Optical Properties: Phenomenological Theory

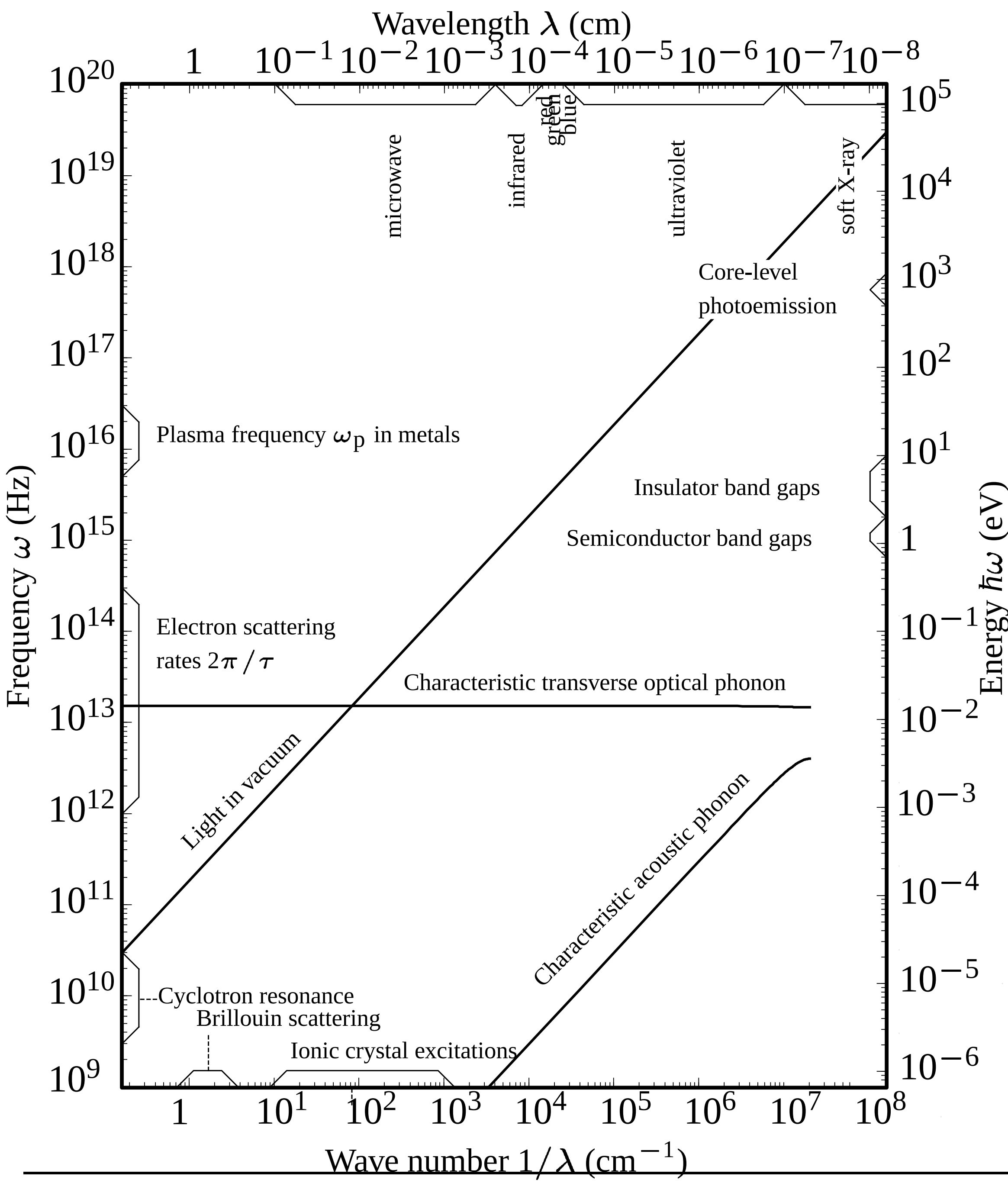
Wavelength λ (cm)
1 10^{-1} 10^{-2} 10^{-3} 10^{-4} 10^{-5} 10^{-6} 10^{-7} 10^{-8}
microwave
infrared
red
green
blue
ultraviolet
soft X-ray
Core-level photoemission
Plasma frequency ω_p in metals
Insulator band gaps
Semiconductor band gaps
Electron scattering rates $2\pi/\tau$
Characteristic transverse optical phonon
Light in vacuum
Characteristic acoustic phonon
Cyclotron resonance
Brillouin scattering
Ionic crystal excitations
Frequency ω (Hz)
10^{20} 10^{19} 10^{18} 10^{17} 10^{16} 10^{15} 10^{14} 10^{13} 10^{12} 10^{11} 10^{10} 10^{9}
Energy $\hbar\omega$ (eV)
10^{5} 10^{4} 10^{3} 10^{2} 10^{1} 1 10^{-1} 10^{-2} 10^{-3} 10^{-4} 10^{-5} 10^{-6}
1 10^{1} 10^{2} 10^{3} 10^{4} 10^{5} 10^{6} 10^{7} 10^{8}
Wave number $1/\lambda$ (cm^{-1})

