

COMPARATIVE STUDY OF EOS (EQUATION OF STATES) MODELS FOR FITTING ENERGY VERSUS VOLUME DATA IN THERMODYNAMICS

David Bandhaso, Arif Lukmantoro, Sholihun*

Department of Physics, Faculty of Mathematics and Natural Sciences, Universitas Gadjah Mada, Sekip Utara BLS 21, Yogyakarta, 5528, Indonesia

*email:sholihun@ugm.ac.id

ABSTRACT

One of the essential aspects of material design research is studying the stability of the model designed. In Thermodynamics, material stability can be expressed by the equation of state (EOS). However, not all EoS will fit with the energy versus volume data from the material being designed. Moreover, if the materials prepared have a unique structure, more factors need to be considered so that the data fitting is carried out more precisely. In this research, a comparative study of 1 mathematical approach (second order polynomial) and 4 EoS (Murnaghan EoS, Birch EoS, Birch EoS, Birch-Murnaghan EoS, and Vinet EoS) was carried out for fitting energy versus volume data on 3D (bulk) and 2D materials. obtained from density functional theory (DFT) calculations. This research found that fitting energy versus volume data in 3D material models can be done using second-order polynomials. In contrast, for 2D models, only two EoS fit (Birch-Murnaghan and Vinet). Apart from that, the result is that the Vinet equation of state is an equation that has the smallest tolerance value in the range of 10^{-4} - 10^{-10} eV.

Keywords: DFT; Equation of States; Material Design; Thermodynamical Stability

INTRODUCTION

In research in the field of material design, researchers can freely model crystals according to their creativity. Crystal models can be designed without considering experimental methods that allow for the realization of the created model. However, one aspect that needs to be considered in developing a model is related to thermodynamic equilibrium. Material equilibrium dynamics involves a subtle interaction between inertial dynamics triggered by molecular thermal energy and structural effects of density correlation. The balance between kinetic and potential energy becomes susceptible to applied pressure or stress (Douglas, 2021). It can be explained in the equation of states (EOS) to express the state of matter. There are several EOS models, such as Birch (Fu, 1983), Murnaghan (Murnaghan, 1944), Birch-Murnaghan (Birch, 1947), and also Vinet (Vinet, 1947). EOS acts as a determinant of material stability in specific pressures, volumes, and temperatures.

Material models that have been made need to be optimized to obtain stable models so that synthesis is possible. Optimization is done by calculating energy as a function of the size variation of the crystal model created (volume, area, or length of cell units). From the data obtained, it is necessary to fit with the existing equation model to find out the equilibrium state of the material. A polynomial function is a

straightforward equation that fits energy data to crystal size (Katsura, 2019; Absor, 2014). However, from the optimization point of view, the second-order polynomial function can only be used for fitting since the higher-order functions have no physical meaning. Therefore, it is necessary to consider fittings by using the thermodynamic function. The known thermodynamic fittings are the equation of states to look for the more precise and accurate minimum point.

This study used material modeling with a 3-dimensional (3D) and 2-dimensional (2D) structure. The crystal model that has been created then minimizes energy to obtain an optimal structure. Energy minimization calculation uses the density functional theory (DFT) method. Then, the most fitting equation of state will be searched to find the minimum value of the energy versus volume data, fitting it with the equation of state (EOS).

RESEARCH METHODS

In optimizing crystal energy, energy calculations were carried out as a function of crystal size variations in this study. The calculation was carried out using the Density Functional Theory (DFT) method with gradient generalized approximation Perdew, Burke, and Enzerhoff (GGA-PBE) as an approach to solving the exchange-correlation potential (Perdew, 1994). In

distinguishing atoms in the calculation process, pseudopotentials are used, and wave functions are expanded from linear combination atomic pseudo-orbitals already available in the OpenMX program (Ozaki, 2009). In calculations, the convergence of energy and force is set until it reaches 2.7×10^{-7} eV and 5.0×10^{-4} eV/Å, respectively. Discretization of k-grid for bulk crystals (SrTiO₃, PbTiO₃, and ZnO) $10 \times 10 \times 10$ and for 2-dimensional crystals (SiGe, SiC, and GeC) is made $8 \times 8 \times 1$.

To obtain the optimum energy value, a fitting is carried out between the volume of the crystal and its energy in such a way that the minimum value is obtained. In research, curve fitting is carried out with a 2nd-order polynomial approach and four types of thermodynamic state equation models for solids, including the Birch state equation, Murnaghan state equation, Birch-Murnaghan state equation, and Vinet state equation.

