Equation of State for a 2D System

Gloria I. Murila, [1] George S. Manyali, [1] James Sifuna, [1,2,3]
[1]Computational and Theoretical physics group (CTheP), Department of Physics,
Masinde Muliro University of Science and Technology, 190-50100, Kakamega, Kenya

[2]Materials Modeling Group, Department of Physics and Space Sciences,
The Technical University of Kenya, 52428-00200, Nairobi, Kenya

[3]Department of Natural Sciences,
The Catholic university of Eastern Africa, 62157 -00200, Nairobi, Kenya

Abstract
We have described a simple theoretical model of an equation of state (EOS) for a two-dimensional system. The goal was to give a clear description of the interplay between hydrostatic change in surface area and the two dimensional in-plane pressure (F). Of interest from this described EOS, was the measure a material's resilience to isotropic stretching (γ) that can in principle be viewed as the layer modulus. To this date, few attempts have been made to obtain accurately the layer modulus of 2D systems. We studied using density functional theory as implemented in the Quantum ESPRESSO computer code, a number of monolayer systems; graphene, Boronitrene, dichalcogenides and Janus chalcogenides. The results found out in this study showed that of the above honeycomb structures, graphene was the most resilient to stretching with a value of C = 206.6 N/m followed by boronitrene BN = 177.3 N/m. The layer modulus of the dichalcogenides and Janus chalcogenides was seen to be competing but not as large as that of graphene or boronitrene. Apart from the layer modulus, we were also able to use the EOS to predict isotropic intrinsic strength of the listed systems. It was observed that the intrinsic stress was proportional to the layer modulus. This project does not just satisfy our knowledge thirst but can also be used by experimental groups in fabricating hard 2D materials.

Key words: EOS, First-principles, Density functional theory, Layer modulus.

1. Introduction

1.1 Two-dimensional materials

A part from electrical and optical properties of materials, mechanical properties feature as important aspects in exploring a new material (Liu & Wu, 2015). Mechanical properties provide a key criteria for discovering, selecting and refining new super hard materials that have wider applications in people's life.

The recent discovery of a two-dimensional (2D) graphene (Novoselov, *et al.,* 2004) & (Liu & Wu, 2015) (Geim, 2009), has opened-up doors for exploring materials whose fundamental properties are depended on its dimensionality. Among explored materials are the transition-metal dichalcogenides (TMDs), which consist of one transition-metal layer such as Hf, Ti, Zr, Mo,W, V, Nb, and Ta sandwiched between two chalcogen layers (S, Se and Te) to form a unit cell, in which metalchalcogens are covalently bonded within the plane (Chhowalla, *et al*., 2013). These

2D TMDs can form both out-of-plane and in-plane heterojunctions (Yifei, et al., 2015), (Duan, et al., 2014) & (Li, et al., 2015).

As far as we know, a mixed monolayer of MoSSe does not exist in nature, but its structure was theoretically predicted for the first time in 2013 (Cheng, Zhu, Tahir, & Schwingenshlogl, 2013), and after a short time it was successfully synthesized using the modified chemical vapour deposition (CVD) method (Lu A. , *et al*., 2017). To fabricate it, Lu and co-workers synthesized a monolayer of MoS_2 using CVD on SiO_2 substrate, then separated the top-layer S atoms and replaced them with H atoms using hydrogen inductively coupled plasma, and, finally, replaced H atoms with Se atoms using thermal salinization. S atoms in MoS_2 were completely replaced by Se atoms with the formation of a mixed MoSSe monolayer. Later, Kandemir and Sahin (Kandemir & Sahin, 2018) studied the structural, vibrational and electronic properties of the stable WSSe single layer. In addition, they studied bilayer stacking order in the hypothetical WSSe 2H-structure. Most recent studies have shown that by breaking the out-of-plane structural symmetry, a new kind of heterojunction is formed leading to a structurally stable Janus SMoSe monolayer (Lu, *et al*., 2017). This particular TMD consists of three layers of atoms formed by sulphur, molybdenum, and selenium. Great efforts have been devoted into the studies of various properties of single layer MoSSe (Ma, *et.al,* 2018) for insistence its hardness

In this study we have described the reaction of Janus to conditions of applied 2D pressure called the force per unit length $\mathcal{F}$ and we have shown how to obtain a layer modulus which is synonymous to the 3D bulk modulus.

