

DEPARTAMENTO DE QUÍMICA FÍSICA Y ANALÍTICA



Universidad de Oviedo

THE FRICTION-LIKE MODE OF GRAPHITE

THESIS

IN ORDER TO OBTAIN THE QUALIFICATION IN THE

MASTER'S DEGREE IN THEORETICAL CHEMISTRY AND COMPUTATIONAL MODELLING

PRESENTED BY

CÉSAR MENÉNDEZ MUÑIZ

Contents

1	Theoretical Background	15
1.1	Quantum Mechanics	15
1.1.1	The Schrödinger equation	15
1.1.2	The variational principle for the ground state	17
1.1.3	The Hartree-Fock approximation	18
1.1.4	Density Functional Theory	20
1.2	Solids	30
1.2.1	Crystallography	30
1.2.2	The Schrödinger equation in a periodic potential	31
1.3	Computational calculations in solids	33

1.3.1	The VASP code	33
1.3.2	The Projector Augmented-Wavefunction (PAW)	33
1.3.3	Monkhorst and Pack method	34
1.3.4	Dealing with non-covalent interactions	35
2	Anharmonicity in the friction-like mode of graphite	38
2.1	Proofs of Anharmonicity from Atomic Arrangements and Energetic Considerations	40
2.2	Modelling the Anharmonicity of the $E_{2g}(1)$ Mode	43
2.2.1	Oscillations	44
2.2.2	The four spring model	53
2.2.3	Fitting parameters: the Morse function	56
2.2.4	Frequency and pressure. The equation of state and the Grüneisen parameter	58
2.3	Frequency Evaluation and Comparison with Experiment	59
2.3.1	Fitting by Morse	59

2.3.2	What does anharmonicity depend on?	61
2.3.3	The anharmonicity understood under the four springs model	64
2.3.4	The final step. Does the analysis reproduce the experimental value?	65
3	Anharmonicity-Temperature relationship	69
3.1	A quantum mechanical perspective of anharmonicity	70
3.2	The average vibrational energy	75
3.3	Heat Capacity at $p = 0$ GPa	78
3.4	Calculation of the temperature coefficient	80
4	Conclusions	83

Introduction

Graphite is among the best solid lubricants, but it is also known that graphite behaves as a poor lubricant in vacuum.[1] Such a diverse behaviour makes graphite a target model in many frictional/tribological studies at both macroscopic[2] and atomic[3, 4, 5] levels. Graphite also was the first system studied in the seminal work by Mate *et al.*,[6] when the friction force microscope was developed. Nowadays graphene has emerged into the scene of frictional studies[7, 8, 9] and many works have been focused on understanding the underlying mechanisms of friction in graphite[10, 11] and graphene.[12] For instance, novel terms like superlubricity[13, 14] have been coined to refer to the near-zero friction force observed between a graphite substrate and a graphite flake in an incommensurate configuration.

The vibrational $E_{2g}(1)$ mode of graphite describes a rigid-layer relative movement of the graphene sheets (see Fig. 1), thus informing on the forces that graphene layers have to overcome in order to initiate relative displacements.[15, 16] By means of the characterization of this vibrational mode and the evaluation of the energetic profile accompanying its atomic movements, it is possible to get insight into the corrugation energy landscape and the frictional behavior of graphite at a microscopic level. One of the relevant points at this regard is to accurately take into account the anharmonicity of this Raman active mode. It is expected to be noticeable, leading to a stress-induced blue shift of its frequency greater

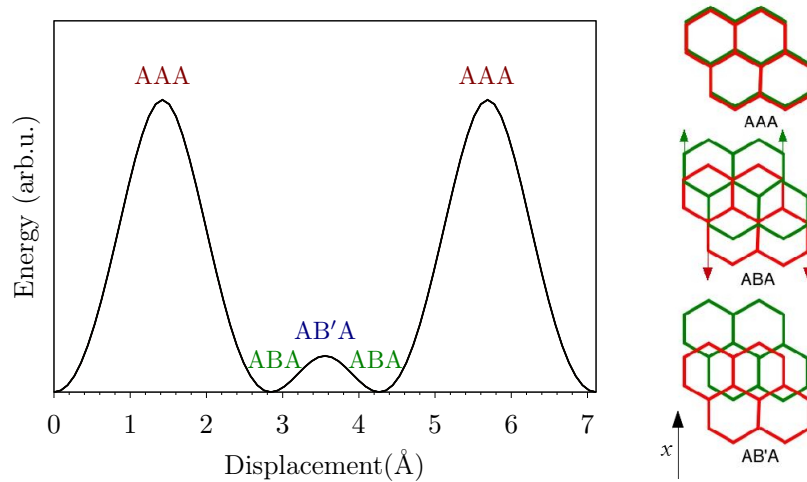


Figure 1: *Left.* Energetic profile versus the relative displacement of the middle layer of the ABA equilibrium configuration for a given interlayer distance along a selected direction (the x direction). *Right.* Arrangements of the tri-layer slab associated with graphite stackings at critical points. C atoms in the central layer B are in green. C atoms in A layers are in red. Arrows indicate the atomic movements involved in the $E_{2g}(1)$ vibrational mode.

