

Aplicación del modelo de dispersión al grafito y al hollín

Nuestro objetivo es entender y aplicar el modelo dispersión utilizado en el artículo:

Lee, S. C., & Tien, C. L. (1981, January). *Optical constants of soot in hydrocarbon flames. In Symposium (international) on combustion (Vol. 18, No. 1, pp. 1159-1166). Elsevier.*

Así, cuando tengamos datos experimentales, a través de una serie de valores (longitud de onda / índice de refracción), podríamos utilizar el modelo de dispersión para tener una curva continua y poder aproximar a cualquier longitud de onda el índice de refracción de un determinado hollín.

En dicho modelo de dispersión, hay varios parámetros que se pueden “fijar” (en base a estudios previos) o se pueden dejar “libres” y utilizar para ajustar el modelo. Idealmente, las densidades electrónicas utilizadas en el modelo no deberían ser parámetros de ajuste, sino que se podrían obtener a través de difracción de rayos X o espectrometría Raman, siendo así entradas del modelo, diferenciando así el grafito de los diferentes tipos de hollín que tengamos. Las denominadas “damping constants” servirían para ajustar el modelo con los datos experimentales.

En el artículo de Lee_Tien_1981 dice:

$$n^2 - k^2 = 1 + \frac{e^2}{m\epsilon} \sum_{j=1}^2 \frac{n_j(\omega_{bj}^2 - \omega^2)}{(\omega_{bj}^2 - \omega^2) + \omega^2 g_{bj}^2} - \frac{e^2}{m^* \epsilon} \frac{n_f}{(\omega^2 + g_f^2)} \quad (1)$$

$$2nk = \frac{e^2}{m\epsilon} \sum_{j=1}^2 \frac{n_j \omega g_{bj}}{(\omega_{bj}^2 - \omega^2) + \omega^2 g_{bj}^2} + \frac{e^2}{m^* \epsilon} \frac{n_f g_f}{\omega(\omega^2 + g_f^2)} \quad (2)$$

where the complex refractive index is $m = n - ik$, e the electron charge, m the electron mass in vacuum, ϵ the permittivity constant, n_j 's and n_f the bound and free electron number densities, ω_{bj} the natural frequency of bound electrons, ω the frequency of radiation, g_{bj} and g_f the damping constants of bound and free electrons, and m^* the effective electron mass. Previous studies on graphite optical properties allow reasonably accurate estimates of ω_{b2} and g_{b2} ¹² as well as ω_{L1} .²³ Since the Fermi energy surface

El modelo de dispersión viene explicado detalladamente en:

Moss, T. S., Burrell, G. J., & Ellis, B. (2013). *Semiconductor opto-electronics*. Butterworth-Heinemann.

Aquí aparece que:

$$n^2 - k^2 - 1 = \sum_j \frac{(Ne^2 f_j / m \epsilon_0) (\omega_j^2 - \omega^2)}{(\omega_j^2 - \omega^2)^2 + \omega^2 g_j^2}$$
$$2nk = \sum_j \frac{(Ne^2 f_j / m \epsilon_0) \omega g_j}{(\omega_j^2 - \omega^2)^2 + \omega^2 g_j^2}$$

Donde:

N is the electron density.

frequency corresponding to an optical transition. **The magnitude of the contribution of each oscillator to the optical constants is determined by the oscillator strength f of each transition. Equations (2.5a and b) would then be replaced by a series of terms for all the allowed transitions**

In principle, the sum of the oscillator strengths $\sum f_j$ is simply determined from the electronic configuration of the atoms (see Ditchburn, 1952, and Houghton and Smith, 1966).

Vemos aquí, comparando con el artículo de Lee_Tien_1981, que:

$$N \cdot f_i = n_i$$

Dejando de lado el término de los “electrones libres” e intentando aclarar cómo se calcula el “ n_j ”:

En el capítulo de Moos_2013, aparece como ejemplo de N :

0.295 μm (Philipp and Taft, 1959). Putting N equal to four times the atomic density, as Ge has four valence electrons per atom, (namely putting $N = 1.8 \times 10^{23} \text{ cm}^{-3}$) and noting that m is the classical electron mass (not an effective mass) one obtains

Por lo que N en el carbono sería la densidad atómica por 4.

