

Atomistic modelling of elasticity and phonons in Diamond and Graphene

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Abstract— We present an atomistic interatomic potential that with a single set of parameters is able to accurately describe at the same time the elastic, vibrational and thermodynamics properties of semiconductors. We also show that the correct inclusion in the potential of short and long range interactions provides a model for the force field that accurately performs Static Dynamics and Molecular Dynamics.

Keywords— *Empirical interatomic potential; dispersion curves; mode-Grüneisen; Molecular Dynamics; Graphene.*

I. INTRODUCTION

Atomistic empirical potential methods are still the only computationally feasible way to model semiconductor materials on nanoscale. When used in Molecular Dynamics these methods drastically reduce the computational time and the number of atoms that is possible to simulate greatly exceeds that of ab initio methods. Since the initial propositions of Keating, Tersoff and others, very little progress has been made in obtaining a suitable potential able of accurately describing the physics of both the elastic, vibrational and thermodynamics properties of semiconductors.

Starting from the Abel-Tersoff model [1] [2], which is one of the most commonly used methods for atomistic modelling, we have designed a many body potential that simultaneously reproduces the elastic constants, dispersion curves and mode-Grüneisen parameters for the group IV semiconductors. The new potential, which we will refer to as the MMP potential,[3] includes the radial and angular forces of the interacting atom pairs (short range) but also takes into account the influence of the broken crystal symmetry when the atomic arrangement is out of equilibrium (long range). These long range interactions are taken into account only up to the second nearest neighbours, which is enough to correctly influence the elastic and vibrational properties and therefore representing only a marginal computational cost compared to the full treatment of other proposed potentials.

II. CLASSIC ATPS AND MMP POTENTIAL

A general feature, observed in the ATPs but also in others potential as the Stillinger-Weber [4] or the Tersoff-Brenner potential [5], is that the limitation of mainly including short

range forces results in the incompatibility between vibrational (phonon frequencies and their dispersions) and elastic properties (e.g. elastic constants). These potentials replicate rather well the elastic constants but they overestimate the phonon dispersion curves. Particularly, the Transverse Acoustic phonon branches are considerably overestimated missing the characteristically flat band near the X high symmetry point. In the MMP potential the inclusion of the second nearest neighbours interactions allows the reproduction of the flat band as well as the splitting between the Transverse Optical (TO) and Longitudinal Optical (LO) far from the Γ point.

One of the obvious implications of the phonons overestimation is that thermodynamic properties such as the coefficient of thermal expansion, which depends on the derivative of the phonon frequencies in respect of deformation, is also incorrectly predicted. Moreover, when the potential does correctly predict the thermal expansion coefficient it dramatically fails to describe the mode-Grüneisen parameters, which is a fundamental inconsistency.[6] In the MMP potential the exact prediction of the elastic property is consistent with good prediction of the mode-Grüneisen parameters. This is mainly due to the introduction in the model of a multi-bond interaction term between first neighbours which accounts for the crystal distortion out of equilibrium.

III. RESULTS AND DISCUSSION

Of the group IV tetrahedrally bonded semiconductors we have chosen C-Diamond as target material. Compared to Silicon and Germanium, Carbon has distinctive mechanical properties: small lattice constant, low cohesive energy and great elastic moduli. The large elastic constants, due to the very strong carbon-carbon bonds, express the tendency to strongly resist to any distortions of the crystal. Furthermore, the short bond length induces a strong bonds interaction and first nearest neighbours interaction which in the MMP are taken into account by a multi-bond term. In Table I the measured mechanical properties of diamond are listed along with the MMP simulated values and are also compared with ab initio results. Whereas, in Table II the mode-Grüneisen parameters are shown for the high symmetry points.

