A Theoretical Framework of Elastic, Thermo-Physical Properties of the Monolayer Stanene

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Abstract: In the 2D materials family, stanene has drawn a specific interest because of its remarkable exhibitions and properties. Stanene is one of the most active areas of nanomaterials research due to their potential for integration into next-generation electronic. Using many body interactions that lead to bond charge model, the elastic, thermo-physical, and Debye temperature variations of monolayer stanene were investigated. The elasticity is a fundamental property of crystalline materials and is of great importance in physical science, including materials science, solid state physics and chemistry, geological sciences. Elastic constants such as Young's modulus, Poisson's ratio, bulk modulus and shear modulus have also been calculated. With the help of Elastic constants, the values longitudinal and transverse sound velocities also have been computed. Various studies of single layer stanene have been carried out to investigate the phonon properties and Phonon Density of States, however, other thermo physical properties such as heat capacity and Grüneisen parameter have been neglected. In this research paper, a comprehensive study on heat capacity and Grüneisen parameter is performed by Python program and all the above mention properties are equally important for engineering applications. Elastic and Thermo-Physical properties were calculated is agreed very close with the result of other researchers.

Keywords: Bond Charge Model, Grüneisen Parameter, Elastic Constants, Heat Capacity, Stanene

1. Introduction

Stanene is one of the most active areas of nanomaterials research due to their potential for integration into next-generation electronic. The use of phenomenological models in the study of the vibrational properties of Stanene allows a complete and straightforward description in highly symmetric direction with little bit greater computational effort. Stanene, the other 2D group-IV materials, with Honey-comb and buckled lattice structures has been discovered by epitaxial growth on substrates [1, 2]. The lattice vibrations are responsible for the characteristic properties of solid such as Phonon properties, Phonon group velocities, Phonon Scattering mechanism, Thermal conductivity and Elastic properties etc. The atoms in a stanene are executing vibrations about their equilibrium positions with energy governed by the temperature of the solid; such vibrations in crystals are called lattice vibrations. The vibration of the atoms depends on the interatomic potentials within the crystal. To determine the vibrational frequencies and the corresponding modes one needs to solve the dynamical matrix, which can be obtained from the interatomic interactions potential [6-10]. There have been several theoretical attempts to understand the lattice vibrations and Thermal properties of Stanene [11-13], which usually employing the force constant model, the rigid ion model, the rigid shell model, the dipole approximation etc, but bond charge model is showing best results for IVth group of semiconductor. The adiabatic bond charge (BCM) method was originally developed by Weber [3]. Very recently, the researchers has discovered that among Group IV elements, Silicene, Germanene apart from Stanene can form stable honey-comb structures with 2D nanostructure [4, 5].

The condition for the non-trival solutions for wave equation of 2D nanostructure, honey-comb and buckled lattice [20, 22] lead to the characteristic or secular equation,

$$\left| D^{eff}(q) - \omega^2(q)mI \right| = 0 \qquad (1)$$

$$\omega = \omega_j(q); j = 1, 2, 3, \ldots 2n$$

This is the secular equation of 2x2 dimensions. The elements of dynamical matrix are defined as

$$D_{\alpha\beta}\left(\frac{kk'}{q}\right) = \sum_{l'} \Phi_{\alpha\beta}(l' - l; kk') exp(iq.r(lk, l'k')) \quad (2)$$

The above equation in matrix form is solved by MATLAB program. And the result is investigated along hexagonal Brillouin zone with symmetry points $\Gamma(0,0), M(\frac{2\pi}{a\sqrt{3}}, 0)$.

The vibrational frequencies for acoustic modes along symmetry line with coupling constant $\gamma_{j\ =8.4\ x\ 10}{}^{-3}\ \gamma$ for stanene is deduce as [20]

$$\Gamma - M$$

$$\omega_1{}^2 = \gamma_j \left[1 - \cos\left(\frac{\sqrt{3}}{2} q_y a\right) \right] \qquad (3)$$

$$\omega_2{}^2 = 3\gamma_j \left[1 - \cos\left(\frac{\sqrt{3}}{2} q_y a\right) \right] \qquad (4)$$

2. Study of Grüneisen Parameters of Stanene

On the basis of oscillator model of the solid, Grüneisen predicted that the three important physical properties of a solid, the thermal expansion coefficient, the lattice specific heat and the compressibility are linked together. To understand the physical importance of the relation, we examine that the frequency of a lattice vibration of specified wave vector changes with the lattice parameter of the solid, this lead to anharmonic effect. For simplicity, we assume that a given change in lattice parameter gives rise to the same relative change of frequency of every mode of vibration. The results of Kamlesh et, al were obtained by calculating individual values of the angular frequencies $\omega_{a;q,j}$ for different modes in high symmetry direction [20, 22, 23].

