Advanced Topics in Condensed Matter

Lecture 11: Kramers-Kronig Relations

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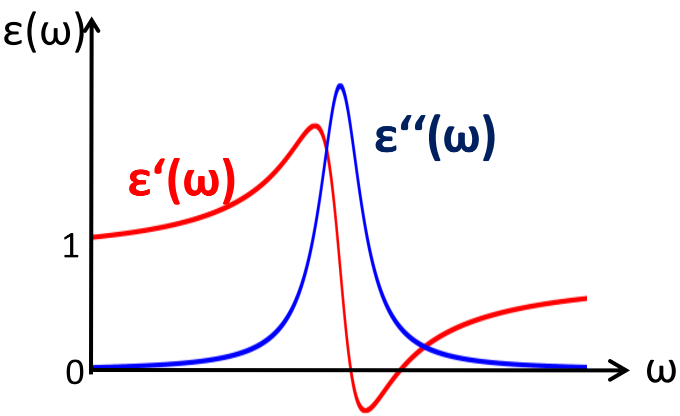
with special thanks to Dr. Clemens Zeiser



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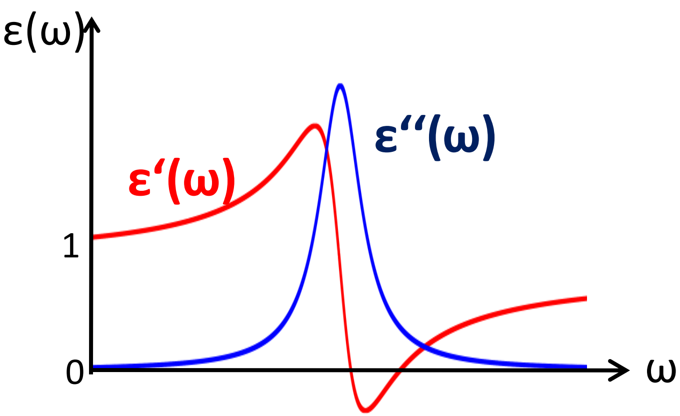
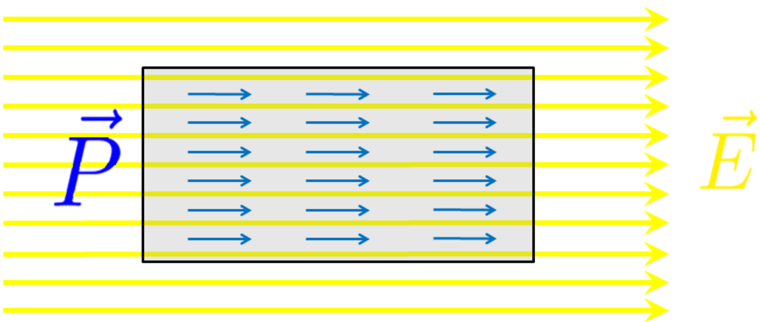




Spectral response of a solid in the visible

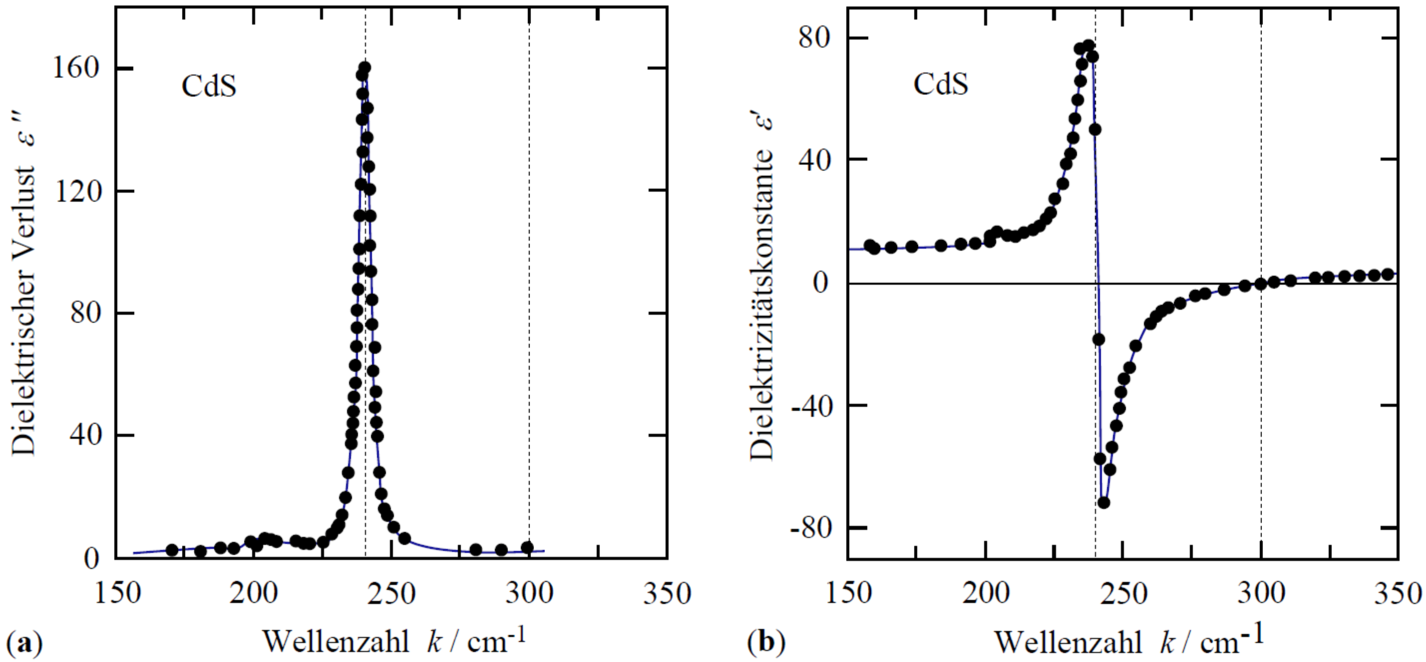
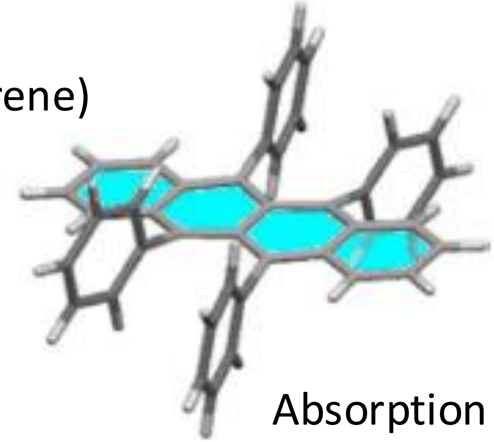