Por otro lado, en el artículo:

Halpern, O., & Hall, H. (1948). The ionization loss of energy of fast charged particles in gases and condensed bodies. Physical Review, 73(5), 477.

Aparecen unas “ f_i ” que podrían coincidir con las “ f_i ” del capítulo de Moss_2013. Dice:

The quantities f_j give the fraction of electrons associated with the various dispersion frequencies, while the quantities g_j take account of the

from empirical data. In assigning the f_j 's, the electrons in each atomic shell (K, L, M, etc.) were generally grouped together, and an average frequency ν_j was assigned on the basis of x-ray ionization data. Table I contains the data ac-

TABLE I. Data employed in constructing Fig. 1.

	Lead	Iron	Water	Carbon	Air (Sea level)	Helium
Z	82	26	10	6	7	2
$2\pi ne^3/mc^2$ (Mev cm ² /gm)	0.0606	0.0710	0.0850	0.0765	0.0765	0.0765
α (volts)	60	53	21	28	0.74	0.40
f_0	0	0	0	1/3	0	0
f_1	22/82	2/26	2/10	1/6	3/7	1
f_2	32/82	14/26	4/10	1/6	2/7	0
f_3	18/82	8/26	2/10	1/3	2/7	0
f_4	8/82	2/26	2/10	0	0	0
f_5	2/82	0	0	0	0	0
g_0	0	0	0	7*	0	0
ν_0 (vapor)	—	—	—	0.33	—	—
ν_1 (vapor)	—	—	0.62	—	—	—
ν_1	2.0	0.25	0.27	1.7	40	100
ν_2	20	4.0	2.2	2.3	115	—
ν_3	100	32	6	15	800	—
ν_4	360	170	40	—	—	—
ν_5	500	—	—	—	—	—
13.5Z (volts)	1100	350	135	81	95	27
ν_{mj} (volts)	1200	430	80	60	96	40

* This value of g_0 (in units of α) for carbon corresponds to a specific resistance of 5000×10^{-6} ohm cm.

Pero aquí aparecen 4 f_i y nosotros solo tenemos 2 n_i (artículo de Lee_Tien_1981).

Por otro lado, el artículo de Lee_Tien_1981 comenta una relación interesante entre los n_1 y n_t :

The number densities of the bound electrons are inter-related by the effective number of electrons n_j^* ($j = 1, 2$) contributing to the optical properties over the frequency range $0 < \omega < \omega_{bj}^{12}$ such that

$$\frac{n_1}{n_t} = \left(\rho \frac{N_0}{M} n_1^* \right) / \left(\rho \frac{N_0}{M} n_2^* \right) = \frac{n_1^*}{n_2^*} = \frac{1}{12} \quad (5)$$

where ρ is the density, N_0 the Avogadro number, and M the molecular mass. An additional relation

Aquí, parece decir que la relación entre la densidad de los n_1 y n_t depende de la relación entre los n_1 y n_2 efectivos (asterisco). La referencia 12:

Taft, E. A., & Philipp, H. R. (1965). *Optical properties of graphite*. *Physical Review*, 138(1A), A197.

Nos da la fórmula para calcular los n_{eff} :

$$\int_0^{\omega_0} \omega \epsilon_2(\omega) d\omega = (2\pi^2 N e^2 / m) n_{\text{eff}}, \quad (3)$$

where n_{eff} is the effective number of electrons per atom (in a crystal of atom density N) contributing to the optical properties in the range to ω_0 .^{5,21} Since transitions

La constante dieléctrica $\epsilon_2(\omega)$ (que se refiere a la parte compleja) quizá se podría obtener de ese mismo artículo digitalizando y estudiando las curvas:

