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A micromorphic model for monolayer hexagonal boron nitride with determined constitutive constants by phonon dispersions

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ABSTRACT

A two dimensional (2D) micromorphic model is developed for monolayer hexagonal boron nitride (h-BN). Theoretical expressions of phonon dispersions for 2D crystals are derived based on the simplified governing equations of specialized three dimensional micromorphic crystals. The constitutive constants of governing equations of the h-BN micromorphic model are determined, which is performed by fitting the available phonon dispersions data of experimental measurements and first-principles calculations with our theoretical expressions. The obtained Young's modulus and Poisson's ratio of h-BN are comparable with the results of *ab initio* calculations and inelastic x-ray scattering experiments, thus the constitutive relations of the h-BN model are verified, which also indicates that mechanical properties of monolayer h-BN could be characterized by our 2D micromorphic model.

1. Introduction

For potential applications of atomically thin two dimensional (2D) crystals, e.g. graphene and monolayer hexagonal boron nitride (h-BN), in nanoelectromechanical systems and sturdy lightweight composite materials [1,2] and nanoscale dielectric capacitors [3,4] etc., their mechanical behaviors have triggered enthusiasm of researchers [5–10]. With the strong covalent sp^2 bonds [11–13] in 2D networks, the in-plane mechanical strength and thermal conductivity of h-BN are close to those of graphene [14]. However, micro-continuum models of monolayer h-BN are seldom reported in literatures as the discrete nature of material particles is neglected in classical continuum theory, whereas the effect of discrete structure is significantly important for polar materials. Peng et al. [10] ever presented a continuum method to describe the elastic properties of monolayer h-BN through density functional theory calculations, and their model is formulated by expanding strain energy density in a Taylor series of strain truncated after the fifth-order term, however, this leads to fourteen non-zero independent constants. Unfortunately, continuum model with too many undetermined constants is limited for its broad applications. Aiming to establish a concise continuum model of monolayer h-BN, we will propose another novel approach based on classic micromorphic theory [15,16].

Micromorphic theory, as a sub-branch of micro-continuum field theory, supposes that a material body was a continuous collection of many deformable particles of finite sizes, in which the primitive cell of a solid crystal or its equivalent unit cell can be taken as a deformable particle. Moreover, micromorphic theory has dramatically extended the application of classical continuum theory in micro-scales for the consideration of additional micro-structure and micro-motion of particle units [17]. Chen et al. [18] ever proposed a specialized micromorphic theory for covalent and ionic crystals without external rotational modes (molecules move as rigid units), which is promising for seizing the mechanical properties of 2D crystals. Continuum models of solid crystals including single crystal diamond and silicon by utilizing the specialized micromorphic theory have been constructed [18], while micromorphic model of monolayer h-BN has not been reported yet.

The constitutive constants of micromorphic models should be determined for its realistic applications. Evidently, traditional experimental measurements are inefficient here since the internal-motions of deformable micro-particles are not considered. As another hint, phonon dispersion relations of atoms, which describe the vibration properties in the primitive cell of crystals, have linked the inter-atomic forces to the constitutive relations of continuum model [19]. The vibrations of atoms can be vividly described by acoustic and optical phonons in lattice dynamics. The atoms of the unit cell move essentially in the same phase, which leads to homogeneous deformations of lattice under acoustic type vibrations, while the atoms move contrarily out of phase within

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the cell, which results in the internal deformations under optical type vibrations. Therefore, the constitutive constants of h-BN micromorphic model can be alternately determined by analyzing their phonon dispersion relations.

Hereafter, a 2D micromorphic model of monolayer h-BN will be constructed, and its constitutive constants of governing equations are determined by analyzing available experimental and theoretical phonon dispersions. The detailed governing equations of our h-BN micromorphic model are given lastly.

