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Temperature effects on the friction-like mode of graphite

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Abstract Since the anharmonicity of the vibrational mode related to the relative rigid motion of graphene layers plays a decisive role in the friction behavior of graphite, a quantitative account of the temperature dependence of the frequency of this $E_{2g}(1)$ mode its worth to be investigated. Starting with the solution of the Morse quantum-mechanical oscillator, a relationship between the populated averaged vibrational quantum number and temperature is proposed. This expression is applied to our previous computed Morse fittings describing the anharmonic potential of this mode (*Phys. Rev. B* 93, 144112 (2016)) with the aim at providing the available vibrational energy at different pressures and temperatures. We show that the average vibrational quantum number decreases under pressure but the available vibrational energy is almost indenpendent on pressure at a given temperature. As a result, the calculated temperature coefficient shows that inter-layer friction in graphite lowers as temperature increases with a lower impact when pressure is applied.

Keywords Graphite · Friction · Anharmonicity · Temperature · DFT calculations

1 Introduction

Anharmonicity is a key property to understand the effect of pressure (p) and temperature (T) on materials. As a recent and pertinent example, Errea *et al.* [1] have demonstrated the important role that anharmonicity plays in the accurate determination of the superconducting transition record temperature of sulphur hydride at high pressure. One of the reasons behind this fact is that these two thermodynamic variables, p and T, induce different crystal strains changing the distances between the atomic and molecular constituents of solids.

Pressure affects interatomic potentials and the shape of the vibrational density of states, whereas temperature mostly modify the relative population of the vibrational energy levels. Although both effects are manifested as volume changes in the unit cell, they are completely different in their physical nature and produce a different response in the crystal behavior [2]. For general and particular purposes, it is desirable to quantify and interpret, from a microscopic point of view, how pressure and temperature are related to the anharmonicity of the crystal if we want to provide a reliable description of the fundamental material properties.

While it is difficult to simulate from first-principles quantum-mechanical simulations, friction is such a fundamental property deserving a deep understanding both

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at the basic and applied realms [3]. In graphite, interlayer friction is associated with the vibrational $E_{2g}(1)$ mode accounting for the relative rigid displacement of its graphene layers. The lowest the frequency of this mode the easiest the relative motion between the layers.

In a previous paper [4], we have shown how a rigorous description of anharmonic effects associated with this friction-like $E_{2g}(1)$ mode of graphite can lead to an accurate evaluation of its frequency (ω) dependence on the available energy of the system. Pressure effects were successfully described showing good agreement with previous Raman experimental data [5]. However, an explicit ω-T relationship was not evaluated. To the best of our knowledge, such an expresion has not been reported so far for the $E_{2g}(1)$ mode of graphite, although for the frequency of the also double degenared $E_{2g}(2)$ mode of graphite, a linear dependence with temperature has been proposed by Koukaras *et al.* [6] very recently.

In this contribution, we make use of the solution of the quantum Morse oscillator and basic statistical mechanics following the Boltzmann distribution to derive an expression for the ω-T dependence of the friction-like $E_{2g}(1)$ mode of graphite. After a detailed analysis of combined pressure and temperature effects, we evaluate the variation of $\omega(E_{2g}(1))$ with temperature at zero pressure and calculate a temperature coefficient for this mode which is essentially independent on pressure. Our results will be successfully compared with the room temperature data of Hanfland *et al.* [5].

The rest of this article contains three more sections. The next one is divided into two subsections: a summary of the computational details of our previous DFT calculations and the algebraic equations leading to the ω-T relationship. Results and discussion will be dealt with in the following section where calculated frequency values with respect to temperature and pressure will be reported along with the comparison to experimental data. The paper ends with the main conclusions of our work.

2 Computational aspects

2.1 Details of the DFT calculations

Our basic system model is a tri-layer graphene (3LG) periodic slab of three graphene layers in an initial ABA stacking representing the Bernal-type configuration of stable bulk graphite. All the results presented here rely on previous electronic structure calculations carried out in our laboratory by Abbasi *et al.* [7] and Menéndez *et al.* [4] using this 3LG system. These calculations were performed within the density-functional theory (DFT) framework using the `VASP` code [8]. We follow the plane-wave pseudopotential approach along with the Perdew-Burke-Ernzerhof (PBE) generalized gradient exchange-correlation functional [9]. For the Brillouin-zone integrals, the Monkhorst-Pack method [10] is used with a k-point mesh of 16×16×8 along with an energy convergence of 1 meV and a plane-wave cutoff of 600 eV. Weak (dispersion) interactions were described using a Grimme-type correction [11]. These computational parameters yield a description of structural and equation of state parameters of graphite in good agreement with available experimental data (see Ref. [7]).

