

Invariant-based hyperelastic constitutive model for hexagonal two-dimensional materials

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A general hyperelastic constitutive model for hexagonal two-dimensional (2D) materials is presented, wherein the strain energy density is expressed in terms of the invariants of the Green–St. Venant strain tensor. The functional dependence of the strain energy density on the strain tensor is elucidated through the introduction of new invariants that capture the contributions of dilatational, deviatoric, and strain-induced anisotropy effects. The strain energy density is formulated in terms of these new invariants and the corresponding second Piola–Kirchhoff stress tensor is obtained. A specific form of the constitutive model, characterized by seven elastic constants, is presented and a methodology for systematically evaluating the elastic constants is provided. A general expression for the tangent stiffness tensor is provided based on the new invariants. Additionally, the constitutive model is linearized for infinitesimal deformations and expressions for the Young’s modulus, Poisson’s ratio, and shear modulus are derived. Expressions for the layer modulus and speed of sound of hexagonal 2D materials are presented in terms of the linearized elastic properties. The nonlinear elastic behavior of graphene and molybdenum disulfide is investigated using the proposed approach. The constitutive model is validated using density functional theory data and the linearized elastic properties of graphene and molybdenum disulfide are compared with values reported in the literature. The proposed constitutive model accurately captures the nonlinear elastic response of graphene and molybdenum disulfide and can be adapted to study other 2D materials of hexagonal symmetry.

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I. INTRODUCTION

Two-dimensional (2D) materials are materials consisting of a single layer of atoms or a few tightly bonded layers of atoms [1–3]. Examples of 2D materials include graphene [4], black phosphorus [5], and molybdenum disulfide [4]. The salient physical properties of 2D materials, such as high stiffnesses and strengths [6,7] and high conductivity [2], have made them an important topic of investigation. The nonlinear elastic behavior of 2D materials is particularly of interest due to applications in fields such as flexible electronics [8] and strain sensing [9,10], where 2D materials may be subjected to large deformations. Furthermore, the electrical properties and band gap of 2D materials can be tuned by applying strains, including large deformations, which is referred to as straintronics or strain engineering (e.g., see [11,12]).

The elastic properties of 2D materials subjected to infinitesimal deformations have been evaluated in the literature through computational methods [6,13,14] and experimental

studies [15–17]. Furthermore, the nonlinear elastic behavior of 2D materials such as graphene [18], molybdenum disulfide [19], silicon carbide [20], and black phosphorus [21] has been studied in the literature. In particular, constitutive models that relate the strain energy density, or the stress, to a strain or deformation tensor have been developed for the nonlinear elastic behavior of 2D materials. Cadelano *et al.* [22] expanded the strain energy density as a cubic function in terms of the strains and used tight-binding atomistic simulations to retrieve the elastic constants of graphene. Wei *et al.* [23] noted that the third-order expansion is insufficient to capture the nonlinear elastic behavior of graphene and presented a fifth-order Murnaghan constitutive model to study graphene. Murnaghan’s constitutive model [24–27] is a thermodynamically consistent series expansion of the strain energy density in terms of the components of the Green–St. Venant strain tensor $\mathbf{E}$ (e.g., see [28,29]) that has been successfully applied to 2D materials of various symmetries such as black phosphorus [30,31], graphene [23], silicon carbide [32], germanium carbide [33], hexagonal boron nitride [34], molybdenum disulfide [17], borophene [35], graphyne [36], and antiferromagnetic MnPS₃ [37]. The effect of the polynomial order of the constitutive model on the accuracy of the strain energy density has been systematically investigated in [30].

A widely used approach for deriving nonlinear constitutive models for elastic materials involves expressing the strain energy density as a function of the invariants of strain tensors or other deformation tensors, as commonly done in

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rubber elasticity (e.g., see [38–40]). Xu *et al.* [41] proposed a phenomenological constitutive model wherein the strain energy density is a function of the invariants of the right Cauchy-Green deformation tensor $\mathbf{C}$ (e.g., see [29]). In order to account for the deformation-induced anisotropy at large strains, they assumed that the strain energy density also depends on the components of the Green–St. Venant strain tensor through Heaviside step functions. Subsequently, they derived an expression for the Cauchy stress based on the proposed form of the strain energy density, and presented results for graphene. Kumar and Parks [42] proposed a constitutive model for graphene based on the invariants of the logarithmic strain [43–46]. The approach presented by Kumar and Parks [42] is rigorously based on the theory of representation of scalar functions of a tensor in terms of isotropic invariants and a structure tensor (e.g., see [47]) that takes into account material symmetry and deformation-induced anisotropy. Ghaffari *et al.* [48] presented a constitutive model for hexagonal blue phosphorus using the approach of Kumar and Parks. Höller *et al.* [49] derived a constitutive model for graphene using the approach proposed by Kumar and Parks [42], but employed the invariants of the Green–St. Venant strain tensor rather than those of the logarithmic strain. In their formulation, they [49] introduce 11 new invariants and express the strain energy density in terms of the new invariants and the three invariants of the Green–St. Venant strain tensor.

When developing constitutive models, the objective is to accurately represent the elastic response of the material for arbitrary deformations with the fewest number of elastic constants. As the number of elastic constants increases, so does the computational effort required to determine the constants. Although Murnaghan’s constitutive model has been successfully applied to hexagonal 2D materials, it involves a large number of elastic constants (e.g., see [30]) along with additional linear relations between them, which complicates the formulation and increases the computational effort required to determine the constants. Furthermore, Murnaghan’s model is based on a series expansion in terms of the components of the Green–St. Venant strain tensor which obscures the mechanics of the material and does not include *a priori* the symmetry information in the constitutive model. As a result, the linear dependence between the elastic constants needs to be separately derived (e.g., see [42]). The constitutive model proposed by Xu *et al.* [41] uses Heaviside step functions, which increases the complexity of the constitutive model and introduces 10 elastic constants that need to be determined. In contrast, the constitutive model proposed by Kumar and Parks [42] includes only seven elastic constants and accurately predicts the stress-strain behavior of graphene up to large strains. However, it requires the evaluation of the eigenvalues and eigenvectors of the deformation gradient to evaluate the strain energy density. Furthermore, the calculation of the Cauchy or the second Piola-Kirchhoff stress tensor in their constitutive model requires the evaluation of fourth-order tensor derivatives, which increases the complexity of the formulation. The constitutive model proposed by Höller *et al.* [49] includes 14 elastic constants. We note that hexagonal 2D materials exhibit isotropic behavior in the linear elastic regime [22]. However, isotropic elasticity does not accurately describe the elastic response of hexagonal 2D materials

under large strains due to the deformation-induced and inherent anisotropy.

In this paper, we propose a constitutive model for free-standing hexagonal 2D materials wherein the strain energy density is expressed as a function of the invariants of the Green–St. Venant strain tensor $\mathbf{E}$, which include the contribution of a structure tensor that captures the effects of material symmetry and deformation-induced anisotropy. The constitutive model in the current work is derived employing a similar approach to that used by Kumar and Parks for graphene [42,47] albeit using a different deformation measure. To distinguish the contributions of different deformation modes, new invariants are introduced to discern the contributions of dilatational deformations, deviatoric deformations, and deformation-induced anisotropy effects. The strain energy density is expressed as a general function of these invariants, and the second Piola-Kirchhoff stress tensor and tangent stiffness tensor are derived in terms of the Green–St. Venant strain tensor and those invariants. A specific form for the strain energy density that involves seven elastic constants is proposed. Relations between the elastic constants of the proposed model and the second- and third-order elastic constants of Murnaghan’s model [24–27] are presented. When expanded as a power series in terms of the Green–St. Venant strain components, the proposed form of the strain energy density is shown to exhibit the correct distribution of linearly independent elastic constants for hexagonal 2D materials. The elastic constants are evaluated using an extension of the ray-based methodology [30,31], which consists of evaluating the strain energy density of 2D materials along rays in deformation space using density functional theory. The constitutive model is then fitted to the density functional theory data to evaluate the elastic constants. The proposed model is linearized for infinitesimal deformations and the linearized elastic properties are obtained. Expressions for the layer modulus [50] and longitudinal and transverse speed of sound (e.g., see [51]) in the material are presented based on the elastic constants. The proposed formulation is used to investigate the nonlinear elastic behavior of graphene and molybdenum disulfide, and their elastic constants are presented. The constitutive model is validated by comparing its predictions for the strain energies, stresses, and Poisson’s effects with results obtained from density functional theory and with those from a fifth-order Murnaghan model. Additionally, the variation of the tangent elastic properties of both materials is compared with those obtained using a fifth-order Murnaghan model. While the predictions of Murnaghan’s model for the strain energies, stresses, Poisson’s effects, and tangent moduli are accurate, the proposed model is simpler to implement and includes a smaller number of elastic constants without significant loss of accuracy. Finally, the linearized elastic properties, layer modulus, and speed of sound are evaluated for both materials and compared to values reported in the literature.

This paper is organized as follows. In Sec. II, we formulate the invariant-based constitutive model. The dilatational, deviatoric, and anisotropic invariants are defined based on the symmetry invariants of the Green–St. Venant strain tensor. Subsequently, expressions for the strain energy density as a function of the newly defined invariants are presented. Furthermore, an expression for the second Piola-Kirchhoff

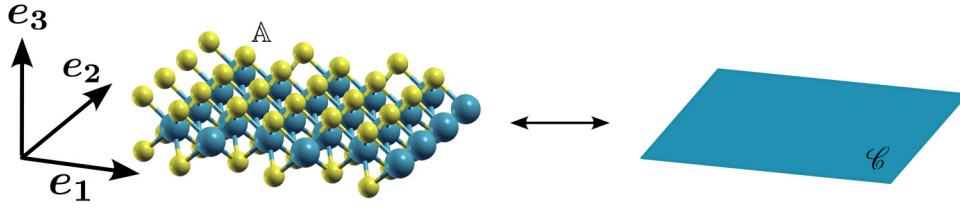


FIG. 1. Schematic of a 2D material with its equivalent continuum. The coordinate basis vectors $\mathbf{e}_1$, $\mathbf{e}_2$, and $\mathbf{e}_3$ are shown.

stress tensor as a function of the Green–St. Venant strain tensor is presented. The constitutive model is linearized and expressions for the linearized elastic properties are presented in Sec. III. Furthermore, a general expression of the tangent moduli in terms of the newly defined invariants and the Green–St. Venant strain tensor is presented. The correspondence of the proposed constitutive model with Murnaghan’s model is discussed in Sec. IV. A methodology for the evaluation of the elastic constants is proposed in Sec. V. The constitutive model is used to study the nonlinear elastic behavior of graphene and molybdenum disulfide in Sec. VI. The summary and conclusions are presented in Sec. VII.

II. HYPERELASTIC CONSTITUTIVE MODEL FOR HEXAGONAL 2D MATERIALS

Figure 1 shows a schematic of a 2D material represented by $\mathbb{A}$ along with its equivalent continuum represented by the domain $\mathcal{C}$, which is assumed to have the same in-plane dimensions and physical response as the 2D material [30]. Since the physical response of the equivalent continuum is assumed to be identical to that of the 2D material, the strain energy density W stored in the equivalent continuum equals that stored in the 2D material for the same deformation, i.e., $W_{\mathbb{A}} = W_{\mathcal{C}}$ (cf. Fig. 1). The general coordinate basis vectors $\mathbf{e}_1$, $\mathbf{e}_2$, and $\mathbf{e}_3$ are shown in Fig. 1. The strain energy density of the 2D material is calculated through density functional theory and used to evaluate the elastic constants of the hyperelastic constitutive model proposed for the equivalent continuum. It is noted that the materials are assumed to be in a state of plane stress since the atoms in 2D materials are generally free to move in the out-of-plane direction (e.g., see [30]).

We adopt a hyperelastic formulation wherein the constitutive model is defined using a strain energy density function (e.g., see [28,40,52]) and a stress tensor is obtained through differentiation of the strain energy density with respect to a strain measure. The strain energy density W is defined as the elastic energy stored in the material per unit undeformed area due to deformation (e.g., see [30,40]) and is expressed as a function of a suitable deformation measure.

In the current work, the strain energy density W of 2D materials is expressed as a function of the Green–St. Venant strain tensor (e.g., see [29]),

$$W = W(\mathbf{E}), \quad (1)$$

where $\mathbf{E}$ is the Green–St. Venant strain tensor, defined as (e.g., see [28,29])

$$\mathbf{E} = \frac{1}{2}(\mathbf{F}^T \mathbf{F} - \mathbf{I}), \quad (2)$$

in which $\mathbf{F}$ is the deformation gradient tensor (e.g., see [28,29,52]) and $\mathbf{I}$ represents the identity tensor. It is noted that the tensor $\mathbf{E}$ is an objective measure of deformation since it satisfies material-frame indifference (e.g., see [28,53]). In the case of 2D materials, tensors, e.g., $\mathbf{E}$, are expressed in a Cartesian coordinate system as 2×2 matrices. We use the ground state of the 2D materials as the undeformed reference configuration for the elastic analysis.