Bild 13.10: Dielektrische Funktion von Kadmiumsulfid. **a)** Imaginärteil ε'', **b)** Realteiteil ε' Die gestrichelten Linien markieren die Werte von ω_t bzw. ω_ℓ. (Nach M. Balkanski, in *Optical Properties of Solids* (F. Abelès ed.), North-Holland Publishing, Amsterdam, 1972).

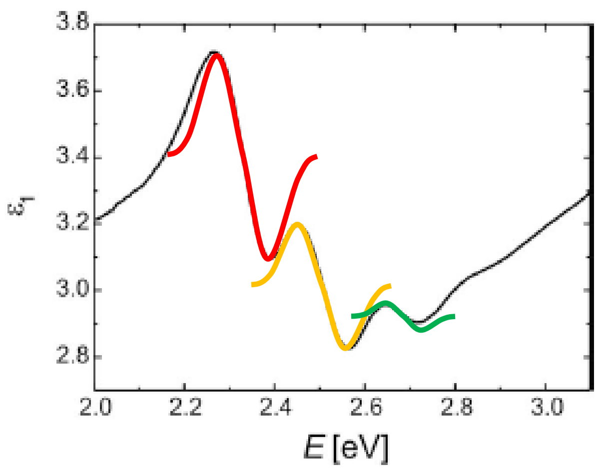
From Hunklinger / TO phonon on CdS / note that 240 cm^{-1} ~ 30 meV

Spectral response of a molecular system in the visible

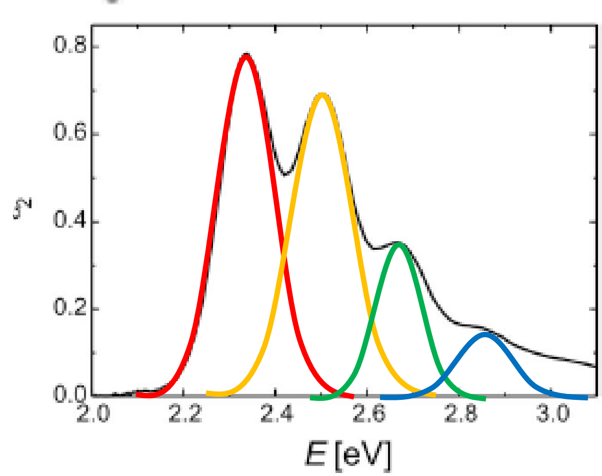
$C_{42}H_{28}$ - Molecule (Rubrene)