Figure 1:

Definitions

- Maxwell's Equations
- Dielectric Functions
- Kramers–Kronig Relations
- Sum Rules
- Kubo–Greenwood Formula

Return of the Drude Model

$$m\dot{\vec{v}} = -e\vec{E} - m\frac{\vec{v}}{\tau}, \tag{L1}$$

$$-i\omega m\vec{v} = -e\vec{E} - m\frac{\vec{v}}{\tau} \tag{L2}$$

$$\Rightarrow \vec{j} = -ne\vec{v} = ? \qquad ? \tag{L3}$$

$$\Rightarrow \sigma(\omega) = ? \qquad ? \tag{L4}$$

Maxwell's Equations

$$\vec{\nabla}\cdot\vec{E} = -4\pi e n \qquad \vec{\nabla}\cdot\vec{B} = 0 \tag{L5a}$$

$$\vec{\nabla}\times\vec{E} = -\frac{1}{c}\frac{\partial\vec{B}}{\partial t} \qquad \vec{\nabla}\times\vec{B} = \frac{4\pi\vec{j}}{c} + \frac{1}{c}\frac{\partial\vec{E}}{\partial t}. \tag{L5b}$$

$$\vec{P} = \int^t dt'\,\vec{j}_{\rm int}(t'). \tag{L6}$$

$$-e\frac{\partial n_{\rm int}}{\partial t} = -\vec{\nabla}\cdot\vec{j}_{\rm int} \tag{L7}$$

$$\Rightarrow e n_{\rm int} = \vec{\nabla}\cdot\vec{P}, \tag{L8}$$

$$\vec{D} = \vec{E} + 4\pi\vec{P}. \tag{L9}$$

$$\vec{\nabla}\cdot\vec{D} = -4\pi e n_{\rm ext} \qquad \vec{\nabla}\cdot\vec{B} = 0 \tag{L10a}$$

$$\vec{\nabla}\times\vec{E} = -\frac{1}{c}\frac{\partial\vec{B}}{\partial t} \qquad \vec{\nabla}\times\vec{B} = \frac{4\pi\vec{j}_{\text{ext}}}{c}+\frac{1}{c}\frac{\partial\vec{D}}{\partial t}. \tag{L10b}$$

$$\vec{j}(\vec{r},t) = \int dt'd\vec{r}'\sigma(\vec{r}-\vec{r}',t-t')\vec{E}(\vec{r}',t') \tag{L11a}$$

$$\equiv \sigma*\vec{E}(\vec{r},t). \tag{L11b}$$

$$\vec{j}(\vec{q},\omega) = \sigma(\vec{q},\omega)\vec{E}(\vec{q},\omega). \tag{L12}$$

$$\vec{D}(\vec{r},t) = \epsilon*\vec{E}(\vec{r},t) \Rightarrow \vec{D}(\vec{q},\omega) = \epsilon(\vec{q},\omega)\vec{E}(\vec{q},\omega). \tag{L13}$$

$$\epsilon(\vec{q},\omega) = 1+\frac{4\pi i}{\omega}\sigma(\vec{q},\omega). \tag{L14}$$

Traveling Waves

$$\vec{\nabla}\times\vec{\nabla}\times\vec{E} = -\frac{1}{c}\frac{\partial}{\partial t}\vec{\nabla}\times\vec{B} = -\frac{1}{c^2}\frac{\partial^2\epsilon * \vec{E}}{\partial t^2} \quad \text{(L15)}$$

$$\Rightarrow q^2\vec{E} - \vec{q}(\vec{q}\cdot\vec{E}) = \epsilon(\vec{q},\omega)\frac{\omega^2}{c^2}\vec{E}. \quad \text{(L16)}$$

$$q^2\vec{E} = \epsilon(\vec{q},\omega)\frac{\omega^2}{c^2}\vec{E} \quad \text{(L17)}$$

$$\Rightarrow q = \omega\tilde{n}/c; \quad \tilde{n}(\vec{q},\omega) = \sqrt{\epsilon(\vec{q},\omega)}, \quad \text{(L18)}$$

$$\vec{E}_0 e^{i\omega[\tilde{n}x/c-t]}. \quad \text{(L19)}$$

$$\epsilon_1 = \bar{n}^2 - \kappa^2 \quad \text{(L20a)}$$

$$\epsilon_2 = 4\pi\mathrm{Re}[\sigma]/\omega = 2\bar{n}\kappa. \quad \text{(L20b)}$$

