \hat{x} \) and \( \hat{y} \)—and the Cartesian unit vectors—\( e_1 \) and \( e_2 \)—indicated. Dashed lines denote the 2-atom reference unit cell used in the \( ab \) \( initio \) calculations. The GGA (LDA) value of the lattice parameter is also indicated. Armchair and zigzag directions parallel the \( e_1 \) and \( e_2 \) axes, respectively. (b) Brillouin zone of graphene, with high symmetry points indicated. (Online version in colour.)
For purposes of constructing the fourth-order tangent modulus tensors, second derivatives of the invariants with respect to $E^{(0)}$ are obtained as follows:

\[
\frac{\partial^2 \epsilon_a}{\partial E^{(0)} \partial E^{(0)}} = 0 ,
\]

(4.10)

\[
\frac{\partial^2 (\gamma_i^2)}{\partial E^{(0)} \partial E^{(0)}} = 4 \left[ I - \frac{1}{2} I \otimes I \right]
\]

(4.11)

and

\[
\frac{\partial^2 (\gamma_i^3)}{\partial E^{(0)} \partial E^{(0)}} = 6 \left( (M : E_0^{(0)}) M \otimes M - (N : E_0^{(0)}) [M \otimes N + N \otimes M + N \otimes N] \right) \equiv S_{E_0^{(0)}}.
\]

(4.12)

Here $\mathbb{O}$ and $I$ are the fourth-order zero and identity tensors, respectively.

(a) Strain energy per unit reference area $\psi$

The proposed hyperelastic model is based on representation of the strain energy per unit reference area $\psi$ in terms of the symmetry invariants of $E^{(0)}$; i.e. $\psi = \psi(\epsilon_a, \gamma_i, \gamma_0)$. For application of invariant-based hyperelasticity, the strain measure $E^{(0)}$ offers substantial simplifications in terms of formulation. First, as is evident from its spectral representation (equation (2.6)), $E^{(0)}$ additively decomposes areal ($U^a$) and isochoric ($\tilde{U}$) parts of the deformation into isotropic and deviatoric parts of the strain, respectively. Secondly, the state nature of $\psi$ in a hyperelastic material enables calculating $\psi$ by integrating $d\psi = (\partial \psi / \partial E^{(0)}) : dE^{(0)}$ along any convenient strain path, where it is understood that $T^{(0)} \equiv \partial \psi / \partial E^{(0)}$ is the work-conjugate stress measure. Let a first, purely isotropic strain path (Path 1) correspond to areal deformation $U^a$ while holding $\tilde{U} = I$, and let a second, purely deviatoric strain path (Path 2) correspond to a subsequently imposed isochoric deformation $\tilde{U}$ while holding $U^a = I^1 / 2 I$. The isotropic/deviatoric decomposition of the work-conjugate stress is $T^{(0)} \equiv 1/2 S^{(0)} I + T_0^{(0)}$, while that of the incremental log strain is $dE^{(0)} = 1/2 de^a I + dE_0^{(0)}$; thus, the incremental energy/work relation is additively decomposed into isotropic and deviatoric parts

\[
d\psi = T^{(0)} : dE^{(0)} = 1/2 S^{(0)} de^a + T_0^{(0)} : dE_0^{(0)}.
\]

(4.13)

The strain energy of an arbitrary deformed state of the lattice—when expressed in terms of invariants of $E^{(0)}$—can be additively decomposed into a term $\psi^{\text{Dil}}(\epsilon_a)$—corresponding to a pure areal deformation $U^a$ while $E_0^{(0)} = 0$—plus a term $\psi^{\text{Dev}}(\gamma_i, \gamma_0; \epsilon_a)$—corresponding to a superimposed isochoric deformation $\tilde{U}$ while $\text{tr} E^{(0)}$ remains fixed at $\epsilon_a$. Thus, we write

\[
\psi = \psi(\epsilon_a, \gamma_i, \gamma_0) = \psi^{\text{Dil}}(\epsilon_a) + \psi^{\text{Dev}}(\gamma_i, \gamma_0; \epsilon_a).
\]

(4.14)

Setting $\psi = 0$ in the undeformed configuration, the areal contribution $\psi^{\text{Dil}}$ equals the isotropic stress working along isotropic strain Path 1, along which $dE_0^{(0)} = 0$; thus $\psi^{\text{Dil}} = \psi^{\text{Dil}}(\epsilon_a)$. The contribution $\psi^{\text{Dev}}$ is numerically equal to the stress working along the subsequent deviatoric strain Path 2, along which $de^a = 0$; thus $\psi^{\text{Dev}}$ depends on invariants $\gamma_i$ and $\gamma_0$ of the imposed deviatoric strain $E_0^{(0)}$, as well as having implicit dependence on the (constant) areal strain $\epsilon_a$ along Path 2, with ‘initial’ condition $\psi^{\text{Dev}}(0; 0; e^a) = 0$.

From elasticity theory, we recall that the flexural stiffness $D$ of a thin structural element scales with its thickness $h$ as $D \sim h^3$, whereas its stretching stiffness $C$ scales linearly as $C \sim h$. Notably, graphene is just one atomic layer thick, so in a superthin structure like graphene, the ratio $D/C$ is exceedingly small and, accordingly, we assume that the contribution of bending to the strain energy is negligible compared to that of in-plane strain. Furthermore, and for the same reason, a suspended graphene sheet under a compressive in-plane loading, i.e. a state of Cauchy stress $\sigma$ with $\mathbf{n} \cdot \mathbf{\sigma} \cdot \mathbf{n} < 0$ for some in-plane direction $\mathbf{n}$, is structurally unstable in the limiting case of vanishing flexural stiffness, and will immediately buckle out-of-plane. Therefore, the scope of the modelling effort is limited to only those in-plane deformation states for which $\mathbf{n} \cdot \mathbf{\sigma} \cdot \mathbf{n} \geq 0 \quad \forall \mathbf{n}$.
For reasons outlined above, the energies associated with various ‘Path 2’ deviatoric deformations are expected to depend on the value of \( \epsilon \). Table 1 lists values of the constants \( \mu \) whereas \( \eta \) is well-fit by an exponentially decreasing function of the areal strain, \( \epsilon_a \) (figure 2b),

\[
\mu(\epsilon_a) = \mu_0 - \mu_1 e^{\beta \epsilon_a},
\]

whereas \( \eta(\epsilon_a) \) is fit by an even quadratic function of \( \epsilon_a \) (figure 2c),

\[
\eta(\epsilon_a) = \eta_0 - \eta_1 \epsilon_a^2.
\]