TABLE I. LATTICE PARAMETERS FOR C-DIAMOND

Property	Exp. ^a	MMP	ab initio
E_{Coh} [eV]	-7.37	-7.24	
L.C. [Å]	3.567	3.561	3.530 ^b
B [Mbar]	4.42	4.51	4.73 ^b
C' [Mbar]	4.76	4.76	
C_{11} [Mbar]	10.76	10.85	10.60 ^c
C_{12} [Mbar]	1.25	1.34	1.25 ^c
C_{44} [Mbar]	5.77	5.77	5.62 ^c

^a Values from [7]
^b Values from [8]
^c Values from [9]

TABLE II. MODE-GRÜNEISEN PARAMETERS FOR DIAMOND

mode-Grüneisen	Exp. ^a	MMP	ab initio
$\gamma_{\text{TO,LO}}(\Gamma)$	0.98	1.31	0.94
$\gamma_{\text{TA}}(\text{X})$	0.40	0.21	0.32
$\gamma_{\text{LA,LO}}(\text{X})$	2.00	1.80	1.43
$\gamma_{\text{LO}}(\text{L})$	1.40	1.40	0.55
$\gamma_{\text{TO}}(\text{L})$	1.40	1.50	1.13

^a Values from [7]
^b Values read from Fig. 4 in [8]

In Fig. 1 and Fig. 2 the dispersion curves of C-Diamond and Graphene are shown. The results show that the proposed potential outperforms all other potentials in the literature and is able to correctly predict a very large set of elastic and vibrational properties of C-Diamond. Furthermore we also tested the reliability of the potential in modelling the vibrational spectrum of Graphene and the results also indicate an excellent agreement with experimental data.

To further show the accuracy of the method we have performed Molecular Dynamics on a Graphene sheet (Fig. 3) in order to reveal more of the physics behind the intrinsic ripples that are experimentally observed in free standing Graphene sheets. Our simulations show that ordered and roughly regular ripples form spontaneously as a means to lower the total elastic and cohesive energy of the system and not as a spontaneous response to thermal fluctuations as previously proposed.

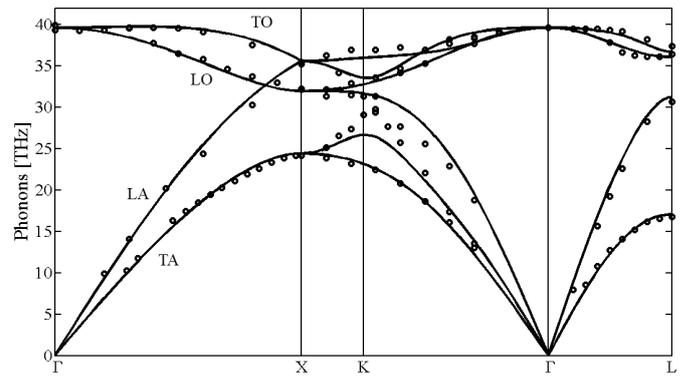


Fig. 1. Phonon dispersion curves of C-Diamond. Experimental data in open circles.

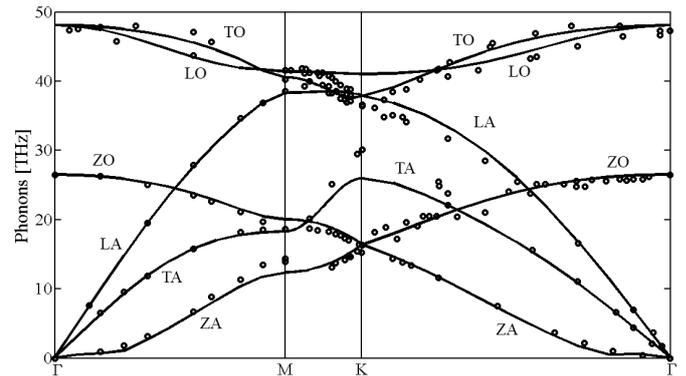


Fig. 2. Phonon dispersion curves of Graphene. Experimental data in open circles.

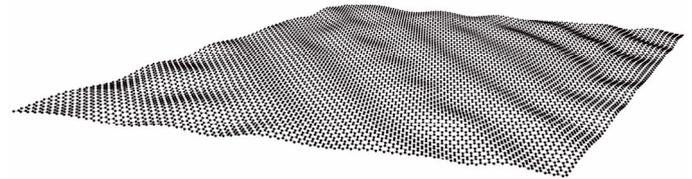


Fig. 3. Intrinsic ripples in a free standing Graphene sheet.

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