Elastic Properties of 2D Materials: Theory and Computation

I. DEFINITION AND CONVERSION OF CRYSTAL STRCUTURES

Crystal structures are described using basis vectors and point coordinates of labeled atoms. Lattice basis vectors $\mathbf{A}$ are represented by three row vectors

$$\mathbf{A} = \begin{bmatrix} \mathbf{a} \\ \mathbf{b} \\ \mathbf{c} \end{bmatrix} = \begin{bmatrix} a_x & a_y & a_z \\ b_x & b_y & b_z \\ c_x & c_y & c_z \end{bmatrix}. \tag{1}$$

The position of an atom is represented by a row vector either in fractional coordinates (x, y, z), relative to the basis vector lengths, or in Cartesian coordinates (X, Y, Z). The relationship between these two coordinate systems is given by

$$\begin{bmatrix} X \\ Y \\ Z \end{bmatrix} = \mathbf{A}^T \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} a_x & b_x & c_x \\ a_y & b_y & c_y \\ c_z & b_z & c_z \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix}, \tag{2}$$

where $\mathbf{A}^T$ denotes the matrix transpose of lattice basis vectors $\mathbf{A}$.

The conversion from one lattice basis $(\mathbf{a}, \mathbf{b}, \mathbf{c})$ to another choice of lattice basis $(\mathbf{a}', \mathbf{b}', \mathbf{c}')$ is given by

$$\begin{bmatrix} \mathbf{a}' \\ \mathbf{b}' \\ \mathbf{c}' \end{bmatrix} = \mathbf{M} \cdot \begin{bmatrix} \mathbf{a} \\ \mathbf{b} \\ \mathbf{c} \end{bmatrix}, \tag{3}$$

where $\mathbf{M}$ is the transformation matrix. Its determinant $|\mathbf{M}|$ defines the ratio between the supercell (SC) and primitive unit cell (PUC) volumes in the real space.

II. ELASTIC MECHANICS

Within the linear elastic region, where stress and strain are linearly related, the stress response $\sigma = (\sigma_1, \sigma_2, \sigma_3, \sigma_4, \sigma_5, \sigma_6) \equiv (\sigma_{xx}, \sigma_{yy}, \sigma_{zz}, \sigma_{yz}, \sigma_{xz}, \sigma_{xy})$ of a solid to an external loading strain $\varepsilon = (\varepsilon_1, \varepsilon_2, \varepsilon_3, \varepsilon_4, \varepsilon_5, \varepsilon_6) \equiv (\varepsilon_{xx}, \varepsilon_{yy}, \varepsilon_{zz}, 2\varepsilon_{yz}, 2\varepsilon_{xz}, 2\varepsilon_{xy})$ follows the generalized Hooke's law. This relationship can be conveniently expressed using Voigt notation:

$$\sigma_i = \sum_{j=1}^{6} C_{ij} \varepsilon_j, \tag{4}$$

C_{ij} is a second-order elastic constant (stiffness) tensor represented as a 6×6 symmetric matrix in units of GPa, kbar, or N/m^2. Second-order elastic constants play a crucial role in determining a material's mechanical and dynamical properties, particularly its stability and stiffness. The C_{ij} tensor can be determined from the first-order derivative of the stress-strain curves (within the linear elastic region). The number of independent elastic constants depends on the crystal symmetry: the lower the symmetry, the greater the number of independent elastic constants.

An alternative theoretical approach to calculating elastic constants involves analyzing energy variations resulting from small strains applied to the equilibrium lattice configuration. This method expands the potential energy surface as a function of long-wavelength acoustic modes, where all atoms move in the same direction. Under the harmonic approximation, the elastic energy $\Delta E(V, \{\varepsilon_i\})$ of a solid is given by:

$$\Delta E(V, \{\varepsilon_i\}) = E(V, \{\varepsilon_i\}) - E(V_0, 0) = \frac{V_0}{2} \sum_{i,j=1}^{6} C_{ij} \varepsilon_j \varepsilon_i, \tag{5}$$

where $E(V_0, 0)$ and $E(V, \{\varepsilon_i\})$ are the total energies of the equilibrium and distorted lattice cells, with the volume of V_0 and V, respectively. In general, the stress-strain method requires higher computational precision to achieve the same accuracy as the energy-strain method [1].