$$\alpha = \frac{2\omega}{c}\kappa = \frac{\omega\epsilon_2}{\bar{n}c}. \tag{L21}$$

$$\epsilon(\vec{q},\omega)\frac{\omega^2}{c^2}\vec{E} = 0 \tag{L22}$$

$$\Rightarrow \epsilon(\vec{q},\omega) = 0. \tag{L23}$$

Mechanical Oscillators as Dielectric Function

$$\vec{E}(\vec{r},t) = \vec{E}e^{-i\omega t}, \tag{L24}$$

$$m_l\ddot{\vec{r}} = -m_l\omega_l^2\vec{r} - m_l\dot{\vec{r}}/\tau_l - e\vec{E}(\vec{r},t) \tag{L25}$$

$$\Rightarrow \vec{r}(\omega) = -\frac{e\vec{E}}{m_l(\omega_l^2 - i\omega/\tau_l - \omega^2)} \tag{L26}$$

$$\vec{j}(\omega) = \frac{-i\omega n_l e^2\vec{E}}{m_l(\omega_l^2 - i\omega/\tau_l - \omega^2)}, \tag{L27}$$

$$\sigma(\omega) = \frac{-i\omega n_l e^2}{m_l(\omega_l^2 - i\omega/\tau_l - \omega^2)}. \tag{L28}$$

$$\epsilon(\omega) = 1 + \sum_l \frac{4\pi n_l e^2/m_l}{\omega_l^2 - \omega^2 - i\omega/\tau_l}. \tag{L29}$$

$$\sigma(\omega) = \frac{ne^2\tau}{m(1 - i\omega\tau)} \tag{L30}$$

Mechanical Oscillators as Dielectric Function

$$\epsilon(\omega) = 1 - \frac{\omega_{\mathrm{p}}^2}{\omega(\omega + i/\tau)}, \tag{L31}$$

Plasma frequency ω_{p}:

$$\omega_{\mathrm{p}} = \sqrt{\frac{4\pi n e^2}{m}}. \tag{L32}$$

$$\epsilon_1(\omega) = \mathrm{Re}[\epsilon(\omega)] = 1 + \sum_l \frac{4\pi n_l e^2 (\omega_l^2 - \omega^2)/m_l}{(\omega_l^2 - \omega^2)^2 + (\omega/\tau_l)^2} \tag{L33a}$$

$$\epsilon_2(\omega) = \mathrm{Im}[\epsilon(\omega)] = \sum_l \frac{4\pi n_l e^2 \omega/(\tau_l m_l)}{(\omega_l^2 - \omega^2)^2 + (\omega/\tau_l)^2}, \tag{L33b}$$