Since the strain energy density is a scalar function of the symmetric tensor $\mathbf{E}$ [cf. Eq. (1)], we use the theory of scalar functions of a tensor (e.g., see [47]) to develop a constitutive model. We represent the symmetry group of hexagonal 2D materials by $\mathcal{G}$. The strain energy function needs to be $\mathcal{G}$ invariant (e.g., see [42]), i.e.,

$$W(\mathbf{E}) = W(\mathbf{\Gamma}^T \mathbf{E} \mathbf{\Gamma}), \quad \forall \mathbf{\Gamma} \in \mathcal{G} \subset \text{SO}(2), \quad (3)$$

where $\text{SO}(2)$ represents the rotation group of 2×2 orthogonal matrices with determinant equal to one (e.g., see [54]). By the isotropicization theorem (e.g., see [47]), a $\mathcal{G}$ -invariant scalar function of a symmetric tensor agency can be written in terms of isotropic invariants and a structure tensor that represents the symmetry of the material (e.g., see [42]). In the case of a hexagonal 2D material, the in-plane, two-dimensional, symmetry group is C_{6v} (e.g., graphene; see [42]) or C_{3v} (e.g., transition-metal dichalcogenides such as molybdenum disulfide; see [55]) and the associated sixth-order structure tensor has the form [42,47]

$$\mathbb{H} = \mathbf{M} \otimes \mathbf{M} \otimes \mathbf{M} - (\mathbf{M} \otimes \mathbf{N} \otimes \mathbf{N} + \mathbf{N} \otimes \mathbf{M} \otimes \mathbf{N} + \mathbf{N} \otimes \mathbf{N} \otimes \mathbf{M}), \quad (4)$$

where $\mathbf{M}$ and $\mathbf{N}$ are symmetric traceless 2×2 tensors defined in the global basis $\{\mathbf{e}_i\}$ as

$$\mathbf{M} = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}, \quad \mathbf{N} = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}. \quad (5)$$

The symmetry invariants of the strain tensor $\mathbf{E}$ with respect to the C_{6v} and the C_{3v} symmetry groups are identical [47]. Therefore, the structure tensor $\mathbb{H}$ is the same for both symmetry groups. The strain energy density function can be expressed in terms of the invariants of the strain tensor $\mathbf{E}$ as follows [47]:

$$W = W(\mathcal{I}_1, \mathcal{I}_2, \mathcal{I}_3), \quad (6)$$

where $\mathcal{I}_1$ is the first invariant and $\mathcal{I}_2$ is the second invariant, which are, respectively, defined as follows:

$$\begin{aligned} \mathcal{I}_1 &= \text{tr} \mathbf{E}, \\ \mathcal{I}_2 &= \det \mathbf{E}. \end{aligned} \quad (7)$$

The third invariant $\mathcal{I}_3$ is defined using the structure tensor $\mathbb{H}$ [42,47,49] and is evaluated as follows [42,48,49]:

$$\mathcal{I}_3 = [(\mathbb{H} : \mathbf{E}) : \mathbf{E}] : \mathbf{E} = (\mathbf{M} : \mathbf{E})^3 - 3(\mathbf{M} : \mathbf{E})(\mathbf{N} : \mathbf{E})^2, \quad (8)$$

where the double-dot product of two tensors is defined as $\mathbf{A} : \mathbf{B} = \text{tr}(\mathbf{A}^T \mathbf{B})$ (e.g., see [28,29]). Accordingly, the third invariant of the Green–St. Venant strain tensor can be expressed as $\mathcal{I}_3 = (E_{11} - E_{22})^3 - 3(E_{11} - E_{22})(2E_{12})^2$. The invariants $\mathcal{I}_1$, $\mathcal{I}_2$, and $\mathcal{I}_3$ are termed the symmetry invariants (e.g., see [42]) of the Green–St. Venant strain tensor.

It is noted that the second invariant $\mathcal{I}_2$ has been modified from that presented in [47], where it is defined as $\text{tr}(\mathbf{E}^2)$. In the case of matrices $\mathbf{E}$ of size 2×2 , $\det \mathbf{E}$ and $\text{tr}(\mathbf{E}^2)$ are related through $\det \mathbf{E} = (1/2)[(\text{tr} \mathbf{E})^2 - \text{tr}(\mathbf{E}^2)]$. Since any combination of the invariants is also an invariant, we define the second invariant $\mathcal{I}_2$ as $\det \mathbf{E}$ for the sake of convenience.

A. Dilatational, deviatoric, and anisotropic invariants

While the strain energy can be expressed in terms of the three symmetry invariants of the Green–St. Venant strain tensor $\mathbf{E}$, the functional dependence on these invariants is unclear. Therefore, we define new invariants that are based on the three symmetry invariants and have physical significance for common deformations such as equibiaxial stretching and pure shear. The invariants, termed the dilatational, deviatoric,

and anisotropic invariants, are defined as follows:

$$\begin{aligned} \mathcal{I}_{\text{dil}} &= \sqrt{1 + 2\mathcal{I}_1 + 4\mathcal{I}_2} - 1, \\ \mathcal{I}_{\text{dev}} &= \mathcal{I}_1^2 - 4\mathcal{I}_2, \\ \mathcal{I}_{\text{aniso}} &= \mathcal{I}_3. \end{aligned} \quad (9)$$

The dilatational invariant $\mathcal{I}_{\text{dil}}$ quantifies the change in area per unit undeformed area of the material. The deviatoric invariant $\mathcal{I}_{\text{dev}}$ quantifies shape-changing deformations. Hexagonal 2D materials behave isotropically for infinitesimal deformations and they exhibit progressively increasing anisotropy as the deformation increases [22]. The anisotropic invariant $\mathcal{I}_{\text{aniso}}$ quantifies the deformation-induced anisotropy by virtue of its dependence on the structure tensor. The anisotropic invariant $\mathcal{I}_{\text{aniso}}$ has a cubic dependence on the components of $\mathbf{E}$ and has a more pronounced effect on the strain energy and stresses as the deformations become larger. The newly defined invariants can be used to model arbitrary 2D materials of hexagonal symmetry.

To illustrate the significance of the new invariants, we consider a general deformation that is characterized by the principal stretches λ_a and λ_b oriented at angle Φ , as depicted in Fig. 2. The principal stretches are the eigenvalues of the right Cauchy stretch tensor (e.g., see [28]). A tensor transformation from the principal coordinate system yields the following Green–St. Venant strain tensor in the $\mathbf{e}_1$ – $\mathbf{e}_2$ basis:

$$\mathbf{E} = \frac{1}{2} \begin{bmatrix} \lambda_a^2 \cos^2 \Phi + \lambda_b^2 \sin^2 \Phi - 1 & (\lambda_a^2 - \lambda_b^2) \cos \Phi \sin \Phi \\ (\lambda_a^2 - \lambda_b^2) \cos \Phi \sin \Phi & \lambda_a^2 \sin^2 \Phi + \lambda_b^2 \cos^2 \Phi - 1 \end{bmatrix}. \quad (10)$$

The dilatational, deviatoric, and anisotropic invariants for this general deformation, obtained using Eqs. (7)–(10), are

$$\begin{aligned} \mathcal{I}_{\text{dil}} &= \lambda_a \lambda_b - 1, \\ \mathcal{I}_{\text{dev}} &= \frac{1}{4}(\lambda_a^2 - \lambda_b^2)^2, \\ \mathcal{I}_{\text{aniso}} &= \frac{1}{8}(\lambda_a^2 - \lambda_b^2)^3 \cos 6\Phi. \end{aligned} \quad (11)$$

Consider the deformation corresponding to equibiaxial stretching, wherein $\lambda_a = \lambda_b = \lambda$. In this case, the dilatational invariant $\mathcal{I}_{\text{dil}} = \lambda^2 - 1$, which correctly captures the change in area per unit reference area of the material. As expected, the deviatoric invariant $\mathcal{I}_{\text{dev}} = 0$ since equibiaxial stretch does not change the overall shape of the material. Furthermore, $\mathcal{I}_{\text{aniso}} = 0$ since equibiaxial stretch does not induce any anisotropy because the atoms continue to remain in a regular hexagonal arrangement after deformation.

When the material is subjected to pure shear, the principal stretch ratios are given by $\lambda_a = \lambda$ and $\lambda_b = 1/\lambda$. The dilatational invariant $\mathcal{I}_{\text{dil}} = 0$, as expected, since the deformation does not induce any change in area. The corresponding deviatoric invariant $\mathcal{I}_{\text{dev}} = (1/4)(\lambda^2 - 1/\lambda^2)^2$ is nonzero and increases with increasing deformation. Furthermore, the anisotropic invariant $\mathcal{I}_{\text{aniso}} = (1/8)(\lambda^2 - 1/\lambda^2)^3 \cos 6\Phi$ depends on both λ and Φ and captures the anisotropy induced by pure shear. It is noted that the $\cos 6\Phi$ term in $\mathcal{I}_{\text{aniso}}$ captures the inherent sixfold rotational symmetry of the hexagonal

material. Similarly, it can be shown that when the material is subjected to simple shear, the dilatational invariant $\mathcal{I}_{\text{dil}} = 0$, as expected, and the deviatoric invariant $\mathcal{I}_{\text{dev}}$ increases with increasing shear strain.

In the present formulation, the strain energy density is expressed in terms of the dilatational, deviatoric, and anisotropic

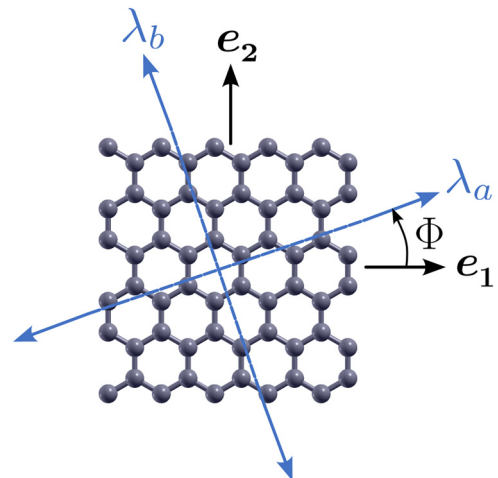


FIG. 2. Schematic of the principal stretches λ_a and λ_b along principal directions oriented at an angle Φ with respect to the $\mathbf{e}_1$ axis.

invariants as

$$W = W(\mathcal{I}_{\text{dil}}, \mathcal{I}_{\text{dev}}, \mathcal{I}_{\text{aniso}}). \quad (12)$$

While the dependence of the strain energy density on the invariants may, in principle, be arbitrary, we express it as a power series in terms of $\mathcal{I}_{\text{dil}}$, $\mathcal{I}_{\text{dev}}$, and $\mathcal{I}_{\text{aniso}}$. For a polynomial of order N , the strain energy density can be written as

$$W = \sum_{m+n+p \leq N} \mathcal{C}_{mnp} \mathcal{I}_{\text{dil}}^m \mathcal{I}_{\text{dev}}^n \mathcal{I}_{\text{aniso}}^p. \quad (13)$$

It is noted that the three invariants $\mathcal{I}_{\text{dil}}$, $\mathcal{I}_{\text{dev}}$, and $\mathcal{I}_{\text{aniso}}$ vanish in the absence of deformation, i.e., when $\mathbf{E} = \mathbf{0}$. Consequently, the strain energy density $W = 0$ in the undeformed configuration, i.e., the ground state. The strain energy density form presented in Eq. (13) is expected to be valid, in principle, for arbitrary 2D materials of hexagonal symmetry. A specific form for the strain energy density used in this paper is given in Sec. II C.

B. Second Piola-Kirchhoff and Cauchy stress tensors

The second Piola-Kirchhoff stress tensor $\mathbf{S}$ (e.g., see [28,29]) is obtained through the differentiation of the strain energy density with respect to the Green–St. Venant strain tensor (e.g., see [28,52,56]),

$$\mathbf{S} = \frac{\partial W}{\partial \mathbf{E}}. \quad (14)$$

In this work, the strain energy density is expressed in terms of the dilatational, deviatoric, and anisotropic invariants, as shown in Eq. (12). The corresponding second Piola-Kirchhoff stress tensor, obtained by differentiating the strain energy density with respect to the Green–St. Venant strain using the invariants, is

$$\mathbf{S} = \frac{\partial W}{\partial \mathcal{I}_{\text{dil}}} \frac{\partial \mathcal{I}_{\text{dil}}}{\partial \mathbf{E}} + \frac{\partial W}{\partial \mathcal{I}_{\text{dev}}} \frac{\partial \mathcal{I}_{\text{dev}}}{\partial \mathbf{E}} + \frac{\partial W}{\partial \mathcal{I}_{\text{aniso}}} \frac{\partial \mathcal{I}_{\text{aniso}}}{\partial \mathbf{E}}. \quad (15)$$

The partial derivatives of the invariants, defined in Eq. (9), with respect to the Green–St. Venant strain tensor, are

$$\begin{aligned} \frac{\partial \mathcal{I}_{\text{dil}}}{\partial \mathbf{E}} &= \frac{1 + 2 \text{tr}(\mathbf{E})}{\mathcal{I}_{\text{dil}} + 1} \mathbf{I} - \frac{2}{\mathcal{I}_{\text{dil}} + 1} \mathbf{E}, \\ \frac{\partial \mathcal{I}_{\text{dev}}}{\partial \mathbf{E}} &= 4\mathbf{E} - 2 \text{tr}(\mathbf{E}) \mathbf{I}, \\ \frac{\partial \mathcal{I}_{\text{aniso}}}{\partial \mathbf{E}} &= 3[(\mathbf{M} : \mathbf{E})^2 - (\mathbf{N} : \mathbf{E})^2] \mathbf{M} - 2(\mathbf{M} : \mathbf{E})(\mathbf{N} : \mathbf{E}) \mathbf{N}. \end{aligned} \quad (16)$$

It is noted that the Cayley-Hamilton theorem (e.g., see [57,58]), i.e., $\mathbf{E}^2 - \text{tr}(\mathbf{E})\mathbf{E} + \det(\mathbf{E})\mathbf{I} = \mathbf{0}$, has been used to obtain the derivative of $\mathcal{I}_{\text{dil}}$ and $\mathcal{I}_{\text{dev}}$ with respect to $\mathbf{E}$.

Substitution of Eq. (16) into Eq. (15) yields the second Piola-Kirchhoff stress tensor,

$$\begin{aligned} \mathbf{S} &= \left[\frac{1 + 2 \text{tr}(\mathbf{E})}{\mathcal{I}_{\text{dil}} + 1} \frac{\partial W}{\partial \mathcal{I}_{\text{dil}}} - 2 \text{tr}(\mathbf{E}) \frac{\partial W}{\partial \mathcal{I}_{\text{dev}}} \right] \mathbf{I} + 2 \left[2 \frac{\partial W}{\partial \mathcal{I}_{\text{dev}}} - \frac{1}{\mathcal{I}_{\text{dil}} + 1} \frac{\partial W}{\partial \mathcal{I}_{\text{dil}}} \right] \mathbf{E} \\ &\quad + 3 \frac{\partial W}{\partial \mathcal{I}_{\text{aniso}}} \{[(\mathbf{M} : \mathbf{E})^2 - (\mathbf{N} : \mathbf{E})^2] \mathbf{M} - 2(\mathbf{M} : \mathbf{E})(\mathbf{N} : \mathbf{E}) \mathbf{N}\}, \end{aligned} \quad (17)$$

where the tensors $\mathbf{M}$ and $\mathbf{N}$ have been defined in Eq. (5), and the double-dot products $\mathbf{M} : \mathbf{E} = E_{11} - E_{22}$, and $\mathbf{N} : \mathbf{E} = 2E_{12}$. The Cauchy stress tensor $\boldsymbol{\sigma}$ is obtained from the second Piola-Kirchhoff stress tensor as follows (e.g., see [28,29]):

$$\boldsymbol{\sigma} = \frac{1}{J} \mathbf{F} \mathbf{S} \mathbf{F}^T, \quad (18)$$

where $J = \det \mathbf{F}$. It is noted that a deformation gradient $\mathbf{F}$ corresponding to a prescribed Green–St. Venant strain tensor $\mathbf{E}$ can be evaluated using the Cholesky decomposition of the right Cauchy-Green deformation tensor $\mathbf{C} = 2\mathbf{E} + \mathbf{I}$, as shown in [13].

