Comparison between calculated LDOS and measured NEXAFS for carbon allotropes and mixtures

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Introduction

Carbon takes many different forms (allotropes) and has a fantastic range of properties. Different electronic configurations give different geometical structures. The "bonds'' between atoms are such that carbon atoms have 3 in-plane nearest neighbours in sheets of graphite bonded by sp2 orbitals and 4 neighbours in an sp3 bonded diamond lattice. The nature and properties of thin diamond films are affected by the growth conditions. Therefore we explore different pure and mixed carbon allotropes including diamond, graphene/graphite, amorphous carbon and mixtures of the above. We plan to include hydrogen atoms in our samples to study the thin film growth process.

After creating carbon samples with specific features (such as vacancies, or graphite/diamond boundaries) we observe our samples with the AViz atomistic visualization package and calculate either the DOS (Density Of States) or LDOS (LocalDOS) spectrum using the PLATO tightbinding molecular dynamics package.

In this project we compare the calculated LDOS spectra of atoms in specific structures with NEXAFS measurements.

Plato

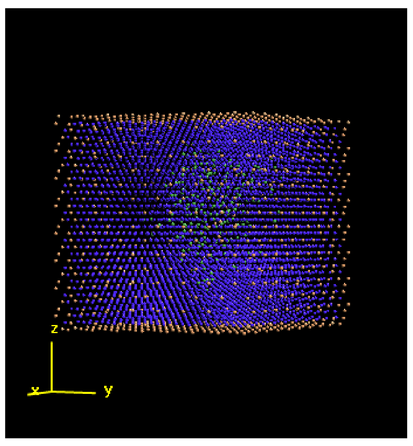
PLATO is a package for Linear-combination of Atomic Orbitals which allows us to perform molecular dynamics, structure optimisation, etc. using atomic orbital based electronic structure methods (tight binding and density functional theory) in an efficient form.

Tight-binding

In a tight-binding model, interior electrons are bound to the nucleus. Solving the Schroedinger equation in this semi-empirical approximation may not be as good as a full "ab-initio" solution, but using a semi-empirical "tight-binding model" enables the introduction of electronic structures calculations into molecular dynamics simulations.

Tight-binding is a technique that produces the accuracy needed to describe complex systems with a relatively small computational cost for large-scale simulations and for relatively long simulation periods.

It is a semi-empirical method which bridges the gap between ab-initio studies and simulations based on empirical classical potentials.



Styles

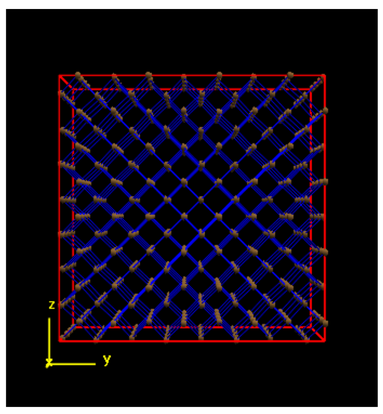
Another way to view samples is by color coding bonds only. A slice of the center of the sample above is shown in detail at right below with bond color coding.

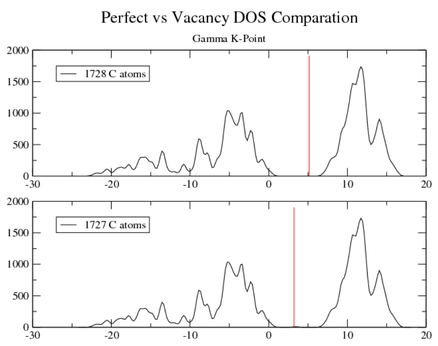
Visualisation

The AViz package was created by Geri Wagner and Adham Hashibon, based on earlier OpenGL routines written by David Segev (Saada) and implemented by Irina Rosenblum amongst others. AViz requires an .xyz file of atomic coordinates, and draws balls at the atomic sites and then adds bonds of specific lengths between specific atoms, thus enabling us to directly observe bond lengths and angles.

Diamond

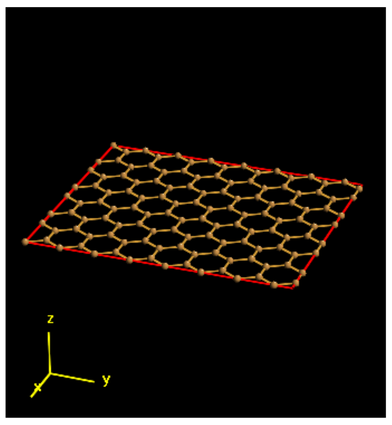
Perfect sample below left and LDOS with/without vacancy below right.

