Drude Model

Free electron gas

$$\bar{E} = \bar{E}_0 e^{-i\omega t}$$

$$m\frac{d^2\bar{r}}{dt^2} + m\Gamma\frac{d\bar{r}}{dt} + K\bar{r} = -e\bar{E}_0 e^{-i\omega t}$$

$$m\frac{d^2\bar{r}}{dt^2} + m\Gamma\frac{d\bar{r}}{dt} = -e\bar{E}_0 e^{-i\omega t}$$

Free electrons

$$\bar{r}(t) = \frac{e\bar{E}_0}{m}\frac{1}{\omega^2 + i\omega\Gamma}e^{-i\omega t} = \frac{e\bar{E}_0}{m}\frac{\omega^2 + i\omega\Gamma}{\omega^4 + (\omega\Gamma)^2}e^{-i\omega t}$$

Drude Model

Free electron gas

$$\bar{p}(t) \equiv -e\bar{r}(t)$$

$$\bar{P} \equiv n\bar{p} = n\varepsilon_0\alpha\bar{E} = \varepsilon_0\chi\bar{E}$$

$$\bar{D} = \varepsilon_0\varepsilon\bar{E} = \varepsilon_0\bar{E} + \bar{P} = \varepsilon_0\bar{E} + \varepsilon_0\chi\bar{E} = \varepsilon_0(1+\chi)\bar{E}$$

$$\varepsilon = 1 + \chi = 1 + n\alpha = 1 - \frac{\omega_P^2}{\omega^2 + i\omega\Gamma} = 1 - \frac{\omega_P^2}{\omega^2 + \Gamma^2} + i\frac{\omega_P^2\Gamma}{\omega(\omega^2+\Gamma^2)}$$

$$\omega_P^2 \equiv \frac{ne^2}{m\varepsilon_0}$$

Bulk plasmon frequency

$$\hbar\omega_P \approx 5 - 20eV$$

Drude Model

High-frequency limit: $\omega \gg \Gamma$

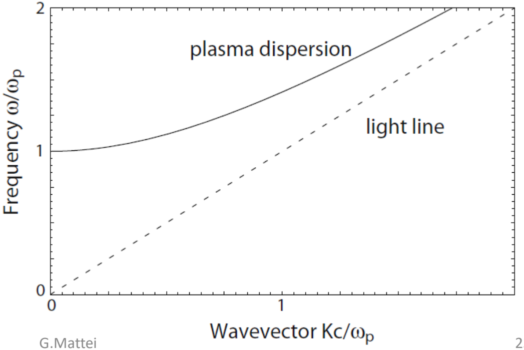
$$\varepsilon = 1 + \chi \approx 1 - \frac{\omega_P^2}{\omega^2} + i\,\frac{\omega_P^2\Gamma}{\omega^3}$$

$$\varepsilon_1 \approx 1 - \frac{\omega_P^2}{\omega^2} \qquad \varepsilon_2 \approx \frac{\omega_P^2\Gamma}{\omega^3}$$

$$k = k_0 n = \frac{\omega}{c}\sqrt{\varepsilon} \approx \frac{\omega}{c}\sqrt{\varepsilon_1} = \frac{\omega}{c}\sqrt{1 - \frac{\omega_P^2}{\omega^2}}$$

$$\varepsilon_1 \begin{cases} < 0 & k \in \mathbb{C}\,,\ E \text{ damped} \\ = 0 & \omega = \omega_P \\ > 0 & k \in \mathbb{R}\,,\ E \text{ oscillating} \end{cases}$$

$$\omega^2 = \omega_P^2 + (kc)^2$$



Drude Model

Relationship between ω_P and ω_{SPR} (high-freq. approx: $\omega \gg \Gamma$)