One-dimensional (1D) energetic profiles corresponding to the atomic movements involved in the $E_{2g}(1)$ mode were evaluated selecting an interlayer spacing, fixing the atoms of the A layers, and displacing the B layer along the x direction (which is parallel to the graphene planes) in steps of 0.09 Å from its equilibrium position up to the next equivalent ABA stacking configuration. At every step, the geometry is relaxed in the following manner: x and y coordinates of one C atom of layer B were fixed, whereas its z coordinate and all the cartesian coordinates of the other C atoms are optimized in the simulations. In order to mimic pressure effects, the inter-layer distance was changed according to the calculated relationship between this distance and hydrostatic pressure [7]. A pressure region between 0 and 14 GPa was investigated.

The shape of these 1D profiles was discussed in depth elsewhere [4], being their asymmetry a clear manifestation of the anharmonicity associated with this mode. Morse fittings to the 1D profiles covering a displacement range of ±0.3 Å around the equilibrium ABA configuration were also obtained in our previous study. These analytical Morse functions constitute the starting point for the analysis of temperature effects on the E_{2g} mode in this contribution.

2.2 Algebraic expressions using the quantum Morse oscillator

As in our previous study [4], we are only interested in the first order anharmonicity. Hence, a single-particle Hamiltonian with a non-harmonic potential can be written as the sum of a harmonic Hamiltonian and a cubic perturbation:

$$\hat{H} = \frac{1}{2}\left(\hat{P}^2 + \hat{X}^2\right) + \hbar\omega\sigma\hat{X}^3, \tag{1}$$

where $\hbar$, ω and σ are, respectively, the reduced Planck constant $h/(2\pi)$, the oscillating frequency and a parameter measuring the strength of the perturbation. $\hat{P}$ and

$\hat{X}$ represents the dimensionless momentum ($\hat{p}$) and position ($\hat{x}$) operators, respectively:

$$\hat{P} = \frac{1}{\sqrt{m\hbar\omega}}\hat{p}; \quad \hat{X} = \sqrt{\frac{m\omega}{\hbar}}\hat{x}. \tag{2}$$

By means of a perturbative expansion of the energy, it is straightforward to derive an expression for the energy levels of the anharmonic potential, as shown in some igorous textbooks [12]:

$$\begin{aligned} E_v = \; & hc\omega\left(v+\frac{1}{2}\right) - \\ & -\frac{15}{4}hc\omega\sigma^2\left(v+\frac{1}{2}\right)^2 - \frac{7}{16}hc\omega\sigma^2 + ... \end{aligned} \tag{3}$$

The quantum effect of the first order anharmonicty is therefore to decrease the energy levels of the harmonic oscillator (whatever the sign of σ), producing an asymmetric and not sinusoidal oscillation. Thus, in this system, the basic understanding of the anharmonicity does not differ from the classical point of view. Aiming at the physical interpretation, we can compare the perturbative treatment result with the quantum-mechanical solution obtained using the Morse potential [13]:

$$E_v = hc\omega\left(v+\frac{1}{2}\right) - \frac{(hc\omega)^2}{4M}\left(v+\frac{1}{2}\right)^2, \tag{4}$$

where M and N are the parameters of the Morse potential in the form:

$$V_M(x) = V_e + M\left(1-e^{-N(x-x_e)}\right)^2, \quad V_e = V_M(x_e). \tag{5}$$

The main advantage of the Morse potential is that the anharmonic correction is a function of the fitting parameters M and N. Incidentally, the comparison of Eqs. (3) and (4) gives us an opportunity to obtain an estimation of the parameter σ, which at zero pressure using the data tabulated in Ref. [4] yields a value as low as -7.45×10^{-2}.