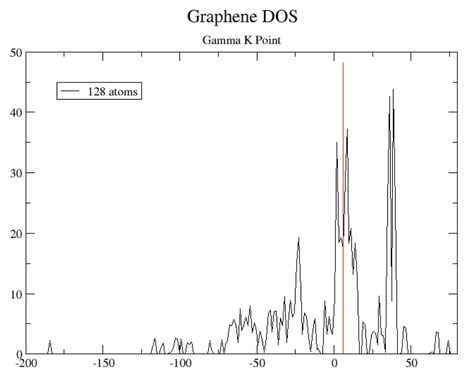




Graphene

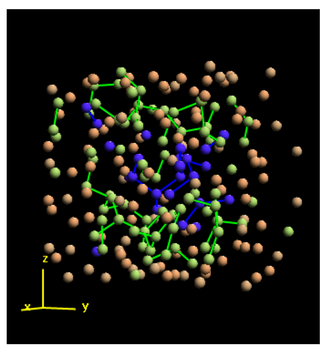
A single graphite layer, image below left, LDOS below right

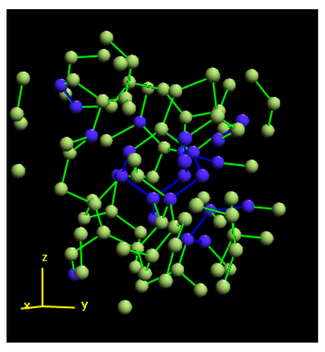


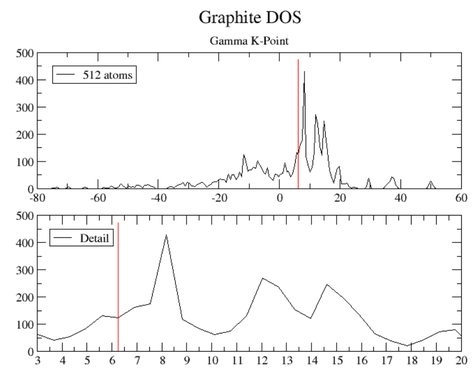


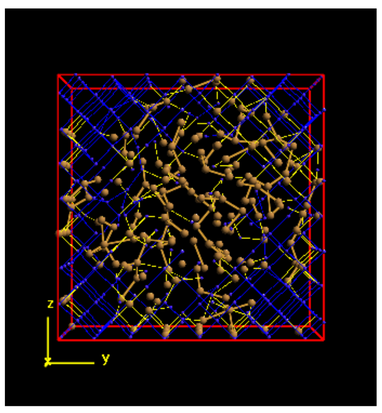
Amorphous

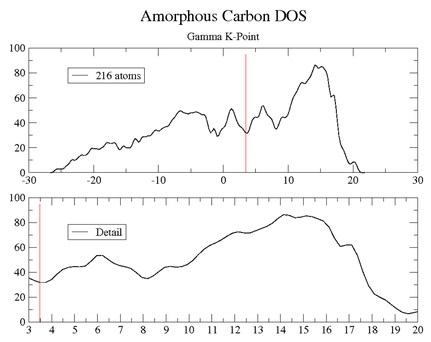
Amorphous diamond has different structural phases, which can be distinguished in models by color coding atoms with different coordination numbers. On the right both images are coded using green for sp2 and blue for sp3. Brown atoms form the sample shell and are not colorcoded here. The image on the far right is a detail of the sample center. The DOS graph is shown lower right, to be compared with the 1000eV NEXAFS.





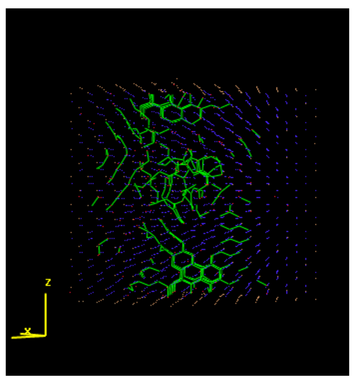


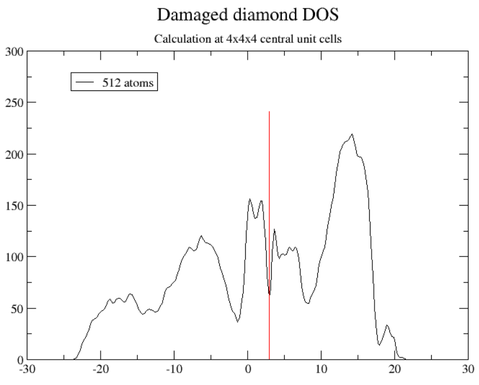




Mixed

We have looked at mixtures of nanodiamonds and amorphous carbon in different configurations. Two types are illustrated here. Above on the left is a sample which under periodic boundary conditions would have nanodiamond and amorphous regions adjacent. At the left is a diamond sample with damage to its core, and at the lower left is an image of the central region of the same sample in a different visualization style. At the lower right is its DOS spectrum, which, as expected, shows a mixture of graphite and diamond features.