1.2 Theoretical frame work

In a 2D set up an in-plane hydrostatic force will by default course a uniform change in its area. This force may be expressed as a derivative of energy with respect to the 2D surface area as

$$\mathcal{F} = -\frac{\partial E}{\partial A} \qquad 1$$

Where E, is the energy and A, is the area of the 2D system. From eqn. 1, can be denotes that if $\mathcal{F}$, is positive then we will have a compression while negative$\mathcal{F}$, denotes a uniform stretching. Proceeding we well represent the layer modulus of a 2D as

$$\gamma = -A\frac{\partial \mathcal{F}}{\partial A} \qquad 2$$

The negative sign in eqn. 2 depicts that the layer modulus is a resistance of a 2D material to - $\mathcal{F}$

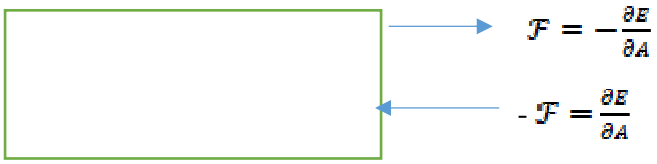

Figure 1 Illustration of force per unit length.

 Available online http://ir.kabarak.ac.ke/handle/123456789/1

In this work we considered a stretching force.

From the work of Andrew and co-works in their PRB 2010 (Andrew, *et.al*, 2012), they indicated that the layer modulus (γ_o) of a monolayer graphitic material can be estimated by the in-plane linear modulus using the eqn. 3 below

$$\gamma_o = \frac{t\beta_o}{2} \qquad 3$$

Where β_o, is a linear modulus with respect to bulk pressure and t is the layer thickness.

Andrew and co-workers went ahead and indicated the possibility of obtaining a 2D EOS relating the force applied $\mathcal{F}$, to the surface area of any 2D material as

$$\mathcal{F} = -2\gamma_o \left\{\epsilon + (1-\gamma_o')\epsilon^2 + \frac{2}{3}[(1-\gamma_o') + \gamma_o\gamma_o'']\epsilon^2\right\} \qquad 4$$

Where $\epsilon = \frac{1}{2}\left[1 - \frac{A_o}{A}\right]$ and is known as the equibiaxial Eulerian strain.

A_0, γ_o, γ_o' and γ_o'' are the optimized values of unit cell area, layer modulus, the force per unit length derivative and second derivative of the layer modulus at $\mathcal{F} = o$

From eqn.1 it implies that $E = \int \mathcal{F}\,\partial A$ then we can integrate eqn.4 to get energy equation of state as

$$E(A) = E_o + 4A_0\gamma_o\left[\frac{1}{2}\epsilon^2 + \frac{1}{3}(5-\gamma_o')\epsilon^3 + \frac{1}{6}[(1-\gamma_o')(8-\gamma_o') + \gamma_o\gamma_o'' + 18]\epsilon^4\right] \qquad 5$$

Which can be fitted to hydrostatic expansion and compression date to extract A_0, γ_o, γ_o' and γ_o''.

2. Computational Details

All calculations were done within the framework of Density-Functional Theory (DFT) (Hohenberg & Kohn, 1964), using the Projector Augmented Wave (PAW) (Blochi, 1994), formalism as implemented in quantum expresso code (Giannozzi, et al., 2009). We used Pardew-Burke-Ernzerhef (PBE) Generalized Gradient Approximation (Perdew, Burke, & Ernzehof, 1996) exchange correction. The K-point sampling was done at 12 12 1 Monkhorst-Park (Monkhorst & Pack, 1976) and each structure was relaxed so that the forces converged to 0.01eV/Å. In all cases the kinetic energy cut off of 55Ry was used. A height of 20 Å was used in order to prevent spurious interactions between unit cells repeating perpendicular to the layer plane.

3. Results and Discussion

In this study we considered graphene, BN and a number of newly synthesized Janus which include WS_2, WSSe, WSe_2, MoS_2, MoSSe and $MoSe_2$. The lattice parameters are arranged in table one in an increasing order, with the Janus having a higher value of a= 3.189 Å, 3.247 Å, .3.2.97 Å, 3.187 Å, 3.256 Å and 3.331 Å for WS_2, WSSe, WSe_2, MoS_2, MoSSe and $MoSe_2$ respectively.

The values of *a* is higher when the transitional metal is combined with Se chalcogen atom than S. This is due to higher molecular mass of Se as compared to S. It can also be seen that the lattice constant a increases in the series MS_2<MSSe<MSe_2 (M=Mo,W) since as sulphur is substituted with Se , the number of electron increases thus high repulsive force that leads to increase in the lattice distance. The relaxed honeycomb structure of graphene has unit cell with lattice constant of 2.467 Å and BN of 2.515 Å, which combers well with values obtained by reference (Andrew, *et.al,* 2012). The lattice parameters of the Janus is generally high than graphene and BN due to increasing in the number of atoms in the structure of the molecule.