As pressure (p) and temperature (T) are thermodynamic variables, evaluation of their effect on the anharmonicity from a quantum mechanical perspective requires an expression able to relate such quantities with the available vibrational energy $\langle E_v\rangle$. In our case, we propose to model such a relationship through basic statistical mechanics using the Boltzman distribution. This procedure is the standard one shown in solid state textbooks [14] and it has been recently applied to study phonon anharmonicities in graphite and graphene [15]. Accordingly, the calculation of $\langle E_v\rangle$ will be performed by replacing the quantum number v of the Morse oscillator eigenvalues by the average quantum number, $\langle v\rangle$:

$$\langle E_v\rangle = hc\omega_H\left(\langle v\rangle+\frac{1}{2}\right) - \frac{(hc\omega_H)^2}{4M}\left(\langle v\rangle+\frac{1}{2}\right)^2, \tag{6}$$

where the conection with temperature appears in $\langle v\rangle$:

$$\langle v\rangle = \frac{1}{e^{-\beta hc\omega_H}-1}, \quad \beta = \frac{1}{k_B T}. \tag{7}$$

The value of ω is related to the observed frequency (wavenumber). Thus, ω is expected to have a harmonic part, ω_H, corrected by an energy dependent anharmonic contribution, ω'. Hence, we can think in ω_H and ω' in terms of the Morse coefficients M and N (see Ref. [4]):

$$\omega = \omega_H + \omega', \quad \omega_H = N\sqrt{\frac{2M}{m_C}}, \quad \omega' = -\frac{15E}{16M}\omega_H, \tag{8}$$

where m_C is the atomic mass of carbon and E corresponds to the average available vibrational energy of the system. Including the expression of ω_H in Eq.(6) we arrive at our final equation for $\langle E_v\rangle$:

$$\langle E_v\rangle = \hbar N\sqrt{\frac{2M}{m_c}}\left(\langle v\rangle+\frac{1}{2}\right) - \frac{(\hbar N)^2}{2m_c}\left(\langle v\rangle+\frac{1}{2}\right)^2 \tag{9}$$

Therefore, in our scheme, the effect of T on the available energy is analitically calculated by inserting the value of $\langle v\rangle$ at a given temperature in Eq. 9 and using the values of the Morse parameters M and N obtained by fitting the potential energy 1D profiles. The main advantage of this procedure is that we can study the effect of T not only on the relative population of the energy levels and on the available energy but also on the frequency as pressure increases, highlighting how these two thermodynamic variables affect the anharmonic behaviour of the $E_{2g}(1)$ mode.

3 Results and discussion

Now, we are in condition of studying the impact of p and T on the $E_{2g}(1)$ mode of graphite. From Eq. (9), it is evident that the available vibrational energy depends not only on the temperature but on pressure as well, inasmuch as both quantities affect either the average vibrational quantum number or the Morse coefficients.

Let us start with the effect of T. Temperature does not affect the harmonic frequency, so at a given pressure the effect of temperature is increasing the vibrational quantum number, and, therefore, the available energy. Since an increase in the available energy of the system produces an increase in the amplitude of the vibrational mode, the frequency will decrease, and the anharmonic effect due to temperature in the $E_{2g}(1)$ mode is expected to reduce the frictional forces between graphite layers. Fig. 1 shows how $\langle v\rangle$ and $\langle E_v\rangle$ are modified by T and p. At a given pressure, the increase of temperature leads to higher values of both $\langle v\rangle$ and $\langle E_v\rangle$. Specifically, at $p = 0$ GPa, $\langle v\rangle$ increases from 0 at 0 K to 5.73 at

