A Determination of Inter-Planar Resonant Frequency of Bulk Graphite

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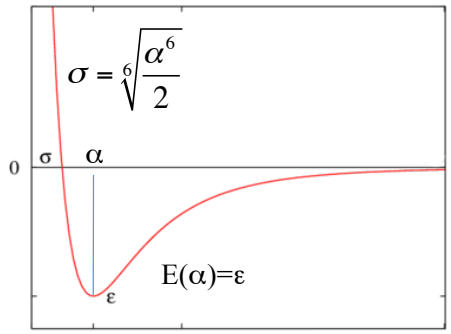
(1) We assume the c_{33} elastic modulus of HOPG (highly ordered pyrolytic graphite) determined by Kelly & Walker (1969)[1] can also model the interaction of two C atoms at some distance α;

$$c_{33} = 3.650 * 10^{11} \frac{dyne}{cm^2} = 3.650 * 10^{10} Pa$$

(2) Given the Lennard Jones potential approximation, E(α), differentiation allows for a value σ to be determined at which E′(α) equals zero at a specific α. Plugging this value into the LJ potential function yields a minimum corresponding to the observed interlayer spacing in bulk graphite (i.e 3.34 A);



$$E(\alpha) = 4\varepsilon\left[\left(\frac{\sigma}{\alpha}\right)^{12} - \left(\frac{\sigma}{\alpha}\right)^{6}\right]$$

$$E'(\alpha) = 4\varepsilon\left[\left(\frac{6\sigma^6}{\alpha^7}\right) - \left(\frac{12\sigma^{12}}{\alpha^{13}}\right)\right] = 0$$

$$\frac{6\sigma^6}{\alpha^7} = \frac{12\sigma^{12}}{\alpha^{13}} \rightarrow \alpha^6 = 2\sigma^6 \rightarrow \sigma = \sqrt[6]{\frac{\alpha^6}{2}}$$

(3) From this, a Δα can be determined which corresponds to a change in interlayer spacing such that E(α) ranges from its absolute minimum to its zero at σ. This Δα value will be used with α, defined as the equilibrium interlayer spacing of bulk graphite (3.34 A) to calculate strain with the elastic modulus mentioned prior to determine some coaxial force required to induce an interlayer spacing change of Δα;

$$\alpha = 3.340 * 10^{-10} m$$

$$\Delta\alpha = \alpha - \sigma = \alpha - \sqrt[6]{\frac{\alpha^6}{2}} = 3.644 * 10^{-11} m$$

(4) At this point, a coaxial force F_{atom} can be determined with the only remaining unknown being the cross sectional area of the object in question. For the sake of this derivation, it is assumed that the known density of Graphene (ρ) can be used to deduce a value corresponding to the area of a single atom;

$$\rho = 7.62 * 10^{-5} \frac{g}{cm^2}$$

$$N_A = 6.022 * 10^{23}$$

$$\therefore$$

$$\frac{cm^2}{7.62 * 10^{-5} g} * \frac{12.011 g}{N_A atoms} * \frac{m^2}{10^4 cm^2} = 2.618 * 10^{-23} \frac{m^2}{atom} = A_{atom}$$

(5) Then the force F_{atom} required to produce a strain $\Delta\alpha/\alpha$ for a pair of C atoms interacting at a distance 3.34 A can be modelled by;

$$F_{atom} = c_{33}(\frac{\Delta\alpha}{\alpha})A_{atom} \approx 1.042 * 10^{-13} N$$

(6) If it is assumed that a change in interlayer spacing $\Delta\alpha$ can be modelled (or at least roughly approximated) by Hooke's Law, then the analogous spring constant k can be calculated by;

$$k = \frac{F_{atom}}{\Delta\sigma} \approx 0.00286 \frac{N}{m}$$

(7) In the case of a spring, the natural harmonic frequency can be determined by the following assuming the mass of the spring system is known. For the purposes of this derivation, it can also be assumed that one C atom is "fixed" corresponding to adhesion to a substrate. Thus the mass of the oscillating system can be set as the mass of a single Carbon atom (M_{atom}) given by;

$$\frac{12.011g}{N_A atoms} * \frac{xg}{atom} = 1.995 * 10^{-23} \frac{g}{atom} = M_{atom}$$

(8) And the first mode given by;

$$f_0 = \frac{1}{2\pi}\sqrt{\frac{k}{M_{atom}}} \approx 1.90597 * 10^9 Hz \approx 1.91 GHz$$

Resonant frequency independence from number of atoms proof

With the assumption of two C atoms interacting with respect to equation (5), it could be inferred that the first harmonic frequency then changes depending on the surface area of the bulk HOPG crystal in question. To this end, the following is presented to show that the resonant frequency of two C atoms interacting at distance α also holds for a graphene crystal of n atoms (2n atoms for the total system).

(9) Considering an aggregated equation for the first mode frequency of the two interacting C atoms, the values of A_{atom} and M_{atom} can be replaced with values A and M respectively where n represents the number of atoms in the system;

$$f_0 = \frac{1}{2\pi}\sqrt{\frac{c_{33}(\frac{\Delta\alpha}{\alpha})A}{\frac{\Delta\alpha}{M}}} = f_0 = \frac{1}{2\pi}\sqrt{\frac{c_{33}(\frac{\Delta\alpha}{\alpha})A_{atom}n}{\frac{\Delta\alpha}{M_{atom}n}}}$$

$$A = A_{atom}n : A_{atom} = \frac{cm^2}{7.62*10^{-5}g} * \frac{12.011g}{N_A atoms} * \frac{m^2}{10^4 cm^2} = 2.618*10^{-23}\frac{m^2}{atom}$$

$$M = M_{atom}n : M_{atom} = \frac{12.011g}{N_A atoms} * \frac{xg}{atom} = 1.995*10^{-23}\frac{g}{atom}$$

(10) Algebraic manipulation leads to the following conclusion;

$$f_0 = \frac{1}{2\pi}\sqrt{\frac{c_{33}(\frac{\Delta\alpha}{\alpha})A_{atom}n}{\frac{\Delta\alpha}{M_{atom}n}}} = \frac{1}{2\pi}\sqrt{\frac{c_{33}(\frac{\Delta\alpha}{\alpha})A_{atom}n}{\Delta\alpha M_{atom}}}$$

Thus, the resonant frequency of a graphitic system does not depend on the number of atoms involved even though the force F required to produce a change in interlayer spacing $\Delta\alpha$ depends on the cross sectional area of the object in question.

[1] Theory of Thermal Expansion of a Graphite Crystal in the Semi-Continium Model
https://www.ems.psu.edu/~radovic/PLW/1970_8_211_Kelly_Carbon.pdf