The Grüneisen parameter for 2D, nanostructure materials of IVth group of semiconductor is derived by Xu-Jin Ge et al [21]

$$\gamma(q,j) = -\frac{a_0}{\omega_{a;q,j}} \left[\frac{\partial \omega_{a;q,j}}{\partial a} \right]_{a_0} \qquad (5)$$

It is now clear that if $\omega_{a;q,j}$ is angular frequency of the solid, $\omega_{a;q,j}$ is the vibrational frequency corresponding to wave vector q, mode j, a_0 is the equilibrium lattice constant.

$\gamma(q,j)$ is independent of compressibility and thus it has the same value for every modes at low temperature. Thus at low frequency modes, the variation is negligible for Grüneisen parameter. But when Grüneisen parameter $\gamma(q,j)$ is associated

with a low stiffness mode, it gets heavily weighted and leads to a decrease in $\gamma(q,j)$ at low temperature. Grüneisen parameter $\gamma(q,j)$ is the same for modes in the dispersive region of any given branch of acoustic modes and here the optics modes can be ignored. The $\gamma(q,j)$ calculated in table 1 comes from the Python program.

In high symmetry direction, $\Gamma - M$

Grüneisen parameter of stanene is determined by acoustics modes in high symmetry direction

$$M\left(\frac{2\pi}{a\sqrt{3}}, 0\right)$$

$$\gamma(q,j) = -a_0 \frac{\sqrt{3}}{4} q_y \left[\cot\left(\frac{\sqrt{3}}{4} q_y a_0\right) \right] \qquad (6)$$
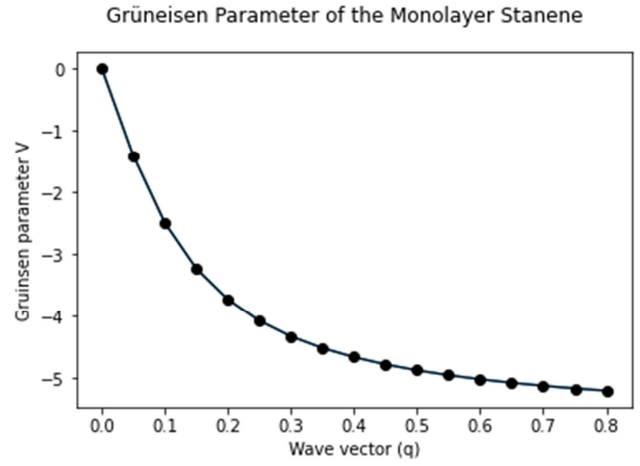

Figure 1. *Variation Grüneisen parameter with wave vector q in Γ- M.*

Using the quasi-harmonic approximation (QHA), we computed the Grüneisen parameter of Stanene, 2D materials. We find that, the Grüneisen parameter of stanene 2D materials is negative for low frequency phonons near Γ.

The calculated the Grüneisen parameter along high symmetry lines within the Brillouin zone is shown in Figure 1. The dispersion lines are similar due to the honey-combed lattice structures. Dispersion of Grüneisen parameter along the high symmetry path is plotted. The acoustic and optical modes along Z direction (ZA and ZO) do not couple with other phonon modes, resulting in crossings of dispersion lines in Stanene along high symmetry direction because of larger buckling. This results in the development of phonon band gaps and the decrement in phonon group velocity. Further, both of them reduce the phonon thermal conductivity. The large buckling in stanene leads to the ZA mode for very low value near Γ points. This means the applied strain should be small enough otherwise harmonic approximation is not valid any more. We have shown the Stanene LA and TO modes have negative and similar Grüneisen parameters; the anomalous hardening of phonon modes upon expansion is a general feature of the 2D buckled mode and the reason why Stanene shows negative. But the TA and LA modes have Grüneisen parameters which are varying from -1.4 to -5.2 for Stanene corresponding to different wave vector q.

3. Longitudinal &Transverse Velocities of Monolayer Stanene

The equation of elasticity is derived from Newton's law:

$$\rho \frac{\partial^2 u_i}{\partial t^2} = \sum_j \frac{\partial^2 \sigma_{ij}}{\partial x_j^2} \qquad (7)$$

Where ρ_{2d} is surface mass density in units of Kilogram per area.

