

Si Observables Results

1 Silicon Equation of State

The equation of state of silicon was studied by varying the input lattice parameter in regular intervals between 95% and 105% of its initial value. A total of 200 data points were obtained. The extracted energy values of a Si atom, (half that of the unit cell) were fitted to three known models for the equation of state, expressing energy as a function of the relative linear compression η . The fitting of the models to the data, as well as the calculation of the best-fit parameters and associated uncertainties, was performed using the tools integrated in the `scipy.optimize` library in Python. In this case, the values E_0 and V_0 were treated as fitting parameters, along with the bulk modulus and its derivative at zero applied pressure, B_0 and B'_0 .

The data points and fitted models are shown in Figure 6. The initial guess for the best-fit parameters was taken from the literature as $V_0 = 20.0 \text{ \AA}^3/\text{atom}$, $B_0 = 100 \text{ GPa}$, $B'_0 = 5$, and $E_0 = -130 \text{ eV}$. For improved visualisation, the figure displays only a third of the calculated data points; however, the complete set of 200 points was used for fitting the models and determining the best-fit parameters.

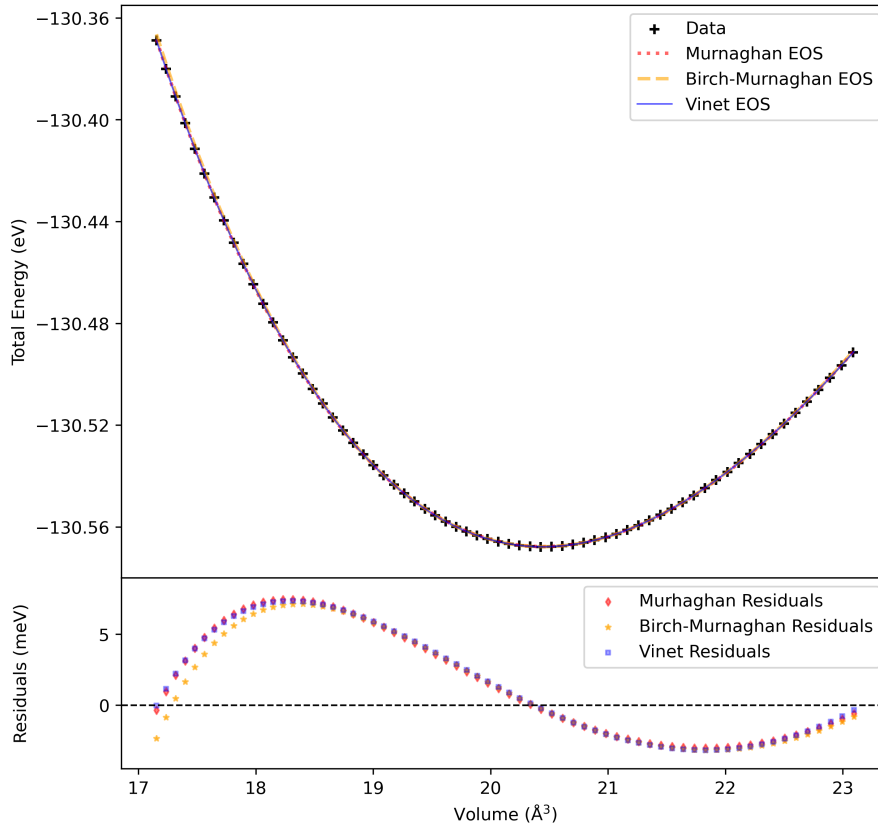


Figure 1: Graph showing the energy obtained for different values of the lattice parameter and the fitting of three known models for the $E(V)$ relationship. Note that the residual axis is plotted in meV.

The best-fit parameters and associated uncertainties for both cases can be found in Table 3.

EOS	V_0 (\AA^3)	E_0 (eV)	B_0 (GPa)	B'_0
Murnaghan	$20.4513 \pm 4 \cdot 10^{-4}$	-130.56770 ± 10^{-5}	88.08 ± 0.03	4.124 ± 0.008
Birch-Murnaghan	$20.4476 \pm 2 \cdot 10^{-4}$	-130.56775 ± 10^{-5}	88.47 ± 0.01	4.239 ± 0.003
Vinet	$20.44590 \pm 4 \cdot 10^{-5}$	-130.567774 ± 10^{-6}	88.751 ± 0.003	$4.2937 \pm 9.0 \cdot 10^{-4}$

Table 1: Best-fit parameters and associated uncertainties for the three equations of state fitted to the data.