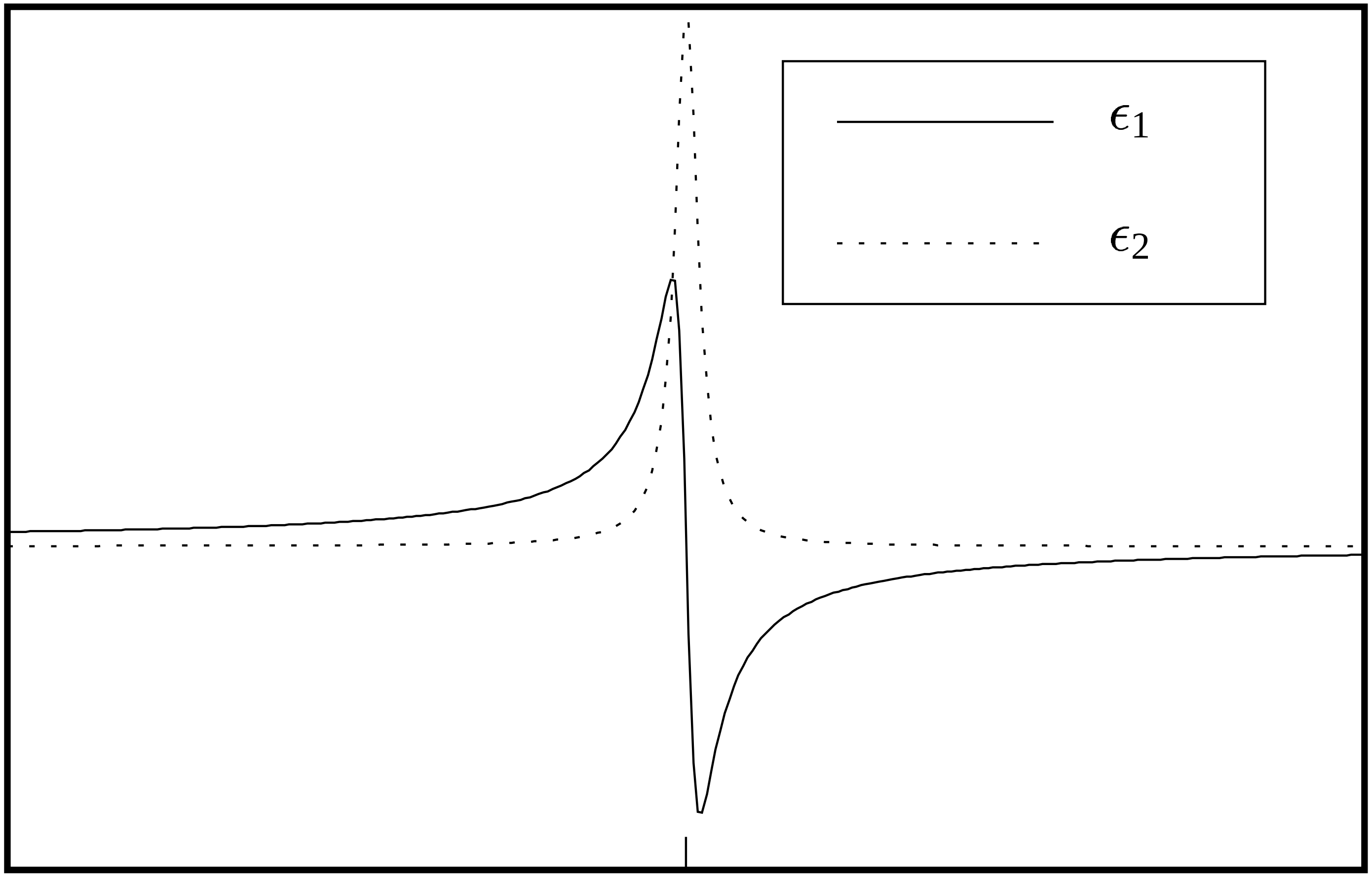

Figure 2: Characteristic shapes of the real and imaginary parts of the dielectric function described in Eq. (L33).

Kramers–Kronig Relations

$$\vec{D}(\omega) = \epsilon(\omega)\vec{E}(\omega) \Rightarrow \vec{D}(t) = \int dt'\, \epsilon(t')\vec{E}(t-t'). \tag{L34}$$

$$\vec{D}(t) = \epsilon(t) t_0 \vec{E}_0. \tag{L35}$$

$$\epsilon(t) = 0 \ \text{ for } t < 0. \tag{L36}$$

$$\epsilon(\omega) = \int_0^\infty dt\, e^{i\omega t} \epsilon(t). \tag{L37}$$

$$\epsilon(\omega) = \oint \frac{d\omega'}{2\pi i} \frac{\epsilon(\omega')}{\omega' - \omega - i\eta}. \tag{L38}$$

$$\epsilon(\omega) - \epsilon^\infty = \oint \frac{d\omega'}{2\pi i} \frac{\epsilon(\omega') - \epsilon^\infty}{\omega' - \omega - i\eta}. \tag{L39}$$