When a crystal is deformed by applying strain ε, the relation of lattice vectors between the distorted and equilibrium cells is given by

$$\begin{bmatrix} \mathbf{a'} \\ \mathbf{b'} \\ \mathbf{c'} \end{bmatrix} = (I + \varepsilon) \cdot \begin{bmatrix} \mathbf{a} \\ \mathbf{b} \\ \mathbf{c} \end{bmatrix}. \tag{6}$$

where I is the 3×3 identity matrix. The strain tensor ε is defined by (matrix notation)

$$\varepsilon = \begin{bmatrix} \varepsilon_1 & \varepsilon_6/2 & \varepsilon_5/2 \\ \varepsilon_6/2 & \varepsilon_2 & \varepsilon_4/2 \\ \varepsilon_5/2 & \varepsilon_4/2 & \varepsilon_3 \end{bmatrix}. \tag{7}$$

III. ELASTICITY in 2D MATERIALS

When dealing with 2D materials, assuming the crystal lies in the xy plane, the relationship between strain and stress can be expressed as follows:

$$\begin{bmatrix} \sigma_1 \\ \sigma_2 \\ \sigma_6 \end{bmatrix} = \begin{bmatrix} C_{11} & C_{12} & C_{16} \\ C_{21} & C_{22} & C_{26} \\ C_{61} & C_{62} & C_{66} \end{bmatrix} \cdot \begin{bmatrix} \varepsilon_1 \\ \varepsilon_2 \\ \varepsilon_6 \end{bmatrix} \tag{8}$$

where C_{ij} ($i, j = 1, 2, 6$) is the in-plane stiffness tensor.

The strain-tensor ε in Eq. (7) is simplified as

$$\varepsilon^{2D} = \begin{bmatrix} \varepsilon_1 & \varepsilon_6/2 & 0 \\ \varepsilon_6/2 & \varepsilon_2 & 0 \\ 0 & 0 & 0 \end{bmatrix} \tag{9}$$

Then the elastic strain energy per unit area based on the strain-energy method can be expressed as

$$\Delta E(S, \{\varepsilon_i\}) = \frac{d_0 S_0}{2}(C_{11}\varepsilon_1^2 + C_{22}\varepsilon_2^2 + 2C_{12}\varepsilon_1\varepsilon_2 + 2C_{16}\varepsilon_1\varepsilon_6 + 2C_{26}\varepsilon_2\varepsilon_6 + C_{66}\varepsilon_6^2), \tag{10}$$

where the S_0 is the equilibrium area of the system and d_0 represents the effective thickness of the layer. Clearly, the C_{ij} is equal to the second partial derivative of strain energy ΔE with respect to strain ε, namely $C_{ij} = (1/d_0 S_0)(\partial^2 \Delta E/\partial \varepsilon_i \partial \varepsilon_j)$. Therefore, the unit of elastic stiffness tensor for 2D materials is force per unit length (N/m)

To compute the Poisson ratio ν and Young modulus Y for 2D materials, we have:

$$\nu^{2D} = \frac{C_{12}}{C_{11}} \tag{11}$$

$$Y^{2D} = \frac{C_{11}^2 - C_{12}^2}{C_{11}}. \tag{12}$$

To compute Eqs. 11 and 12, normal strains (compressive and tensile) are required. These strains are associated with C_{11} (strain in the x-direction), C_{22} (strain in the y-direction), and C_{12} (xy-biaxial strain). It is important to note that when a biaxial strain is applied, C_{11}, C_{22}, and C_{12} coexist. In Eq. 10, the first three terms contribute to energy variations as a function of `normal strain`, while the last three terms correspond to `shear strain effects`.

IV. COMPUTATIONAL APPROACH

To obtain ν^{2D} and Y^{2D} for a 2D system:

(1) A standard conventional cell needs to be adopted in the following calculations since the components of C_{ij} are dependent on the choice of the coordinate system and lattice vectors (the lattice vectors should be perpendicular).

(2) The minimum-energy cell data are first derived. For 2D materials, in order to avoid mirror interaction the periodic slabs are required to separated by sufficiently large vaccum layer in c direction.

(3) The space group number and the type of input structure can be analyzed to determine how many independent elastic constants need to be calculated. The system is then strained, preserving as much crystal symmetry as possible, in order to extract corresponding stiffness values. We suggest up to 10% strain.

(4) The elastic energies are calculated for each distorted structure. We use Hotbit code. Several strain magnitudes are applied for each strain type, giving an energy parabola.

(5) Fit $y = ax^2 + b$ curve to the data. y and x represent energy and strain. It calculates the second derivative at the equilibrium of energy with respect to the strain. The elastic stiffness values can be extracted from a value. Only simple arithmetic computations! However, the magnitude of stiffness appropriate for the type of strain is then derived from the curvature of the parabola.

[1] Y. Le Page and P. Saxe, Symmetry-general least-squares extraction of elastic coefficients from ab initio total energy calculations, Phys. Rev. B **63**, 174103 (2001).