A sound wave has a displacement given by

$$u(r) = u_0 exp[i(q.r - \omega t)] \qquad (8)$$

Time derivative give $-i\omega$, and space derivative $\frac{\partial y}{\partial x} \to iq$. The strains are

$$e_1 = iq_x u_x, \ e_2 = iq_y u_y, \ e_6 = i(q_x u_y + q_y u_x)$$

then equation of motion become

$$(c_{11}q_x^2 + \frac{(c_{11}-c_{12})}{2}q_y^2 - \rho\omega^2)u_x +$$
$$\left((c_{11} + \frac{(c_{11}-c_{12})}{2})\right)q_x q_y u_y = 0$$

$$(c_{11}q_y^2 + \frac{(c_{11}-c_{12})}{2}q_x^2 - \rho\omega^2)u_y +$$
$$\left((c_{11} + \frac{(c_{11}-c_{12})}{2})\right)q_x q_y u_x = 0$$

It has solution only if the determinant of coefficient of u_x and u_y should be vanishes i.e

$$\begin{vmatrix} (c_{11}q_x^2 + \frac{(c_{11}-c_{12})}{2}q_y^2 - \rho\omega^2) & \left((c_{11} + \frac{(c_{11}-c_{12})}{2})\right)q_x q_y \\ \left((c_{11} + \frac{(c_{11}-c_{12})}{2})\right)q_x q_y & (c_{11}q_y^2 + \frac{(c_{11}-c_{12})}{2}q_x^2 - \rho\omega^2) \end{vmatrix} = 0$$

Simplify this we obtain

$$\rho^2\omega^4 - \rho\omega^2(c_{11} + \left(\frac{c_{11}-c_{12}}{2}\right))q^2 + c_{11}\frac{(c_{11}-c_{12})}{2}q^4 = 0 \ (9)$$

This is quadratic equation of $\rho\omega^2$ and its solutions have two values give the longitudinal and transverse acoustic velocities.

$$V_{LA} = \sqrt{\frac{c_{11}}{\rho}} \qquad (10)$$

$$V_{TA} = \sqrt{\frac{c_{11}-c_{12}}{2\rho}} \qquad (11)$$

Table 1. *Variation of sound velocities.*

Materials	Longitudinal velocity (Km/Sec)	Transverse velocity (Km/Sec)
Graphene	21.59	13.82
Stanene	3.70	2.04

Table 2 shows the variation of Longitudinal &Transverse velocities of monolayer stanene. It is clear that Longitudinal &Transverse velocities are decreasing for Stanene in comparison to Graphene [18, 19]. It is understandable that the variation of Longitudinal &Transverse velocities is affected by the Phonon group velocities. It may be

determined that the average sound wave velocity is a maximum when a sound wave travels with the z- axis of the material.

4. Elastic Modulus of Monolayer Stanene

In the linear theory of elasticity, the infinitesimal deformations are assumed, and second-order elastic constants (SOEC) are sufficient to describe the elastic stress-strain response and wave propagation in solids. For very small strain according to Hook's law strain in linear with stress, give the relation

$$\sigma_i = \sum_j c_{ij} \epsilon_j \qquad (12)$$

Where c_{ij} are elastic stiffness constantsr

$$\epsilon_i = s_{ij}\sigma_j$$

S_{ij} is called elastic compliance constant;
C_{ij} are the forth rank tensor matrices.

Graphene has C_{6v} symmetry while stanene has D_{3d} symmetry, C_{ij} matrices for graphene and stanene is given

$$c_g = \begin{bmatrix} c_{11} & c_{12} & c_{13} & 0 & 0 & 0 \\ c_{12} & c_{11} & c_{13} & 0 & 0 & 0 \\ c_{13} & c_{13} & c_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & c_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & c_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & 1/2(c_{11}-c_{12}) \end{bmatrix}$$

$$c_s = \begin{bmatrix} c_{11} & c_{12} & c_{13} & c_{14} & 0 & 0 \\ c_{12} & c_{11} & c_{13} & -c_{14} & 0 & 0 \\ c_{13} & c_{13} & c_{33} & 0 & 0 & 0 \\ c_{14} & -c_{14} & 0 & c_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & c_{44} & c_{14} \\ 0 & 0 & 0 & 0 & c_{14} & 1/2(c_{11}-c_{12}) \end{bmatrix}$$

2D materials z tends to zero these matrices are same and have only two Elastics constants c_{11} and c_{12}. Hexagonal crystals have the feature that the waves are isotropic in basal plane ($q_z=0$) that is not true for cubic crystal.