Since the ground state of 2D materials is stress free, the stress tensor $\mathbf{S}$ must vanish in the absence of deformation. This restriction imposes a consistency condition that the constitutive model must satisfy. When $\mathbf{E} = \mathbf{0}$, we have $\mathcal{I}_{\text{dil}} = 0$, $\mathcal{I}_{\text{dev}} = 0$ and $(\mathbf{M} : \mathbf{E}) = (\mathbf{N} : \mathbf{E}) = 0$, and it follows from Eq. (17) that

$$\left. \frac{\partial W}{\partial \mathcal{I}_{\text{dil}}} \right|_{\mathbf{E}=\mathbf{0}} = 0. \quad (19)$$

The functional form of the strain energy density in terms of the invariants in Eq. (12) may, in general, be arbitrary provided the consistency condition in Eq. (19) is satisfied.

C. Proposed form for the strain energy density

We examined the effectiveness of the power series representation of the strain energy density, given in Eq. (13), in capturing the elastic response of representative 2D materials, such as graphene and molybdenum disulfide. The order of the series was increased and the accuracy of the strain energy was systematically evaluated. The only terms retained were those that exhibited a significant influence on the strain energy density. To further reduce the number of elastic constants, the polynomial terms involving only the dilatational invariant $\mathcal{I}_{\text{dil}}$ were replaced by a two-parameter function inspired by the Varshni potential [59,60]. The resulting strain energy density has the following functional form:

$$\begin{aligned} W &= D(1 - e^{-\beta \mathcal{I}_{\text{dil}}})^2 + (C_0 + C_1 \mathcal{I}_{\text{dil}} + C_2 \mathcal{I}_{\text{dil}}^2) \mathcal{I}_{\text{dev}} \\ &\quad + (A_0 + A_1 \mathcal{I}_{\text{dil}}) \mathcal{I}_{\text{aniso}}, \end{aligned} \quad (20)$$

where D , β , C_i , and A_j are elastic constants. The proposed constitutive model includes a total of seven elastic constants and satisfies the consistency condition shown in Eq. (19). The first term in Eq. (20), namely, $D(1 - e^{-\beta \mathcal{I}_{\text{dil}}})^2$, captures the contribution of area-changing deformations to the strain energy density and is based on the functional form of the Varshni potential [59,60]. For example, under equibiaxial stretch, both $\mathcal{I}_{\text{dev}} = 0$ and $\mathcal{I}_{\text{aniso}} = 0$, so this term captures the strain energy response due to the change in area when the material is subjected to dilatational deformations. It is noted that it is possible to use a polynomial function in terms of $\mathcal{I}_{\text{dil}}$ to capture the effect of the dilatational deformations on the strain energy density. However, a quadratic function in terms of $\mathcal{I}_{\text{dil}}$, which includes three elastic constants, is generally insufficient to accurately capture the dilatational strain energy curve of arbitrary hexagonal 2D materials. While higher-order polynomials can be used, they require additional elastic constants, as opposed to the chosen exponential form which includes only two elastic constants.

The second term of the strain energy function in Eq. (20) captures the contribution of shape-changing deformations, such as pure shear and simple shear. The coefficient of the deviatoric invariant $\mathcal{I}_{\text{dev}}$ in Eq. (20), namely, $C_0 + C_1 \mathcal{I}_{\text{dil}} + C_2 \mathcal{I}_{\text{dil}}^2$, reflects the observed dependence of the shear response on the underlying dilatational deformation. Similarly, the term $(A_0 + A_1 \mathcal{I}_{\text{dil}})\mathcal{I}_{\text{aniso}}$ accounts for the anisotropic material response due to deformation. In the absence of this term, the strain energy density function would describe a purely isotropic response.

The strain energy form proposed in Eq. (20) is expected to be applicable to arbitrary 2D materials of hexagonal symmetry. However, additional terms may be necessary for increased accuracy. The second Piola-Kirchhoff stress tensor $\mathbf{S}$ and the Cauchy stress tensor $\boldsymbol{\sigma}$ corresponding to the proposed strain energy function in Eq. (20) are obtained using Eq. (17) and Eq. (18), respectively.

III. TANGENT AND LINEARIZED ELASTIC PROPERTIES

A. Linearized constitutive equation for infinitesimal deformations

In the case of infinitesimal deformations, the Green–St. Venant strain tensor $\mathbf{E}$ reduces to the infinitesimal strain tensor $\boldsymbol{\epsilon}$ (e.g., see [52]) and the second Piola-Kirchhoff stress tensor reduces to the Cauchy stress $\boldsymbol{\sigma}$ (e.g., see [28]). Furthermore, $\mathcal{I}_{\text{dil}}$ reduces to $\text{tr } \boldsymbol{\epsilon}$ and the invariants $\mathcal{I}_{\text{dev}}$ and $\mathcal{I}_{\text{aniso}}$ reduce to zero. Using Eq. (17) and the form of the strain energy presented in Eq. (20), we systematically eliminate higher-order terms of $\boldsymbol{\epsilon}$ to obtain the following linearized constitutive equation:

$$\boldsymbol{\sigma} = \zeta \text{tr}(\boldsymbol{\epsilon})\mathbf{I} + 2\mu\boldsymbol{\epsilon}, \quad (21)$$

where the Lamé constants ζ and μ are given by

$$\zeta = 2(D\beta^2 - C_0), \quad \mu = 2C_0. \quad (22)$$

Equation (21) implies that hexagonal 2D materials behave as isotropic materials under infinitesimal in-plane deformations. In the case of 2D materials, the inverse relations which follow from Eq. (21) are

$$\boldsymbol{\epsilon} = \frac{1}{2\mu}\boldsymbol{\sigma} - \frac{\zeta}{4\mu(\zeta + \mu)}\text{tr}(\boldsymbol{\sigma})\mathbf{I}. \quad (23)$$

The linearized elastic moduli, which follow from Eq. (23), are

$$Y = 8 \frac{D\beta^2 C_0}{D\beta^2 + C_0}, \quad \nu = \frac{D\beta^2 - C_0}{D\beta^2 + C_0}, \quad G = \mu = 2C_0, \quad (24)$$

where Y is the Young's modulus, ν is the Poisson's ratio, and G is the in-plane shear modulus for infinitesimal deformations. These elastic moduli are related by the isotropic relation $G = Y/[2(1 + \nu)]$ (e.g., see [28,61]).

It is possible to compute the longitudinal sound velocity (v_l) and transverse sound velocity (v_t) in the 2D materials using the linearized elastic properties, as follows [42,51,62,63]:

$$v_l = \sqrt{\frac{Y}{(1 - \nu^2)\rho}}, \quad v_t = \sqrt{\frac{G}{\rho}}, \quad (25)$$

respectively, where ρ represents the mass per unit area of the 2D material.

The 2D bulk modulus B , which is known as the layer modulus, represents the 2D material's resistance to stretching [50] when subjected to equibiaxial compressive stress of magnitude p , i.e., $\boldsymbol{\sigma} = -p\mathbf{I}$. The layer modulus is given by [50,51,62,63]

$$B = -\Omega \left. \frac{\partial p}{\partial \Omega} \right|_{\Omega \rightarrow \Omega_0} = \frac{Y}{2(1 - \nu)} = 2D\beta^2, \quad (26)$$

where Ω_0 is the ground-state area of the material and Ω is the deformed area of the material. It is noted that the expression shown in Eq. (26) can be derived using $(\Omega - \Omega_0)/\Omega_0 = \text{tr}(\boldsymbol{\epsilon})$ (e.g., see [28]).

B. Tangent stiffness tensor

Using the relation between the second Piola-Kirchhoff stress tensor $\mathbf{S}$ and the Green–St. Venant strain tensor $\mathbf{E}$ presented in Eq. (17), it is possible to evaluate the tangent stiffness tensor $\mathbf{T}$ as (e.g., see [64])

$$\mathbf{T} = \frac{1}{2} \left(\frac{\partial \mathbf{S}}{\partial \mathbf{E}} + \frac{\partial \mathbf{S}}{\partial \mathbf{E}^T} \right). \quad (27)$$

It is noted that $\mathbf{T}$ respects the major and minor symmetries, i.e., $\mathbb{T}_{ijkl} = \mathbb{T}_{klij} = \mathbb{T}_{jikl} = \mathbb{T}_{iljk}$, by virtue of the definition in Eq. (27). In order to evaluate $\partial \mathbf{S} / \partial \mathbf{E}$, we first determine

$$\frac{\partial}{\partial \mathbf{E}} \left(\frac{\partial W}{\partial \mathcal{I}_X} \right) = \left(\frac{2 \text{tr}(\mathbf{E}) + 1}{\mathcal{I}_{\text{dil}} + 1} \mathbf{I} - \frac{2}{\mathcal{I}_{\text{dil}} + 1} \mathbf{E} \right) \frac{\partial^2 W}{\partial \mathcal{I}_{\text{dil}} \partial \mathcal{I}_X} + [4\mathbf{E} - 2 \text{tr}(\mathbf{E})\mathbf{I}] \frac{\partial^2 W}{\partial \mathcal{I}_{\text{dev}} \partial \mathcal{I}_X} + \frac{\partial \mathcal{I}_{\text{aniso}}}{\partial \mathbf{E}} \frac{\partial^2 W}{\partial \mathcal{I}_{\text{aniso}} \partial \mathcal{I}_X}, \quad (28)$$

where $\mathcal{I}_X$ represents either $\mathcal{I}_{\text{dil}}$, $\mathcal{I}_{\text{dev}}$, or $\mathcal{I}_{\text{aniso}}$. The second derivative of $\mathcal{I}_{\text{aniso}}$ with respect to the strain tensor $\mathbf{E}$ is given as follows:

$$\frac{\partial}{\partial \mathbf{E}} \left(\frac{\partial \mathcal{I}_{\text{aniso}}}{\partial \mathbf{E}} \right) = 6[(\mathbf{M} : \mathbf{E})(\mathbf{M} \otimes \mathbf{M} - \mathbf{N} \otimes \mathbf{N}) - (\mathbf{N} : \mathbf{E})(\mathbf{M} \otimes \mathbf{N} + \mathbf{N} \otimes \mathbf{M})], \quad (29)$$

where $\otimes$ represents the tensor outer product, i.e., $(\mathbf{A} \otimes \mathbf{B})_{ijkl} = A_{ij}B_{kl}$ (e.g., see [28]). Finally, the following differential, given by

$$\begin{aligned} \frac{\partial}{\partial \mathbf{E}} \left(\frac{1 + 2 \text{tr}(\mathbf{E})}{\mathcal{I}_{\text{dil}} + 1} \right) &= (1 + 2 \text{tr}(\mathbf{E})) \frac{\partial}{\partial \mathbf{E}} \left(\frac{1}{\mathcal{I}_{\text{dil}} + 1} \right) + \frac{1}{\mathcal{I}_{\text{dil}} + 1} \frac{\partial}{\partial \mathbf{E}} [1 + 2 \text{tr}(\mathbf{E})] \\ &= \frac{1 + 2 \text{tr}(\mathbf{E})}{(\mathcal{I}_{\text{dil}} + 1)^3} [2\mathbf{E} - [1 + 2 \text{tr}(\mathbf{E})]\mathbf{I}] + \frac{2}{\mathcal{I}_{\text{dil}} + 1} \mathbf{I}, \end{aligned} \quad (30)$$

is also helpful for the evaluation of $\partial \mathbf{S} / \partial \mathbf{E}$. The derivative of the second Piola-Kirchhoff stress tensor $\mathbf{S}$ with respect to the Green–St. Venant strain tensor $\mathbf{E}$ is given by

$$\begin{aligned} \frac{\partial \mathbf{S}}{\partial \mathbf{E}} &= \left[\frac{\partial}{\partial \mathbf{E}} \left(\frac{1 + 2 \text{tr}(\mathbf{E})}{\mathcal{I}_{\text{dil}} + 1} \right) \frac{\partial W}{\partial \mathcal{I}_{\text{dil}}} + \frac{1 + 2 \text{tr}(\mathbf{E})}{\mathcal{I}_{\text{dil}} + 1} \frac{\partial}{\partial \mathbf{E}} \left(\frac{\partial W}{\partial \mathcal{I}_{\text{dil}}} \right) - 2 \frac{\partial W}{\partial \mathcal{I}_{\text{dev}}} \mathbf{I} \right. \\ &\quad \left. - 2 \text{tr}(\mathbf{E}) \frac{\partial}{\partial \mathbf{E}} \left(\frac{\partial W}{\partial \mathcal{I}_{\text{dev}}} \right) \right] \otimes \mathbf{I} + \left(2 \frac{\partial W}{\partial \mathcal{I}_{\text{dev}}} - \frac{1}{\mathcal{I}_{\text{dil}} + 1} \frac{\partial W}{\partial \mathcal{I}_{\text{dil}}} \right) \mathbb{I} \\ &\quad + \left[2 \frac{\partial}{\partial \mathbf{E}} \left(\frac{\partial W}{\partial \mathcal{I}_{\text{dev}}} \right) - \frac{\partial W}{\partial \mathcal{I}_{\text{dil}}} \frac{\partial}{\partial \mathbf{E}} \left(\frac{1}{\mathcal{I}_{\text{dil}} + 1} \right) - \frac{1}{\mathcal{I}_{\text{dil}} + 1} \frac{\partial}{\partial \mathbf{E}} \left(\frac{\partial W}{\partial \mathcal{I}_{\text{dil}}} \right) \right] \otimes \mathbf{E} \\ &\quad + \frac{\partial}{\partial \mathbf{E}} \left(\frac{\partial W}{\partial \mathcal{I}_{\text{aniso}}} \right) \otimes \frac{\partial \mathcal{I}_{\text{aniso}}}{\partial \mathbf{E}} + \frac{\partial W}{\partial \mathcal{I}_{\text{aniso}}} \frac{\partial}{\partial \mathbf{E}} \left(\frac{\partial \mathcal{I}_{\text{aniso}}}{\partial \mathbf{E}} \right), \end{aligned} \quad (31)$$

where $\mathbb{I}$ is a fourth-order identity tensor defined in index notation as $\mathbb{I}_{ijkl} = \delta_{ik}\delta_{jl}$ and δ_{ij} is the Kronecker delta (e.g., see [28]). The fourth-order tangent stiffness tensor $\mathbb{T}$ can be written in Voigt notation [65,66] as a second-order tensor as (e.g., see [28])

$$\mathbf{Q}^{(t)} = \begin{bmatrix} \mathbb{T}_{1111} & \mathbb{T}_{1122} & \mathbb{T}_{1112} \\ \mathbb{T}_{2211} & \mathbb{T}_{2222} & \mathbb{T}_{2212} \\ \mathbb{T}_{1211} & \mathbb{T}_{1222} & \mathbb{T}_{1212} \end{bmatrix}. \quad (32)$$