2. Governing equation and its simplification

The governing equations for specialized three dimensional micromorphic crystals can be expressed in the macro-displacement u_p and micro-strain φ_{pq} of the deformable particle in global coordinates as [20]:

$$\rho\,\ddot{u}_p = a_1 u_{m,mp} + a_2(u_{p,qq}+u_{q,pq}) + (c_1-a_1)\varphi_{mm,p} + 2(c_2-a_2)\varphi_{pq,q}, \tag{1}$$

$$\begin{aligned}\rho\, j\ddot{\varphi}_{pq} = {} & (a_2-c_2)(u_{p,q}+u_{q,p}) + (a_1-c_1)\delta_{pq}u_{m,m} \\ & + (2c_1-a_1-b_1)\delta_{pq}\varphi_{mm} + 2(2c_2-a_2-b_2)\varphi_{pq} \\ & + 2d_1(\varphi_{nn,pq}+\delta_{pq}\varphi_{rn,rn}) + 4d_2(\varphi_{pn,qn}+\varphi_{qn,pn}) + d_3\delta_{pq}\varphi_{nn,rr} \\ & + 2d_4\varphi_{pq,rr},\end{aligned} \tag{2}$$

where ρ is the mass density, j the micro-inertia density, and a_1, a_2, b_1, b_2, c_1, c_2, d_1, d_2, d_3 and d_4 are ten undetermined constitutive constants. For 2D crystals, each index in Eqs. (1) and (2) should be 1 or 2. The number of the undetermined constants could be reduced if one considers the links between the governing equations and phonon dispersion relations of 2D micromorphic model [20]. Therefore, the constitutive relations of 2D micromorphic model are derived as:

$$T_{\alpha\beta} = a_1\delta_{\alpha\beta}(\varepsilon_{mm}+\varphi_{mm}) + a_2(\varepsilon_{\alpha\beta}+\varepsilon_{\beta\alpha}) + 2c_2\varphi_{\alpha\beta}, \tag{3}$$

$$S_{\alpha\beta} = a_1\delta_{\alpha\beta}(\varepsilon_{mm}+\varphi_{mm}) + c_2(\varepsilon_{\alpha\beta}+\varepsilon_{\beta\alpha}) + 2b_2\varphi_{\alpha\beta}, \tag{4}$$

$$\begin{aligned}M_{\lambda\alpha\beta} = {} & d_1(\delta_{\lambda\alpha}\gamma_{\beta nn}+\delta_{\lambda\beta}\gamma_{\alpha nn}+2\delta_{\alpha\beta}\gamma_{n\lambda n}-2\delta_{\alpha\beta}\gamma_{\lambda nn}) \\ & + 2d_2(\delta_{\lambda\alpha}\gamma_{n\beta n}+\delta_{\lambda\beta}\gamma_{n\alpha n}) + 2d_2(\gamma_{\beta\lambda\alpha}+\gamma_{\alpha\lambda\beta}) + 2d_4\gamma_{\lambda\alpha\beta},\end{aligned} \tag{5}$$

where $T_{\alpha\beta}$ is the Cauchy stress, $S_{\alpha\beta}$ the average micro-stress, $M_{\lambda\alpha\beta}$ the moment stress, $\varepsilon_{\alpha\beta}$ the macro-strain (relative strain), and $\gamma_{\lambda\alpha\beta}$ the micro-strain gradient, in which only seven undetermined constants remain.

3. Phonon dispersion relations of 2D crystals

3.1. Phonon dispersions of specialized 2D micromorphic crystals

On the assumption of crystals without external rotational modes, there are total nine branches of phonon dispersion relations [18], of which five branches are in-plane modes. Namely, two acoustic modes, i.e. LA and TA waves, are associated with the macro-displacements u_1 and u_2; three optical modes, i.e. LO_1, LO_2 and TO waves, have relevance to the micro-deformations φ_{11}, φ_{22} and φ_{12} (φ_{21}).

It is assumed that harmonic waves propagate along the x (or y) direction, which can be expressed as

$$u_\alpha = iU_\alpha\exp(ikx-i\omega t), \quad \varphi_{\alpha\beta} = \Phi_{\alpha\beta}\exp(ikx-i\omega t) \tag{6}$$

Thus, the secular equations of the in-plane phonon dispersion relations of 2D micromorphic models can be obtained and grouped as:

(1) LA, LO_1 and LO_2

$$\begin{vmatrix} A_{11}k^2-\rho\omega^2 & A_{12}k & A_{13}k \\ A_{12}k & A_{22}k^2+B_{22}-\rho j\omega^2 & A_{23}k^2+B_{23} \\ A_{13}k & A_{23}k^2+B_{23} & A_{33}k^2+B_{33}-\rho j\omega^2 \end{vmatrix} \begin{vmatrix} U_1 \\ \Phi_{11} \\ \Phi_{22} \end{vmatrix} = 0, \tag{7}$$