1. Murnaghan Equation of State

Murnaghan's equation is proposed to answer research problems for minerals and rocks, as well as where to determine the mechanical properties of their internal structure. The equation model proposed by F.D. Murnaghan is an equation that relates volume pressure and temperature with bulk modulus being a lineation of pressure:

$$E(V) = E_0 + B_0 V_0 \left[\frac{\varphi^{(1-B'_0)}}{B'_0(B'_0-1)} + \frac{\varphi}{B'_0} - \frac{1}{B'_0-1} \right] \quad (1.1)$$

(Murnaghan, 1944).

2. Birch State Equation

The Birch equation of state is an equation of state proposed by geophysicist Francis Birch, who considered that the speed of wave propagation in materials is directly proportional to the density of the rock. From this law, the relationship between energy and volume is as follows:

$$E(V) = E_0 + \frac{9B_0V_0}{8} [\varphi^2 - 1]^2 + \frac{9}{16} B_0V_0(B'_0 - 4) [\varphi^2 - 1]^3 \quad (1.2)$$

(Fu, 1983).

3. Birch-Murnaghan Equation of State

Before discovering Birch's law, Francis Birch in 1944 corrected Murnaghan's equation of state. If Murnaghan considers the bulk modulus to undergo a linear change with pressure, in this case, birch adds the derived terms of the bulk modulus to the pressure:

$$E(V) = E_0 + \frac{9B_0V_0}{16} \{ [\varphi^2 - 1]B'_0 + [\varphi^2 - 1]^2 [6 - 4\varphi^2] \} \quad (1.3)$$

(Birch, 1947).

4. Vinet Equation of State

The equations of state mentioned earlier describe the state of materials in a low-temperature range. This limitation causes the state of the material to be inaccessible when a phase transition occurs at high temperatures. Pascal Vinet et al. proposed a new equation of state model in which thermal stress does not depend on volume, and the change is linear to the temperature change when it reaches $T > T_d$, where T_d is the Debye temperature. The Energy function to volume in the Vinet equation is different from other equations where, in this equation, the energy function is an exponential function volume:

$$E(V) = E_0 + \frac{2B_0V_0}{(B'_0-1)^2} \left(2 - (5 + 3B'_0(\varphi - 1)) \left(\exp\left(-3(B'_0 - 1)\frac{\varphi-1}{2}\right) \right) \right) \quad (1.4)$$

(Vinet, 1947).

Energy minimization in the four equations of the state above is done using the least square method. This minimization method combines three methods: Levenberg-Marquardt (LM), Gauss-Newton, and steepest-descent. With these three combinations, values can be converged by short iterations. To minimize value, a guess value is needed as initial input. In this study, the initial guess was obtained from the value of the fitting result with a second-order polynomial equation. This is done so that the guess value does not deviate far from the value to be addressed, making convergence easier to achieve.

RESULTS AND DISCUSSION

Based on Density Functional Theory (DFT), calculations have been made on ZnO and SrTiO₃ bulks. The two materials have different structures, where ZnO forms a wurtzite structure, and the atoms bind to each other and create a hexagonal structure. Meanwhile, SrTiO₃ is a cubic crystal with the Sr atom surrounded by TiO₃ ions in the center. Obtained grid parameter calculation results for bulk materials are shown in Table 1. Figures 1 (a), (b), (d), and (e) show the optimal structure of SrTiO₃ and ZnO. As a comparison, calculations are also carried out for group IV diatomic 2-dimensional materials that have a structure resembling graphene. This study optimized the group IV diatomic model using a combination of SiC, GeC, and SiGe. The optimal model is shown in Figure 1 (c). The diatomic structure of group IV is flat, and each atom

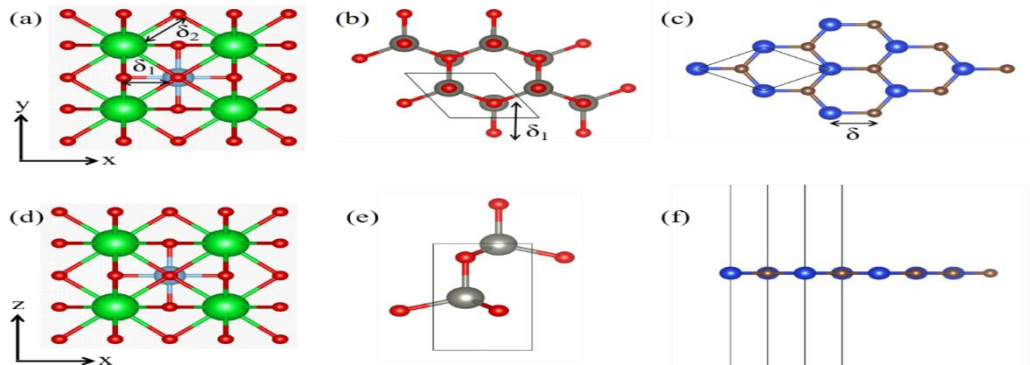


Figure 1. The crystal structure is seen from -z (out of plane) axis (a) ATiO3 (A: Sr, Pb) (b) ZnO (c) Diatomic group IV XY (X) and visible from -y-axis (in-plane) (d) SrTiO3 (e) ZnO (f) Diatomic group IV (SiGe/GeC/SiC