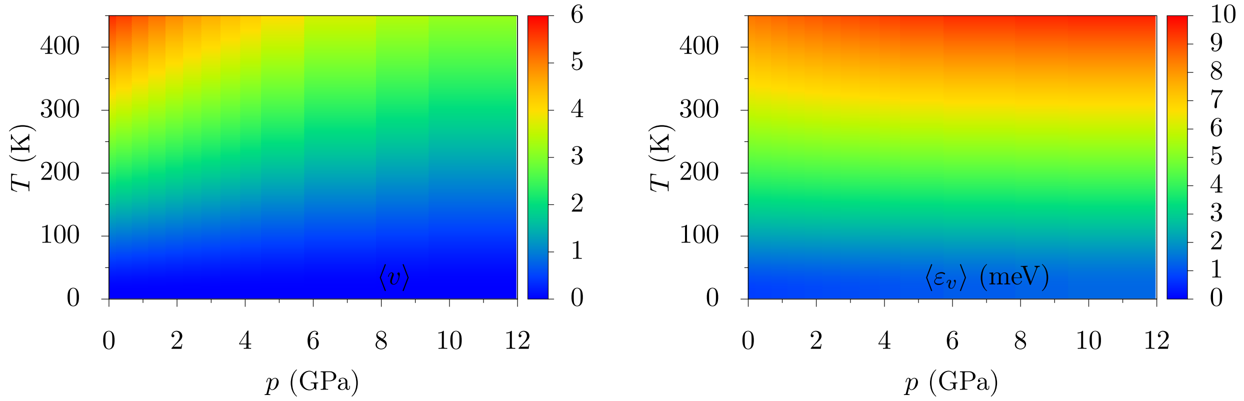

Fig. 1 (Left) Variation of $\langle v \rangle$ with pressure and temperature. (Right) Variation of $\langle E_v \rangle$ with pressure and temperature. Values of both magnitudes are displayed in terms of a color scale.

450 K, whereas the value of $\langle E_v \rangle$ increases from 1 meV to 10 meV.

It is worthwhile to compare the calculated effect of temperature on the $E_{2g}(1)$ mode with the classical limit. In Fig. 2 (left), we show the variation of the available energy with temperature at 0 GPa. Between 0 and 25 K, the available energy of this mode remains almost constant and therefore no anharmonic effects are expected. However, at temperatures from 25 to 50 K, the available energy starts to increase softly with a positive curvature, indicating that $E_{2g}(1)$ is thermally activated and higher vibrational levels are occupied. At a temperature close to T=70 K, the characteristic vibrational temperature $\Theta_v = \frac{h\nu}{k_B T}$ is reached and the $E_{2g}(1)$ mode begins to behave following the classical limit $k_B T$.

To get further insight on the classical behaviour of this mode as temperature increases, we have calculated the heat capacity of the lattice at constant volume (C_{lat}) associated with the friction-like $E_{2g}(1)$ mode. In graphite, the unit cell has four atoms and, therefore, there are three acoustic and nine optical vibrational modes. Since the $E_{2g}(1)$ mode is the vibrational mode with the lowest frequency at the Γ-point, the contribution at very low temperatures to C_{lat} is mainly made by this degenerated mode. This fact allows us to avoid including the whole vibrational density of states function. Thus, due to the lack of translational and rotational contributions, the total energy of the lattice at T increases from 0 K can be evaluated using Eq. 9, and the low T behavior of C_{lat} can be easily estimated by:

$$C_{lat} = 2N_A \frac{(hc\omega\langle v \rangle)^2}{K_B T^2} \left(1 - \frac{hc\omega}{2M}\left[\langle v \rangle + \frac{1}{2}\right]\right) e^{\beta hc\omega} \tag{10}$$

Using the calculated frecuency of the $E_{2g}(1)$ mode at 0 GPa, the lattice heat capacity of this mode is shown in Fig. 2 (right). As it can be seen, C_{lat} shows an asymptotic behaviour at temperatures close to 70 K, clearly informing that the classical limit is reached.

Concerning pressure, its effect is to increase the harmonic frequency and to reduce the anharmonic contribution. Therefore, it produces two opposite effects on the energy. On the one hand, pressure increases the $\langle E_v \rangle$ as the harmonic frequency does. On the other hand, the value of $\langle v \rangle$ is expected to be lower as a consequence of the higher energy gap between vibrational levels when pressure is applied. This behavior is illustrated in Fig. 1 (left), where the decreasing of $\langle v \rangle$ as pressure is increased at a given temperature is aparent specially at high temperature. The value of $\langle v \rangle$ reaches its maximum at low pressure and high temperature. At p = 0 GPa and T = 450 K, $\langle v \rangle$ is 5.73. The value at the same temperature but at 12 GPa is 3.06. At room temperature (293 K), $\langle v \rangle$ values are 3.56 and 1.84 at 0 and 12 GPa, respectively. From our previous results [4], the harmonic frequency at 0 GPa is around 50 cm^{-1} and higher than 90 cm^{-1} at 12 GPa. Therefore, since the changes in ω_H and $\langle v \rangle$ are of the same order but with opposite trends, it is not *a priori* clear if the average vibrational energy will increase or not as pressure is applied at a given temperature. Nonetheless, it is expected that these opposed trends cancel out with each other. The data plotted in 1 (right) confirms this statement since we clearly observe a nearly constant height for each of the colors in the figure.