than in other IR and Raman higher frequency modes.[17, 18] This vibrational mode may be also used to verify the presence of graphene among graphite-like samples containing few layers graphene. Although present in graphite and absent in graphene, the Raman active $E_{2g}(1)$ mode “cannot be (directly) used as method for an experimental verification of graphene”[19] due to its low Raman intensity.[20] However, since the frequency of this mode is a measure of the splitting experienced by the E_{2g} mode in graphene into the infrared active E_{1u} and the Raman active $E_{2g}(2)$ modes of graphite,[21] the lower frequency of this $E_{2g}(2)$ mode in graphite with respect to graphene could be used as a potential way to discriminate between graphite and graphene, albeit this is a matter of current controversy.[22]

From a more theoretical perspective, it should be noticed that in the $E_{2g}(1)$ mode, the in-plane and out-of-phase atomic movements (see Fig. 1) yield negligible modifications in the intralayer C-C network. The frequency of this shear-like mode was observed below 50 cm^{-1} at ambient conditions (see for example Refs.[21, 23, 24] and references therein) and

provides a direct and accurate manifestation of the weak van der Waals (vdW) interactions between graphene sheets in graphite. This is a relevant issue that deserves some comments since the interplay between vibrational modes and vdW and covalent interactions in graphite has aroused interest with detailed analysis for decades. In the pioneer works of Dresselhaus *et al.*[21, 23] and the more recent studies of Cousins *et al.*,[24] the focus was on the simultaneous modelization of both types of interactions (also introducing anharmonic contributions) to account for experimental elastic data and Γ -point vibrational frequencies. As highlighted in these works, difficulties in the parametrization of C interactions appear not only due to the coexistence of both strong and weak interactions but for the fact that the former are well localized and the later are of a non-directional type. Clearly, a theoretical determination of the energy profile involved in the $E_{2g}(1)$ mode would benefit an unambiguous characterization of vdW interactions in graphite-based materials.

By performing detailed first principles calculations, it is possible to accurately describe the simultaneous energetics involved in intra- and inter-layer C-C interactions. Among the number of computational simulations related to this topic, and in the context of our study, it is worth mentioning the early works of di Vincenzo *et al.*[17] (with explicit reference to anharmonicity in the $E_{2g}(1)$ mode) and Gonze *et al.*,[25] where the lack of an accurate computational methodology was discussed. More recently, vdW contributions were specifically taken into account in the calculations,[15, 26, 27, 16, 28, 29] and the particular energetic barrier involved in the transition from the stable ABA to the AAA stacking of graphene sheets in graphite was calculated.[15, 16, 27, 26] From the energetic profiles connecting both stackings, the vibrational frequency of the $E_{2g}(1)$ mode can be straightforwardly calculated.[16] Anharmonicity of phonons in carbon-based materials has also been the subject of rigorous theoretical studies by Bonini *et al.*[22] and Paulatto *et al.*[30] (and references therein). In these works, the focus is on the phonon scattering mechanisms and the characterization of phonon decays[22] with the aim at determining thermal transport properties of these materials,[30] though nor explicit neither implicit

reference to friction phenomena was reported.

Fortunately, an extensive experimental work,[18] including effects of hydrostatic pressure on this frequency, provides a pertinent source of information to compare with these computational studies. Moreover, from the frequency (ω)-pressure (p) experimental data of Hanfland *et al.*,[18] linear Grüneisen parameters were derived, thus allowing for a comprehensive discussion of anharmonicity in the $E_{2g}(1)$ mode.