As a comparison, calculations are also carried out for group IV diatomic 2-dimensional materials that have a structure resembling graphene. This study optimized the group IV diatomic model using a combination of SiC, GeC, and SiGe. The optimal model is shown in Figure 1 (c). The diatomic structure of group IV is flat, and each atom binds three atoms to its nearest neighbor, which in Figure

1 (c) and (f) are similar to the structure of graphene. The optimized model shows that lattice parameters and distances between atoms change for different variations in atomic composition. SiGe is the material with the largest lattice size of the three combinations. This shows that the greater the atomic number, the greater the unit size of the crystalline cell.

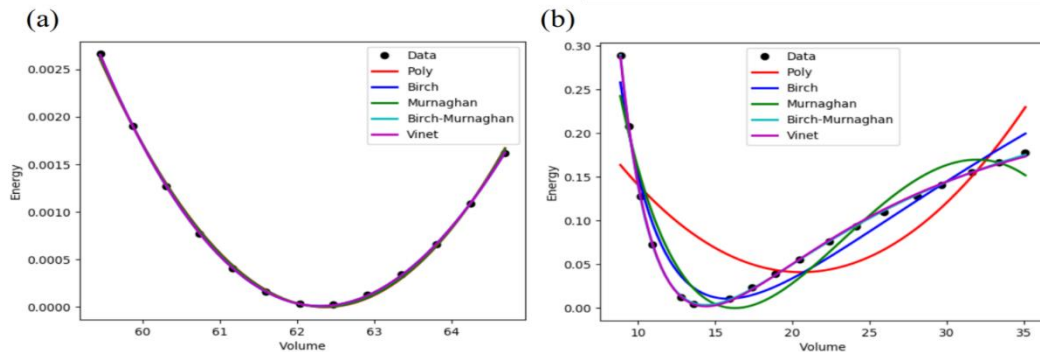


Figure 2. Energy versus volume fitting curve at (a) SrTiO3(b) SiGe with five equations of state

Energy data as a function of crystal size obtained from DFT calculations are then fitted to get the minimum energy value more precisely. Figures 2 (a) and (b) result from fitting DFT data with the five equations of state mentioned earlier. To compare fitting materials with high (bulk) and low (2D) dimensions, SrTiO3 is used to represent bulk material and SiGe as 2D material. The curve shows the difference between SrTiO3 and SiGe, where the SrTiO3 curve is shaped like a quadratic curve, while the SiGe curve is unique, unlike the usual quadratic curve. The formed is extreme enough, second-order polynomials are no longer accurate when approaching minimum values.

results of fitting DFT data with all five equations of state are shown in Table 2, with the smallest error value obtained when fitting with the Vinet equation of state.

Of the five equations of state, second-order polynomials are the simplest equations used to guess the minimum value from the data obtained. Second-order polynomials can still apply the minimum value approach to bulk materials with small tolerance values ($\Delta < 10^{-6}$ eV). However, when the curve

Table 1. Parameters of structure optimization results with the DFT method for bulk materials

No.	Materials	V_{\min} (\AA^3)	E_{\min} (eV)	Distance Between Atoms	
				δ_1 (\AA)	δ_2 (\AA)
1	SrTiO ₃	62.30	-141.62	1.96	2.77
2	PbTiO ₃	63.89	-173.19	2.01	2.83
3	ZnO	149.8	-478.22	2.07	-

Table (2). Parameters of structure optimization results with the DFT method for 2D materials

No.	Materials	A_{\min} (\AA^2)	E_{\min} (eV)	δ (\AA)
1	SiC	8.23	-9.92	1.80
2	GeC	14.05	-9.90	1.87
3	SiGe	14.40	-9.19	2.16

Table 3. Results of energy versus volume fittings with five different types of state equations

No.	Materials	Polynomial		Birch		Murnaghan	
		E_m (eV)	Δ (eV)	E_m (eV)	Δ (eV)	E_m (eV)	Δ (eV)
1	SrTiO ₃	-140.43	13.5×10^{-10}	-142.94	3×10^{-10}	-141.62	93×10^{-10}
2	PbTiO ₃	-171.88	67×10^{-7}	-174.58	8.6×10^{-7}	-173.19	4×10^{-7}
3	ZnO	-477.57	188×10^{-6}	-479.4	10×10^{-6}	-478.21	7.3×10^{-6}
4	SiC	-9.88	0.3833	-10.57	851×10^{-5}	-9.89	881×10^{-5}
5	GeC	-5.89	0.1834	-10.34	11×10^{-4}	-9.21	69×10^{-4}
6	SiGe	-8.77	0.480	-9.74	4.9×10^{-3}	-9.19	0.086