$$c = \begin{bmatrix} c_{11} & c_{12} & 0 \\ c_{12} & c_{11} & 0 \\ 0 & 0 & 1/2(c_{11}-c_{12}) \end{bmatrix}$$

Elastic compliance constants matrix is inverse of elastic stiffness constants matrix i.e

$$s = c^{-1}$$

$$s = \begin{bmatrix} \frac{c_{11}}{c^2_{11}-c^2_{12}} & \frac{-c_{12}}{c^2_{11}-c^2_{12}} & 0 \\ \frac{-c_{12}}{c^2_{11}-c^2_{12}} & \frac{c_{11}}{c^2_{11}-c^2_{12}} & 0 \\ 0 & 0 & \frac{2}{c_{11}-c_{12}} \end{bmatrix}$$

$$s = \begin{bmatrix} s_{11} & s_{12} & 0 \\ s_{12} & s_{11} & 0 \\ 0 & 0 & 2(s_{11}-s_{12}) \end{bmatrix}$$

Young s modulus

$$E = \frac{1}{s_{11}} = \frac{c^2_{11} - c^2_{12}}{c_{11}} \quad \upsilon = \frac{-s_{12}}{s_{11}} = \frac{c_{12}}{c_{11}} \quad s_{66} = 2(s_{11} - s_{12})$$

Shear modulus is inverse of s_{66} i.e

$$G = \frac{1}{s_{66}} = \frac{c_{11} - c_{12}}{2} \qquad (13)$$

Bulk modulus of 2D materials that is equivalent to in-plane stiffness constant.

The elastic energy density U is a quadratic function of the strains.

$$U = \frac{1}{2} \sum_{i=1}^{2} \sum_{j=1}^{2} c_{ij} \, e_i e_j$$

For isotropic e1=e2=1/2δ this give

$$U = \left(\frac{c_{11} + c_{12}}{2}\right) \delta^2$$

$$B = \left(\frac{c_{11} + c_{12}}{2}\right) \qquad (14)$$

Table 2. Calculated and Compared Young's modulus Y2D, Poisson's ratio σ, bulk modulus B and shear modulus G for Graphene and Stanene.

Materials	M(amu)	ρ_{2d} (x10^{-6} Kg/m^2)	Y_{2D}(N/m)	B_{2D}(N/m)	G_{2D}(N/m)	σ
Graphene	12.01	0.755	340.8	207.2	144.6	0.18
Stanene	118.71	2.088	24.14	19.95	8.6	0.39

Table 1 shows the Young's modulus Y2D, Poisson's ratio υ, bulk modulus B and shear modulus G for Stanene estimated at room temperature. It is found that the value of B, Y, and G of Stanene are smaller than Graphene [15, 16, 24, 25]. Thus Stanene have little Stiffness and bonding with respect to Graphene B/G and 'σ' are the measure of brittleness and ductility of solid. If σ ≤ 0.26 and the solid is generally brittle, otherwise it is ductile in nature. Our finding of lower values of B/G and σ compared to their critical values indicates that Stanene is not brittle in nature at room temperature. It is well known that for stable and elastic material the value of σ should be less than 0.5. The values of 'σ' evaluated for Stanene are smaller than its critical value.

5. Debye Temperatures Variation of Stanene

The Debye formula for heat capacity of stanene as 2D material is derived as

$$C = 4R \left(\frac{T}{\theta}\right)^2 \int_0^{\theta/T} \frac{x^3 e^x}{(e^x - 1)^2} dx \qquad (15)$$

here $x = \frac{\hbar \omega}{k_B T}$

The value of $R = N_0 k_B$ depends on the units involved, but is usually stated with S.I. units as R = 8.314 J/mol·K. The parameter Θ entering into our present discussion is usually referred to as the Debye temperature. It plays the role of a characteristic temperature of solid. At the Debye temperature at sufficiently low temperatures T, here only long wavelength acoustic modes are excited. These are just the modes which may be treated as in elastic continuum with macroscopic elastic constants. The energy of short-wavelength modes is too high to allow these to be excited at low temperatures. This is a universal function of only a ratio $\frac{T}{\theta}$.
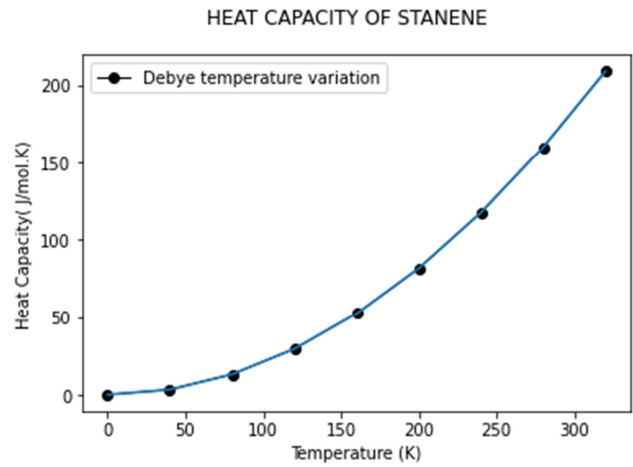