Table 1. Values of \( \mathcal{E} \) and \( \alpha \) obtained by fitting the UBER form (equation (4.15)) to \( \textit{ab initio} \) energies. The UBER constitutive form exhibits a tangent area modulus \( \kappa \) —defined in equation (4.29)—that decreases with increasing areal strain, ultimately vanishing at a critical areal strain value given in equation (4.31) by \( \epsilon_a|_{\kappa=0} = 1/(1 + \alpha) \).

|         | \( \alpha \) | \( \mathcal{E} \) | \( \epsilon_a|_{\kappa=0} = 1/(1 + \alpha) \) |
|---------|-------------|-----------------|---------------------------------|
| GGA     | 1.53        | 93.84           | 0.40                            |
| LDA     | 1.38        | 116.43          | 0.42                            |

(i) Energetic response under pure dilation, \( \psi^{\text{Dil}} \)

The energetic response under ‘Path 1’ deformations characterized by \( U = U^a = J^{1/2} I \) is well described by a function based on the universal binding energy relation (UBER) proposed by Rose et al. [25,26]. The UBER relation is

\[
\psi^{\text{Dil}}(\epsilon_a) = \mathcal{E}[1 - (1 + \alpha \epsilon_a) \exp(-\alpha \epsilon_a)].
\]  

(ii) Energetic response under shape-changing deformations, \( \psi^{\text{Dev}} \)

For reasons outlined above, the energies associated with various ‘Path 2’ deviatoric deformations are expected to depend on the value of \( \epsilon^a \) at the end of ‘Path 1’; accordingly, we assume that \( \psi^{\text{Dev}} = \hat{\psi}^{\text{Dev}}(\gamma_y, \gamma_{y^3}; \epsilon_a) \).

A simple linear combination of monomials in \( J_2 = (\gamma_y/2)^2 \), and in \( J_3 = (\gamma_{y^3}/2)^3 \), with coefficients that are functions of \( \epsilon_a \), i.e.

\[
\hat{\psi}^{\text{Dev}}(\gamma_y, \gamma_{y^3}; \epsilon_a) = \frac{1}{2} \mu(\epsilon_a) \gamma_y^2 + \frac{1}{8} \eta(\epsilon_a) \gamma_{y^3}^3,
\]

fits the \( \textit{ab initio} \) calculations well using simple functional forms for \( \mu(\epsilon_a) \) and \( \eta(\epsilon_a) \). The shear modulus \( \mu \) is well-fit by an exponentially decreasing function of the areal strain, \( \epsilon_a \) (figure 2b),

\[
\mu(\epsilon_a) = \mu_0 - \mu_1 e^{\beta \epsilon_a},
\]

whereas \( \eta(\epsilon_a) \) is fit by an even quadratic function of \( \epsilon_a \) (figure 2c),

\[
\eta(\epsilon_a) = \eta_0 - \eta_1 \epsilon_a^2.
\]
Table 2. Coefficients \( \mu_0 \) and \( \mu_1 \) and exponent \( \beta \) in equation (4.16) for shear modulus \( \mu(e_a) \), and coefficients \( \eta_0 \) and \( \eta_1 \) in equation (4.17) for \( \eta(e_a) \), determined by least-square fits to a set of \textit{ab initio} energies. The data and the functional form suggest that \( \mu \) vanishes at a critical value of areal strain given by \( e_a|_{\mu=0} = (1/\beta) \ln(\mu_0/\mu_1) \), tabulated in the right-most column.

| \( \mu_0 \) (N m\(^{-1}\)) | \( \mu_1 \) (N m\(^{-1}\)) | \( \beta \) | \( \eta_0 \) (N m\(^{-1}\)) | \( \eta_1 \) (N m\(^{-1}\)) | \( e_a|_{\mu=0} = (1/\beta) \ln(\mu_0/\mu_1) \) |
|-----------------------------|-----------------------------|-----|-----------------------------|-----------------------------|--------------------------------------------------|
| GGA                        | 172.18                      | 27.03 | 5.16                        | 94.65                       | 4393.26                                           |
| LDA                        | 164.17                      | 17.31 | 6.22                        | 93.17                       | 4408.76                                           |

Thus, the overall expression proposed for the free energy \( \psi \) is

\[
\dot{\psi} = \mathcal{E} - \mathcal{E}(1 + \alpha e_a \exp(-\alpha e_a) + \frac{1}{2}(\mu_0 - \mu_1 e^{\beta e_a})\gamma^2_i + \frac{1}{8}(\eta_0 - \eta_1 e^{\beta e_a})\gamma^3_i. \tag{4.18}
\]

The constants in the expressions for \( \mu \) and \( \eta \) are determined by fitting the set of \textit{ab initio} energies calculated for a number of deformed states described in the electronic supplementary material; fitted values are summarized in table 2.

Using a total of only seven scalar fitting parameters, half the number used in the formulation of Wei et al., the proposed functional form fits the entire DFT dataset very well.