1. To excite ω_P (after Drude)

$$\varepsilon_1(\omega_P) = 0$$

2. To excite ω_{SPR} (after Mie)

$$\varepsilon_1(\omega_{SPR}) = -2\varepsilon_m$$

$$\varepsilon_1(\omega_{SPR}) \approx 1 - \frac{\omega_P^2}{\omega_{SPR}^2} = -2\varepsilon_m$$

$$\omega_{SPR}^2 = \frac{\omega_P^2}{1 + 2\varepsilon_m}$$

$$\omega_{SPR} = \frac{\omega_P}{\sqrt{1 + 2\varepsilon_m}}$$

$$\lambda_{SPR} = \lambda_P\sqrt{1 + 2\varepsilon_m} > \lambda_P$$

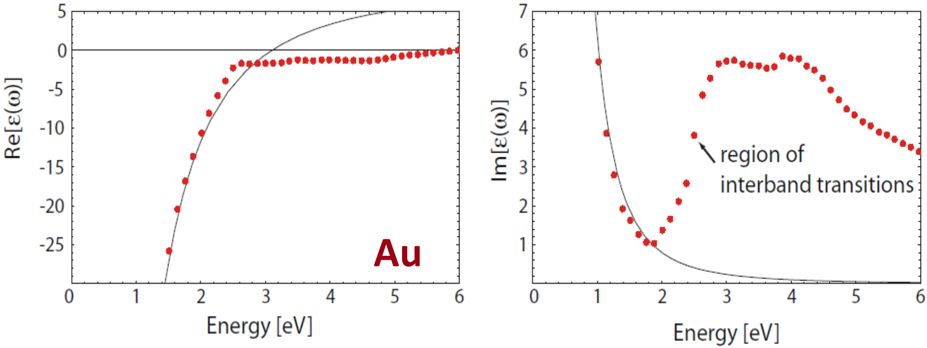
Drude Model

Correction due to higher polarizability of core d electrons

$$\varepsilon = \varepsilon_\infty - \frac{\omega_P^2}{\omega^2 + i\omega\Gamma}$$

$$1 \leq \varepsilon_\infty \leq 10$$

Drude vs. Experiment (Johnson-Christy, 1972)



P.B. Johnson & R. W. Christy, Phys. Rev. B 6 (1972) 4370

Drude Model

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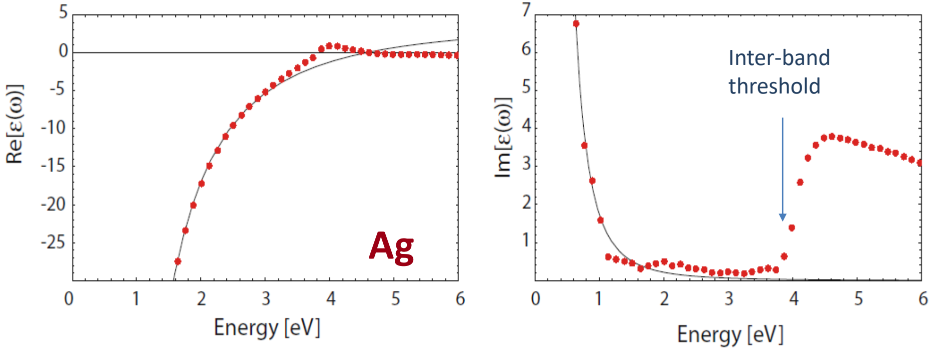

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Drude-Lorentz model

Generalization to bound-electrons

$$\bar{E} = \bar{E}_0 e^{-i\omega t}$$

$$m\frac{d^2\bar{r}}{dt^2} + m\Gamma\frac{d\bar{r}}{dt} + K\bar{r} = -e\bar{E}_0 e^{-i\omega t}$$

$$m\frac{d^2\bar{r}}{dt^2} + m\Gamma\frac{d\bar{r}}{dt} + m\omega_0^2\bar{r} = -e\bar{E}_0 e^{-i\omega t} \qquad \omega_0^2 \equiv \frac{K}{m}$$

$$\bar{r}_{bound}(t) = \frac{e\bar{E}_0}{m}\frac{1}{\omega^2 - \omega_0^2 + i\omega\Gamma}e^{-i\omega t}$$

$$\bar{r}_{free}(t) = \frac{e\bar{E}_0}{m}\frac{1}{\omega^2 + i\omega\Gamma}e^{-i\omega t}$$

Drude-Lorentz model

Generalization to bound-electrons

$$\varepsilon_{bound} = 1 - \frac{\omega_P^2}{\omega^2 - \omega_0^2 + i\omega\Gamma}$$

$$\omega_{P,bound}^2 \equiv \frac{n_{bound}\ e^2}{m_{bound}\varepsilon_0}$$

Add as many Lorentzian oscillators as the bound states in the system (QM).