The tensor $\mathbf{Q}^{(t)}$ is symmetric due to the major symmetry of $\mathbb{T}$. The study of the tangent elastic properties involves superimposing infinitesimal deformations to a predeformed material; therefore, the tangent elastic moduli can be obtained using the inverse of the tangent stiffness tensor $\mathbf{Q}^{(t)}$ (e.g., see [13]) as follows:

$$\begin{bmatrix} \frac{1}{Y_1^t} & -\frac{\nu_{21}^t}{Y_2^t} & \frac{\eta_{16}^t}{G^t} \\ -\frac{\nu_{12}^t}{Y_1^t} & \frac{1}{Y_2^t} & \frac{\eta_{26}^t}{G^t} \\ \frac{\eta_{61}^t}{Y_1^t} & \frac{\eta_{62}^t}{Y_2^t} & \frac{1}{G^t} \end{bmatrix} = (\mathbf{Q}^{(t)})^{-1}, \quad (33)$$

where Y_i^t represents the tangent Young's modulus in the $\mathbf{e}_i$ direction, G^t represents the in-plane tangent shear modulus, ν_{ij}^t are the tangent Poisson's ratios, and η_{ij}^t are the tangent coefficients of mutual influence (e.g., see [13]). It is noted that in the linear elastic regime, i.e., for infinitesimal deformations where $\|\boldsymbol{\varepsilon}\| \ll 1$, the tangent elastic moduli reduce to the linearized elastic properties wherein as $\boldsymbol{\varepsilon} \rightarrow \mathbf{0}$, $Y_i^t \rightarrow Y$, $G^t \rightarrow G$, $\nu_{ij}^t \rightarrow \nu$, and $\eta_{ij}^t \rightarrow 0$.

IV. CORRESPONDENCE OF THE PROPOSED CONSTITUTIVE MODEL WITH MURNAGHAN'S MODEL

In this section, the constitutive model presented in Eq. (20) is related to the classical Murnaghan constitutive model [24–27,30] by expanding the strain energy density as a Maclaurin series in terms of the components of the Green–St. Venant strain tensor. Murnaghan's model has been previously used in the literature to study 2D materials [17,23,30–36,67], most commonly using a fifth-order expansion. In Murnaghan's polynomial-based constitutive model, the strain energy density is typically expressed in Voigt notation [65,66] as (e.g., see [30])

$$\begin{aligned} W &= W_0 + \sum_{l=1}^N \frac{1}{l!} Q_{i_1 i_2 \dots i_l} E_{i_1} E_{i_2} \dots E_{i_l} \\ &= W_0 + Q_i E_i + \frac{1}{2} Q_{ij} E_i E_j + \frac{1}{6} Q_{ijk} E_i E_j E_k + \dots, \end{aligned} \quad (34)$$

where N is the order of the constitutive polynomial, $E_1 = E_{11}$, $E_2 = E_{22}$, $E_6 = 2E_{12}$, and summation over repeated dummy indices is implied hereinafter (e.g., see [61]) unless otherwise specified, and the indices vary in $\{1, 2, 6\}$. The constant term W_0 of the series expansion vanishes since $W = 0$ when $\mathbf{E} = \mathbf{0}$ [cf. Eq. (20)]. The remaining constants can be determined using (e.g., see [30])

$$Q_{i_1 i_2 \dots i_n} = \left. \frac{\partial^n W}{\partial E_{i_1} \partial E_{i_2} \dots \partial E_{i_n}} \right|_{\mathbf{E}=\mathbf{0}}, \quad (35)$$

where n is the order of the elastic constant $Q_{i_1 i_2 \dots i_n}$. After differentiation of the strain energy density shown in Eq. (20), using Eq. (35) for $n = 1$, the constants Q_i vanish, which conforms to the Murnaghan model for 2D materials in their

ground state (e.g., see [30]). By symbolically differentiating Eq. (20) with respect to the strain components, we determine the second-order elastic constants as follows:

$$\begin{aligned} Q_{11} &= Q_{22} = 2C_0 + 2D\beta^2, \\ Q_{12} &= -2C_0 + 2D\beta^2, \\ Q_{16} &= Q_{26} = 0, \\ Q_{66} &= \frac{1}{2}(Q_{11} - Q_{12}). \end{aligned} \quad (36)$$

The expressions presented in Eq. (36) satisfy the hexagonal symmetry conditions (e.g., see [17,23]) where there are only two linearly independent second-order elastic constants. The third-order elastic constants of Murnaghan's model are determined similarly as

$$\begin{aligned} Q_{111} &= 6A_0 + 6C_1 - 6D\beta^2(1 + \beta), \\ Q_{222} &= -6A_0 + 6C_1 - 6D\beta^2(1 + \beta), \\ Q_{112} &= -6A_0 - 2C_1 + 2D\beta^2(1 - 3\beta), \\ Q_{116} &= Q_{126} = Q_{226} = Q_{666} = 0, \\ Q_{122} &= Q_{111} - Q_{222} + Q_{112}, \\ Q_{166} &= \frac{1}{4}(3Q_{222} - 2Q_{111} - Q_{112}), \\ Q_{266} &= \frac{1}{4}(2Q_{111} - Q_{222} - Q_{112}). \end{aligned} \quad (37)$$

The expressions presented in Eq. (37) satisfy the hexagonal symmetry conditions (e.g., see [17,23]) where there are only three linearly independent third-order elastic constants. Similarly, the same process can be repeated to verify that higher-order elastic constants satisfy the hexagonal symmetry conditions, e.g., an additional four linearly independent fourth-order elastic constants.

It is noted that Eq. (14) can be used to obtain expressions for the second Piola-Kirchhoff stress tensor in Voigt notation [65,66] as follows:

$$\begin{aligned} S_i &= \frac{\partial W}{\partial E_i} = Q_{ij}E_j + \frac{1}{2!}Q_{ijk}E_jE_k + \dots \\ &= \sum_{l=1}^N \frac{1}{l!}Q_{ik_1\dots k_l}E_{k_1}\dots E_{k_l}. \end{aligned} \quad (38)$$

Similarly, the tangent stiffness tensor in Voigt notation [65,66] can be obtained using Eq. (27) for Murnaghan's model as follows:

$$\begin{aligned} Q_{ij}^{(t)} &= \frac{\partial S_i}{\partial E_j} = Q_{ij} + Q_{ijk}E_k + \frac{1}{2!}Q_{ijkl}E_kE_l + \dots \\ &= Q_{ij} + \sum_{l=1}^N \frac{1}{(l-1)!}Q_{ijk_1\dots k_l}E_{k_1}\dots E_{k_l}. \end{aligned} \quad (39)$$

V. EVALUATION OF THE ELASTIC CONSTANTS

We adapt the ray-based methodology [30,31] to evaluate the elastic constants associated with constitutive models of the form given in Eq. (12). In this approach, the strain energy density is evaluated using density functional theory for deformation states sampled along rays in deformation space. Each ray is defined as a line segment that extends from the

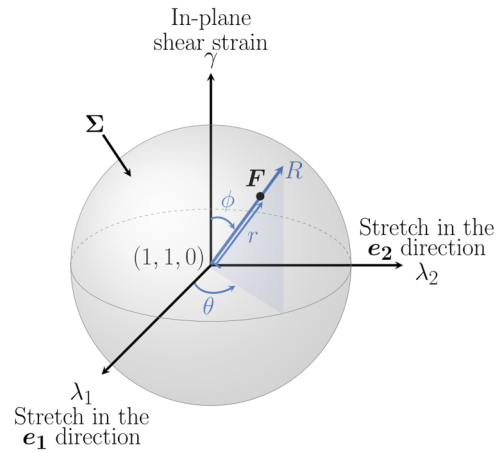


FIG. 3. Deformation space, spanned by the stretch ratios λ_1 and λ_2 , and the shear strain γ , used to sample for the strain energy densities. An example of a ray is shown in blue along with a point on the ray represented by its spherical coordinates r , θ , and ϕ .

origin (i.e., the undeformed state) to a specified deformation norm. To ensure consistency of the deformation magnitudes, the deformation states are restricted to a spherically bounded region of deformation space, denoted by Σ . The elastic constants are determined by fitting the constitutive model to the density functional theory data.

The deformation space is defined as the space spanned by λ_1 , λ_2 , and γ , as shown in Fig. 3, where λ_1 and λ_2 are the stretch ratios (e.g., see [29,52]) in the $\mathbf{e}_1$ and $\mathbf{e}_2$ directions, respectively, and γ is the in-plane shear strain (angle of shear) in the $\mathbf{e}_1$ - $\mathbf{e}_2$ plane (e.g., see [52]). The stretch ratio is defined as the ratio of the deformed length to the undeformed length of a material line element (e.g., see [29,52]). When the stretch ratios λ_1 or λ_2 equal 1.0, the material is unstretched in the corresponding direction. A deformation state for a point on a ray is given by its spherical coordinates r , θ , and ϕ (cf. Fig. 3) as

$$\begin{aligned} \lambda_1 &= 1 + r \cos \theta \sin \phi, \\ \lambda_2 &= 1 + r \sin \theta \sin \phi, \\ \gamma &= r \cos \phi. \end{aligned} \quad (40)$$

The deformation gradient corresponding to a deformation state characterized by the stretch ratios λ_1 and λ_2 , and the shear strain γ , is composed of a biaxial stretch followed by a simple shear deformation (e.g., see [52]), i.e.,

$$\mathbf{F} = \begin{bmatrix} \lambda_1 & \lambda_2 \tan \gamma \\ 0 & \lambda_2 \end{bmatrix}. \quad (41)$$

For any deformation represented by λ_1 , λ_2 , and γ , the Green–St. Venant strain tensor is evaluated using Eq. (2) and the deformation gradient given in Eq. (41). The ground-state lattice parameters of the unit cell are represented by the matrix $\mathcal{L}^0$ and the deformed lattice parameters by $\mathcal{L}$, wherein $\mathcal{L}_{ij}$ represents the i th component of the j th lattice vector and $i, j \in \{1, 2\}$. The deformation gradient $\mathbf{F}$ is applied to the periodic unit cell by updating the lattice vectors according to

TABLE I. Converged density functional theory parameters used in the QUANTUM ESPRESSO simulations of graphene and molybdenum disulfide. r_0 represents the Bohr radius (e.g., see [56]).

Parameter	Graphene	Molybdenum disulfide
K_x, K_y	20	12
K_z	2	2
Total energy convergence threshold	10^{-8} Ry	10^{-10} Ry
Electron energy convergence threshold	10^{-8} Ry	10^{-10} Ry
Force convergence threshold	10^{-8} Ry/ r_0	10^{-8} Ry/ r_0
Kinetic-energy cutoff τ	150 Ry	125 Ry
z lattice vector dimension	10 Å	30 Å

the relation (e.g., see [30])

$$\mathcal{L} = F \mathcal{L}^0. \quad (42)$$

The elastic constants are obtained using the ray-based methodology through the following sequence of steps. First, the ground state of the material is determined by relaxing both the atomic coordinates and lattice parameters to obtain the ground-state energy $\mathcal{E}_0$ and the ground-state lattice parameters $\mathcal{L}^0$. Next, a set of rays is defined in deformation space where the i th ray is represented by its directions θ_i and ϕ_i and the number of points along a ray, e.g., $\mathcal{N}$, is chosen. Subsequently, for each ray and each point on the ray, the unit cell is deformed according to Eqs. (40)–(42) and the atomic coordinates are relaxed while holding the lattice parameters fixed to obtain the energy $\mathcal{E}$ of the deformed unit cell using density functional theory. The corresponding strain energy density W per unit undeformed area is computed as

$$W = \frac{1}{\Omega_0}(\mathcal{E} - \mathcal{E}_0), \quad (43)$$

where Ω_0 is the ground-state area of the unit cell obtained using $\mathcal{L}^0$. For each deformation state, the corresponding dilatational, deviatoric, and anisotropic invariants are computed and the constitutive model is curve fitted to the strain energy densities obtained from density functional theory to determine the elastic constants.

VI. RESULTS AND DISCUSSIONS

In this section, the constitutive model proposed in Sec. II C is used to investigate the nonlinear elastic behavior of representative hexagonal 2D materials. This section is organized as follows. We begin by presenting the computational details of the simulations. We then examine the nonlinear elastic behavior of graphene and molybdenum disulfide.