Kramers–Kronig Relations

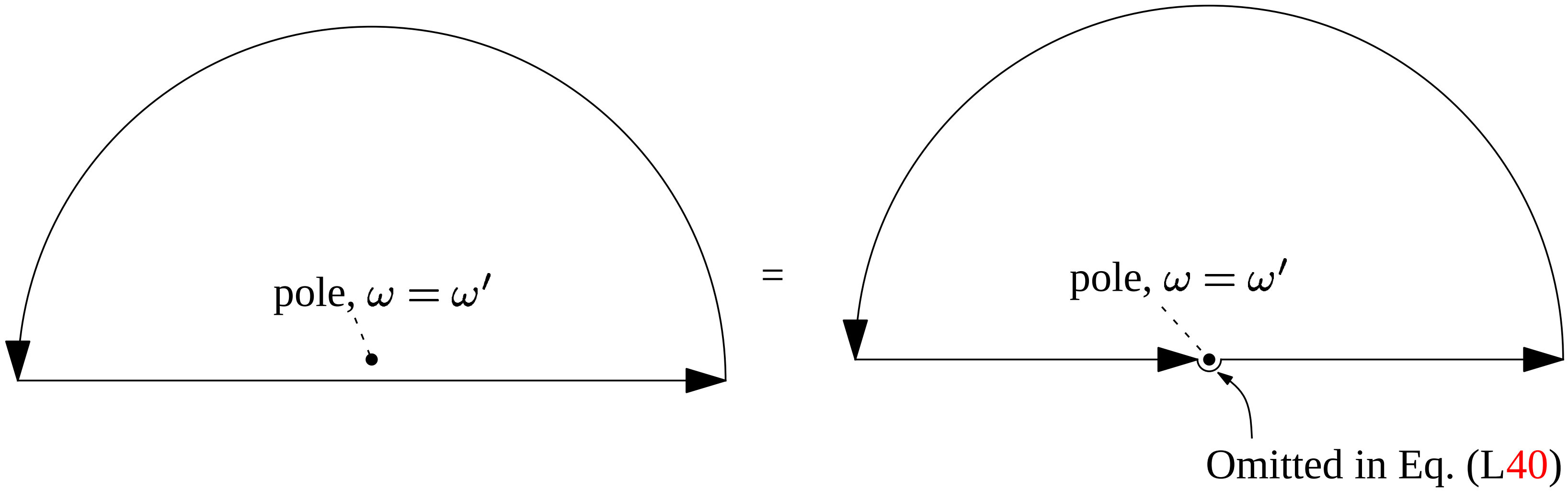

Figure 3: Contours for Kramers Kronig integrals

$$\epsilon(\omega) - \epsilon^{\infty} = \mathcal{P} \int \frac{d\omega'}{\pi i} \frac{\epsilon(\omega') - \epsilon^{\infty}}{\omega' - \omega} \tag{L40}$$

$$\mathrm{Re}[\epsilon(\omega) - \epsilon^{\infty}] = \mathcal{P} \int \frac{d\omega'}{\pi} \frac{\mathrm{Im}[\epsilon(\omega') - \epsilon^{\infty}]}{\omega' - \omega} \tag{L41a}$$

$$\mathrm{Im}[\epsilon(\omega) - \epsilon^{\infty}] = -\mathcal{P} \int \frac{d\omega'}{\pi} \frac{\mathrm{Re}[\epsilon(\omega') - \epsilon^{\infty}]}{\omega' - \omega}. \tag{L41b}$$

Kramers–Kronig Relations

$$\epsilon_1(\omega) - \epsilon^{\infty} = \mathcal{P}\int_0^{\infty} \frac{2\omega' d\omega'}{\pi} \frac{\epsilon_2(\omega')}{\omega'^2 - \omega^2} \qquad \text{(L42a)}$$

$$\epsilon_2(\omega) = -\mathcal{P}\int_0^{\infty} \frac{2\omega d\omega'}{\pi} \frac{\epsilon_1(\omega') - \epsilon^{\infty}}{\omega'^2 - \omega^2}. \qquad \text{(L42b)}$$

Application to Optical Experiments

$$\tilde{r} = \frac{\tilde{n}-1}{\tilde{n}+1} \equiv \rho e^{i\theta}. \tag{L43}$$

$$\ln\left(\frac{\tilde{r}(\omega)}{\tilde{r}(0)}\right) = \ln(\rho(\omega)/\rho(0)) + i(\theta(\omega) - \theta(0)), \tag{L44}$$

$$\theta(\omega) - \theta(0) = -\frac{1}{\pi}\mathcal{P}\int d\omega' \ln\left[\frac{\rho(\omega')}{\rho(0)}\right]\left[\frac{1}{\omega'-\omega} - \frac{1}{\omega'}\right] \tag{L45}$$

$$\Rightarrow \theta(\omega) = -\frac{2\omega}{\pi}\mathcal{P}\int_0^\infty d\omega' \frac{\ln\rho(\omega')}{\omega'^2-\omega^2}. \tag{L46}$$

$$\epsilon_1(0) - 1 = \frac{2}{\pi}\int_0^\infty d\omega' \frac{\epsilon_2(\omega')}{\omega'}. \tag{L47}$$

