MESOSCALE ELASTIC THEORY IN GRAPHITE

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First principles density functional calculations within the Local Density Approximation (LDA) have provided highly plausible [1-3] results but the folklore of interlayer interactions is that LDA does not include an important part of the physical interaction between layers (dispersion forces *i.e.* van der Waals force) and therefore should not be relied upon.

The main disagreement between theory and experiment is the value of the elastic constant C_{13} (positive for experimental studies [4, 5] and negative for theoretical studies [6]). The sign of this elastic constant is crucial for the elastic properties of the material; a positive (negative) value of C_{13} means that under compression of the in-plane lattice constant, the out-plane lattice constants tend to expand (contract), respectively. Therefore theory and experiment describe graphite as a material with an opposite elastic behavior.

In this work we have demonstrated that LDA performs excellently for graphite and reproduces with precision all the elastic properties. We have shown that, under compression, graphite tends to bend with amplitude directly proportional to the applied strain. These bending modes introduce a new kind of elastic constants called *mesoscale elastic constants*.

We have developed a elastic theory beyond the harmonic approximation that describes the behaviour of graphite/graphene under any applied strains ε. Within this theory the elastic formation energy $E(\varepsilon)$ describing the behaviour of a graphite layer under any applied strain ε can be written as [7]:

$$E(\varepsilon) = \left\{ K \cdot \frac{-\varepsilon + \varepsilon_{critical}}{L(1+\varepsilon)^2} + C \cdot \varepsilon_{critical}^2 \right\} \cdot \vartheta(-\varepsilon + \varepsilon_{critical}) + C \cdot \varepsilon^2 \cdot \vartheta(+\varepsilon - \varepsilon_{critical})$$

where K is the bending constant of graphene, C is the elastic constants along the bending direction, θ is the Heaviside step function, L is the length of the plane along the bending direction and $\varepsilon_{critical}$ is the critical strain.

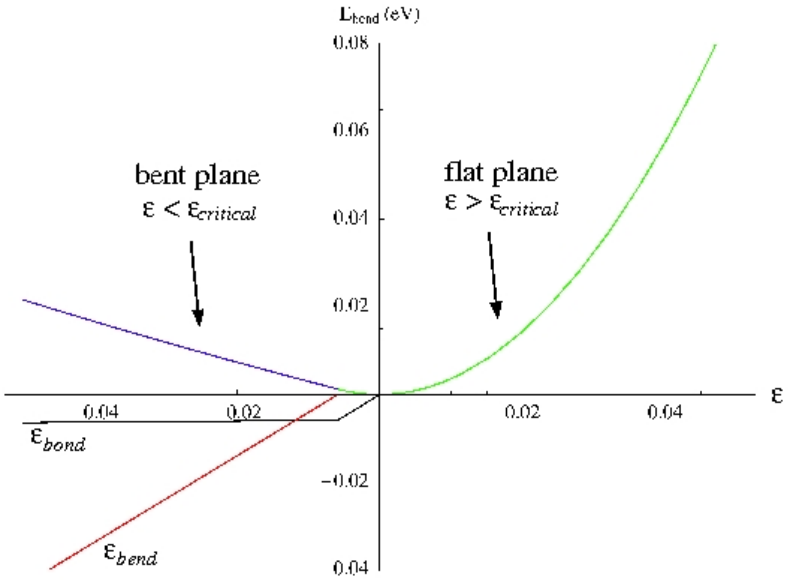
Therefore a graphite layers can be flat or bent depending on the value of the applied strain ε. The critical strain separates homogeneous in-plane compression (at low compression) from the bent plane behaviour (at high compression). Under small deformation the critical strain $\varepsilon_{critical}$ can be written as:

$$\varepsilon_{critical} : -\frac{K}{2 \cdot L \cdot C}$$

This theory predict that under the critical strain the elastic behaviour is due to the classical elastic constants while above the critical strain the elastic behaviour is dominated by the mesoscale elastic constants. The corresponding C_{13} classical and mesoscale elastic constants are -2.3 GPa and +6.2 GPa, respectively both in agreement the previous theoretical calculations (C_{13} = -2.8 GPa, [6]) and experiments (C_{13} = 7.9±3.5 GPa, [4, 5]).

Therefore the elastic constants measured by experimental studies are the mesoscale elastic constants (the elastic constants that really describes the elastic behaviour of HOPG graphite samples) while the elastic constants determined by *ab-initio* studies are the common elastic constants.

We observe that, different quality of graphite samples could favourite the rising of one elastic behaviour over the other. For instance, polycrystalline graphite samples should favourite the mesoscale elastic behaviour while single crystal graphite (Kish graphite) should favourite the classical elasticity. Furthermore different experimental measures could be able to detect the mesoscale or classic elasticity depending on the type of the techniques (x-ray, ultrasonic, sonic resonance or static test methods).



Figures: The formation energy of a graphite plane when compressed ($\varepsilon < 0$) or expanded ($\varepsilon > 0$). The green and blue curves represent the formation energies when the strain ε is above or under the critical strain $\varepsilon_{critical}$, respectively. The red line represents the strain component due to the bending, while the black line represents the strain component in-plane compression.

We must observe that the only theoretical value that is not completely in agreement with respect to the experimental data is the mesoscale elastic constant C_{13}^{M} = 31.8 GPa (the respective experimental value is 36.5 ± 1 [4.5]). Nevertheless, the temperature effects [6] and/or crystal defects [2] can explain this relatively small difference (10.4 %) between theory and experiment.

Finally using the same background theory but applied for the graphene case, we have demonstrated:

1. The bending modes possess always sinusoidal solutions;
2. The 1-dimensional bending is always more favourable than a 2-dimensional one;

The latter results give new insight into the structural atomic properties of 2-dimensional materials with strong implications for the new field of graphene science. We observe that the mesoscale elastic theory should extend to all the other important layered materials like BN, clays and MgB_2.

References:

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