(b) Work-conjugate stress tensor \( T^{(0)} \)

Using the proposed functional forms for \( \psi \), the stress measure \( T^{(0)} \) work-conjugate to \( E^{(0)} \) is calculated as

\[
T^{(0)}(e_a, \gamma_i, \gamma_i) = \frac{\partial \psi}{\partial E^{(0)}} = \left[ \frac{\partial \psi^{\text{Dev}}(e_a, \gamma_i, \gamma_i)}{\partial e_a} + \frac{\partial \psi^{\text{Dev}}(e_a, \gamma_i, \gamma_i)}{\partial \gamma_i} \right] I + 4 \frac{\partial \psi^{\text{Dev}}(e_a, \gamma_i, \gamma_i)}{\partial \gamma^2_i} E^{(0)} + \frac{\partial \psi^{\text{Dev}}(e_a, \gamma_i, \gamma_i)}{\partial \gamma^3_i} S E^{(0)}, \tag{4.19}
\]

where the prime notation \((\ldots)'\) denotes differentiation with respect to \( e_a \). Following the hyperelastic work-conjugacy relation [27,28], the conversion from work-conjugate stress \( T^{(0)} \) to Cauchy stress \( \sigma \) is obtained as follows. Letting a superposed dot denote the material time derivative, the power balance of isothermal hyperelasticity identifies measures of stress that are power-conjugate to differing measures of strain-rate by

\[
\dot{\psi} = T^{(2)} : E^{(2)} = T^{(0)} : E^{(0)}, \tag{4.20}
\]

etc. where, for example, \( E^{(2)} = \frac{1}{2}(C - I) = \frac{1}{2}(F^TF - I) \) is the Green–Lagrange strain tensor, and \( T^{(2)} \) is its power-conjugate stress tensor, often denoted as the second Piola–Kirchhoff stress tensor. Using the chain rule, and viewing \( E^{(0)} \) as a function of \( E^{(2)} \), we obtain

\[
\dot{E}^{(0)} = \begin{bmatrix} \frac{\partial E^{(0)}}{\partial E^{(2)}} \end{bmatrix} E^{(2)} = 2 \begin{bmatrix} \frac{\partial E^{(0)}}{\partial C} \end{bmatrix} \dot{E}^{(2)}. \tag{4.21}
\]

where the fourth-order tensor \( L^{(1)} = \partial E^{(0)}/\partial C \) has major symmetry, i.e. \( L^{(1)T} = L^{(1)} \), and it is understood that \( L^{(1)} \) operates on the second-order tensor appearing on its immediate right to produce a resultant second-order tensor. Substituting equation (4.21) into equation (4.20) gives

\[
T^{(2)} : \dot{E}^{(2)} = T^{(0)} : \left[ 2L^{(1)} E^{(2)} \right] = \left[ 2L^{(1)T} T^{(0)} \right] : \dot{E}^{(2)} = \left[ 2L^{(1)} T^{(0)} \right] : E^{(2)}. \tag{4.22}
\]

In order for equation (4.22) to hold for arbitrary \( E^{(2)} \), we obtain the transformation relation

\[
T^{(2)} = 2L^{(1)} T^{(0)}. \tag{4.23}
\]
The Cauchy stress $\sigma$ can be similarly obtained from power balance relations [28] as

$$\sigma = \frac{1}{J} F T^{(2)} F^T = \frac{1}{J} F \left[ 2 \mathcal{L}^{(1)} T^{(0)} \right] F^T. \quad (4.24)$$

Evaluation of $\mathcal{L}^{(1)}$ in a general state of deformation is carried out in the electronic supplementary material, §2.

As a particular illustration, we can use equation (4.19) to evaluate $T^{(0)}$ for equi-biaxial stretch. In the absence of shape change, $E^{(0)}_0 = 0$ and hence $\gamma_i = \gamma_0 = 0$, so that

$$T^{(0)}(\epsilon_a) = \frac{\partial \hat{\psi} \text{Dil}}{\partial \epsilon_a} = E \alpha^2 \epsilon_a \exp(-\alpha \epsilon_a) I. \quad (4.25)$$

Further, in this special deformation case, $\mathcal{L}^{(1)}$ has the simple form:

$$\mathcal{L}^{(1)} = \frac{\partial E^{(0)}}{\partial C} = \frac{1}{2J} \|, \quad (4.26)$$

so that $\sigma$ under equi-biaxial stretch becomes

$$\sigma|_{\text{F} = \frac{1}{\sqrt{2}}} I = 2 \frac{1}{2J} I \left\{ \| T^{(0)}|_{\text{F} = \frac{1}{\sqrt{2}}} I \right\} I = \frac{1}{J} T^{(0)}|_{\text{F} = \frac{1}{\sqrt{2}}} I, \quad (4.27)$$

thus, the equi-biaxial Cauchy stress is

$$\sigma|_{\text{F} = \frac{1}{\sqrt{2}}} I = \frac{1}{J} \frac{\partial \hat{\psi} \text{Dil}}{\partial \epsilon_a} I = E \alpha^2 \epsilon_a \exp(-(1+\alpha)\epsilon_a) I \equiv p I. \quad (4.28)$$

where $p \equiv \frac{1}{2} \text{tr} \sigma$, and a corresponding tangent areal modulus $\kappa$ is

$$\kappa(\epsilon_a) \equiv \frac{dp(\epsilon_a)}{d\epsilon_a} = E \alpha^2 (1 - (1 + \alpha)\epsilon_a) \exp(-(1+\alpha)\epsilon_a). \quad (4.29)$$

Under equi-biaxial stretch, the equi-biaxial Cauchy stress reaches its maximum when

$$\kappa = 0 \Rightarrow 1 - (1 + \alpha)\epsilon_a = 0. \quad (4.30)$$

Thus, the peak equi-biaxial Cauchy stress occurs at a critical areal strain given by

$$\epsilon_a|_{\kappa = 0} = \frac{1}{1 + \alpha}. \quad (4.31)$$

(c) Work-conjugate tangent moduli tensor $\mathbb{L}^{(0)}$

The fourth-order tensor of tangent moduli connecting $\dot{T}^{(0)}$ to $\dot{E}^{(0)}$ is defined as

$$\mathbb{L}^{(0)} = \frac{\partial T^{(0)}}{\partial E^{(0)}} = \frac{\partial^2 \psi}{\partial E^{(0)} \partial E^{(0)}}. \quad (4.32)$$