No.	Materials	Birch-Murnaghan		Vinet	
		E_m (eV)	Δ (eV)	E_m (eV)	Δ (eV)
1	SrTiO ₃	-141.62	3×10^{-10}	-141.62	3×10^{-10}
2	PbTiO ₃	-173.19	2.8×10^{-7}	-173.19	2.4×10^{-7}
3	ZnO	-478.22	8.1×10^{-6}	-478.22	7.8×10^{-6}
4	SiC	-9.92	12×10^{-5}	-9.92	5.1×10^{-5}
5	GeC	-9.20	4.8×10^{-4}	-9.90	1.8×10^{-4}
6	SiGe	-9.19	2.8×10^{-3}	-9.19	7×10^{-5}

The first fitting is done with a 2nd-order polynomial approach, which is still suitable for high-

dimensional materials. It can be seen that the data obtained do not deviate far from the polynomial curve. However, problems arise when fittings are

carried out on low-dimensional materials. The energy versus volume data is quite extreme in low-dimensional materials, making it impossible to fit with a second-order polynomial approach. Therefore, approaches that consider the thermodynamic properties of materials are needed for intense energy versus volume curves. The Birch, Murnaghan, Birch-Murnaghan, and Vinet EoS can be applied to 3D materials. Furthermore, in the case of 2D materials, it is shown that the Vinet and Birch-Murnaghan EoS produce more reliable results of fitting data.

CONCLUSION

This study's DFT-based calculations were done on 3D materials (SrTiO₃ and ZnO) and 2D (SiGe, SiC, GeC). There is a significant difference in the crystal size optimization results curve with energy for 3D and 2D materials. The Birch-Murnaghan and Vinet EoS present accurate results from the five equations used for fittings.

BIBLIOGRAPHY

- Absor, M. A. U., Kotaka, H., Ishii, F., & Saito, M. 2014. *Tunable Rashba effect on strained ZnO: First-principles density-functional study*. Applied Physics Express, 7(5), 053002. <https://doi.org/10.7567/APEX.7.053002>
- Birch, F. 1947. *Finite Elastic Strain Of Cubic Crystals*. Physical Review, 71(11), 809. <https://doi.org/10.1103/PhysRev.71.809>
- Douglas, J. F., & Xu, W.-S. 2021. *Equation Of State And Entropy Theory Approach To Thermodynamic Scaling In Polymeric Glass-Forming Liquids*. Macromolecules, 54(10), 3247-3269. <https://doi.org/10.1021/acs.macromol.1c00075>
- Fu, C. L., & Ho, K. M. 1983. *First-Principles Calculation Of The Equilibrium Ground-State Properties Of Transition Metals: Applications To Nb And Mo*. Physical Review B, 28(10), 5480. <https://doi.org/10.1103/PhysRevB.28.5480>
- Katsura, T., & Tange, Y. 2019. *A Simple Derivation Of The Birch–Murnaghan Equations Of State (Eoss) And Comparison With Eoss Derived From Other Definitions Of Finite Strain*. Minerals, 9(12), 745. <https://doi.org/10.3390/min9120745>
- Murnaghan, F. D. 1944. *The Compressibility Of Media Under Extreme Pressures*. Proceedings of the National Academy of Sciences, 30(9), 244-247. <https://doi.org/10.1073/pnas.30.9.244>
- Perdew, J. P., Burke, K., & Ernzerhof, M. 1996. *Generalized Gradient Approximation Made Simple*. Physical Review Letters, 77(18), 3865. <https://doi.org/10.1103/PhysRevLett.77.3865>
- Ozaki, T. 2003. *Variationally Optimized Atomic Orbitals For Large-Scale Electronic Structures*. Physical Review B, 67, 155108. <https://doi.org/10.1103/PhysRevB.67.155108>
- Ozaki, T., & Kino, H. 2004. *Numerical Atomic Basis Orbitals From H To Kr*. Physical Review B, 69, 195113. <https://doi.org/10.1103/PhysRevB.69.195113>
- Ozaki, T., Kino, H., Yu, J., Han, M. J., Kobayashi, N., Ohfuti, M., & Terakura, K. (2009). *OpenMx (Open Source Package For Material Explorer) Version 3.8*.
- Vinet, P., Smith, J. R., Ferrante, J., & Rose, J. H. 1987. *Temperature Effects On The Universal Equation Of State Of Solids*. Physical Review B, 35(4), 1945. <https://doi.org/10.1103/PhysRevB.35.1945>