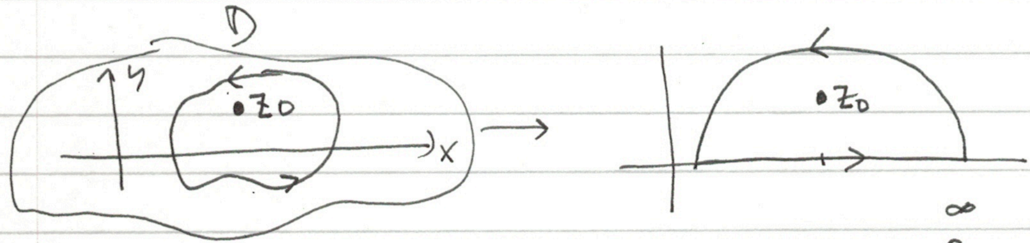
Relaciones de Kramers - Kronig

sea $f(z)$ analítica en D, con $\lim\limits_{|z|\to\infty} |f(z)| = 0$

Cauchy $\Rightarrow$ $$f(z_0) = \frac{1}{2\pi i}\oint_C \frac{f(z)}{z-z_0}\,dz \qquad (1)$$



$$f(z_0) = \frac{1}{2\pi i}\int_{-\infty}^{\infty} \frac{f(x)}{x-z_0}\,dx$$

$z_0 \to x_0$ $$f(x_0) = \frac{1}{i\pi}\, P\!\!\int_{-\infty}^{\infty} \frac{f(x)}{x-x_0}\,dx \qquad (2)$$

$$f(x_0) = u(x_0) + i\,v(x_0) = \frac{1}{\pi}\, P\!\!\int_{-\infty}^{\infty} \frac{v(x)}{x-x_0}\,dx - \frac{i}{\pi}\, P\!\!\int_{-\infty}^{\infty} \frac{u(x)}{x-x_0}\,dx$$

$\Rightarrow$ $$u(x_0) = \frac{1}{\pi}\, P\!\!\int_{-\infty}^{\infty} \frac{v(x)}{x-x_0}\,dx \qquad (3)$$

$$v(x_0) = -\frac{1}{\pi}\, P\!\!\int_{-\infty}^{\infty} \frac{u(x)}{x-x_0}\,dx \qquad (4)$$

cuando $f(-x) = f^*(x)$ (caso de $n^2(\omega)-1$)

Kramers-Kronig

$\Rightarrow$ $$\boxed{\begin{aligned} u(x_0) &= \frac{2}{\pi}\, P\!\!\int_0^{\infty} \frac{x\,v(x)}{x^2-x_0^2}\,dx \\ v(x_0) &= -\frac{2}{\pi}\, P\!\!\int_0^{\infty} \frac{x_0\,u(x)}{x^2-x_0^2}\,dx \end{aligned}} \qquad (5)$$

Caso particular, $f(\omega) = \epsilon(\omega) - \epsilon_0 \equiv \epsilon'(\omega) - \epsilon_0 - i\epsilon''(\omega)$

$$\Rightarrow \quad \epsilon'(\omega) - \epsilon_0 = \frac{2}{\pi} P \int_0^\infty \frac{\epsilon''(\omega')\,\omega'}{\omega'^2 - \omega^2}\, d\omega'$$

$$\epsilon''(\omega) = \frac{2\omega}{\pi} P \int_0^\infty \frac{(\epsilon'(\omega') - \epsilon_0)\, d\omega'}{\omega'^2 - \omega^2}$$

Dispersión y Absorción están íntimamente relacionadas.

$$D(t) = \int_{-\infty}^{\infty} \epsilon(t-t')\, E(t')\, dt' = \int_{-\infty}^{\infty} \epsilon(t')\, E(t-t')\, dt'$$

$$\Rightarrow \boxed{D(\omega) = \epsilon(\omega) E(\omega)}$$

y como $\epsilon(\omega) \xrightarrow[\omega \to \infty]{} \epsilon_0 \Rightarrow$ aplico Cauchy a $\epsilon(\omega) - \epsilon_0$

$$\lim_{|z| \to \infty} (\epsilon(z) - \epsilon_0) = 0 \quad ✓$$

Relaciones de Kramers-Kronig (ver apuntes)

Ejemplo: $\gamma_j \simeq 0$

$$\Rightarrow n^2 = 1 + \frac{Ne^2}{\epsilon_0 m} \sum_j \frac{f_j}{\omega_j^2 - \omega^2}$$

$$\Rightarrow \underbrace{\varepsilon(\omega) - \varepsilon_0}_{\varepsilon'(\omega) - \varepsilon_0} = \frac{Ne^2}{m} \sum_j \frac{f_j}{\omega_j^2 - \omega^2}$$

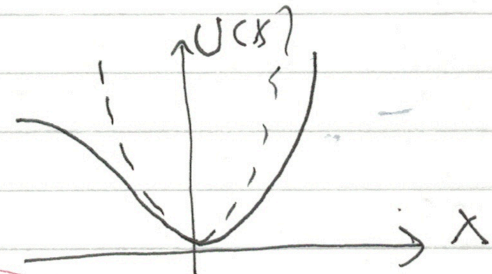
re-escribir como, $\varepsilon'(\omega) - \varepsilon_0 = \frac{Ne^2}{m} P \int_0^\infty \sum_j \frac{f_j \, \delta(\omega' - \omega_j)}{\omega'^2 - \omega^2} d\omega'$

lo cual implica, $\varepsilon''(\omega) = \frac{\pi N e^2}{2\omega m} \sum_j f_j \, \delta(\omega - \omega_j)$.