On using equation (4.19) with previous results, $\mathbb{L}^{(0)}$ can be straightforwardly expressed as

$$\mathbb{L}^{(0)} = \left\{ E \alpha^2 (1 - \alpha \epsilon_a) \exp(-\alpha \epsilon_a) + \frac{\mu''(\epsilon_a)}{2} \gamma_i^2 + \frac{\eta''(\epsilon_a)}{8} \gamma_0^2 \right\} I \otimes I$$
$$+ 2\mu'(\epsilon_a) \left\{ I \otimes E^{(0)}_0 + E^{(0)}_0 \otimes I \right\} + \frac{1}{8} \eta'(\epsilon_a) \left\{ I \otimes S^{(0)}_{E_0} + S^{(0)}_{E_0} \otimes I \right\}$$
$$+ 2\mu(\epsilon_a) \left\{ I - \frac{1}{2} I \otimes I \right\} + \frac{1}{8} \eta(\epsilon_a) S^{(0)}_{E_0}. \quad (4.33)$$
(d) Acoustic tensor $\tilde{A}$

The acoustic tensor is defined as the second derivative of the $\psi$ with respect to the deformation gradient tensor $F$ [7,28,29]:

$$\tilde{A} = \frac{\partial^2 \psi}{\partial F \partial F}.$$  

(4.34)

The first derivative of $\psi$ with respect to $F$ gives the generally non-symmetric first Piola–Kirchhoff stress tensor, $T^{PK1}$, which can be evaluated using the chain rule as:

$$\left[ \frac{\partial \psi(E^{(0)})}{\partial F} \right]_{ij} = \left[ T^{PK1} \right]_{ij} = \left[ \frac{\partial \psi(E^{(0)})}{\partial E} \right]_{mn} \left[ \frac{\partial E^{(0)}}{\partial C_{pq}} \right] \left[ \frac{\partial C_{pq}}{\partial F_{ij}} \right].$$  

(4.35)

Then the second derivative, which is the acoustic tensor, is obtained as

$$\tilde{A}_{ijkl} = \left[ \frac{\partial^2 \psi(E^{(0)})}{\partial F^2} \right]_{ijkl} = \left[ L^{(0)} \right]_{mnpqrs} \left[ \frac{\partial E^{(0)}}{\partial C} \right]_{mn} \left[ \frac{\partial C}{\partial F} \right]_{pqij} \left[ \frac{\partial E^{(0)}}{\partial C} \right]_{rsab} \left[ \frac{\partial C}{\partial F} \right]_{abkl} + \left[ T^{(0)} \right]_{mn} \left[ \frac{\partial^2 C}{\partial C \partial C} \right]_{mn} \left[ \frac{\partial C}{\partial F} \right]_{pqij} \left[ \frac{\partial C}{\partial F} \right]_{rs}.$$  

(4.36)

where the evaluation of the various tensor derivatives has been explicitly demonstrated in the electronic supplementary material, §2.

In the present applications, the acoustic tensor $\tilde{A}$ is a fourth-order tensor in two dimensions. Representation of $\tilde{A}$ with respect to the orthonormal basis $\{e_i \otimes e_j \otimes e_k \otimes e_l \}_{1 \leq i,j,k,l \leq 2}$ is given by

$$\tilde{A} = \tilde{A}_{ijkl} e_i \otimes e_j \otimes e_k \otimes e_l,$$  

(4.37)

with Cartesian components $\tilde{A}_{ijkl} = (e_i \otimes e_j) \cdot \tilde{A} \cdot (e_k \otimes e_l)$, with $1 \leq i,j,k,l \leq 2$. By definition, $\tilde{A}$ has the major symmetry $\tilde{A}_{ijkl} = \tilde{A}_{klji}$. We can define another orthonormal basis set [30] as $\{ \tilde{e}_a \otimes \tilde{e}_\beta \}_{1 \leq a, \beta \leq 4}$ where $\tilde{e}_{(a, \beta)} = e_i \otimes e_j$ with $f(1, 1) = 1, f(2, 2) = 2, f(1, 2) = 3,$ and $f(2, 1) = 4$. In this alternate basis, $\tilde{A}$ can be represented by a four-dimensional second-order tensor $\tilde{A}$ given by

$$\tilde{A} = A_{a\beta} \tilde{e}_a \otimes \tilde{e}_\beta.$$  

(4.38)

We can thus express components of $\tilde{A}$ in terms of a $4 \times 4$ matrix.

5. Validation of the constitutive model

As detailed below, we validate our continuum model for a number of homogeneous deformations by comparison with small-strain elastic constants inferred from experiments, comparison of stress–strain curves with independent $ab$ initio calculations, and comparisons of predictions of elastic stability limits to independent phonon calculations.

(a) Comparison of small-strain elastic constants and wave-velocities with measured values

The in-plane elastic constants—recovered from the constitutive model in the limit of infinitesimal strain—are compared with the measured values of Lee et al. [1]. The predicted values for the in-plane Young’s modulus $Y^{(0)}$, shear modulus $\mu^{(0)}$, bulk modulus $k^{(0)}$ and Poisson’s ratio $\nu^{(0)}$ are all in good accord with the experimentally reported values (table 3). The acoustic wave-velocities $c_{LA}$ and $c_{TA}$ obtained from the continuum model also compare very well with measured values, as well as with values obtained from phonon dispersion, as shown in table 4.
Table 3. In-plane elastic constants recovered from our constitutive model in the limit of infinitesimal strain, compared with values reported by Lee et al. [1], based on their experimental results.