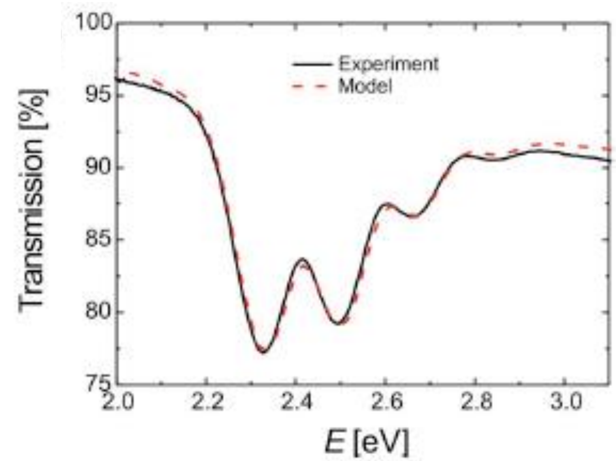
Dispersion



Absorption



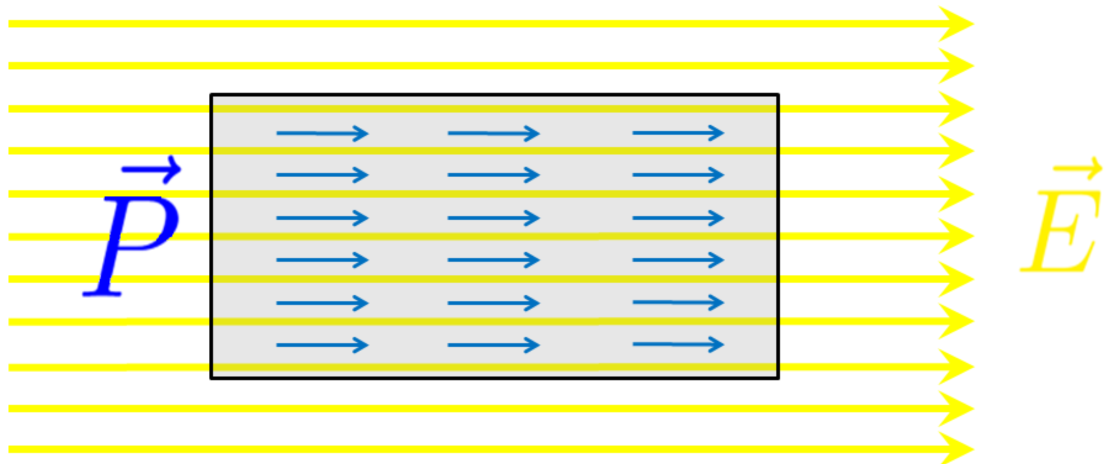
Transmission



- looks like the three quantities are related
- look for general relationship

E field in a medium

Polarisation of a medium: $\vec{P} = \epsilon_0 \chi \vec{E}$



Total field: $\vec{D} = \epsilon_0 \vec{E} + \vec{P} = \epsilon_0 \left(1 + \chi\right) \vec{E} = \epsilon_0 \epsilon_r \vec{E}$

Susceptibility is frequency-dependent: $\chi = \chi_{ij}(\omega)$
(and in general a tensor)

Permittivity / dielectric function: $\epsilon_r = 1 + \chi(\omega) = \epsilon_r(\omega)$

EM wave in a medium

Solution of Maxwell equations: $$\vec{E} = \vec{E}_0 \cdot e^{i(kx-\omega t)}$$

New index of refraction: $$n = \sqrt{\mu\epsilon} = n_0\sqrt{\mu_r\epsilon_r}$$

In medium: $$\frac{\omega}{k} = \frac{c}{n} =: c_n$$

Complex quantities: $$\epsilon = \epsilon_1 + i\epsilon_2 \qquad \epsilon_1 = n^2 + \kappa^2$$
$$N = n + i\kappa \qquad \epsilon_2 = 2n\kappa$$

Phase and absorption: $$\vec{E} = \vec{E}_0 \cdot \exp\left[ik\Big(nx - c_1 t\Big)\right] \cdot \exp\left[-\frac{\alpha}{2}x\right]$$

Absorption coefficient: $$\alpha = 2\kappa k = \frac{4\pi\kappa}{\lambda}$$

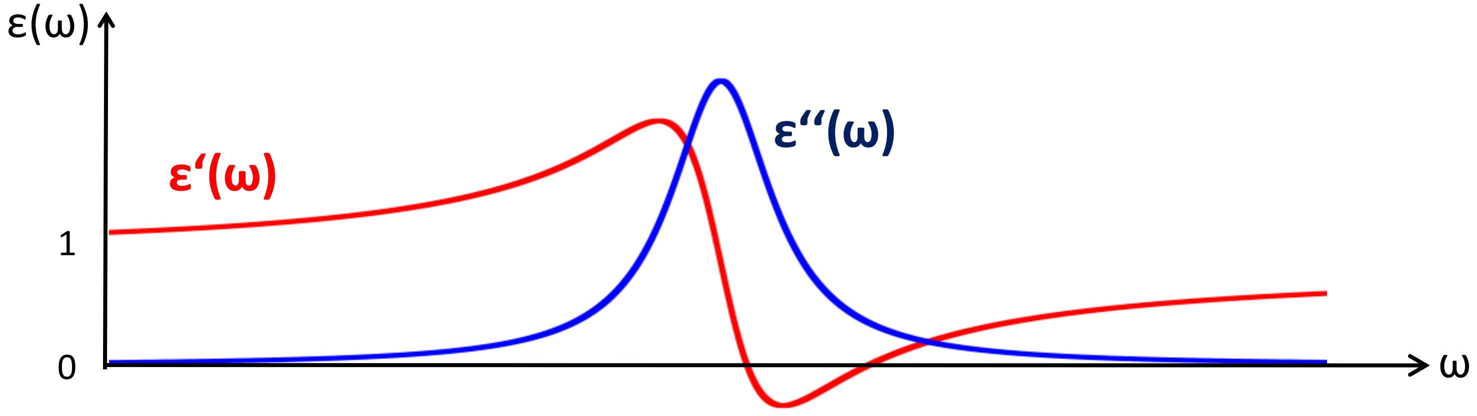
Lorentz model of a spectral resonance

Spectral dependence of permittivity ?