De $\sum_j f_j = Z$, $\Rightarrow \int_0^\infty \omega \varepsilon''(\omega) \, d\omega = \frac{\pi N e^2 Z}{2m}$ Regla de suma.

Susceptibilidad No lineal de un oscilador anarmónico clásico (Modelo de Lorentz)

(i) Medio No-centrosimétrico



$$U \simeq \frac{1}{2} m \omega_0^2 x^2 + \frac{1}{3} m a x^3 \qquad (1)$$

→ notar que $U(-x) \neq U(x)$

$$F_{rest} \simeq -m\omega_0^2 x - m a x^2 \qquad (2)$$

$$\Rightarrow \quad \ddot{x} + 2\gamma \dot{x} + \omega_0^2 x + a x^2 = -eE(t)/m \qquad (3)$$

Tomamos $E(t) = E_1 e^{-i\omega_1 t} + E_2 e^{-i\omega_2 t} + c.c.$ (4)

"buena" elección para mostrar la fenomenología de los medios cuadráticos.

usar Teo. de perturbación: [x es pequeño]

$$E(t) \rightarrow \lambda E(t) \quad , \quad \lambda \in [0,1]$$

$$\ddot{x} + 2\gamma \dot{x} + \omega_0^2 x + a x^2 = -\lambda e E/m \qquad (4')$$

$$x = \lambda x^{(1)} + \lambda^2 x^{(2)} + \lambda^3 x^{(3)} + \cdots \qquad (5)$$

reempl. en (4') e igualar potencias de λ.

$$(6)\begin{cases} \Rightarrow \ddot{x}^{(1)} + 2\gamma\dot{x}^{(1)} + \omega_0^2 x^{(1)} = -eE^{(t)}/m & \text{(orden } \lambda) \\ \ddot{x}^{(2)} + 2\gamma\dot{x}^{(2)} + \omega_0^2 x^{(2)} + a[x^{(1)}]^2 = 0 & \text{(orden } \lambda^2) \\ \ddot{x}^{(3)} + 2\gamma\dot{x}^{(3)} + \omega_0^2 x^{(3)} + 2a x^{(1)} x^{(2)} = 0 & \text{(orden } \lambda^3) \end{cases}$$

Como $E(t) = E_1(t) + E_2(t)$, tomamos $x^{(1)}(t) = x_1^{(1)}(t) + x_2^{(1)}(t)$

$$x^{(1)}(t) = x^{(1)}(\omega_1)e^{-i\omega_1 t} + x^{(1)}(\omega_2)e^{-i\omega_2 t} + c.c. \qquad (7)$$

se obtiene: $$x^{(1)}(\omega_j) = -\frac{e}{m}\frac{E_j}{D(\omega_j)} \qquad (8)$$

donde $$\boxed{D(\omega) \equiv \omega_0^2 - \omega^2 - 2i\gamma\omega} \qquad (9)$$

se toma ahora $[x^{(1)}(t)]^2$ y se reemplaza en la ec. para $x^{(2)}$:

$$\ddot{x}^{(2)} + 2\gamma\dot{x}^{(2)} + \omega_0^2 x^{(2)} = \underbrace{-a[x^{(1)}]^2}_{\text{contiene frecuencias } \pm 2\omega_1,\ \pm 2\omega_2,\ \pm(\omega_1+\omega_2),\ \pm(\omega_1-\omega_2),\ \phi.} \leftarrow \vec{F} \text{ efectiva} \qquad (10)$$

Por lo tanto,

$$x^{(2)}(t) = x^{(2)}(2\omega_1)e^{-i2\omega_1 t} + x^{(2)}(2\omega_2)e^{-i2\omega_2 t} + x^{(2)}(\omega_1+\omega_2)e^{-i(\omega_1+\omega_2)t} +$$
$$+ x^{(2)}(\omega_1-\omega_2)e^{-i(\omega_1-\omega_2)t} + x^{(2)}(\phi) + c.c. \qquad (11)$$

se obtiene:

$$x^{(2)}(2\omega_1) = \frac{-a(e/m)^2 E_1^2}{D(2\omega_1)D^2(\omega_1)} \quad ; \quad x^{(2)}(2\omega_2) = \frac{-a(e/m)^2 E_2^2}{D(2\omega_2)D^2(\omega_2)}$$

$$x^{(2)}(\omega_1+\omega_2) = \frac{-2a(e/m)^2 E_1 E_2}{D(\omega_1+\omega_2)D(\omega_1)D(\omega_2)}$$

$$x^{(2)}(\omega_1-\omega_2) = \frac{-2a(e/m)^2 E_1 E_2^*}{D(\omega_1-\omega_2)D(\omega_1)D(-\omega_2)}$$

$$x^{(2)}(\phi) = \frac{-2a(e/m)^2 E_1 E_1^*}{D(0)D(\omega_1)D(-\omega_1)} + \frac{-2a(e/m)^2 E_2 E_2^*}{D(0)D(\omega_2)D(-\omega_2)}$$