<table>
<thead>
<tr>
<th></th>
<th>(Y^{(0)}) (N m(^{-1}))</th>
<th>(\nu^{(0)})</th>
<th>(\kappa^{(0)}) (N m(^{-1}))</th>
<th>(\mu^{(0)}) (N m(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>exp.</td>
<td>342 ± 30</td>
<td>0.165</td>
<td>205 ± 18</td>
<td>147 ± 12</td>
</tr>
<tr>
<td>DFT (GGA)</td>
<td>349</td>
<td>0.203</td>
<td>219</td>
<td>145</td>
</tr>
<tr>
<td>DFT (LDA)</td>
<td>354</td>
<td>0.203</td>
<td>222</td>
<td>147</td>
</tr>
</tbody>
</table>

Table 4. In-plane longitudinal and transverse wave velocities calculated from the LDA-fitted continuum model closely agree with measured values and the values calculated from DFPT phonon dispersion. \(\rho\)\(_{2D}\) is the mass per reference area of graphene, calculated from the atomic mass of carbon and the lattice constant of the reference unit cell.

\[
\begin{align*}
\rho_{2D} & = \frac{\sqrt{Y^{(0)}/(1 - \nu^{(0)2})}}{\mu^{(0)}} \\
\frac{d\omega_{LA}}{dq} |_{q=0} & = 21.15 \\
\frac{d\omega_{TA}}{dq} |_{q=0} & = 21.82
\end{align*}
\]

(b) Comparison with directly calculated \textit{ab initio} stress response curves

The constants of the continuum model are determined by a least-squares fit to the strain energies alone (stress values were not used in the fitting), so the agreement of predicted stress values with those determined directly from \textit{ab initio} calculations remains to be examined. Next we compare the continuum model’s predictions of stress response with corresponding \textit{ab initio}-calculated values in a few important modes of large homogeneous deformation, including equi-biaxial tension, and uniaxial stretching and stressing in the armchair and the zigzag directions. In obtaining the stress response, the elastic and soft-mode instabilities—discussed in previous sections—have been suppressed in both \textit{ab initio} and continuum calculations.

(i) Pure biaxial stretch

Cauchy stress as a function of strain for pure equi-biaxial deformation as obtained from the continuum model (equation (4.28)) is shown in figure 3a. The Cauchy biaxial stress as a function of areal strain \(\epsilon_a\), as predicted by the UBER-based model, compares well with the \textit{ab initio} values. Our model predicts that the Cauchy stress reaches its maximum value at nearly 42% areal strain. In figure 3b, we show the softening of the dilatant tangent modulus, defined in equation (4.29), with areal strain \(\epsilon_a\). The areal tangent modulus vanishes when the Cauchy stress approaches its maximum value.

(ii) Uniaxial stretching along the armchair and the zigzag directions

Cauchy stress components as a function of stretch, obtained from the continuum model for the case of uniaxial stretching along the armchair and the zigzag directions, are shown in figure 4a, b, respectively. Orientation-dependent differences in response at large deformation evidence a limited anisotropy that is fully captured by the strain energy contribution \(\eta(e_a)J_5\).
Figure 3. (a) Variation of Cauchy mean normal stress with areal strain as predicted by the UBER-based continuum model, along with corresponding ab initio values. (b) Variation of the dilatational tangent modulus $\kappa$ with areal strain $\epsilon_a = \ln J$, as predicted by the UBER-based continuum model. (Online version in colour.)

Figure 4. (a) Stress–stretch curves obtained from the continuum model for uniaxial strain along armchair direction. Also shown are the ab initio stress values. (b) The continuum stress–stretch curves and the ab initio stress values for uniaxial strain in zigzag direction. The arrows show locations of maximum stress. Solid lines are LDA results; dashed lines are GGA counterparts. (Online version in colour.)

(iii) Uniaxial tension along the armchair and the zigzag directions

Cauchy stress components as functions of stretch obtained from the continuum model for the case of uniaxial tensile stress along the armchair and the zigzag directions are shown in figure 5a, b, respectively. The ratios of transverse strain (due to Poisson contraction) to longitudinal strain obtained from the continuum model for uniaxial stress along the armchair and zigzag directions are also in good agreement with the ab initio values (see the electronic supplementary material, Fig. [S2]).

6. Predictive capability: elastic stability limits for some biaxial deformation modes

Material elastic stability requires that the speed of propagation of all acceleration waves in a solid should be non-negative [32]. This condition is satisfied when the acoustic tensor is positive-definite, which is equivalent to the condition that the continuum elasto-dynamic equations are hyperbolic.

The acoustic tensor-based prediction of elastic instability involves detecting a deformed state at which $\cal A$ loses positive-definiteness [29,33] (or, equivalently, when the slope of an acoustic...
phonon branch in the long-wavelength limit vanishes, i.e. \( \frac{d\omega}{dk} \big|_{k \to 0} = 0 \). In addition to elastic instabilities, there may also be instabilities causing abrupt rearrangement of the atoms within the basis set of the unit cell. Such instabilities—which cannot be detected by acoustic tensor analysis—are accompanied by abrupt changes in energy/stress of the deformed state; e.g. as shown in the excluded regions in the electronic supplementary material, Fig. [S1].

Employing the continuum expression for \( A \) (equation (4.36)), we can monitor its positive-definiteness at all points along a deformation path, and thus can precisely locate the initial loss of elastic stability in that mode of deformation. In the following subsections, we predict elastic stability limits for some certain homogeneous deformation modes, and compare these with predictions obtained from independent \textit{ab initio} linear response phonon calculations.

**a) Pure biaxial stretch**

For this deformation state, Cartesian components of \( A \) obtained from the present constitutive model are

\[
A_{ijkl} = \varepsilon \alpha^2 e^{-\varepsilon_a(1+\alpha)}((1 - \varepsilon_a \alpha)\delta_{ij}\delta_{kl} - \varepsilon_a \delta_{jk}\delta_{il}) + \mu (\varepsilon_a) e^{-\varepsilon_a(\delta_{ik}\delta_{jl} - \delta_{kl}\delta_{ij} + \delta_{il}\delta_{jk})}. \tag{6.1}
\]

The condition of strong ellipticity requires

\[
(m \otimes n):A:(m \otimes n) = A_{ijkl}m_i m_j n_k n_l > 0, \tag{6.2}
\]

for arbitrary unit vectors \( m \) and \( n \). If, for any two unit vectors, equation (6.2) does not hold, then the deformed crystal is said to have lost strong ellipticity. Substituting for \( A \) from equation (6.1), the strong ellipticity condition becomes

\[
(m \otimes n):A:(m \otimes n) = e^{-\varepsilon_a(1+\alpha)} \varepsilon \alpha^2 (1 - \varepsilon_a (1 + \alpha)) m_i m_j n_i n_j + e^{-\varepsilon_a} \mu (\varepsilon_a) m_i m_j n_i n_j > 0. \tag{6.3}
\]