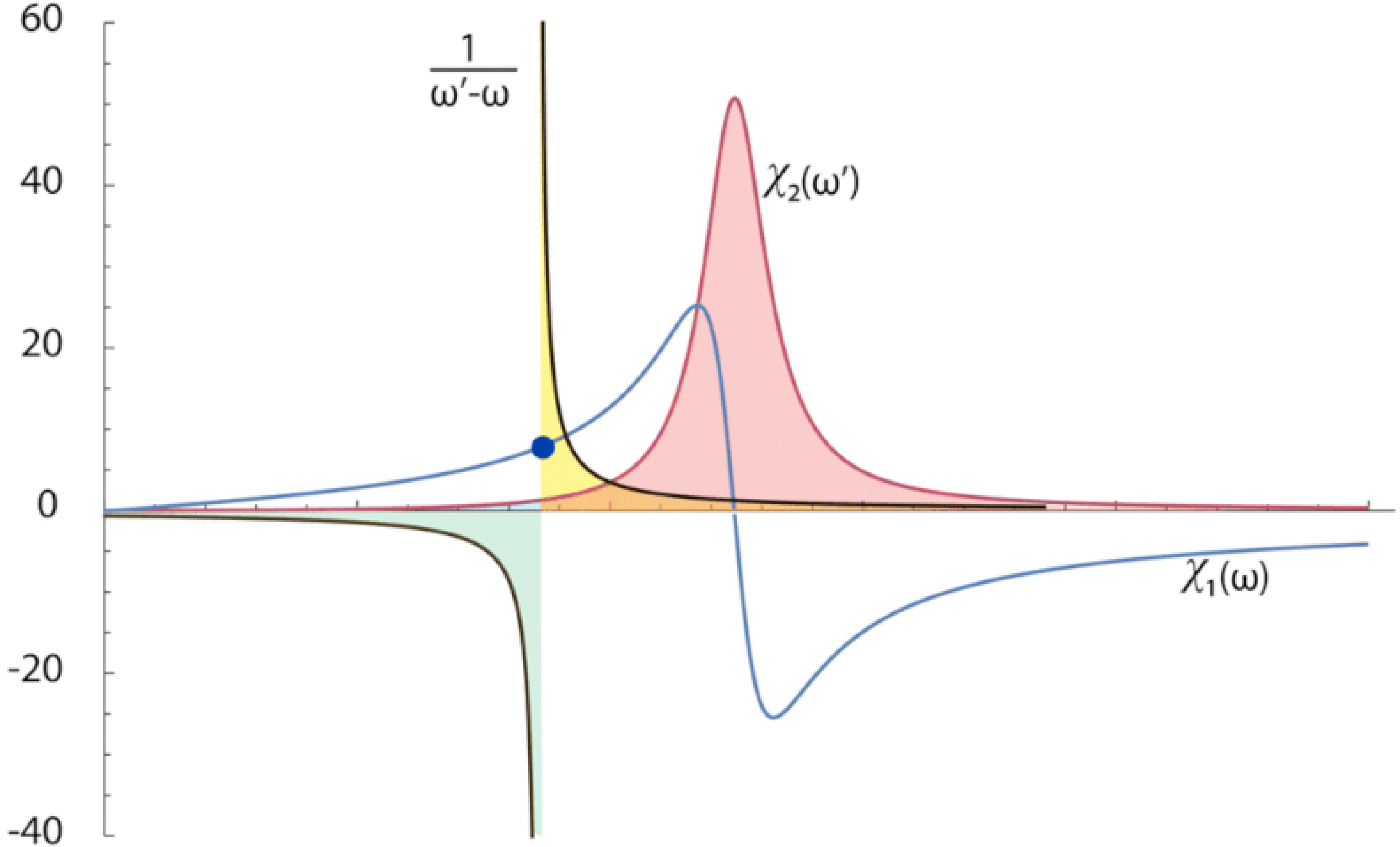
Classical Lorentz model of dispersion and absorption:

- harmonic coupling of electron to nucleus
- damping (friction) and periodic external force (oscillating el. field)
- solve equation of motion, obtain polarization and permittivity

$$\varepsilon'(\omega) = 1 + \frac{N_v e^2}{\varepsilon_0 m} \frac{\omega_1^2 - \omega^2}{(\omega_1^2 - \omega^2)^2 + \beta^2\omega^2} \qquad \varepsilon''(\omega) = \frac{N_v e^2}{\varepsilon_0 m} \frac{\beta\omega}{(\omega_1^2 - \omega^2)^2 + \beta^2\omega^2}$$