Application to Optical Experiments

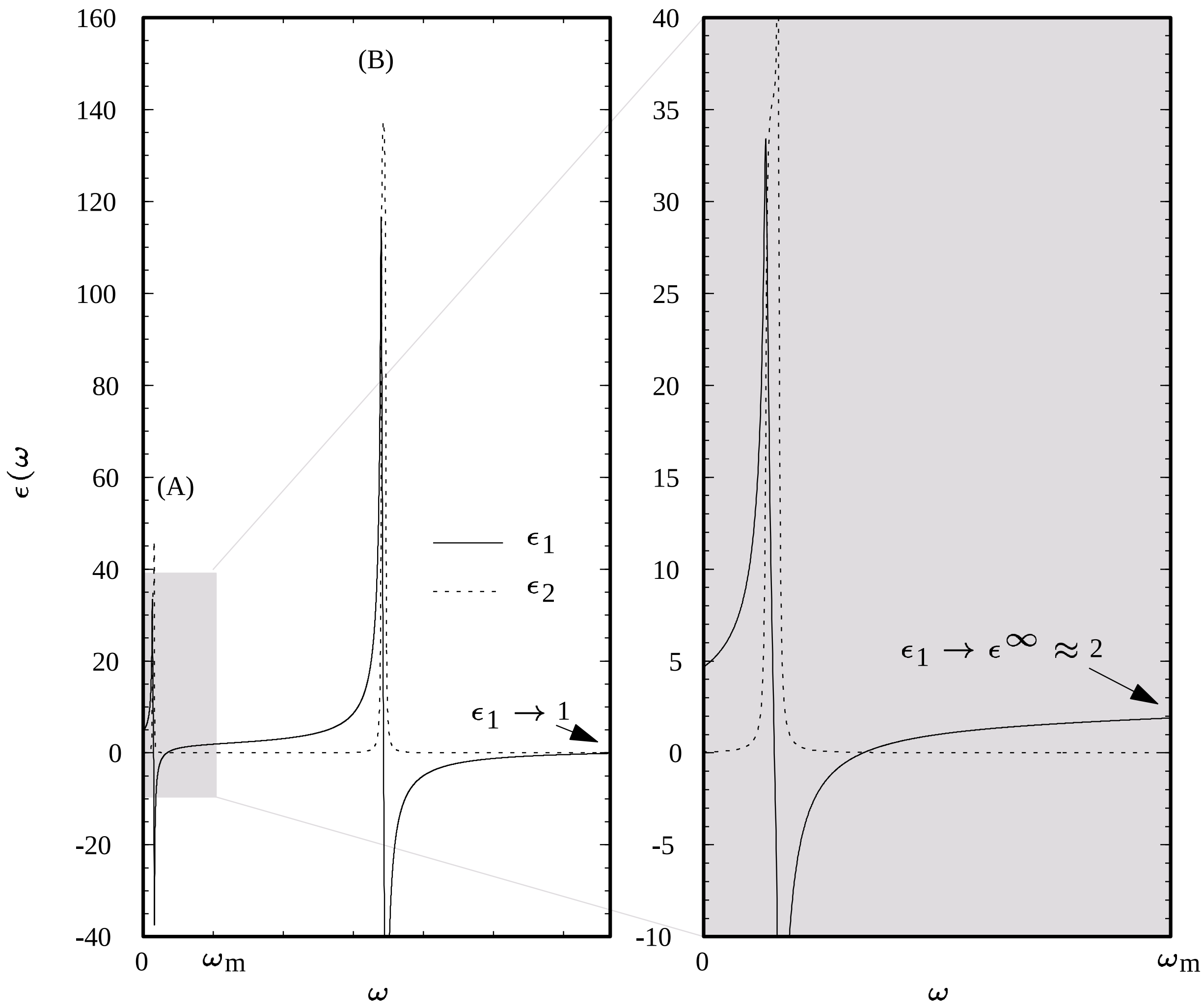

Figure 4: Dielectric functions from widely separated sets of modes.

$$\mathrm{Re}[\epsilon(\omega)] = 1 - \frac{2}{\pi\omega^2}\int_0^{\omega_\mathrm{m}} d\omega'\,\omega'\epsilon_2(\omega') + \frac{2}{\pi}\int_{\omega_\mathrm{m}}^{\infty} d\omega'\,\frac{\epsilon_2(\omega')}{\omega'} \tag{L48}$$

$$= \epsilon^\infty - \frac{\omega_\mathrm{p}^2}{\omega^2}, \tag{L49}$$

where

$$\epsilon^\infty = 1 + \frac{2}{\pi}\int_{\omega_\mathrm{m}}^{\infty} d\omega'\,\frac{\epsilon_2(\omega')}{\omega'} \tag{L50}$$

and

$$\omega_\mathrm{p}^2 \equiv \frac{4\pi n e^2}{m_\mathrm{opt}} = \frac{2}{\pi}\int_0^{\omega_\mathrm{m}} d\omega'\,\omega'\,\epsilon_2(\omega') \tag{L51}$$

$$\Rightarrow \int_0^{\omega_\mathrm{m}} d\omega'\,\omega'\epsilon_2(\omega') = \frac{2\pi^2 n e^2}{m_\mathrm{opt}}. \tag{L52}$$

$$\mathcal{E}_l = \hbar\omega_l \tag{L53}$$

Born approximation:

$$|\tilde{l}(t)\rangle \approx \mathcal{N}\Big[e^{-i\hat{\mathcal{H}}\frac{t}{\hbar}}|l\rangle + \int_{-\infty}^{t} dt' e^{-i\hat{\mathcal{H}}\frac{(t-t')}{\hbar}} \frac{\hat{U}(t')}{i\hbar} e^{-i\hat{\mathcal{H}}\frac{t'}{\hbar}}|l\rangle\Big] \tag{L54}$$