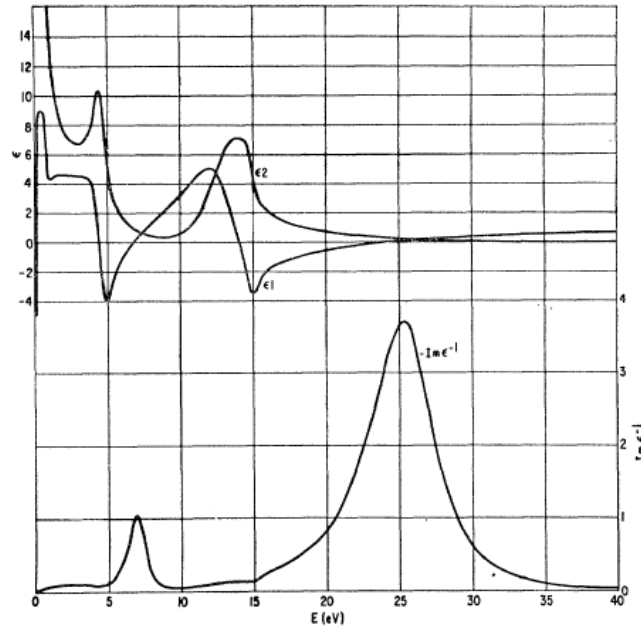


FIG. 2. The spectral dependence of the real and imaginary parts of the dielectric constant, ϵ_1 and ϵ_2 , and the energy-loss function $-\text{Im}\epsilon^{-1}$ for graphite obtained by Kramers-Kronig analysis of the curve of Fig. 1.

Conociendo el valor de la integral se podrían calcular los n_{eff} . Pero para ello necesitamos también los ω_0 , que en nuestro caso serían las ω_{bj} del artículo de Lee_Tien_1981, las frecuencias naturales de los “bound electrons”. Dichas frecuencias naturales son (artículo Lee_Tien_1981):

TABLE I
Dispersion constants at 300°K

Electrons	Number density, n		Natural frequency $\omega \times 10^{-15}, \text{sec}^{-1}$	Damping constants $g \times 10^{-15}, \text{sec}^{-1}$	
	Present	Dalzell & Sarofim ¹⁵		Present	Dalzell & Sarofim ¹⁵
free	n_f	n_f	—	0.54	6.0
bound, 1	$n_1 = \frac{1}{12} n_t$	n_1	1.25	g_{b1}	6.0
bound, 2	$n_2 = n_t - n_1 - n_f$	n_2	7.25	2.53	7.25

Los valores de 1.25 y 7.25, se supone que se obtienen en los artículos:

Yasinsky, J. B., & Ergun, S. (1965). *Transmittance of single crystals of graphite in the infrared spectrum. Carbon*, 2(4), 355-358.

Taft, E. A., & Philipp, H. R. (1965). *Optical properties of graphite. Physical Review*, 138(1A), A197.

Pero al leerlos, dichos números no aparecen. Por ejemplo, en el artículo de Yasinsky, solo aparecen los números 0.82 eV y 0.41 eV:

Figure 3 shows the reciprocal transmittance spectra over the range 0.2–1.6 eV. The profile of each of the three curves indicates a peak near 0.82 eV. Since $\log I_0/I$ is proportional to the extinction coefficient, it seems probable that the extinction coefficient spectrum peaks near 0.82 eV. Preliminary evidence indicates that the index of refraction does not vary rapidly with wavelength in this region. Thus the nk curve should peak near 0.82 eV. Since $\gamma_1 = \hbar\omega/2$ where the theoretical conductivity curve is discontinuous, we arrive at a value of $\gamma_1 = 0.41$ eV. The calculation of γ_2 must

Siendo el parámetro de 0.41 eV, según McClure_1957:

The parameter γ_1 represents the chief splitting of bands caused by the interlayer interaction. Wallace estimated 0.1 eV and Johnston's work yields 0.35 eV.

En cualquier caso, todo lo anterior se basa en las transiciones (visible e infrarroja) existentes en el grafito. Como dice Lee_Tien_1981:

dimension.¹⁰ It is therefore reasonable to assume that soot particles possess the same π bands as in graphite. Since the graphite optical transitions involving the π bands are in the visible and infrared^{11,12} (0.26 μm and 1.5 μm), while the σ band transitions occur well below the ultraviolet (<0.1 μm), an accurate account of the optical properties in the visible and infrared can be obtained by considering the π bands only.