Ahora como $P^{(1)}(\omega) = \chi^{(1)}(\omega)E(\omega)$

y como $P^{(1)}(\omega) = -Nex^{(1)}(\omega)$ $\Rightarrow$ $\boxed{\chi^{(1)}(\omega_j) = \frac{N(e^2/m)}{D(\omega_j)}}$ (12)

Suscept. No-lineal:

$$P^{(2)}(2\omega) = \chi^{(2)}(2\omega,\omega,\omega)E^2(\omega)$$

donde, $P^{(2)}(2\omega) = -Nex^{(2)}(2\omega)$

$$\Rightarrow \chi^{(2)}(2\omega_1,\omega_1,\omega_1) = \frac{N(e^3/m^2)a}{D(2\omega_1)D^2(\omega_1)} \qquad (13)$$

que puede re-escribirse como:

$$\chi^{(2)}(2\omega_1,\omega_1,\omega_1) = \frac{ma}{N^2e^3}\,\chi^{(1)}(2\omega_1)\left[\chi^{(1)}(\omega_1)\right]^2 \qquad (14)$$

De manera similar, se obtiene:

$$\chi^{(2)}(\omega_1+\omega_2,\omega_1,\omega_2) = \frac{N(e^3/m^2)a}{D(\omega_1+\omega_2)D(\omega_1)D(\omega_2)} \qquad (15)$$

o $$\chi^{(2)}(\omega_1+\omega_2,\omega_1,\omega_2) = \frac{ma}{N^2e^3}\,\chi^{(1)}(\omega_1+\omega_2)\,\chi^{(1)}(\omega_1)\,\chi^{(1)}(\omega_2) \qquad (15')$$

$$\chi^{(2)}(\omega_1-\omega_2,\omega_1,\omega_2) = \frac{N(e^3/m^2)a}{D(\omega_1-\omega_2)D(\omega_1)D(-\omega_2)} \qquad (16)$$

$$= \frac{ma}{N^2e^3}\,\chi^{(1)}(\omega_1-\omega_2)\,\chi^{(1)}(\omega_1)\,\chi^{(1)}(-\omega_2) \qquad (16')$$

$$\chi^{(2)}(0,+\omega_1,-\omega_1) = \frac{N(e^3/m^2)a}{D(0)D(\omega_1)D(-\omega_1)} = \frac{ma}{N^2e^3}\,\chi^{(1)}(0)\,\chi^{(1)}(\omega_1)\,\chi^{(1)}(-\omega_1) \qquad (17)$$

<u>Regla de Miller</u>: $$\underbrace{\frac{\chi^{(2)}(\omega_1+\omega_2,\omega_1,\omega_2)}{\chi^{(1)}(\omega_1+\omega_2)\,\chi^{(1)}(\omega_1)\,\chi^{(2)}(\omega_2)}}_{\simeq\ \text{cte. (obs. experimental)}} = \frac{ma}{N^2e^3}$$

$$\Rightarrow \frac{ma}{N^2e^3} \simeq \text{cte.}$$

Estimación de $\chi^{(2)}$

$$\chi^{(2)}(\omega_1+\omega_2, \omega_1, \omega_2) = \frac{N(e^3/m^2)a}{D(\omega_1+\omega_2)D(\omega_1)D(\omega_2)}$$

N es más o menos cte ($\approx 10^{22}$ 1/cc)
m ✓ e ✓ a no se conoce

Asumi. contribu. lineal y cuadrática son del mismo Orden
$\Rightarrow \quad m\omega_0^2 d = ma d^2$, donde d ~ tamaño atómico
$\Rightarrow \boxed{a = \omega_0^2/d}$

Aprox. $D(\omega) \simeq \omega_0^2$, $N \simeq 1/d^3$, $a = \omega_0^2/d$

$$\Rightarrow \chi^{(2)} \simeq \frac{e^3}{m^2\omega_0^4 d^4}$$

$\left.\begin{array}{l} \omega_0 \simeq 10^{16} \text{ rad/sec.} \\ d \simeq 3\,\mathring{A} \\ e = 4.8 \times 10^{-10} \text{ esu} \\ m = 9.1 \times 10^{-28} \text{ gr.} \end{array}\right\} \Rightarrow \chi^{(2)} \simeq 1.7 \times 10^{-8} \text{ (esu)}$

$\downarrow$

en acuerdo con valores experimentales