Real and imaginary part of resonance



- looks like real and imaginary part are related (integral or derivative or alike ?)
- look for general relationship

https://en.wikipedia.org/wiki/Kramers-Kronig_relations

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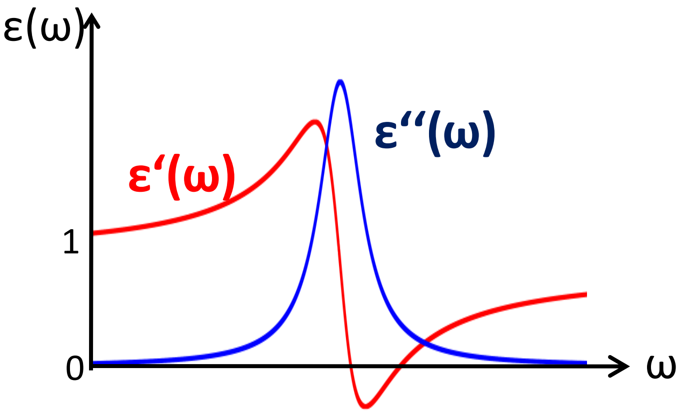
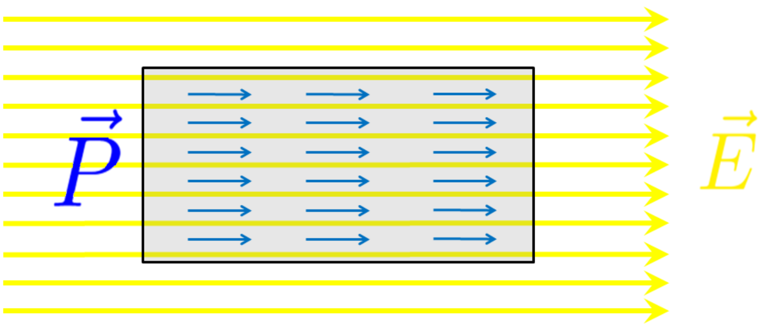




Derivation & mathematical excursion (Cauchy et al.)

- see blackboard for details of calculation
- note that there are several versions / approaches, all with the same result
- all have in common the key assumptions
  … linear response
  … causality (response does not come before stimulus cause)

Kramers-Kronig relations (KKR)

With the above we find $\chi(z) = \chi_1(z) + i\chi_2(z)$

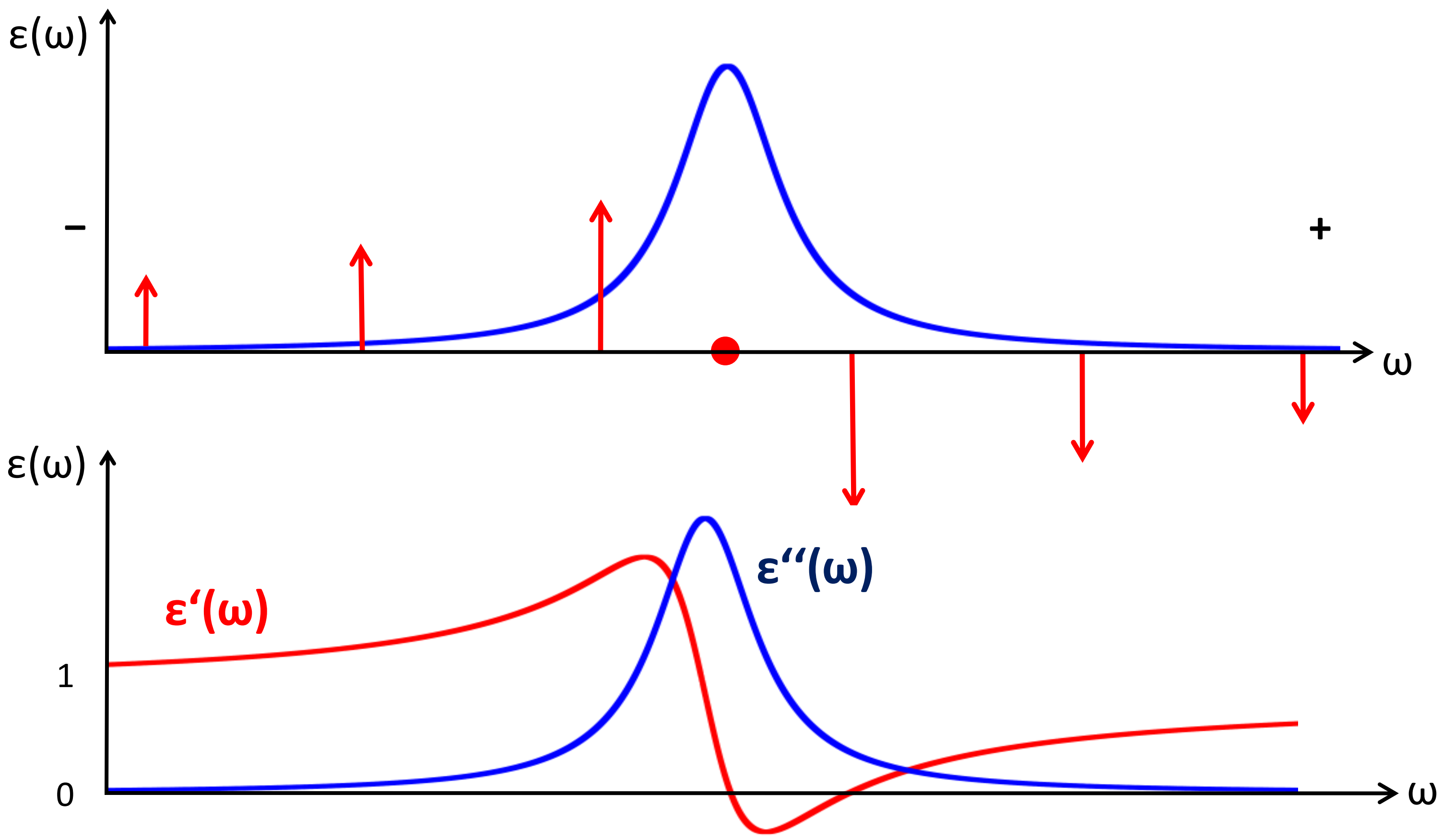
$$\boxed{\begin{aligned} \chi_1(z) &= +\frac{1}{\pi}\,\mathrm{CH}\int_{-\infty}^{\infty}\frac{\chi_2(z')}{z'-z}\,dz' \\ \chi_2(z) &= -\frac{1}{\pi}\,\mathrm{CH}\int_{-\infty}^{\infty}\frac{\chi_1(z')}{z'-z}\,dz' \end{aligned}}$$