1.5 μm coincide con los 0.82 eV del artículo de Yasinsky_1965, no sabemos si por casualidad.

0.82	eV	1512.00235	nm	6613.74632	cm ⁻¹	5.04350	fs
820.00000	meV	1.51200	μm	198.27513	THz	0.00504	ps

Las referencias mencionadas (11 y 12), siendo 12 Taft_1965 y la 11:

Boyle, W. S., & Nozières, P. (1958). *Band structure and infrared absorption of graphite. Physical Review*, 111(3), 782.

No muestran de forma clara esos valores de 0.26 y 1.5 μm .

El artículo de Boyle_1958 y otros artículos mencionados remiten a la estructura de bandas del grafito, lo cual es la base para entender las transiciones que buscamos. Los dos artículos principales son:

Wallace, P. R. (1947). *The band theory of graphite. Physical review, 71(9), 622.*

McClure, J. W. (1957). *Band structure of graphite and de Haas-van Alphen effect. Physical Review, 108(3), 612.*

En Wallace_1947, por ejemplo, se dice:

Now C. A. Coulson³ has estimated that γ_0 is about 20 kcal./mole, or about 0.9 ev. At room temperature $kT=0.025$ ev. Therefore the "effective number of free electrons" n_{eff} , per atom, is

$$n_{\text{eff}} = 2.3 \times 10^{-4}.$$

$$\sigma = N_{\text{eff}} e^2 \tau / m_{\text{eff}}, \quad (3.15)$$

we can calculate the "mean effective mass," m_{eff} , of our conductivity electrons. This is found to be

$$m_{\text{eff}} = \frac{h^2 k T}{36 \log 2 \cdot a^2 \gamma_0^2} \quad (3.16)$$

which yields, on numerical evaluation, at room temperature

$$m_{\text{eff}} = 1/18 \text{ electron mass.} \quad (3.17)$$

the four atoms of a unit cell.

The volume of the unit cell is

$$V_{\text{cell}} = \mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3) = \frac{\sqrt{3}}{2} a^2 c,$$

so that the atomic volume is

$$V_{\text{atomic}} = \frac{\sqrt{3} a^2 c}{8}. \quad (4.2)$$

horizontal boundaries of the first zone are therefore at $k_z = \pm(1/c)$. The lowest Brillouin zone so described has the volume $4/\sqrt{3} a^2 c$. But the density of states is twice the volume of the crystal, that is,

$$2 \times (\text{number } N \text{ of cells}) \times (\text{volume of cell}) = \sqrt{3} a^2 c N.$$

Thus there are 4 N electron states in the lowest Brillouin zone, or one per atom. Since as in the

Now the number of free electrons per atom is $n_{\text{eff}} = N_{\text{eff}}/N_a$, N_a being the number of atoms. Since the atomic volume is $\sqrt{3}a^2c/8$,

$$N_a = 8V/\sqrt{3}a^2c.$$

So

$$n_{\text{eff}} = \frac{4}{\sqrt{3}\pi} \frac{kT\gamma_1}{\gamma_0^2} \left[s_1 + \frac{\pi}{2} \frac{kT}{\gamma_1} s_2 + \frac{3}{2} \left(\frac{kT}{\gamma_1} \right)^2 s_3 + O\left(\left(\frac{kT}{\gamma_1} \right)^3 \right) + \dots \right] \quad (5.7)$$

$$= 2.25 \times 10^{-3}$$

at room temperature. This is not at all in agreement with the value of 2.3×10^{-4} obtained by treating a single hexagonal layer; in fact, the dependence of n_{eff} on T is quite different in the two cases. On the other hand, as we shall see in the next section, the conductivities in the plane agree to the first order. Thus the discrepancy is merely caused by our definition of n_{eff} , and is compensated by a corresponding change in m_{eff} , the effective mass.

En McClure_1957 se comenta que:

In the three-dimensional case there are two conduction and two valence bands (not counting spin degeneracy),

Band 1 corresponds to the sum of Bloch waves made up from $2p_z$ orbitals based on A and A' atoms and is generally the highest in energy; Band 2 corresponds to the difference of the same Bloch waves based on A and A' atoms and is generally the lowest in energy. Bands 1