Let the unit vectors \( m \) and \( n \) be represented by

\[
m = (\cos \phi, \sin \phi) \quad \text{and} \quad n = (\cos \varphi, \sin \varphi); \tag{6.4}
\]

using this parametrization in equation (6.3) provides

\[
(m \otimes n):A:(m \otimes n) = e^{-\varepsilon_a(1+\alpha)} \varepsilon \alpha^2 (1 - \varepsilon_a (1 + \alpha)) \cos^2 (\phi - \varphi) + e^{-\varepsilon_a} \mu (\varepsilon_a) > 0. \tag{6.5}
\]
Based on values of the fitted constants, \( A \) can be represented by a block-diagonal 4 \times 4 matrix of the form:

\[
A = \begin{bmatrix}
A_{1111} & A_{1122} & 0 & 0 \\
A_{1122} & A_{2222} & 0 & 0 \\
0 & 0 & A_{1212} & A_{1221} \\
0 & 0 & A_{1221} & A_{2121}
\end{bmatrix}.
\]

Figure 6. (a) The instability due to loss of positive-definiteness of \( A \) in equi-biaxial stretch \( (F = f/4) \) corresponds to the vanishing of \( \mu(\epsilon_a) \) that occurs at the critical equi-biaxial areal strain of \( \epsilon_a = 0.355 \) (GGA) and 0.36 (LDA). (b) LDA phonon dispersion along the \( \Gamma - M \) direction shows a long-wavelength transverse acoustic phonon at \( \Gamma \) going unstable near \( \epsilon_a = 0.347 \); softening of this branch is associated with the vanishing shear modulus \( \mu(\epsilon_a) \). (c) Phonon dispersions along the \( \Gamma - K \) direction show a soft-phonon mode appearing just before \( \epsilon_a = 0.297 \), well before the acoustic instability. The \( k \)-vector is expressed in terms of \( 2\pi/a \), where \( a = f/2a_0 \) is the dilated lattice constant, \( a_0 \) being the undeformed lattice constant. (Online version in colour.)

When \( \epsilon_a < 1/(1 + \alpha) = \epsilon_{a|\epsilon_a=0} \), the minimum value of the term containing the factor \( \cos^2(\phi - \varphi) \) is zero, occurring when \( \mathbf{m} \cdot \mathbf{n} = 0 \); therefore, in this range of deformation

\[
[(\mathbf{m} \otimes \mathbf{n}) : \mathbf{A} : (\mathbf{m} \otimes \mathbf{n})]_{\min} = e^{-\epsilon_a} \mu(\epsilon_a).
\]

Thus, the loss of strong ellipticity under equi-biaxial stretch first occurs when (also see table 2)

\[
\mu(\epsilon_a) = \mu_0 - \mu_1 e^{\beta\epsilon_a} = 0.
\]

This condition occurs at a critical value of \( \epsilon_a \) given by

\[
\epsilon_{a|\mu=0} = \frac{1}{\beta} \ln \left( \frac{\mu_0}{\mu_1} \right).
\]

Based on values of the fitted constants, \( \epsilon_{a|\mu=0} < \epsilon_{a|\epsilon_a=0} \), as assumed. Since the associated directions \( \mathbf{m} \) and \( \mathbf{n} \) are perpendicular, the predicted dynamic instability is of transverse acoustic nature. The model’s capture of this instability is confirmed in independent linear-response-based phonon calculations for equi-biaxially strained graphene. The LDA phonon dispersion shows a vanishing long-wavelength transverse acoustic wave speed emerges at \( \epsilon_a = \ln f = 0.354 \), associated with the vanishing of \( \mu \) (figure 6). Based on our constitutive modelling and on independent phonon calculations, the loss of elastic stability under equi-biaxial loading occurs prior to the stress peak associated with the zero tangent modulus condition.

(b) Uniaxial strain in armchair and zigzag directions

Uniaxial stretching along both armchair and zigzag directions preserves reflection symmetries w.r.t the \( \hat{x} \) - and \( \hat{y} \)-axes. Therefore, for such deformations, the \( A_{1112}, A_{1121}, A_{1211}, A_{2111}, A_{2212}, A_{2221}, A_{1222} \) and \( A_{2122} \) components of the acoustic tensor are all zero. The resultant acoustic tensor can be represented by a block-diagonal 4 \times 4 matrix of the form:

\[
A = \begin{bmatrix}
A_{1111} & A_{1122} & 0 & 0 \\
A_{1122} & A_{2222} & 0 & 0 \\
0 & 0 & A_{1212} & A_{1221} \\
0 & 0 & A_{1221} & A_{2121}
\end{bmatrix}.
\]
acoustic instability in this direction, at \( \lambda \)-phonon dispersion calculations shown in figure 7.

At the first loss of strong ellipticity, \( \Lambda_e \) loses positive-definiteness at \( \lambda \approx 1.18 \) for GGA, and \( \approx 1.19 \) for LDA, indicating an acoustic instability in the material. The associated eigenvector of the unstable mode occurs in the \( e_1 \)-direction with polarization along the \( e_i \)-direction, implying a longitudinal instability mode. Solid/dashed lines are from constitutive fits to GGA/LDA results. (b) LDA phonon dispersion curves along the \( \Gamma - M \) direction for increasing stretch. A long-wavelength longitudinal instability emerges at \( \lambda_e \approx 1.188 \). The \( \mathbf{k} \)-vector is expressed in units of \( 2\pi/a \), where \( a = \lambda_a a_0 \). (Online version in colour.)