A. Computational details

In the present study, density functional theory [68,69] is used to compute the strain energy densities and stresses (e.g., see [70]) of deformed 2D materials. A plane-wave basis (e.g., see [56]) is used through the open-source software package QUANTUM ESPRESSO [71,72]. Projector augmented wave pseudopotentials [73] are used in this work to obtain accuracies comparable to using full electron potentials. In addition, the Perdew-Burke-Ernzerhof generalized gradient approximation [74] is used for the exchange and correlation functional. The pseudopotentials used for graphene and molybdenum disulfide originated from PSLIBRARY 1.0.0 [75]. The accuracy and precision of the pseudopotentials in PSLIBRARY 1.0.0 have been assessed in [76,77]. The QUANTUM ESPRESSO parameters used in our simulations, which are chosen based on a convergence study, are presented in Table I. It is noted that the kinetic-energy cutoff shown in Table I is related to the number of plane waves used, i.e., the number of terms in the Fourier expansion of the electronic wave function, through (e.g., see [56])

$$\tau = \frac{\hbar^2}{2m^{\text{el}}} \Lambda^2, \quad (44)$$

where τ is the kinetic-energy cutoff, m^{el} is the electron mass, $\hbar$ is the reduced Planck constant, and Λ represents the cutoff wavelength which controls the number of plane waves (e.g., see [56]).

The parameters K_x , K_y , and K_z shown in Table I represent the number of points in the Monkhorst-Pack K -space sampling mesh [78] in each reciprocal space direction. The z lattice vector dimension represents the length of the out-of-plane lattice vector used to create a vacuum between the 2D material layers to avoid interactions between the layers due to the periodic boundary conditions. It is noted that the study is performed at 0 K.

TABLE II. The rays used to sample for the strain energy densities in deformation space and subsequently evaluate the elastic constants in the current work.

No. rays	Azimuthal angles θ (deg)	Polar angles ϕ (deg)	Physical significance
8	{0, 180, ± 90 , ± 45 , ± 135 }	90	Uniaxial and equibiaxial stretches
2	0	{0, 180}	Simple shear
8	{0, 180, ± 90 }	{45, 135}	Uniaxial stretch and superimposed shear
8	{ ± 45 , ± 135 }	{45, 135}	Equibiaxial stretch and superimposed shear

TABLE III. The elastic constants of Murnaghan's constitutive model for graphene and molybdenum disulfide.

Constant (N/m)	Graphene	Molybdenum disulfide
Q_{11}	349.71	131.47
Q_{12}	61.25	32.33
Q_{111}	-3 055.06	-1 273.88
Q_{222}	-2 894.04	-1 487.83
Q_{112}	-417.49	-141.42
Q_{1111}	25 431.24	12 048.57
Q_{2222}	21 756.14	18 403.89
Q_{1112}	3 523.58	2 909.37
Q_{1122}	4 099.90	-1 619.52
Q_{11111}	-199 013.39	-79 264.50
Q_{22222}	-201 006.86	-156 830.23
Q_{11112}	-30 366.28	-36 685.22
Q_{12222}	-32 530.57	-6 838.10
Q_{11122}	-24 001.63	10 072.32
Root-mean-square error (J/m ²)	0.0056	0.0046

To analyze a 2D material using density functional theory, we first determine the ground-state configuration of its unit cell. This involves minimizing the energy of the unit cell by varying the lattice parameters and atomic coordinates. As the energy is minimized, the atomic forces [79] are also minimized in addition to the stresses in the unit cell [70]. The minimization procedure used for the ground-state determination and subsequent optimizations is the Broyden-Fletcher-Goldfarb-Shanno (BFGS) algorithm [80–83] (e.g., see [84]).

The elastic constants of the materials are evaluated using the rays listed in Table II with a radius $R = 0.2$ for the spherical domain in deformation space and $\mathcal{N} = 10$ points per ray. A nonlinear least-squares algorithm (e.g., see [85]) is used to curve fit the constitutive model to the computed strain energy data by minimizing the root-mean-square (RMS) error. Multiple sets of rays are used for each material to assess the convergence of the elastic constants.

B. Murnaghan's constitutive model

The results obtained using the proposed constitutive model are compared with those from Murnaghan's model [24–27], which is based on a polynomial expansion of the strain energy density in terms of the components of the Green–St. Venant

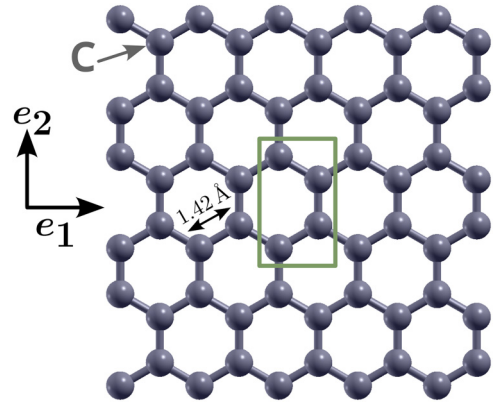


FIG. 4. Ground-state geometry of graphene along with the unit cell used for the analysis shown in green.

strain tensor E (cf. Sec. IV). The strain energy density is expressed as a fifth-order polynomial in Voigt notation [65,66] as [cf. Eq. (34)]

$$W = \frac{1}{2!} Q_{ij} E_i E_j + \frac{1}{3!} Q_{ijk} E_i E_j E_k + \frac{1}{4!} Q_{ijkl} E_i E_j E_k E_l + \frac{1}{5!} Q_{ijklm} E_i E_j E_k E_l E_m, \quad (45)$$

where $Q_{ij\dots}$ are the elastic constants of Murnaghan's model, E_i are the components of the Green–St. Venant strain tensor in Voigt notation, and the subscript indices take values in $\{1, 2, 6\}$. The components of the second Piola–Kirchhoff stress tensor (e.g., see [28,53]) in Voigt notation are obtained using Eq. (38) as follows:

$$S_i = \frac{\partial W}{\partial E_i} = Q_{ij} E_j + \frac{1}{2!} Q_{ijk} E_j E_k + \frac{1}{3!} Q_{ijkl} E_j E_k E_l + \frac{1}{4!} Q_{ijklm} E_j E_k E_l E_m. \quad (46)$$

For a hexagonal 2D material, the total number of linearly independent elastic constants is 14 for a fifth-order polynomial expansion for the strain energy density [23,30] based on material symmetry. The relations for the linearly dependent elastic constants are given in [23]. We use the ray-based methodology (cf. Sec. V) along with the rays shown in Table II to evaluate the elastic constants of Murnaghan's model for graphene and molybdenum disulfide. The elastic constants, which are extracted by curve fitting Murnaghan's model to

TABLE IV. Elastic constants of hexagonal graphene for the proposed constitutive model. The elastic constants corresponding to 26 rays are used to evaluate the strain energy density and stresses in the current work.

Elastic constant	Value (8 rays)	Value (10 rays)	Value (18 rays)	Value (26 rays)
D (N/m)	32.32	32.29	32.34	32.26
β	1.82	1.82	1.82	1.82
C_0 (N/m)	69.71	69.97	70.07	70.22
C_1 (N/m)	-200.24	-199.88	-200.20	-199.86
C_2 (N/m)	114.98	106.72	107.00	101.86
A_0 (N/m)	-11.41	-11.27	-11.66	-11.82
A_1 (N/m)	76.84	76.71	76.19	76.96
Root-mean-square error (J/m ²)	0.0201	0.0186	0.0182	0.0179

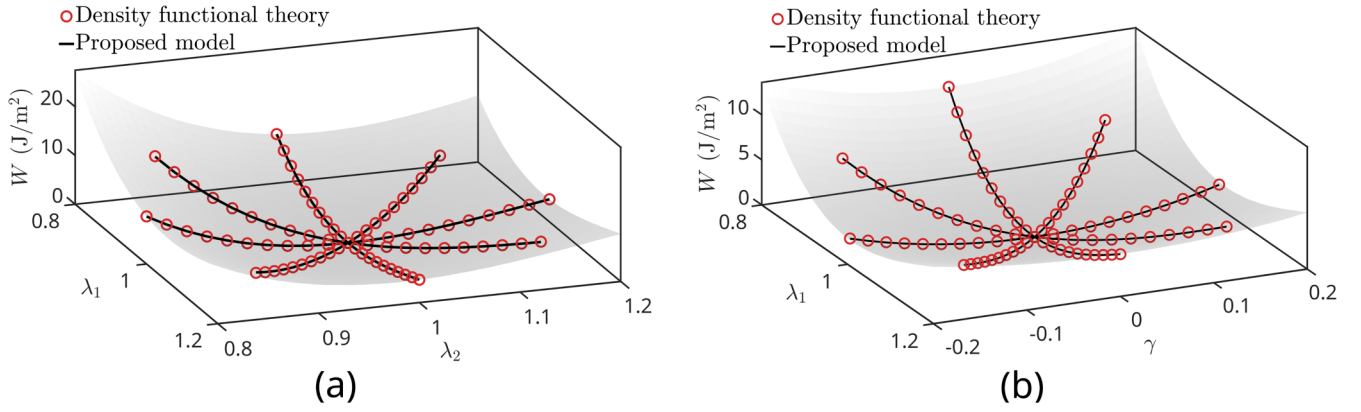


FIG. 5. Strain energy density plots of graphene under different loading conditions, as obtained from density functional theory computations and compared to the predictions of the constitutive model. (a) Strain energy density landscape as a function of the stretches λ_1 and λ_2 for biaxial stretch. (b) Strain energy density landscape as a function of the stretch ratio λ_1 and the shear strain γ .

the strain energy densities obtained from density functional theory, are listed in Table III.

The lower-order, e.g., second-order, elastic constants of Murnaghan's model presented in Table III show good agreement with those presented in [23,30] for graphene. In addition, the elastic constants obtained for molybdenum disulfide compare well with those presented in [17]. There are some numerical differences in the higher-order elastic constants since they are highly dependent on the curve fitting approach and curve fitting range. In the current work, a different curve fitting range and different rays are used compared to [30]. Furthermore, the curve fitting in [17,23] is performed using the stress-strain relations, but in [30] it is done using the strain energy densities. Despite these differences, the resulting strain energy densities are numerically comparable. We note that the configuration of molybdenum disulfide used in [17] is a 90 degree rotation of the configuration in the current paper.

C. Graphene

The ground-state geometry of graphene is shown in Fig. 4, where the unit cell used in the analysis, consisting of four carbon atoms, is highlighted in green. Energy minimization yields the lattice parameters $\mathcal{L}_{11}^0 = 2.47 \text{ \AA}$ and $\mathcal{L}_{22}^0 = 4.27 \text{ \AA}$. The geometry of graphene in its ground state consists of regular hexagons with internal angles of 120° and bond length between adjacent carbon atoms of $1.42 \text{ \AA}$, which is consistent with the values reported in [31]. It is noted that the $\mathbf{e}_1$ direction shown in Fig. 4 corresponds to graphene's zigzag direction and the $\mathbf{e}_2$ direction corresponds to the armchair direction. The mass density per unit area of graphene, which is used to compute the sound velocity in graphene, is given by

$$\rho = \frac{4m_C}{\mathcal{L}_{11}^0 \mathcal{L}_{22}^0} = 7.56 \times 10^{-7} \text{ kg/m}^2, \quad (47)$$

where $m_C = 1.994 \times 10^{-26} \text{ kg}$ represents the atomic mass of carbon, the factor 4 represents the number of atoms in the unit cell, and the product $\mathcal{L}_{11}^0 \mathcal{L}_{22}^0$ is the ground-state area of the periodic unit cell.

Using the procedure outlined in Sec. V and the computational details presented in Sec. VIA, we evaluate the elastic constants D , β , C_0 , C_1 , C_2 , A_0 , and A_1 of the proposed

constitutive model [cf. Eq. (20)] for graphene. The resulting elastic constants are summarized in Table IV. The elastic constants are evaluated for increasing number of rays by considering successive rows of ray directions in Table II. The root-mean-square error in the curve fit using the strain energy density is calculated as

$$\text{RMS} = \sqrt{\frac{\sum_{i=1}^M (W_{\text{model}} - W_{\text{DFT}})^2}{M}}, \quad (48)$$

where the total number of samples is $M = 286$ (26 rays $\times$ 11 points per ray including the origin), W_{model} is the strain energy density obtained using the constitutive model with the elastic constants listed in the corresponding column of Table IV, and W_{DFT} are the strain energy densities obtained directly from density functional theory. As can be seen in Table IV, the root-mean-square error does not significantly improve between 8 and 26 rays. The values of the elastic constants exhibit little variation with increasing number of rays. While 8 rays would have been sufficient, we utilize the elastic constants corresponding to 26 rays for the subsequent analyses since they yielded the lowest root-mean-square error.

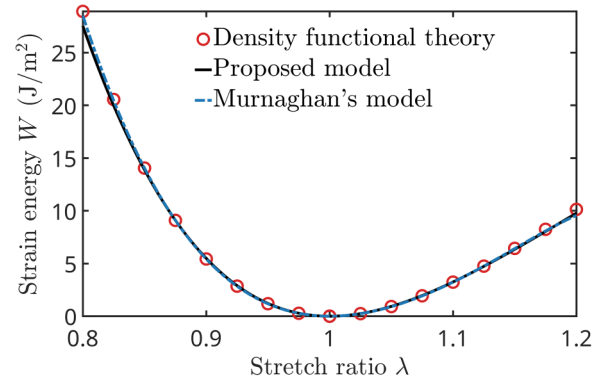


FIG. 6. Variation of the strain energy density of graphene as a function of the stretch ratio λ for equibiaxial stretching conditions. The energies obtained from density functional theory are compared to that predicted by the constitutive model that uses the Varshni potential, and a fifth-order Murnaghan model.