(2) TA, TO

$$\begin{vmatrix} \bar{A}_{11}k^2-\rho\omega^2 & \bar{A}_{12}k \\ \bar{A}_{12}k & \bar{A}_{22}k^2+\bar{B}_{22}-2\rho j\omega^2 \end{vmatrix} \begin{vmatrix} U_2 \\ \Phi_{12} \end{vmatrix} = 0, \tag{8}$$

where

$$\begin{aligned} & A_{11}=a_1+2a_2,\ A_{12}=a_1+2a_2-c_1-2c_2,\ A_{13}=a_1-c_1, \\ & A_{22}=4d_1+8d_2+d_3+2d_4,\ A_{23}=2d_1+d_3,\ A_{33}=d_3+2d_4, \\ & B_{22}=B_{33}=a_1+2a_2+b_1+2b_2-2c_1-4c_2,\ B_{23}=a_1+b_1-2c_1, \\ & \bar{A}_{11}=a_2,\ \bar{A}_{12}=2(a_2-c_2),\ \bar{A}_{22}=8d_2+4d_4,\ \bar{B}_{22}=4(a_2+b_2-2c_2), \end{aligned} \tag{9}$$

3.2. 2D Brillouin zone of monolayer h-BN

Monolayer h-BN crystal is made up of alternating boron and nitrogen atoms arranged in planar hexagonal structure, and its 2D Brillouin zone (BZ) is represented by its primitive cell in Fig. 1. With reciprocal lattice vectors $\boldsymbol{b}_1$ and $\boldsymbol{b}_2$ defined in terms of the real lattice unit vectors $\boldsymbol{a}_1$ and $\boldsymbol{a}_2$ by the relationship $\boldsymbol{b}_\alpha \times \boldsymbol{a}_\beta = 2\pi\delta_{\alpha\beta}$ [21] in Fig. 1, we can obtain the coordinates of points M, K' as

$$M = \frac{2\pi}{a_0}\left(\frac{\sqrt{3}}{3}, 0\right), \quad K' = \frac{2\pi}{a_0}\left(\frac{\sqrt{3}}{3}, \frac{1}{3}\right),$$

where a_0 is the lattice constant of monolayer h-BN. For abundant data of phonon dispersions on the high-symmetry directions of Γ–$M(x)$, Γ–$K(y)$ used in fitting procedure afterwards, the lengths of ΓM and ΓK defined under the framework of phonon wave vector $(2\pi/a_0)$ could be determined.

3.3. Phonon dispersion relations of monolayer h-BN

It is known that a continuum is isotropic when it has third order axial symmetry under the condition of small deformations [22]. Thus, monolayer h-BN in Fig. 2a can be taken as an isotropic continuum since its lattice satisfies the symmetry. Therefore, Eqs. (7) and (8) are applicable for monolayer h-BN. Furthermore, the rhombic basal element in Fig. 2b is taken as the basal element

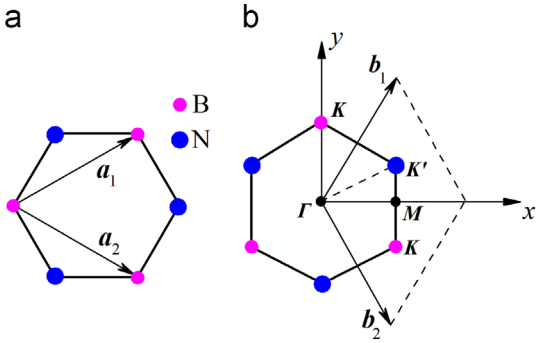

Fig. 1. The hexagonal structure and Brillouin zone of monolayer h-BN. (a) The real lattice unit vectors $\boldsymbol{a}_1$ and $\boldsymbol{a}_2$ in the primitive cell. (b) The reciprocal lattice vectors $\boldsymbol{b}_1$ and $\boldsymbol{b}_2$ in 2D Brillouin zone. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)