EOS fit parameters of equilibrium, layer modulus γ_o = 206.7 N/m, 177.3N/m force per unit length derivative , γ'_o = 4.338N/m, 4.414N/m double force per unit length derivative $\ddot{\gamma}_o$ = −0.0306 N/m, -0.034N/m for graphene and BN respectively. The higher layer modulus value indicates the material are more resilient to stretching thus maintains its structure properties when changing form 3D to 2D state. The resilience to stretching in Janus is low as listed in the table 1 below. Generally a transitional metal bonded to Se chalcogen atom is less resilient the when bonded to S atom.

TABLE I.

	A_0	a	γ_0	γ'_0	γ''_0	Bs	A_f
Graphene	5.271	2.467	206.6	4.368	-0.034	31.5	27.27
BN	5.479	2.515	177.3	4.414	-0.034	27.7	28.9
WS_2	8.807	3.189	110.8	4.301	-0.052	17.8	47.1
WSSe	9.134	3.247	101.6	4.378	-0.053	16.4	49.4
MoS_2	8.796	3.187	100.9	4.311	-0.065	16.0	46.6
WSe_2	9.413	3.297	93.3	4.454	-0.054	15.1	51.5
MoSSe	9.184	3.256	92.8	4.379	-0.062	14.7	49.0
$MoSe_2$	9.610	3.331	85.2	4.408	-0.065	13.6	51.7

References

Andrew, R., Mapesha, E., Ukpong, A. M., & Chetty, N. (2012). Mechanical properties of graphene and boronitrene. *American Physical Society, 85*, 125428-125437.

Blochi, P. (1994). Projector Augmented Wave methods. *Physical Review, 50*, 17953.

Chhowalla, M., Shin, S., Eda, G., Li, J., Loh, K., & Zhang, H. (2013). The chemistry of two-dimensional layered transition metal dichalcogenide nanosheets. *Natire chemisty., 5*, 263-275.

Duan, X., Wang, C., Shaw, J., Cheng, R., Chen, Y., Li, H., . . . Duan, X. (2014). Lateral epitaxial growth of two-dimensional layered semiconductor heterojunctions. *Nature Nanotechnology, 9*, pages 1024–1030.

Geim, K. (2009). Graphene: Status and Prospects. *Science, 324*, 1530-1534.

Giannozzi, P., Baroni, S., Baonini , N., Calandra, M., Car, R., & Cavazzoni, C. (2009). QUANTUM EXPRESSO: A modular and open source softwere project for quantum simulations of materials. *Physicaal Condensed Matter, 21*, 395502.

Hohenberg, P., & Kohn, W. (1964). Inhomogeneous electron gas. *Physical Review, 136*, 864-871.

Li, M., Shi, Y., Cheng, C., Lu, L., Lin, Y., Tang, H., & Tsai, M. (2015). Epitaxial growth of a monolayer WSe2-MoS2 lateral p-n junction with an atomically sharp interface. *Science, 349*, 524-528.

Liu, K., & Wu, J. (2015). Journal of materials Research Mechanical properties os 2D Metarials and heterostuctures. *Journal of materials research, 31*, 822-844.

Lu, A., Zhu, H., Xiao, J., Chuu, C., Han, Y., Ming, C., . . . Yang, Y. (2017). Janus monolayers of transition metal dichalcogenides. *Nature Nanotechnology, 12*, 744–749.

Ma, X., Wu, X., Wang, H., & Wang, Y. (2018). A Janus MoSSe monolayer: a potential wide solar-spectrum water-splitting photocatalyst with a low carrier recombination rate. *material chemistry A, 6*, 2295-2301.

Monkhorst, H., & Pack, J. (1976). Special points for brillion-zone intergrations. *Phyical Review, 13*, 5188.

Novoselov, K., Geim, K., Movozov, S., Jiang, D., Ziang, X., Dubonos, S., . . . Firsov, A. (2004). Electric field Effect in Atomically Thin carbon Films. *Science, 306*, 666-669.

Perdew, P., Burke, K., & Ernzehof, M. (1996). generalised Gradient Apeoximation made simple. *Physical Review, 77*, 3865.

van der Waals Layered Materials: Opportunities and Challenges. (2017). *American Chemical Society, 11*, 11803-11830.

Yifei, Y., Liqin, S., Shi, H., Lujun, H., Liu, Y., Zhenghe, J., . . . Cao, L. (2015). Equally Efficient Interlayer Exciton Relaxation and Improved Absorption in Epitaxial and Nonepitaxial MoS2/WS2 Heterostructures. *American Chemical Society, 15*, 481-496.