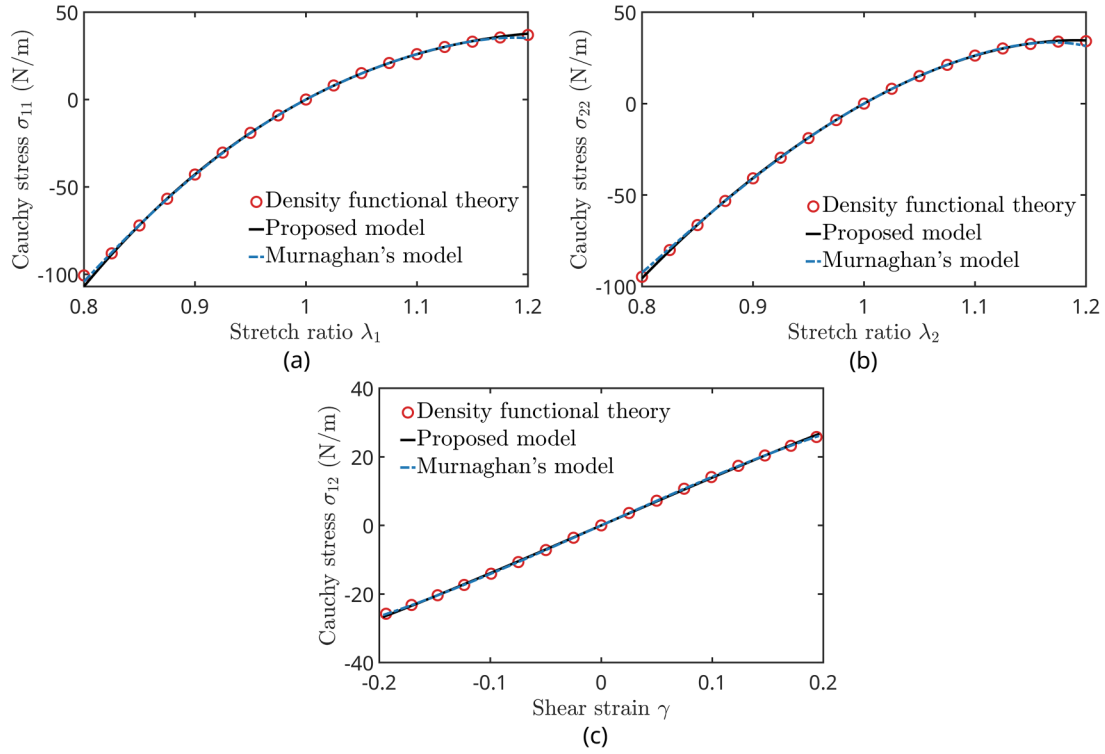


FIG. 7. Plots of the normal stress vs stretch ratio and shear stress vs shear strain of graphene. (a) Normal stress σ_{11} as a function of the stretch ratio λ_1 . (b) Normal stress σ_{22} as a function of the stretch ratio λ_2 . (c) Shear stress σ_{12} as a function of the shear strain γ . Stretch ratios λ_1 or λ_2 of 1.0 correspond to the undeformed state.

Figure 5(a) shows the strain energy density landscape of graphene for biaxial stretching, obtained using density functional theory and the proposed constitutive model. The strain energy density of graphene for simultaneous stretch λ_1 and shear strain γ is shown in Fig. 5(b). As can be seen, the predictions of the constitutive model for the strain energy density closely match the density functional theory data used for the curve fit.

Figure 6 shows the strain energy density of graphene for equibiaxial stretch deformations ($\lambda_1 = \lambda_2 = \lambda$) as predicted by the constitutive model, density functional theory, and Murnaghan's model. It is noted that equibiaxial stretch corresponds to equibiaxial contraction when $\lambda < 1$. Equibiaxial

stretch has been considered since $\mathcal{I}_{\text{dev}} = 0$ and $\mathcal{I}_{\text{aniso}} = 0$ for this deformation mode. As such, the strain energy density depends only on $\mathcal{I}_{\text{dil}}$ and Eq. (20) reduces to $W = D(1 - e^{-\beta \mathcal{I}_{\text{dil}}})^2$, which is the form of the Varshni potential [59,60]. As can be seen in Fig. 6, the proposed constitutive model replicates the density functional theory data very well for equibiaxial stretch with only two elastic constants D and β , almost as accurately as Murnaghan's model with 14 linearly independent elastic constants.

The elastic constants presented in Table IV are validated by considering the nonlinear response of graphene for uniaxial stress conditions. It is noted that the uniaxial stress data were not included in the curve fitting process to obtain the elastic

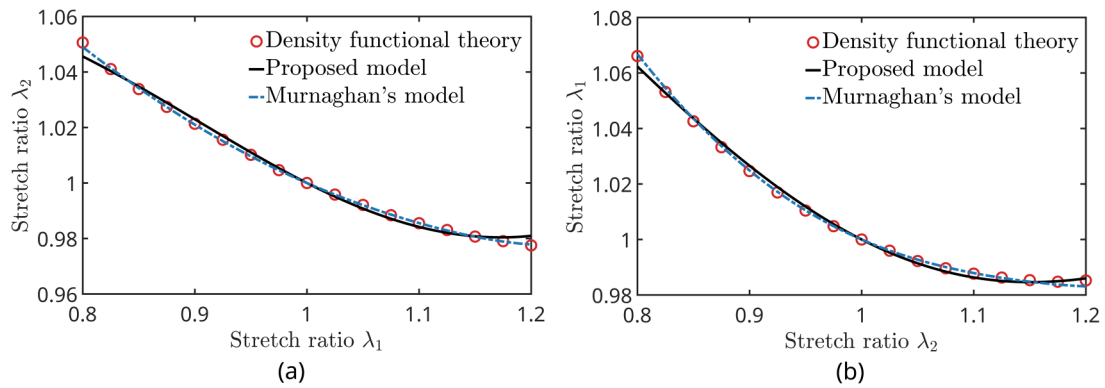


FIG. 8. Stretching of graphene due to Poisson's effect, as predicted by the proposed constitutive model and Murnaghan's model in comparison with the density functional theory data. (a) Stretch λ_2 caused by an applied λ_1 when $\sigma_{22} = 0$. (b) Stretch λ_1 caused by an applied λ_2 when $\sigma_{11} = 0$.

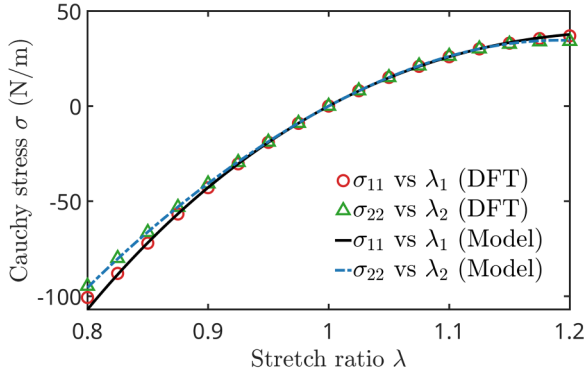


FIG. 9. Comparison of the nonlinear normal Cauchy stress vs stretch curves of graphene in the $\mathbf{e}_1$ and $\mathbf{e}_2$ directions. The predictions of the proposed constitutive model (Model) are presented alongside the density functional theory data (DFT).

constants. In order to simulate the uniaxial stress response in the $\mathbf{e}_1$ direction, a stretch λ_1 is applied and the stretch λ_2 and shear strain γ are evaluated from the stress-free boundary conditions $\sigma_{22} = 0$ and $\sigma_{12} = 0$. In the density functional theory simulations, this corresponds to prescribing the unit cell lattice parameter $\mathcal{L}_{11}$ while allowing the atomic coordinates and the lattice parameters $\mathcal{L}_{12}$ and $\mathcal{L}_{22}$ to relax when minimizing the energy. The resulting plots of σ_{11} versus λ_1 from density functional theory and from the constitutive model are shown in Fig. 7(a) along with the plot obtained using Murnaghan's model. In Fig. 7(b), we plot the stress component σ_{22} as a function of the stretch λ_2 using the stress-free boundary conditions $\sigma_{11} = \sigma_{12} = 0$. Next, we investigate the shear response of graphene wherein the material is subjected to a shear strain γ , while it is free to expand or contract in the longitudinal and lateral directions. In the density functional theory simulations, the lattice parameters $\mathcal{L}_{11}$ and $\mathcal{L}_{22}$ are allowed to relax. In the case of the constitutive models, the shear strain γ is prescribed and the strain energy density W is minimized to obtain λ_1 and λ_2 . Figure 7(c) shows the variation of the shear stress σ_{12} as a function of the shear strain γ . As can be seen, the proposed constitutive model matches well with

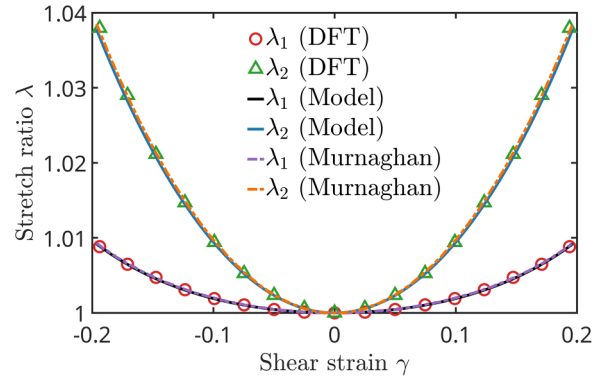


FIG. 10. Curves showing the stretches λ_1 and λ_2 induced from an applied shear strain for uniaxial shear stress states of graphene. The predictions of the constitutive model (Model) are compared with the density functional theory (DFT) data and the predictions of Murnaghan's constitutive model (Murnaghan).

the density functional theory data, demonstrating its predictive capability. Furthermore, the proposed constitutive model with seven elastic constants compares equally well with the density functional theory data as the fifth-order Murnaghan model that involves 14 linearly independent elastic constants.

The Poisson contractions/elongations for uniaxial stress states are presented in Fig. 8. Figure 8(a) shows the stretch ratio λ_2 obtained for an applied λ_1 using density functional theory along with the predictions of the proposed constitutive model and Murnaghan's model. Similarly, Fig. 8(b) shows the stretch ratio λ_1 obtained for an applied λ_2 . It is observed that the constitutive model accurately captures the Poisson's effects, even for large deformations.

To illustrate the significance of the anisotropic invariant $\mathcal{I}_{\text{aniso}}$, we plot σ_{11} versus λ_1 , and σ_{22} versus λ_2 , for uniaxial stress states in Fig. 9. It can be seen that the stress-stretch curves overlap for stretches in the range $0.95 \leq \lambda_i \leq 1.15$, indicating that the effect of $\mathcal{I}_{\text{aniso}}$ is not significant in this regime and that graphene acts almost as an isotropic material for moderate in-plane deformations. For larger stretches outside this range, the deformation-induced

TABLE V. Linearized elastic properties (Y , ν , and G), layer modulus (B), and longitudinal and transverse speed of sound (v_l and v_t) in graphene evaluated based on the proposed constitutive model and compared to values presented in the literature. The presented results are based on first-principles calculations, except those marked with a star * which are experimentally obtained. The symbol $\dagger$ is used to denote a shear modulus obtained from that of a carbon nanotube.

Source	Y (N/m)	ν	G (N/m)	B (N/m)	v_l (km/s)	v_t (km/s)
Current work	338.99	0.207	140.44	213.72	21.57	13.58
Reference [30]	342.30	0.178	145.30			
Reference [23]	348.00	0.169				
Reference [18]	350.70	0.186				
Reference [86]	347.1	0.18				
Reference [15]*	340 ± 50					
Reference [16]*			95.2 ± 12.24			
Reference [87]*, $\dagger$			139.4 ± 122.4			
Reference [50]	342.20	0.173	145.90	206.60		
Reference [88]*					19.90	12.90
Reference [89]					21.40	13.60

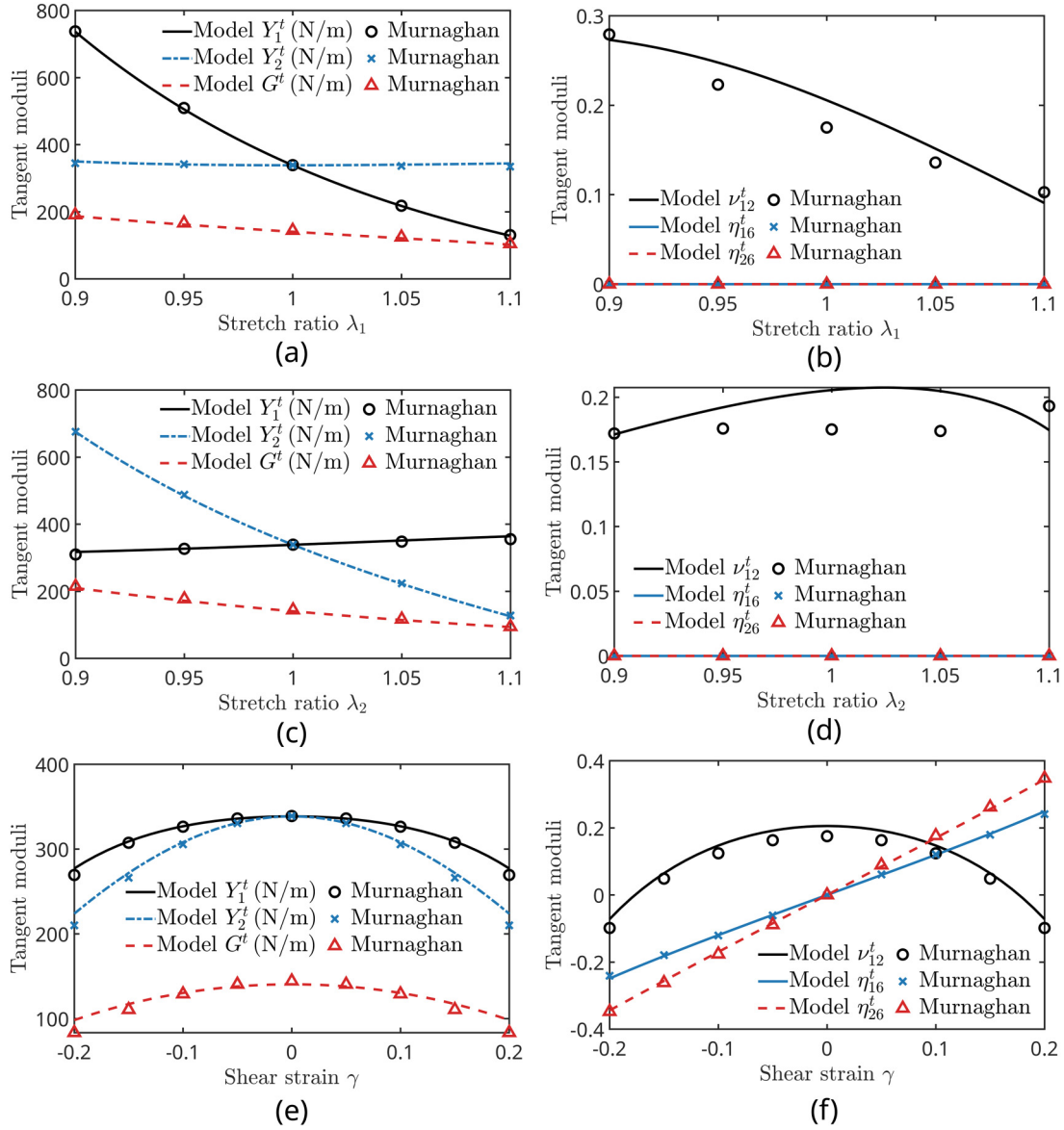


FIG. 11. The variation of the tangent elastic properties of graphene for uniaxial stress states as obtained using the proposed constitutive model (Model) and using Murnaghan's model (Murnaghan). (a) Young's moduli and shear modulus under uniaxial stress in the 1-direction. (b) Poisson's ratio ν_{12} and the coefficients of mutual influence under uniaxial stress in the 1-direction. (c) Young's moduli and shear modulus under uniaxial stress in the 2-direction. (d) Poisson's ratio ν_{12} and the coefficients of mutual influence under uniaxial stress in the 2-direction. (e) Young's moduli and shear modulus under shear stress. (f) Poisson's ratio ν_{12} and the coefficients of mutual influence under shear stress.

anisotropy becomes more significant and the curves begin to deviate.