The goodness of fit was assessed by computing the coefficient of determination, R^2 , yielding values of 0.99333, 0.99386, and 0.99331 for the Murnaghan, third-order Birch-Murnaghan, and Vinet equations of state (EOS), respectively. This indicates that, while the Birch-Murnaghan EOS provides a slightly better fit, the difference is not significant. Furthermore, there does not appear to be a substantial variation in the best-fit parameters across the three models. As shown in Table 1, the equilibrium volume remains relatively stable across models, with values ranging from $V_0 = 20.4459 \text{ \AA}^3$ (Vinet) to $V_0 = 20.4513 \text{ \AA}^3$ (Murnaghan). This represents an overestimation of approximately 2.2% compared to the experimental reference of $V_0 = 20.0 \text{ \AA}^3$. This overestimation of the equilibrium volume is a common feature of most generalised gradient approximation (GGAs) functional, including the PBE. This overestimation naturally leads to an underestimation of the bulk modulus, as from

$$B_0 = V_0 \left(\frac{\partial^2 E}{\partial V^2} \right)_{V=V_0} \quad (1)$$

one would expect $B_0 \propto \frac{1}{V_0}$. Although this effect would predict bulk modulus values of approximately 97 GPa, the best-fit values range from $B_0 = 88.08$ GPa (Murnaghan) to $B_0 = 88.751$ GPa (Vinet), which still deviates from this estimate. The discrepancy of the bulk modulus with the experimental result is likely due to the pseudopotential used, which may be underestimating the converged energy values. The pressure derivative of the bulk modulus B'_0 varies slightly between models, ranging from 4.124 (Murnaghan) to 4.2937 (Vinet), although this variation is relatively small. It was also observed that the results do not significantly change depending on the portion of the data fitted.

2 Silicon Observables

Various observable quantities of silicon have been calculated using the equilibrium volume V_0 and zero-pressure bulk modulus B_0 obtained from the best-fit equations of state. The results are presented in Table 2.

EOS	Density (g/cm ³)	c_L (m/s)	n (atoms/ \AA^3)	Θ_D (K)
Murnaghan	$2.28039 \pm 4 \cdot 10^{-5}$	6215 ± 1	0.048910 ± 10^{-6}	676.6 ± 0.1
Birch-Murnaghan	$2.28081 \pm 2 \cdot 10^{-5}$	6228.1 ± 0.3	$0.0489053 \pm 5 \cdot 10^{-7}$	678.08 ± 0.03
Vinet	$2.281000 \pm 4 \cdot 10^{-6}$	6237 ± 0.1	0.0489096 ± 10^{-7}	679.14 ± 0.01

Table 2: Density, longitudinal sound velocity, atomic number density, and Debye temperature calculated from fitting the three EOS. The uncertainties were found by propagating those on the best fitting parameters.

The computed density values are slightly lower than the experimental value of approximately 2.33 g/cm³. This discrepancy is due to the slight overestimation of the equilibrium volume V_0 , typical of GGAs approximations and discussed above.

In this case, the sound velocity was calculated using the simple form valid for isotropic solids, $c_L = \sqrt{\frac{B}{\rho}}$, which is clearly not valid for Si. The longitudinal sound wave speed (c_L) values obtained are significantly lower than those commonly reported in the literature, which typically cite values around 8400 m/s. However, direct comparison with experiment or other first-principles calculations is challenging due to variations in converged energies and the use of different pseudopotentials in different studies. The discrepancy is partly due to the underestimation of the bulk

modulus, but also because the longitudinal sound speed is typically calculated as

$$c_L = \sqrt{\frac{C_{11}}{\rho}} \quad (2)$$

for a wave propagating along the [100] direction,

$$c_L = \sqrt{\frac{C_{11} + C_{12} + 2C_{44}}{2\rho}} \quad (3)$$

for a wave propagating along the [110] direction, and

$$c_L = \sqrt{\frac{C_{11} + 2C_{12} + 4C_{44}}{3\rho}} \quad (4)$$

for a wave propagating along the [111] direction of the material, with C_{ij} the elements of the stiffness tensor and with

$$B = \frac{C_{11} + 2C_{12}}{3} \quad (5)$$

The computed atomic number density values are in close agreement with the commonly reported value of 0.049 atoms/Å³, with deviations of less than 0.01%, indicating that the structural properties are well captured by the fitting process.

The Debye temperatures (Θ_D) obtained are higher than the experimental value of approximately 645 K. This discrepancy is expected, as the values here were computed using only the longitudinal sound velocity, whereas most accepted values are derived using the effective sound velocity, defined by

$$\frac{3}{c_s^3} = \frac{1}{c_L^3} + \frac{2}{c_T^3}, \quad (6)$$

where c_L and c_T are the longitudinal and transverse sound velocities, respectively. Since c_L alone is used in our calculations, an overestimation of Θ_D is expected. A more accurate determination would require incorporating transverse wave speeds into the analysis.