Taking into account the above considerations, we pursue in this Master Thesis to provide a thorough understanding of anharmonicity in the $E_{2g}(1)$ mode of graphite by rendering, modeling and evaluating this vibrational mode under different stress conditions. By rendering we mean an illustrative description of the atomic arrangements with specific attention to the local anisotropy around the absolute energy minima, and an interpretation of the surface energy potential landscape using intuitive images of charge density interactions. A simple four-spring model and a perturbative treatment using Morse-like functions are enough to reasonably account for the anharmonicity associated to this mode. The evaluation stage consists in a detailed analysis of part of our previous DFT-based calculations in graphite under different stress conditions.[16] Specifically, we examined the results of a three-layer graphene slab in which the middle layer is forced to slide between other two ones, which remain fixed at different interlayer distances, thus mimicking the atomic movements involved in the $E_{2g}(1)$ mode.[16] Morse functions accurately account for energy changes along the vibrational coordinate of this mode at different interlayer separations. It will be shown that anharmonicity decreases as this parameter decreases or, equivalently, hydrostatic pressure or uniaxial stress is applied. Overall, our calculations provide a quantitative assessment of the anharmonic contribution of this rigid-layer frequency mode of graphite under different strain scenarios, and inform on the trends that frictional forces show as temperature increases and pressure is applied.

This document contains two more chapters and the conclusions section. The next chapter collects the basic concepts of the theoretical background needed to perform a study in Computational Materials Science. The Bloch theorem or the DFT formalism are examples of what is included in it. Because many of these concepts appear later in the rest of the Master Thesis, I found it important providing this preliminary chapter. Since this document will not pursue to be in any case a reference for those who look for an insight understanding of these theoretical concepts, I have tried to avoid tedious developments and explanations, being the search for a fluent language and rational organization the main characteristics of this chapter. The referenced bibliography will provide a deeper scope to the reader, if it were necessary.

The main part of this work is contained in Chapter 2 and must be read with care due to its extent and because the most important conclusions obtained in this work come from this chapter. The study of the friction-like mode of graphite starts with the qualitative analysis of the energetic profiles at different interlayer distances. The identification of the interactions responsible for the shape of the potential energy curves are important in the way that will provide information needed to understand the anharmonic contribution once this is quantified in subsequent sections. The potential energy curve obtained when the inner layer (B) is displaced between the outer fixed layers (A) is asymmetric from the equilibrium point, associated to the ABA stacking of graphite. This asymmetry is due to the existence of two less stable stackings (AAA and AB'A) emerging when the displacement is done to the left or to the right. The amount of non-covalent interactions between graphene layers have been mainly related to the electrostatic repulsions arising when atoms or bonds in layers B are on top (under) of their counterpart in layers A placed below (above).

In order to determine numerically the deviation from a harmonic potential, the following section in this chapter shows different ways to modelize this behaviour. Firstly, a

perturbative treatment of a classic oscillator is presented. The idea which remains under this model is that in harmonic oscillations the potential is symmetric around the equilibrium point and the period does not depend on the energy. Hence, the movement in each moment is described by a simple sinusoidal function. In contrast, in an anharmonic oscillator the displacement to the left and to the right from the equilibrium point is not longer the same. And, although the oscillation remains periodic, the period is not energy independent and the movement needs a Fourier series expansion to be accurately explained. Thus, treating the period and the displacements to the left and to the right like perturbations from the harmonic oscillator, it is possible to obtain an expression for the observed frequency in terms of the harmonic frequency and a small anharmonic contribution which depends on the energy. The second model presented is based on the idea that the friction like movement can be approximated to a system with four springs attached to an atom in layer B. These four springs share all of them the same force constant but their lengths are equal in pairs. Therefore, two different springs are attached to two atoms in the upper layer A and the other pair of non equal springs to two atoms in the other (lower) layer A. The small displacements of the atom in layer B are modelized by a given potential from this imaginary system of four springs. Following the perturbative treatment, the anharmonicity emerging from this system can be determined. To end this chapter, a set of equation of states previously employed in experimental works will give us appropriate expressions to relate frequency and pressure variations. As we have previously noticed, it must be remarked that the computational data were fitted to a Morse function, whose strengths and weakness are also discussed in this section.

This chapter ends with a full evaluation of all the models studied. The last section is focussed on answering all the questions which emerged previously. Which external effects increase/decrease anharmonicity, how reliable the models are or if the available experimental results can be explained in terms of the existence of an anharmonic contribution and, in case of being true, how important this contribution is, are examples of such of these

questions.

Finally, Chapter 3 is a short study of different considerations derived from Chapter 2: the calculation of the average vibrational energy and the coefficient of temperature are addressed in this part. To quantify the anharmonic vibrational energy a quantum mechanical treatment took from the Cohen-Tannoudji text-book [46, 47] for anharmonic oscillations is followed. The final target is to achieve an expression capable of relating temperature and anharmonicity. However, other different side products are also included here and their study is carried out in this chapter too.