$$= \mathcal{N}\Big[e^{-i\omega_l t}|l\rangle + \sum_{l'}\int_{-\infty}^{t} dt'|l'\rangle e^{-i\omega_{l'}(t-t')} \frac{\langle l'|\hat{U}|l\rangle}{i\hbar} e^{-i\omega t' - i\omega_l t'}\Big] \tag{L55}$$

$$= \Big\{|l\rangle + \sum_{l'\neq l}|l'\rangle \frac{\langle l'|\hat{U}|l\rangle e^{-i\omega t}}{\hbar(\omega_l - \omega_{l'} + \omega)}\Big\} e^{-i\omega_l t}. \tag{L56}$$

If, on the other hand, the time dependent potential were to have the form $U^* \exp[i\omega^* t]$, then one would have instead

$$|\tilde{l}(t)\rangle = \Big\{|l\rangle + \sum_{l'\neq l}|l'\rangle \frac{\langle l'|\hat{U}^*|l\rangle e^{i\omega^* t}}{\hbar(\omega_l - \omega_{l'} - \omega^*)}\Big\} e^{-i\omega_l t}. \tag{L57}$$

The Kubo–Greenwood Formula

$$\vec{A} = \frac{c\vec{E}}{i\omega} e^{-i\omega t} + \text{c.c.}. \tag{L58}$$

$$\hat{j} = -\frac{e}{m}[\hat{P} + \frac{e}{c}\vec{A}], \tag{L59}$$

$$\hat{P} \rightarrow \hat{P} + \frac{e}{c}\vec{A}, \tag{L60}$$

$$\frac{(\hat{P} + \frac{e}{c}\vec{A})^2}{2m} \tag{L61}$$

$$= \frac{\hat{P}^2}{2m} + \frac{e}{2mc}[\vec{A}\cdot\hat{P} + \hat{P}\cdot\vec{A}] + \ldots \tag{L62}$$

$$= \frac{\hat{P}^2}{2m} + \frac{e}{mc}[\vec{A}\cdot\hat{P}] + \ldots. \tag{L63}$$

$$\hat{U}(t) = \frac{e}{mi\omega}[\vec{E}\cdot\hat{P}]e^{-i\omega t} - \frac{e}{mi\omega^*}[\vec{E}\cdot\hat{P}]e^{i\omega^* t}. \tag{L64}$$

The Kubo–Greenwood Formula

$$\begin{aligned}
\vec{J} &= \mathcal{V}\vec{j} = -\frac{e}{m}\langle\tilde{l}|\hat{P}+\frac{e\vec{A}}{c}|\tilde{l}\rangle && \text{(L65)}\\
&= -\frac{e}{m}\langle l|\hat{P}|l\rangle - [\frac{e^2\vec{E}}{im\omega}e^{-i\omega t}+\text{c.c.}]\\
&- \frac{e^2}{i\hbar m^2}\sum_{l'\neq l}\langle l|\hat{P}|l'\rangle\langle l'|\vec{E}\cdot\hat{P}|l\rangle\left\{\frac{e^{-i\omega t}}{\omega(\omega_l-\omega_{l'}+\omega)}-\frac{e^{i\omega^* t}}{\omega^*(\omega_l-\omega_{l'}-\omega^*)}\right\}\\
&- \frac{e^2}{i\hbar m^2}\sum_{l'\neq l}\langle l|\vec{E}\cdot\hat{P}|l'\rangle\langle l'|\hat{P}|l\rangle\left\{\frac{e^{-i\omega t}}{\omega(\omega_l^*-\omega_{l'}^*-\omega)}-\frac{e^{i\omega^* t}}{\omega^*(\omega_l^*-\omega_{l'}^*+\omega^*)}\right\}. && \text{(L66)}
\end{aligned}$$

$$\begin{aligned}
&\sigma_{\alpha\beta}(\omega)\\
&= \frac{-e^2}{im\omega\mathcal{V}}\sum_l\left[f_l\delta_{\alpha\beta}+\sum_{l'}\frac{f_l}{\hbar m}\left\{\frac{\langle l|\hat{P}_\alpha|l'\rangle\langle l'|\hat{P}_\beta|l\rangle}{\omega_l-\omega_{l'}+\omega}+\frac{\langle l|\hat{P}_\beta|l'\rangle\langle l'|\hat{P}_\alpha|l\rangle}{\omega_l^*-\omega_{l'}^*-\omega}\right\}\right]. && \text{(L67)}
\end{aligned}$$