References

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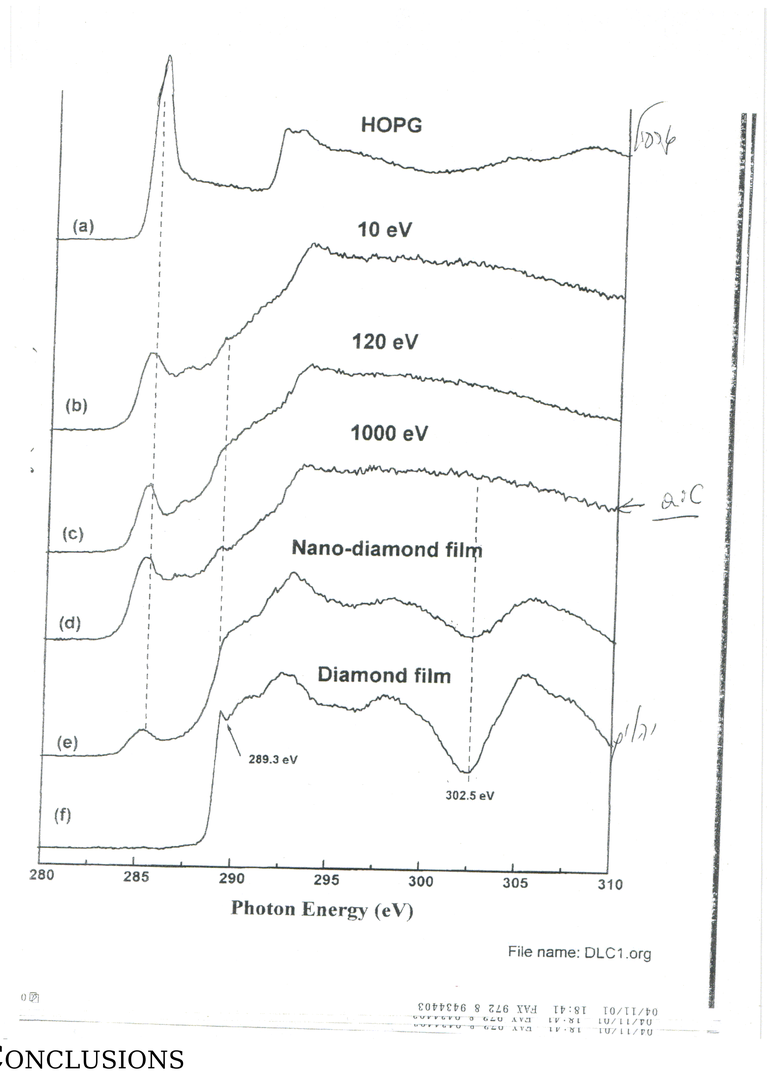
Experiment

The NEXAFS (Near Edge X-ray Absorption Fine Structure) spectroscopic technique can be used to measure the unoccupied density of states (DOS).

For carbon the photon adsorption was measured as a function of photon energy in the 280-320 eV range, and carried out in the partial electron yield (PEY) mode by recording the emission of secondary electron of 8 eV kinetic energy as a function of incident photon energy with a resolution of 0.1 eV. Under these measuring conditions the NEXAFS measures transitions from occupied (C(1s)) core level electronic states to unoccupied electronic states above the Fermi level and therefore it reflects the unoccupied local electronic density of states (U-LDOS) in the near-surface region of the solid. Just as the bonding between carbon atoms in different carbon allotropes (graphite and diamond) is different so are their U-LDOS.

Due to the fact that the initial state of the transition is highly localized (C(1s)) NEXAFS is sensitive to nanosize clusters of carbon allotropes making it a highly sensitive spectroscopic method for the investigation of nanostructures. NEXAFS is also very sensitive to the presence of defects and impurities.

Immediately below we show calculated LDOS for graphite and below that a series of NEXAFS for different carbon allotropes are presented.



Conclusions

The HOPG (Highly Oriented Pyrolithic Graphite) NEXAFS graph has characteristics similar to the LDOS of our simulated graphite sample.

Calculations for samples with vacancies in the diamond crystal present a characteristic blip within the band gap similar to the experimental measurements (not shown).

The diamond film NEXAFS present a second band gap that can also be observed in our diamond samples DOS calculations.

Mixed samples (intermediate energies in the NEXAFS) present a combination of these characteristics.