$$\varepsilon = \varepsilon_{Drude} + \varepsilon_{bound} = \varepsilon_s + \varepsilon_d =$$

$$= 1 - \frac{\omega_P^2}{\omega^2 + i\omega\Gamma} - \sum_j \frac{\omega_{P,j}^2\ f_j}{\omega^2 - \omega_{0,j}^2 + i\omega\Gamma_j}$$

$\varepsilon = \varepsilon(\omega, R)$

$$\varepsilon(\omega) = \varepsilon_d(\omega) + \varepsilon_s(\omega)$$

Interband (d electrons)

s electrons (Drude)

$R \sim \lambda_e$ Quantum confinement

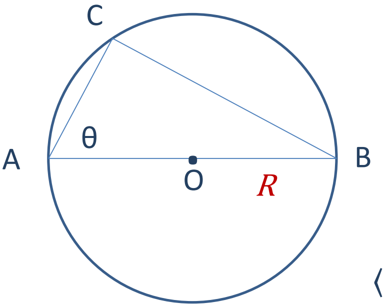
- ε_d (interband) does not depend on R
- Drude correction for ε_{bulk}
- Relaxation frequency correction (size-equation) $\Gamma = \Gamma(R)$

$$\Gamma(R) = \Gamma_{bulk} + A\frac{v_F}{R}$$

$A \sim 1$
v_F Fermi velocity

$$\varepsilon(\omega, R) = \varepsilon_d(\omega) + \varepsilon_s(\omega, R)$$

Semiclassical correction: size equation



$$AC = 2R\cos(\theta)$$

$$\tau_{AC}(\theta) = \frac{AC}{v_F} = \frac{2R\cos(\theta)}{v_F}$$

$$\langle\tau\rangle = \frac{\int_0^{\frac{\pi}{2}} d\theta\, \tau_{AC}(\theta)}{\int_0^{\frac{\pi}{2}} d\theta} = \frac{2R}{v_F\,\frac{\pi}{2}} = \frac{4R}{v_F\,\pi}$$

$$\Gamma(R) = \Gamma_{bulk} + \Gamma_{sup} = \Gamma_{bulk} + \frac{1}{\langle\tau\rangle} = \Gamma_{bulk} + \frac{\pi}{4}\frac{v_F}{R}$$

$\boldsymbol{\varepsilon = \varepsilon(\omega, R)}$

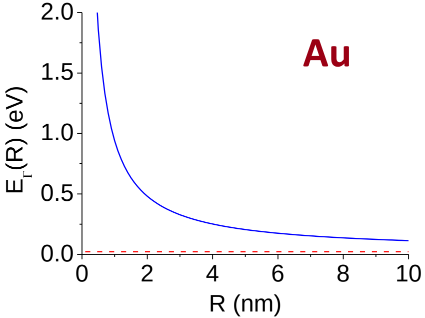
$$\varepsilon(\omega, R) = \varepsilon_d(\omega) + \varepsilon_s(\omega, R)$$

$$\varepsilon(\omega)_{Drude} = 1 - \frac{\omega_P^2}{\omega^2 + \Gamma^2} + i\,\frac{\omega_P^2 \Gamma}{\omega(\omega^2 + \Gamma^2)}$$

$$\varepsilon(\omega, R) = \varepsilon(\omega, \infty) + \omega_P{}^2 \left(\frac{1}{\omega^2 + \Gamma_\infty^2} - \frac{1}{\omega^2 + \Gamma(R)^2} \right) - i\,\frac{\omega_P{}^2}{\omega} \left(\frac{\Gamma_\infty}{\omega^2 + \Gamma_\infty^2} - \frac{\Gamma(R)}{\omega^2 + \Gamma(R)^2} \right)$$

$$\hbar\Gamma(R) = \hbar\Gamma_{bulk} + \hbar A \frac{v_F}{R}$$

$$E_\Gamma(R) = E_\Gamma(\infty)\left(1 + \frac{C}{R}\right)$$



$\varepsilon = \varepsilon(\omega, R)$

Au NP