- The KKR connect real and imaginary part of a complex function!
- Illustration: Integral “compares“ areas left and right of z

Execution

$$\chi_1(z) \quad = \quad +\frac{1}{\pi}\,\mathrm{CH}\int_{-\infty}^{\infty}\frac{\chi_2(z')}{z'-z}\,dz'$$

Function compares the areas right and left “near“ the point:



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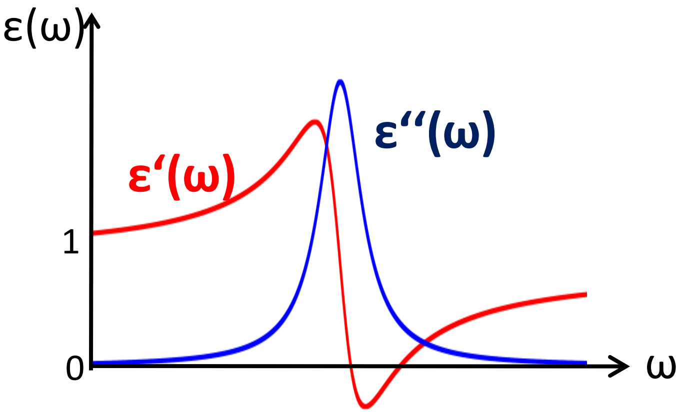

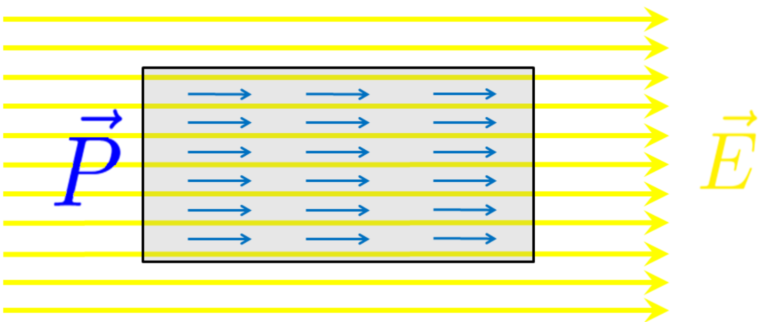

Kramers-Kronig relations (KKR) for permittivity

Frequency-dependent, complex susceptibility: $\chi(\omega) = \chi_1(\omega) + i\chi_2(\omega)$

KKR of susceptibility so far:

$$\begin{aligned}\chi_1(\omega) &= +\frac{1}{\pi}\,\mathrm{CH}\int_{-\infty}^{\infty}\frac{\chi_2(\omega')}{\omega'-\omega}\,d\omega' \\ \chi_2(\omega) &= -\frac{1}{\pi}\,\mathrm{CH}\int_{-\infty}^{\infty}\frac{\chi_1(\omega')}{\omega'-\omega}\,d\omega'\end{aligned}$$

After extension:

$$\chi_1(\omega) = +\frac{1}{\pi}\,\mathrm{CH}\int_{-\infty}^{\infty}\frac{\omega'\,\chi_2(\omega')}{\omega'^2-\omega^2}\,d\omega' + \frac{\omega}{\pi}\,\mathrm{CH}\int_{-\infty}^{\infty}\frac{\chi_2(\omega')}{\omega'^2-\omega^2}\,d\omega'$$

$$\chi_2(\omega) = -\frac{1}{\pi}\,\mathrm{CH}\int_{-\infty}^{\infty}\frac{\omega'\,\chi_1(\omega')}{\omega'^2-\omega^2}\,d\omega' - \frac{\omega}{\pi}\,\mathrm{CH}\int_{-\infty}^{\infty}\frac{\chi_1(\omega')}{\omega'^2-\omega^2}\,d\omega'$$