The eigenvalues of this matrix are

\[
\Lambda_1 = \frac{1}{2} [A_{1111} + A_{2222} + \left( (A_{1111} - A_{2222})^2 + 4A_{1212}^2 \right)^{1/2}],
\]

\[
\Lambda_2 = \frac{1}{2} [A_{1111} + A_{2222} - \left( (A_{1111} - A_{2222})^2 + 4A_{1212}^2 \right)^{1/2}],
\]

\[
\Lambda_3 = \frac{1}{2} [A_{1212} + A_{2121} - \left( (A_{1212} - A_{2121})^2 + 4A_{2222}^2 \right)^{1/2}],
\]

and

\[
\Lambda_4 = \frac{1}{2} [A_{1212} + A_{2121} + \left( (A_{1212} - A_{2121})^2 + 4A_{2222}^2 \right)^{1/2}].
\]

At the first loss of strong ellipticity, \( \Lambda_1 \to 0 \) for one or more eigenvalues of \( \Lambda \) at a certain critical value of stretch. In order to determine the critical stretch \( \lambda_c \) at which \( \Lambda \) loses positive-definiteness, we track the variation of the eigenvalues \( \Lambda_1, \Lambda_2, \Lambda_3 \) and \( \Lambda_4 \) with increasing uniaxial stretch.

First we consider uniaxial stretching along the zigzag direction, oriented along the Cartesian \( e_1 \)-axis, with \( \mathbf{U} = \lambda_s \mathbf{e}_1 \otimes \mathbf{e}_1 + \lambda e_2 \otimes \mathbf{e}_2 \). For this case, the loss of strong ellipticity occurs at a critical stretch, \( \lambda_{c} \approx 1.18 \) for GGA, and \( \approx 1.19 \) for LDA, when the \( \Lambda_2 \)-eigenvalue of \( \Lambda \) vanishes, as shown in figure 7a. The associated eigenvector corresponds to \( \mathbf{m} = \mathbf{n} = \mathbf{e}_1 \) (see equation (6.2)), so the unstable longitudinal mode coincides with the maximum principal eigenvector of \( \mathbf{U} \). Independent phonon dispersion calculations shown in figure 7b, confirm the occurrence of a longitudinal acoustic instability in this direction, at \( \lambda_{c} \approx 1.188 \). Now consider uniaxial stretching along the armchair direction, which is taken to parallel Cartesian axis \( e_2 \), with \( \mathbf{U} = \mathbf{e}_1 \otimes \mathbf{e}_1 + \lambda_a \mathbf{e}_2 \otimes \mathbf{e}_2 \). In this case, \( \Lambda \) loses positive-definiteness at \( \lambda_{c} \approx 1.23 \) (GGA) and \( \approx 1.24 \) (LDA), when \( \Lambda_2 \to 0 \), as shown in the electronic supplementary material, Fig. (S3-a). The associated eigenvector in this case corresponds to \( \mathbf{m} = \mathbf{n} = \mathbf{e}_2 \), again being a longitudinal elastic instability in the direction of maximum principal stretch. This is confirmed by independent LDA phonon calculations shown in the electronic supplementary material, Fig. (S3-b), which exhibits a vanishing slope of the LA branch at \( \Gamma \) when \( \lambda_{c} \approx 1.252 \).
by Uniaxial tensile stress along the zigzag direction corresponds to the right stretch tensor given shown in equation (6.9), and the corresponding eigenvalues are given by equations (6.10)–(6.13). In cases of uniaxial stress along the armchair and zigzag directions, A (c) Uniaxial stress in armchair and zigzag directions

\[ \lambda \text{ a vector is expressed in units of } 2\pi / a, \text{ where } a = \lambda_s a_0. \] (Online version in colour.)

Table 5. Summary of instability analyses based on acoustic tensor analysis of the constitutive models and corresponding phonon calculations for the various homogeneous deformation modes considered.

<table>
<thead>
<tr>
<th>deformation mode</th>
<th>acoustic tensor analysis</th>
<th>phonon analysis (LDA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>equi-biaxial stretch</td>
<td>elastic shear instability at ( f/2 = 1.19 )</td>
<td>short-wavelength transverse instability at ( f/2 = 1.145 ) and transverse acoustic instability at ( f/2 = 1.18 )</td>
</tr>
<tr>
<td>uniaxial stretch (zigzag)</td>
<td>elastic longitudinal instability at ( \lambda_s = 1.188 ) (GGA) ( \lambda_s = 1.194 ) (LDA)</td>
<td>longitudinal acoustic instability at ( \lambda_s = 1.188 )</td>
</tr>
<tr>
<td>uniaxial stretch (armchair)</td>
<td>elastic longitudinal instability at ( \lambda_s = 1.23 ) (GGA) ( \lambda_s = 1.24 ) (LDA)</td>
<td>longitudinal acoustic instability at ( \lambda_s = 1.25 )</td>
</tr>
<tr>
<td>uniaxial stress (zigzag)</td>
<td>elastic longitudinal instability at ( \lambda_s = 1.186 ) (GGA) ( \lambda_s = 1.192 ) (LDA)</td>
<td>longitudinal acoustic instability at ( \lambda_s = 1.20 )</td>
</tr>
<tr>
<td>uniaxial stress (armchair)</td>
<td>elastic longitudinal instability at ( \lambda_s = 1.238 ) (GGA) ( \lambda_s = 1.25 ) (LDA)</td>
<td>longitudinal acoustic instability at ( \lambda_s = 1.25 )</td>
</tr>
</tbody>
</table>

(c) Uniaxial stress in armchair and zigzag directions

In cases of uniaxial stress along the armchair and zigzag directions, \( A \) again has the form as shown in equation (6.9), and the corresponding eigenvalues are given by equations (6.10)–(6.13). Uniaxial tensile stress along the zigzag direction corresponds to the right stretch tensor given by \( \mathbf{U} = \lambda_s \mathbf{e}_1 \otimes \mathbf{e}_1 + f(\lambda_s) \mathbf{e}_2 \otimes \mathbf{e}_2 \), where the transverse stretch \( f(\lambda_s) \leq 1 \), and its value, for a given \( \lambda_s \), is determined by setting \( \sigma_{22} = \mathbf{e}_2. \sigma. \mathbf{e}_2 = 0 \). For uniaxial stress along the zigzag direction, the

\[ \lambda = 1.20 \text{, indicating an acoustic instability.} \]
loss of strong ellipticity occurs at \( \lambda_s^{(c)} = 1.19 \), when \( \Lambda_2 \to 0 \) (figure 8). The associated eigenvector again corresponds to \( \mathbf{m} = \mathbf{n} = \mathbf{e}_1 \), an unstable longitudinal mode parallels to the principal stretch direction. Independent phonon calculations confirm the occurrence of an acoustic instability in the longitudinal branch of the phonon dispersion at \( \lambda_s^{(c)} \approx 1.20 \), as was also indicated by phonon calculations of Liu et al. [14].