We investigate the effects of the shear strain on the elongation or contraction in longitudinal and lateral directions when the material is free to expand in both directions. We minimize the strain energy density W for a prescribed shear strain γ in order to evaluate the corresponding stretches λ_1 and λ_2 . Figure 10 shows the stretches λ_1 and λ_2 induced in graphene from shear strains γ . It is found that a shear strain in graphene induces elongation in the longitudinal and lateral directions. The predictions of the constitutive model match well with Murnaghan's constitutive model and density functional theory. Therefore, the proposed constitutive model is able to

accurately capture the stretches induced by the shearing of a graphene sheet.

The tangent stiffness tensor of graphene is determined using the invariant-based constitutive model and Murnaghan's model employing Eq. (27) [cf. Eq. (31)] and Eq. (39), respectively. Subsequently, the tangent stiffness tensors, in Voigt notation, are inverted and the tangent elastic properties of graphene are evaluated using Eq. (33) and are presented in Fig. 11 for both the proposed constitutive model and Murnaghan's model. Figures 11(a) and 11(b) show the tangent elastic properties of graphene under uniaxial stress in the e_1 direction. Figures 11(c) and 11(d) show the tangent elastic properties of graphene under uniaxial stress in the e_2 direction.

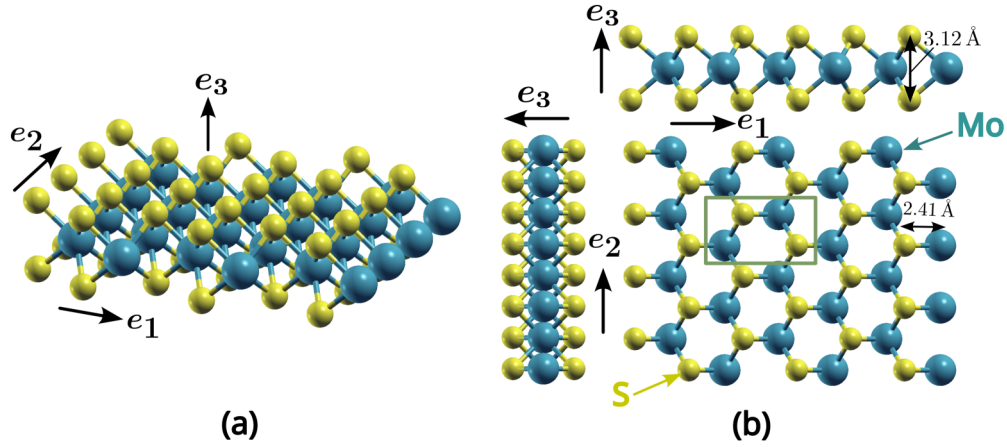


FIG. 12. Geometry of molybdenum disulfide. (a) Three-dimensional perspective view of the ground-state geometry of molybdenum disulfide along with the coordinate axes. (b) Projection views of the ground-state geometry of molybdenum disulfide on the coordinate planes. Rendering of the crystal done using XCRYSDEN [90].

Figures 11(e) and 11(f) show the tangent elastic properties of graphene under uniaxial in-plane shear stress conditions. It can be seen that the predictions of the constitutive model for the tangent moduli generally compare well with those of the Murnaghan model.

Graphene exhibits anisotropic elastic behavior when subjected to shear strains. This is observed by the coefficients of mutual influence being nonzero, as can be seen in Fig. 11(f). Therefore, a sheared graphene sheet exhibits extension-shear coupling (e.g., see [13]). Under uniaxial stress conditions in the e_i direction, we notice that Y_i^t decreases monotonically in tension. This shows that the material exhibits a softening behavior and could become unstable if Y_i reaches zero at larger stretches. Further stability studies can be carried out using the tangent stiffness tensor through the Born-Huang stability criterion [91] (e.g., see [51]) or using the acoustic tensor of the material (e.g., see [42]). The softening behavior is also observed when graphene is sheared [cf. Fig. 11(e)]. We note that the remaining tangent elastic properties which are not shown in the plots, namely, ν_{21}^t , η_{61}^t , and η_{62}^t , can be obtained using the symmetry of the tangent stiffness tensor [cf. Eq. (33)].

The Lamé constants of graphene obtained from the elastic constants in Table IV and Eq. (22) are $\zeta = 73.28$ N/m and $\mu = 140.44$ N/m. The linearized elastic properties of graphene are presented in Table V. As can be seen, the linearized elastic properties obtained in this work are in good agreement with those reported in the literature. The layer modulus B and longitudinal v_l and transverse v_t sound velocities in graphene, obtained using the elastic constants in the current work, are also presented in Table V and compared with values presented in the literature.

D. Molybdenum disulfide

Molybdenum disulfide is a hexagonal 2D material with three tightly bonded layers of atoms consisting of a layer of molybdenum atoms in-between two layers of sulfur atoms. The ground-state geometry of molybdenum disulfide, obtained using density functional theory, is shown in Fig. 12. The bond length between a sulfur atom and a molybdenum atom of 2.41 Å and the vertical distance between the sulfur layers of 3.12 Å are in good agreement with the values reported using density functional theory in [92]. The projected view of molybdenum disulfide in the e_1 - e_2 plane consists

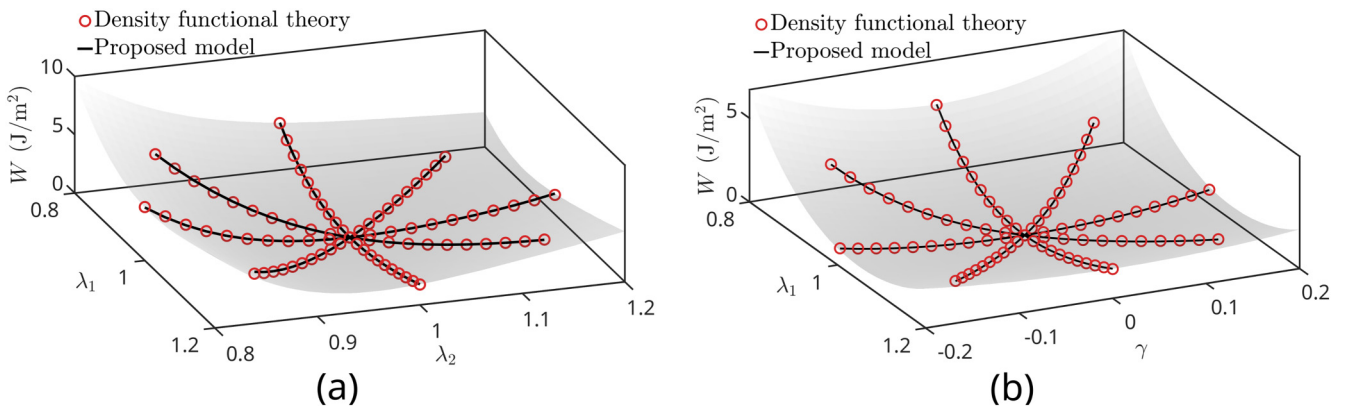


FIG. 13. Strain energy density landscapes of molybdenum disulfide as a function of the stretches and shear strain; the strain energy data obtained from density functional theory is compared to the predictions of the proposed constitutive model. (a) Strain energy density landscape as a function of the stretches λ_1 and λ_2 . (b) Strain energy density landscape as a function of the stretch λ_1 and the shear strain γ .

TABLE VI. Elastic constants of hexagonal molybdenum disulfide for the proposed constitutive model.

Elastic constant	Value
D (N/m)	18.02
β	1.54
C_0 (N/m)	22.56
C_1 (N/m)	-125.47
C_2 (N/m)	331.62
A_0 (N/m)	20.48
A_1 (N/m)	-107.18

of regular hexagons of alternating molybdenum and sulfur atoms. We use the unit cell shown in green in Fig. 12(b) for the analysis of molybdenum disulfide. The unit cell is orthogonal with lattice parameters $\mathcal{L}_{11}^0 = 5.52 \text{ \AA}$ and $\mathcal{L}_{22}^0 = 3.18 \text{ \AA}$ and consists of two molybdenum atoms and four sulfur atoms. It is noted that the $\mathbf{e}_1$ direction shown in Fig. 12 corresponds to molybdenum disulfide's armchair direction and the $\mathbf{e}_2$ direction corresponds to the zigzag direction. We note that the symmetry group of monolayer molybdenum disulfide is D_{3h} (e.g., see [93]) since the plane parallel to the $\mathbf{e}_1$ - $\mathbf{e}_2$ plane passing through the layer of molybdenum atoms is a plane of symmetry. However, since we are considering exclusively the in-plane elastic response of molybdenum disulfide, its two-dimensional symmetry class is C_{3v} (e.g., see [55]). The mass density per unit area of molybdenum disulfide, which is used to compute the sound velocity in molybdenum disulfide,

is given by

$$\rho = \frac{4m_S + 2m_{Mo}}{\mathcal{L}_{11}^0 \mathcal{L}_{22}^0} = 3.03 \times 10^{-6} \text{ kg/m}^2, \quad (49)$$

where $m_S = 5.325 \times 10^{-26} \text{ kg}$ is the atomic mass of sulfur, $m_{Mo} = 1.593 \times 10^{-25} \text{ kg}$ is the atomic mass of molybdenum, the factors 4 and 2 represent the number of sulfur and molybdenum atoms in the unit cell, respectively, and the product $\mathcal{L}_{11}^0 \mathcal{L}_{22}^0$ is the ground-state area of the unit cell.

The elastic constants of molybdenum disulfide are evaluated using the procedure outlined in Sec. V and are listed in Table VI. Although not reported, the convergence of the elastic constants of molybdenum disulfide is assessed as in the case of graphene. The root-mean-square error in the curve fit to obtain the elastic constants presented in Table VI is 0.0230 J/m^2 .

Figure 13 shows the strain energy landscapes for biaxial stretch, and simultaneous stretch λ_1 and shear strain γ . As can be seen, the predictions of the constitutive model compare well with the density functional theory data used for curve fitting.

The variation of the Cauchy stress of molybdenum disulfide as a function of the stretches λ_i and the shear strain γ is shown in Fig. 14 for uniaxial stress states. As can be seen, the proposed model accurately predicts the density functional theory data with minor discrepancies for large deformations. The predictions of the proposed model also compare generally well with the predictions of the Murnaghan model.

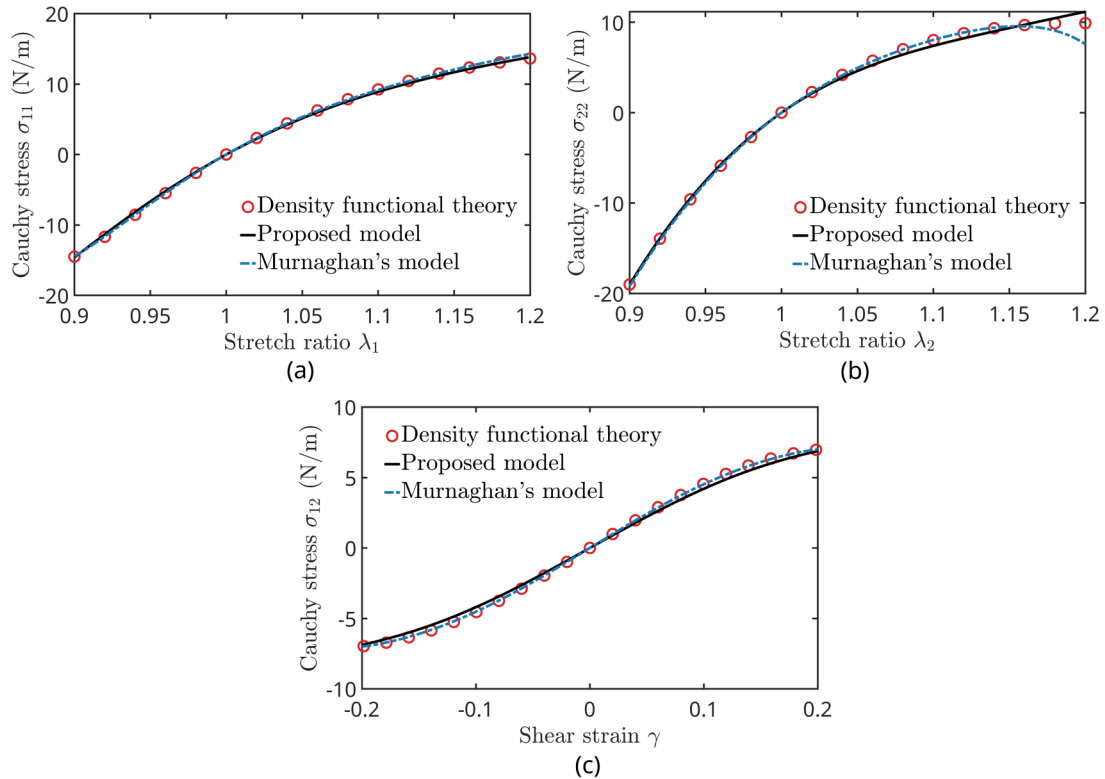


FIG. 14. Plots of the Cauchy stress vs stretch and shear strain. (a) Normal stress σ_{11} as a function of the stretch λ_1 . (b) Normal stress σ_{22} as a function of the stretch λ_2 . (c) Shear stress σ_{12} as a function of the shear strain γ . Stretch ratios λ_1 or λ_2 of 1.0 correspond to the undeformed state.