Figure 2. Variation of Heat Capacity with temperature of Stanene.

Table 3. Variation of Heat Capacity with temperature of Stanene.

Temperature (K)	Heat Capacity with Riemann Zeta function ζ (3)	Heat Capacity (J/mol.K)
0	0	0
40	2.71319253137435*ζ (3)	3.26
80	10.8527701254974*ζ (3)	13.04
120	24.4187327823691*ζ (3)	29.35
160	43.4110805019896*ζ (3)	52.18
200	67.8298132843587*ζ (3)	81.53
240	97.6749311294766*ζ (3)	117.40
280	132.946434037343*ζ (3)	159.81
320	173.644322007958*ζ (3)	208.72

The variation of the experimentally measured specific heats is compared with that computed phonon spectra data. This comparison is usually done by plotting the Debye temperatures against the temperature. For calculating the exact variation of Debye temperatures we have used Python Program. In this technique, the specific heat is expressed in

terms of Riemann-Zeta function ζ (3). ζ (3) has a special value of the Riemann Zeta Function which is equal to 1.202056903…… From the calculated specific heats at different temperatures, heat capacity of monolayer Stanene is calculated by means of standard tables. We make a plot of this function by using the Python Program. It is seen from this plot that the heat capacity approaches the zero value as T→0. For higher temperature, heat capacity is not varying abruptly and almost constant as shown in figure below.
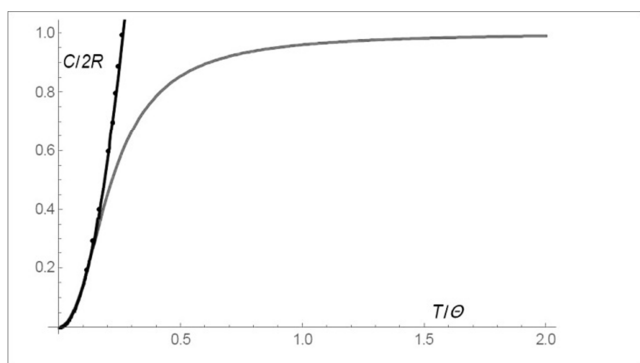

Figure 3. *Variation of Heat Capacity at higher temperature of Stanene.*

Let us now examine it at the low temperature range more closely. Plot of C / (2R) as a function of $\left(\frac{T}{\theta}\right)$ for the 2D phonon system is shown in figure 3. The saturated line denotes the exact expression, while the variation line denotes the low temperature limit. C / (2R) tend to the unity in the high temperature limit. The specific heat at constant volume behavior of the Stanene does not show any anomaly. Figure 3 illustrates the higher order of agreement with other researchers [14, 15, 17].

6. Conclusions

Based on the discussion above, it is important to note that the notion of using a simple interaction potential technique to calculate higher-order elastic coefficients for hexagonally organized 2D monolayer Stanene remains valid. The elasticity of materials concerns the cohesion of solids and the thermo-Physical properties, such as phonon group velocities and Debye temperatures [19]. In this regard, elastic constants are important parameters for construction of inter-atomic potentials and the mechanical stability of crystal [18, 21]. It indicates that Stanene is stable corresponding to shear. The compressibility, hardness, ductility, toughness, brittleness and bonding nature of the Stanene are too well connected with the SOECs. We have also calculated the values longitudinal and transverse sound velocities of monolayer Stanene. The calculated values of sound velocities would be compared with available theoretical results [25]. Grüneisen parameter of material is strongly dependent on phonon polarization and wave vector. We evaluate it along high symmetry directions for acoustic modes because this mode play greater role in thermal expansion. The computed Grüneisen parameters of LA and TA branches are highest among the 2D materials of IVth group elements. Both modes are showing similar results. The theory thus gives a quite satisfactory account of observed variation of heat capacity in the low temperature region and compared with the available experimental data which shows a fairly good agreement.

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