Kramers-Kronig relations (KKR) for permittivity

Additional assumption: $\chi_1(\omega)$ is gerade, $\chi_2(\omega)$ ungerade function (even and odd):

$$\chi_1(\omega) \quad = \quad +\frac{2}{\pi}\,\mathrm{CH}\int_0^\infty \frac{\chi_2(\omega')\,\omega'}{\omega'^2-\omega^2}\,d\omega'$$

$$\chi_2(\omega) \quad = \quad -\frac{2\omega}{\pi}\,\mathrm{CH}\int_0^\infty \frac{\chi_1(\omega')}{\omega'^2-\omega^2}\,d\omega'$$

Definition of permittivity: $\epsilon = 1+\chi = 1+\chi_1+i\chi_2$

Kramers-Kronig-Relations of permittivity:

$$\boxed{\begin{aligned}\epsilon_1(\omega)-1 \quad &= \quad +\frac{2}{\pi}\,\mathrm{CH}\int_0^\infty \frac{\epsilon_2(\omega')\,\omega'}{\omega'^2-\omega^2}\,d\omega' \\ \epsilon_2(\omega) \quad &= \quad -\frac{2\omega}{\pi}\,\mathrm{CH}\int_0^\infty \frac{\epsilon_1(\omega')-1}{\omega'^2-\omega^2}\,d\omega'\end{aligned}}$$

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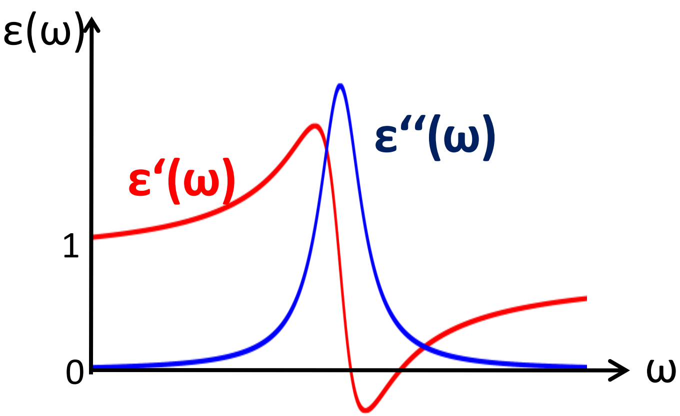
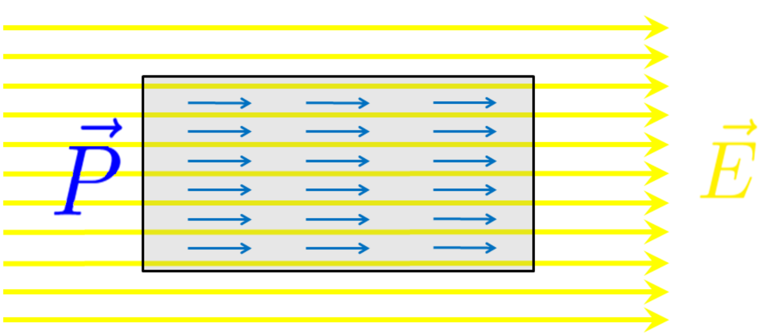
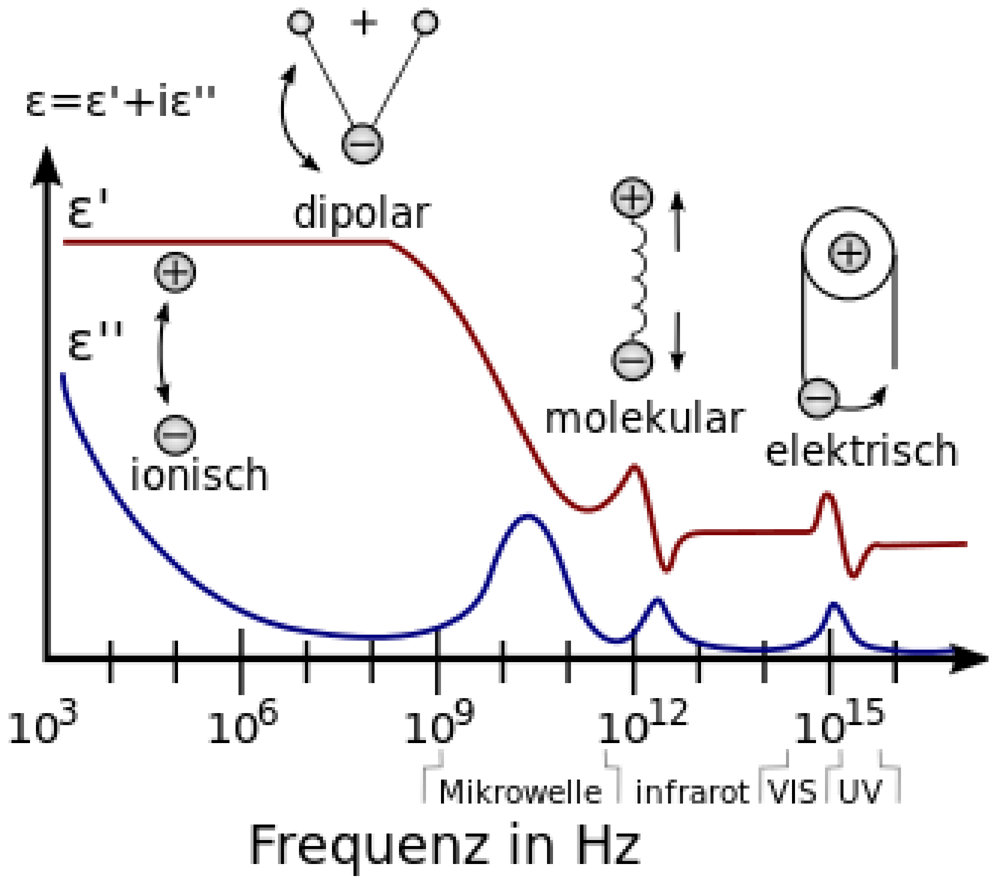
- Introduction
- Derivation
- Application to permittivity
- Applications in spectroscopy
- Summary and sources