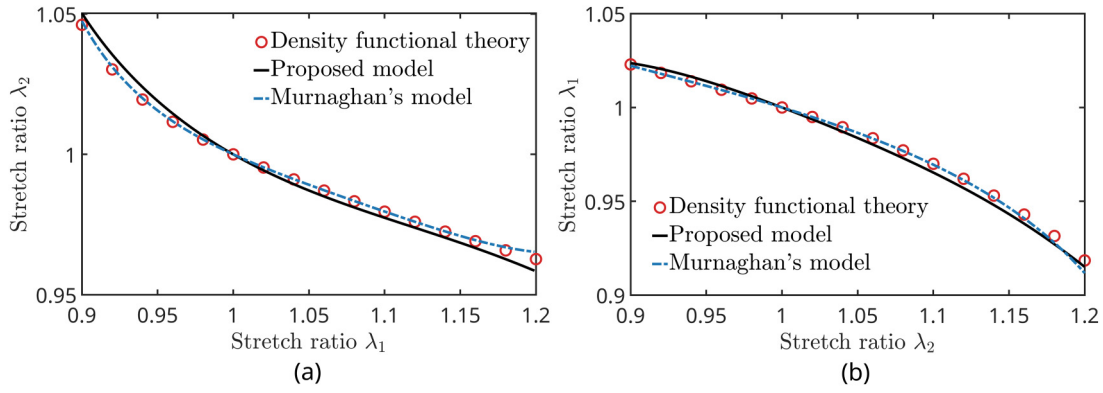


FIG. 15. Variation of the stretches induced by the Poisson's effect in molybdenum disulfide as a function of the applied stretches, as obtained by the proposed constitutive model and Murnaghan's model, in comparison with the density functional theory data. (a) Stretch λ_2 caused by an applied λ_1 when $\sigma_{22} = 0$. (b) Stretch λ_1 caused by an applied λ_2 when $\sigma_{11} = 0$.

The contraction/elongation curves due to the Poisson's effect in molybdenum disulfide are shown in Fig. 15. Some minor discrepancies exist between the predictions of the constitutive model and the density functional theory data. These discrepancies can be remedied by using a higher-order constitutive model that includes additional elastic constants. The Murnaghan model with its 14 elastic constants compares better with the density functional theory data, although it also exhibits some minor discrepancies for large stretches.

The stress versus stretch curves, σ_{11} vs λ_1 and σ_{22} vs λ_2 , for uniaxial stress states are plotted in Fig. 16. The curves overlap only in a narrow range of $0.97 \leq \lambda \leq 1.02$, where molybdenum disulfide acts almost as an isotropic material. The curves do not overlap outside this range since the deformation-induced anisotropy is more pronounced than in the case of graphene. The anisotropic effects in molybdenum disulfide become apparent even at relatively small stretches, beginning at $\lambda = 1.02$.

Figure 17 shows the stretches λ_1 and λ_2 induced in molybdenum disulfide due to shear strains γ when the material is free to expand in the longitudinal and lateral directions. As can be seen in the figure, the predictions of the constitutive model capture the density functional theory behavior with minor

differences. Murnaghan's model with its 14 elastic constants more accurately captures the stretches induced by the shear deformations.

The tangent elastic properties of molybdenum disulfide for uniaxial stress boundary conditions are presented in Fig. 18. It can be seen in the figure that the predictions of the proposed model compare well with those of Murnaghan's model. Similar softening behavior can be observed as in the case of graphene. Furthermore, molybdenum disulfide exhibits an anisotropic elastic behavior when subjected to shear strains, as in the case of graphene.

The Lamé constants of molybdenum disulfide obtained from the elastic constants in Table VI and Eq. (22) are $\zeta = 40.35$ N/m and $\mu = 45.12$ N/m. The linearized elastic properties of molybdenum disulfide, presented in Table VII, are in good agreement with values published in the literature. The layer modulus B and longitudinal v_l and transverse v_t sound velocities in molybdenum disulfide, obtained using the elastic constants in the current work, are also presented in Table VII and compared with values presented in the literature.

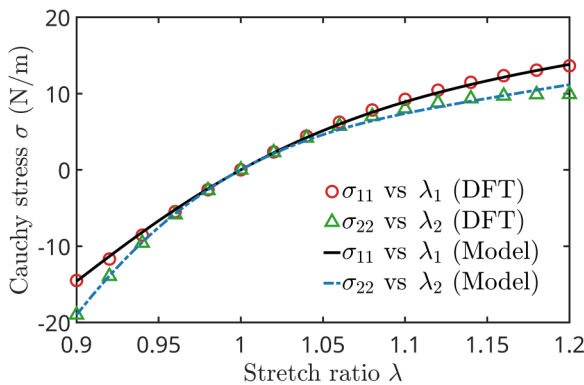


FIG. 16. Comparison of the nonlinear normal Cauchy stress vs stretch curves of molybdenum disulfide in the $\mathbf{e}_1$ and $\mathbf{e}_2$ directions. The predictions of the proposed constitutive model (Model) are presented alongside the density functional theory data (DFT).

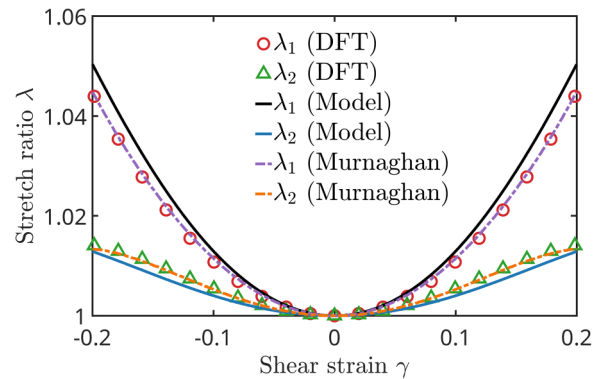


FIG. 17. Curves showing the stretches λ_1 and λ_2 induced from an applied shear strain when molybdenum disulfide is free to expand in the longitudinal and lateral directions. The predictions of the constitutive model (Model) are compared with the density functional theory (DFT) data and the predictions of Murnaghan's constitutive model (Murnaghan).

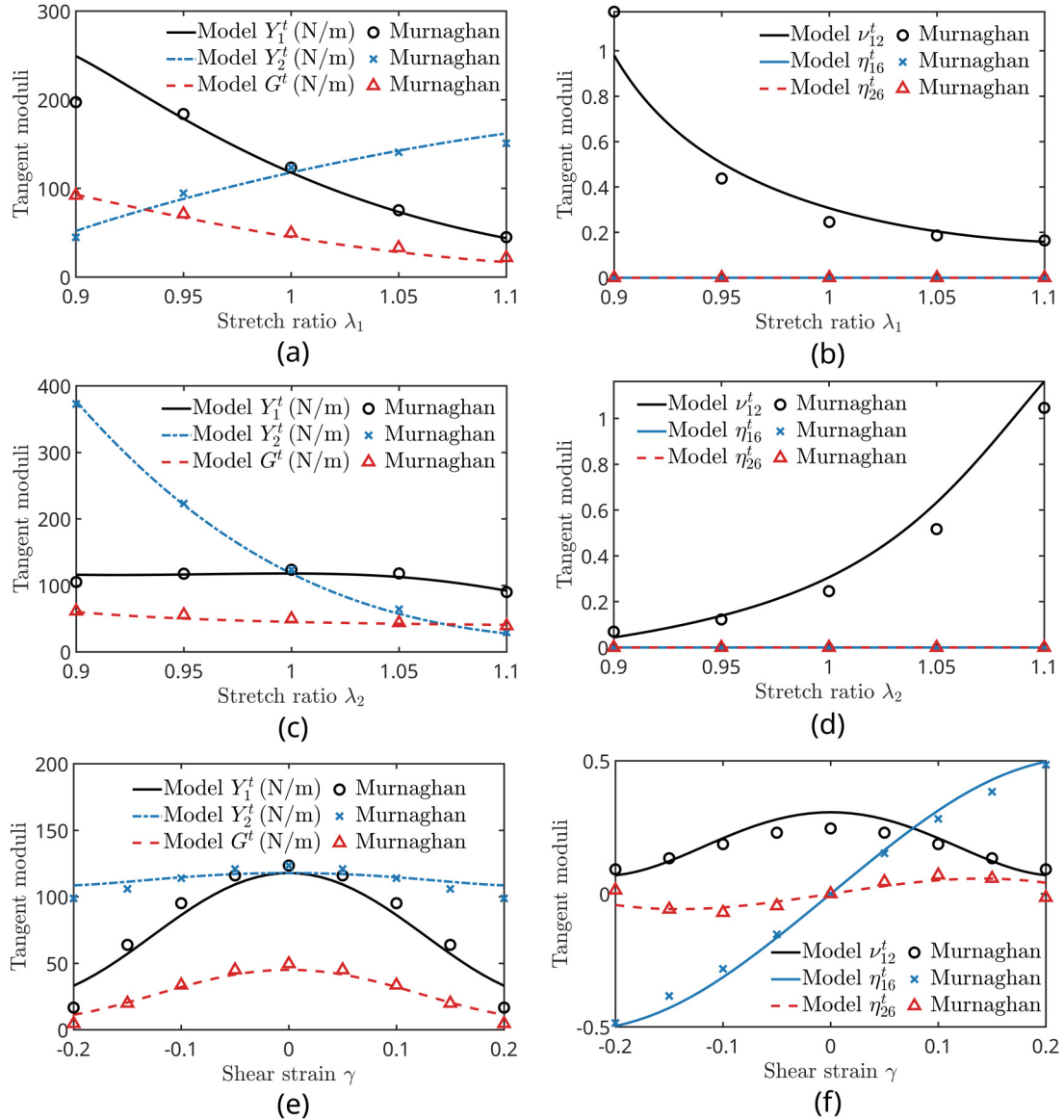


FIG. 18. The variation of the tangent elastic properties of molybdenum disulfide for uniaxial stress states as obtained using the proposed constitutive model (Model) and using Murnaghan's model (Murnaghan). (a) Young's moduli and shear modulus under uniaxial stress in the 1-direction. (b) Poisson's ratio ν_{12} and the coefficients of mutual influence under uniaxial stress in the 1-direction. (c) Young's moduli and shear modulus under uniaxial stress in the 2-direction. (d) Poisson's ratio ν_{12} and the coefficients of mutual influence under uniaxial stress in the 2-direction. (e) Young's moduli and shear modulus under shear stress. (f) Poisson's ratio ν_{12} and the coefficients of mutual influence under shear stress.

VII. SUMMARY AND CONCLUSIONS

A hyperelastic constitutive model is proposed for hexagonal 2D materials. New dilatational, deviatoric, and anisotropic invariants are introduced to separate the effects of area-changing deformations, shape-changing deformations, and deformation-induced anisotropy for large deformations, respectively. The strain energy density of 2D materials is expressed in terms of the newly proposed invariants, and expressions for the second Piola-Kirchhoff stress tensor are derived. The newly defined invariants and general expressions for the strain energy density and stress tensors are expected to be applicable to arbitrary 2D materials of hexagonal symmetry. A specific form of the strain energy function is proposed

for hexagonal 2D materials wherein the dependence of the strain energy on dilatation is captured by the Varshni potential. There are a total of seven elastic constants in the final form of the proposed constitutive model. General expressions for the tangent stiffness tensor are presented in terms of the new invariants and the Green–St. Venant strain tensor. Furthermore, expressions for the linearized elastic properties are obtained in terms of the elastic constants of the constitutive model.

A methodology is presented for the systematic evaluation of the elastic constants for hexagonal 2D materials. It is based on evaluating the strain energy densities using density functional theory along rays in deformation space and then curve fitting the constitutive model to obtain the elastic constants. Using the methodology, the elastic constants of graphene and

TABLE VII. Linearized elastic properties (Y , ν and G), layer modulus (B), and longitudinal and transverse speed of sound (v_l and v_t) in molybdenum disulfide evaluated based on the proposed constitutive model and compared to values presented in the literature. The results presented are based on first-principles calculations, except those marked with a star * which are experimentally obtained.

Source	Y (N/m)	ν	G (N/m)	B (N/m)	v_l (km/s)	v_t (km/s)
Current work	118.12	0.309	45.12	85.47	6.56	3.86
Reference [17]	129	0.29				
Reference [14]	123.07	0.28	48.6			
Reference [86]	124.1	0.25				
Reference [94]	124.5	0.25				
Reference [95]	120.1	0.254				
Reference [96]*	180 ± 60					
Reference [17]*	120 ± 30					
Reference [51]	126.5	0.216	52.05	80.65	6.61	4.14
Reference [97]					6.60	4.30

molybdenum disulfide are evaluated over the spherical region of radius 0.2 in deformation space. Subsequently, we study the nonlinear elastic behavior of the materials under uniaxial stress conditions to validate the constitutive model. It is found that the predictions of the constitutive model for the strain energy density, stresses, and the stretches due to Poisson effects are in good agreement with the density functional theory data. Furthermore, the accuracy of the proposed model is comparable to that of a fifth-order Murnaghan model with 14 linearly independent elastic constants.

The proposed constitutive model provides relations for the strain energy density and the second Piola-Kirchhoff stress in terms of the Green–St. Venant strain tensor and its associated invariants. The formulation, including the methodology for determining the elastic constants, is applicable to large deformations. Due to its generality, the proposed constitutive model can be readily applied to a broad class of hexagonal 2D materials.

ACKNOWLEDGMENTS

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DATA AVAILABILITY

The data that support the findings of this article are not publicly available. The data are available from the authors upon reasonable request.

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