For uniaxial tensile stress along the armchair direction, \( \mathbf{U} = g(\lambda_a) \mathbf{e}_1 \otimes \mathbf{e}_1 + \lambda_s \mathbf{e}_2 \otimes \mathbf{e}_2 \), where the transverse stretch \( g(\lambda_a) \leq 1 \), its value, for a given \( \lambda_a \), being determined by setting \( \sigma_{11} = 0 \). In this case, acoustic tensor analysis gives an elastic instability at \( \lambda_a^{(c)} = 1.24 \), as shown in the electronic supplementary material, Fig. (S4-a). This instability is also longitudinal, in the \( \mathbf{e}_2 \)-direction, and is also in good agreement with phonon calculations shown in the electronic supplementary material, Fig. (S4-b). The predicted elastic stability limits for various deformation modes considered in this work are summarized in table 5. Respective stretch limits for elastic stability under both uniaxial stress and stretch, and in both zigzag and armchair directions, are quite close; this is presumably related to graphene’s relatively small Poisson ratio, and the diminishing ratio of transverse to axial strain magnitude as the lattice is deformed under uniaxial stress (see the electronic supplementary material, Fig. (S2)).

### 7. Discussion and conclusion

Using as a basis scalar-valued symmetry invariants of the logarithmic strain tensor, we derived a nonlinear hyperelastic constitutive response for graphene. Because the model employs symmetry invariants, the material symmetry group of the underlying lattice is built-into the model, and the need for externally imposing the symmetry restrictions is eliminated. The derivation is coordinate-free, facilitating computational implementation. Derivation of higher order tensor variables such as work-conjugate tangent moduli tensors and the acoustic tensor is likewise coordinate-free. The model elucidates the respective contributions to the strain energy density due to purely equi-biaxial area change, and due to purely isochoric shape-changing deformations. The model correctly follows the stress–strain response of graphene in both uniaxial stretching and tension, along both the zigzag and armchair directions, and in equi-biaxial tension. Values of the isotropic small-strain elastic constants deduced from the model are also in good agreement with experimentally reported values. Acoustic-tensor-based stability analysis of the constitutive model provides predictions of the deformation at the limits of strong ellipticity, and the corresponding critical modes, that are in good agreement with the results of independent lattice dynamics calculations based on linear response perturbation theory.

Our model predicts that the initial loss of elastic stability in graphene under pure biaxial stretch occurs at a logarithmic areal strain of \( \epsilon_a = 0.35 \), owing to a vanishing in-plane tangent shear modulus, rather than being due to the vanishing tangent area modulus at \( \epsilon_a = 0.40 - 0.42 \). This latter instability mode was previously reported by Wei et al. [8], but it could occur only at a larger deformation than that of the presently identified elastic shearing instability. Moreover, as noted previously by Yevick & Marianetti [34], phonon calculations for equi-biaxial deformation of graphene also show that, prior to the onset of the long-wavelength shear instability, a short-wavelength instability (or ‘soft mode’) at \( K \) emerges at \( \epsilon_a = 0.28 - 0.30 \), as seen also in figure 6c.

The experimental results of Lee et al. [1] have been interpreted, based in part on continuum finite-element modelling [4], as suggesting that local equi-biaxial Cauchy stress levels in the suspended graphene beneath the tip of a frictionless diamond nanoindenter reach the ideal peak value occurring at \( \epsilon_a = 0.42 \); if this is indeed the case, the earlier occurring soft mode lattice instability identified by Yevick and Marianetti must have been somehow suppressed, perhaps because of the proximity of the diamond nanoindenter. Here we have identified another elastic (shearing) instability in equi-biaxially strained graphene that also occurs at a deformation less than that of the ideal equi-biaxial strength. It is our opinion that a critical assessment of the constitutive assumptions governing graphene/nanoindenter interaction under the extreme...
loading conditions near final failure is required to properly reconcile the inferred failure strains in these nanoindentation experiments with model calculations based on lattice stability; results on this topic will be reported elsewhere [35].

References

Correction to ‘On the hyperelastic softening and elastic instabilities in graphene’

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There is a typographical error in equation (4.12) of the article. This equation is currently published as

$$\frac{\partial^2 (\gamma_3^3)}{\partial E^{(0)} \partial E^{(0)}} = 6 \left( (M : E^{(0)}_0) M \otimes M - (N : E^{(0)}_0) \right) \times \left[ M \otimes N + N \otimes M + N \otimes N \right] \equiv S_{E^{(0)}_0}. \quad (4.12)$$

The correct equation should read as follows:

$$\frac{\partial^2 (\gamma_3^3)}{\partial E^{(0)} \partial E^{(0)}} = 6 \left( (M : E^{(0)}_0) M \otimes M - (N : E^{(0)}_0) \right) \times \left[ M \otimes N + N \otimes M \right]$$

$$- (M : E^{(0)}_0) N \otimes N \equiv S_{E^{(0)}_0}. \quad (4.12)$$

Further, the LDA-fitted values of the coefficients $\eta_0$ and $\eta_1$, as given in table 2, are incorrect. These values are currently published as $\eta_0 = 93.17 \text{ N m}^{-1}$ and $\eta_1 = 4408.76 \text{ N m}^{-1}$. The correct values of these coefficients are $\eta_0 = 86.99 \text{ N m}^{-1}$ and $\eta_1 = 3611.35 \text{ N m}^{-1}$. 