$$\sigma_{\alpha\beta}(\omega) = \frac{-e^2}{im\omega\mathcal{V}}\left[\sum_l f_l\delta_{\alpha\beta} + \sum_{l'}\frac{f_l - f_{l'}}{\hbar m}\frac{\langle l|\hat{P}_\alpha|l'\rangle\langle l'|\hat{P}_\beta|l\rangle}{\omega_l - \omega_{l'} + \omega + i\eta}\right]. \tag{L68}$$

$$\mathrm{Re}\left[\sigma_{\alpha\beta}(\omega)\right] = -\mathrm{Im}\frac{e^2}{m\omega\mathcal{V}}\left[\sum_{ll'}\frac{f_l - f_{l'}}{\hbar m}\frac{\langle l|\hat{P}_\alpha|l'\rangle\langle l'|\hat{P}_\beta|l\rangle}{\omega_l - \omega_{l'} + \omega + i\eta}\right] \tag{L69}$$

$$= \frac{\pi}{\omega\mathcal{V}}\sum_{ll'}(f_l - f_{l'})\langle l|\frac{e\hat{P}_\alpha}{m}|l'\rangle\langle l'|\frac{e\hat{P}_\beta}{m}|l\rangle\delta(\mathcal{E}_{l'} - \mathcal{E}_l - \hbar\omega). \tag{L70}$$

$$\mathrm{Re}\left[\sigma_{\alpha\beta}(\omega)\right] = \frac{e^2}{m\omega\mathcal{V}}\sum_{\substack{l\ \text{occupied}\\ l'\ \text{unoccupied}}}\frac{\gamma_{l'}}{\hbar m}\frac{\langle l|\hat{P}_\alpha|l'\rangle\langle l'|\hat{P}_\beta|l\rangle}{[\omega - (\omega_{l'} - \omega_l)]^2 + \gamma_{l'}^2}. \tag{L71}$$

The Kubo–Greenwood Formula

$$\mathrm{Re}\left[\sigma_{\alpha\beta}(\omega)\right] = \frac{e^2\pi}{\hbar\omega m^2\mathcal{V}}\sum_{ll'}(f_l - f_{l'})\langle l|\hat{P}_\alpha|l'\rangle\langle l'|\hat{P}_\beta|l\rangle F_{ll'}(\omega), \tag{L72}$$

$$U(\vec{q},\omega)e^{i\vec{q}\cdot\vec{r}-i\omega t}+\text{c.c.} \tag{L73}$$

$$n(\vec{r},t)=\sum_{l} f_l\langle\tilde{l}(t)|\vec{r}\rangle\langle\vec{r}|\tilde{l}(t)\rangle. \tag{L74}$$

$$U(\vec{q},\omega)=-eV(\vec{q},\omega), \tag{L75}$$

$$-en(\vec{q},\omega)=\chi_{\text{c}}(\vec{q},\omega)V(\vec{q},\omega) \tag{L76}$$

$$\chi_{\text{c}}(\vec{q},\omega)=e^2\sum_{\vec{k}\sigma}\frac{1}{\hbar\mathcal{V}}\frac{\left(f_{\vec{k}+\vec{q}}-f_{\vec{k}}\right)}{\omega_{\vec{k}+\vec{q}}-\omega_{\vec{k}}-\omega}. \tag{L77}$$

$$\begin{aligned}
\nabla^2V &= \nabla^2V_{\text{ext}}+4\pi en=4\pi en_{\text{ext}}+4\pi en && \text{(L78)}\\
\Rightarrow\nabla^2V &= -\vec{\nabla}\cdot\vec{D}+4\pi en && \text{(L79)}\\
\Rightarrow -q^2V(\vec{q},\omega) &= -i\vec{q}\cdot\vec{D}+4\pi en(\vec{q},\omega) && \text{(L80)}
\end{aligned}$$

Susceptibility

$$\Rightarrow -q^2 V(\vec{q},\omega) = -i\vec{q}\cdot\vec{D} - 4\pi\chi_c(\vec{q},\omega)V(\vec{q},\omega) \quad \text{(L81)}$$

$$\Rightarrow (4\pi\chi_c - q^2)V(\vec{q},\omega) = -i\vec{q}\cdot\vec{D} \quad \text{(L82)}$$

$$\Rightarrow (q^2 - 4\pi\chi_c)\vec{E} = \vec{q}(\vec{q}\cdot\vec{D}) \quad \text{(L83)}$$

Dynamic Lindhard dielectric function

$$\epsilon(\vec{q},\omega) = 1 - \frac{4\pi\chi_c}{q^2} \quad \text{(L84)}$$

Classics....

- ☞ Kadanoff and Baym (1962)
- ☞ Abrikosov, Gor’kov, and Dzyaloshinskii (1965)
- ☞ Fetter and Walecka (1971)