In order to further clarify the effect of pressure on the E_{2g} mode, we show in Fig. 3 the variation of $\langle E_v \rangle$

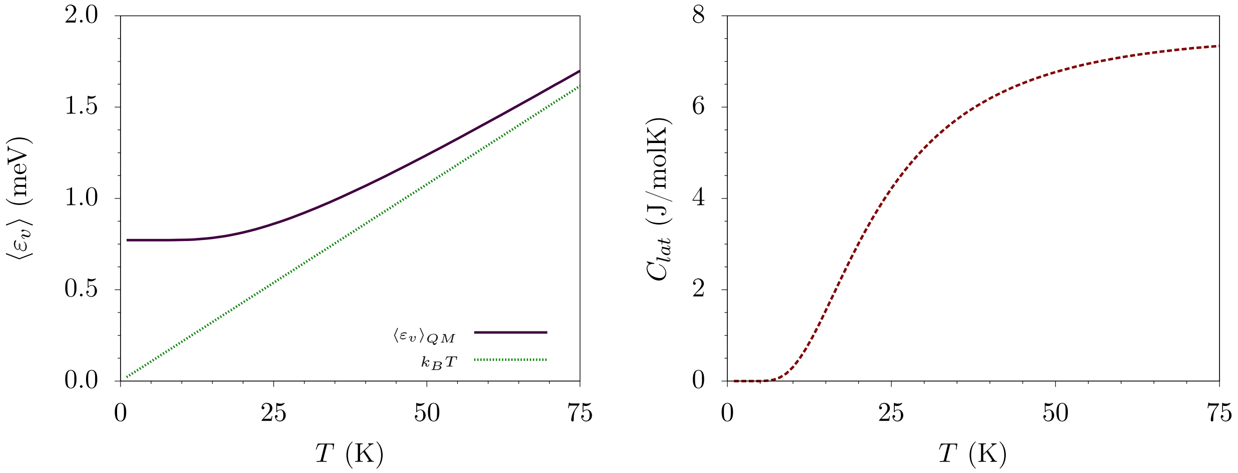

Fig. 2 (Left) Temperature dependence on the available energy of the $E_{2g}(1)$ mode at 0 GPa. Green dotted line represents the classical limit. (Right) $E_{2g}(1)$ mode contribution to the heat capacity at constant volume as a function of temperature.

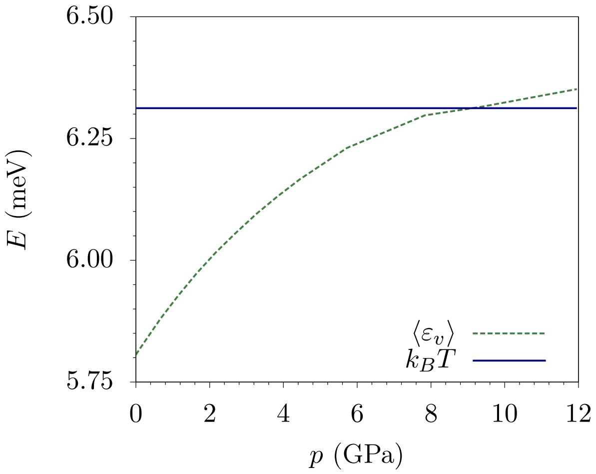

Fig. 3 Change in the available energy of the $E_{2g}(1)$ mode as a function of pressure. Blue line represents the classical limit at 70 K.

with pressure at room temperature along with the classical limit $k_B T$. It can be seen that application of pressure only leads to a small increasing of the average vibrational energy. Overall, the effect of pressure does not seem to have significant importance in the available energy of this mode. At room temperature, the difference in energy between 12 GPa and 0 GPa is 0.55 meV (6.35 and 5.80 meV). So that, our analysis highlight the idea that pressure modifies the form of the potential energy curve but it does not change the relative population of the energy levels at a given temperature.

So far, we have studied the impact of temperature and pressure in the available energy concluding that the classical limit ($k_B T$) can be a reasonable estimation of this property for the $E_{2g}(1)$ mode at temperatures beyond 70 K. Nevertheless, it would be very useful if it were possible to express the frequency dependence of this mode (instead of the available energy) on temperature in terms of a linear coefficient. To do this, we need to recall the expression of the frequency in terms of the harmonic and non-harmonic correction (see Eq. 8).

Then, the corrected frequency can be understood in terms of a linear function of T. The procedure is analogous to what Koukaras *et al.* performed on the also double degenerate high frequency raman active $E_{2g}(2)$ mode in graphene [6].

$$\omega = \omega_H + \chi T \tag{11}$$

According to our previous results, the available energy beyond room temperature is given by the classical limit. However, it must be taken into account that all the energetic calculations were obtained for one atom of C. This means that an estimation of the anharmonic contribution has to consider that the mean vibrational energy or k_BT must be divided by four (in graphite, Z=4). Notice that this does not affect the harmonic frequency because it does not depend on the available energy, but the anharmonic term does. Accordingly, by comparing Eqs. 8 and 11, we have:

$$\omega' = \frac{-15}{32}\frac{k_b}{M}\omega_H T; \quad \chi = \frac{-15}{32}\frac{k_B}{M}\omega_H. \tag{12}$$

In order to give a reasonable value for the parameter χ for the whole range of pressure studied, it would be recommendable to avoid any dependence of χ on p. Interestingly enough, our results allow us to introduce such approximation since we have found that the variation of the available energy with pressure remains almost constant at a given temperature as a consequence of the opposite trends in ω_H and $\langle v \rangle$, *i.e.* the variation with pressure of the anharmonic contribution to the vibrational frequency is approximately constant. Bearing this in mind, χ can be customized with the following expression:

$$\chi = \frac{-15}{32}\frac{k_B}{M_0}\omega_{H,0}, \tag{13}$$

where the subscript 0 stands for the evaluation of the Morse parameter M and the harmonic frequency at 0 GPa.

Under this assumption, we have estimated the value of χ in the pressure range studied as -0.0136 cm^{-1}/K. This value is in concordance with the value of the $E_{2g}(2)$ mode obtained by Koukaras *et al.* [6], -0.05 cm^{-1}/K. It should be pointed out, that at $p = 0$ GPa, the frequency of the $E_{2g}(1)$ mode is around 40-50 cm^{-1} and the value of the $E_{2g}(2)$ frequency is around 1500 cm^{-1}. Thus, our value evidences the expected stronger anharmonic behaviour found in the $E_{2g}(1)$ mode of graphite. Using our estimation of χ, we show in Table 1 the calculated $E_{2g}(1)$ frequencies in the temperature range from 250 K to 450 K at zero pressure. Each increase of 100 K makes the frequency goes down 0.70 cm^{-1}. Furthermore, it should be highlighted that the calculated value for ω at room temperature (293 K) is 48.2 cm^{-1}, very close to the experimental one (44 cm^{-1}) [5].

To conclude our analysis, we have adapted our calculated frequencies to the data obtained by Hanfland *et al.* [5], in order to test if our combined analysis of temperature-pressure frequency dependence is able to reproduce the experimental data. In Fig. 4, we show the experimental values obtained by Hanfland *et al.* at 293 K with those obtained assuming that the effect of the pressure is negligible on the anharmonic part and only affects the harmonic frequency, whereas the temperature effect can be modulated through the linear coefficient χ. Inspection of Fig. 4 clearly shows that our temperature-pressure model is able to reproduce the experimental data surprisingly well.

Table 1 Frequencies of the $E_{2g}(1)$ mode of graphite in the range of 250-450 K and differences ($\delta\omega$) with respect to the harmonic frequency according to our calculations.

T (K)	ω (cm^{-1})	$\delta\omega$ (cm^{-1})
250	48.6	-1.7
300	48.2	-2.1
350	47.9	-2.4
400	47.6	-2.7
450	47.2	-3.1

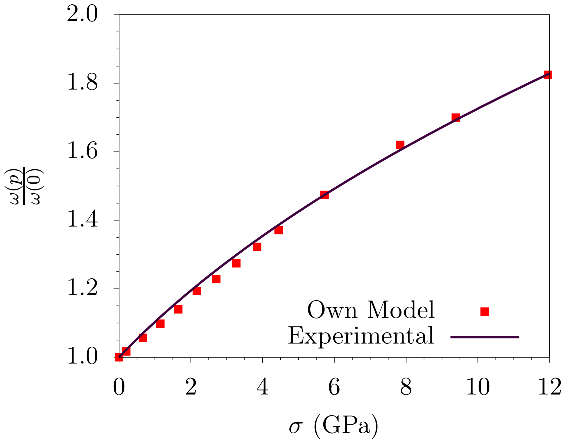

Fig. 4

4 Conclusions

5 Acknowledgements

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