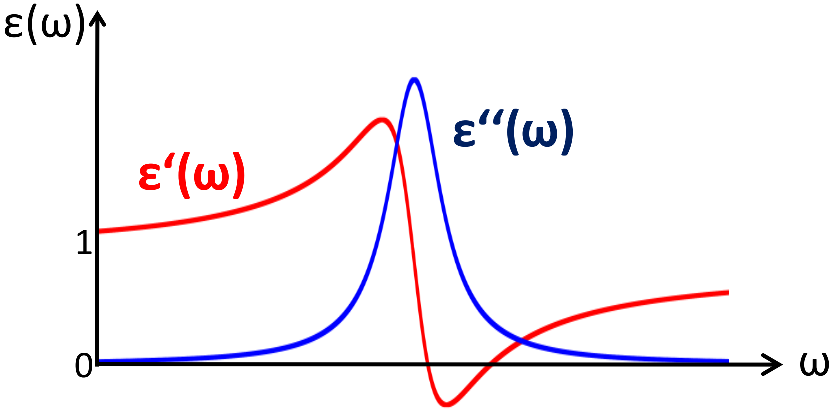
Kramers-Kronig relations (KKR) for spectroscopy

Spectroscopy of condensed matter



Kramers-Kronig relations (KKR) for spectroscopy

$$\epsilon_1(\omega) - 1 = +\frac{2}{\pi}\,\mathrm{CH}\int_{-\infty}^{\infty} \frac{\epsilon_2(\omega')\,\omega'}{\omega'^2 - \omega^2}\,d\omega'$$
$$\epsilon_2(\omega) = -\frac{2\omega}{\pi}\,\mathrm{CH}\int_{-\infty}^{\infty} \frac{\epsilon_1(\omega') - 1}{\omega'^2 - \omega^2}\,d\omega'$$



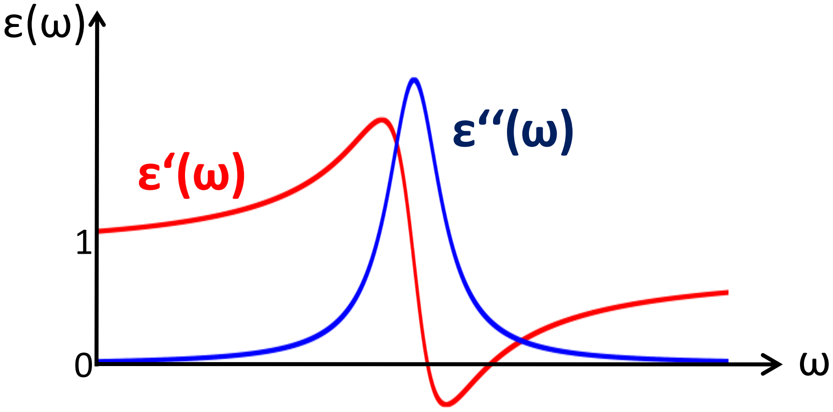
Note:

- unambiguous relation between spectral dependence of both quantities
- applies to all spectral ranges, from IR to magnetic resonance to optics to X-rays to …
- applies also locally: (very) distant frequencies are (linearly) suppressed

Kramers-Kronig relations (KKR) for spectroscopy

$$\epsilon_1(\omega) - 1 = +\frac{2}{\pi}\,\mathrm{CH}\int_{-\infty}^{\infty} \frac{\epsilon_2(\omega')\,\omega'}{\omega'^2 - \omega^2}\,d\omega'$$

$$\epsilon_2(\omega) = -\frac{2\omega}{\pi}\,\mathrm{CH}\int_{-\infty}^{\infty} \frac{\epsilon_1(\omega') - 1}{\omega'^2 - \omega^2}\,d\omega'$$



Applications:

- Complementarity: get dispersion from absorption (if hard to measure; e.g. for X-rays)
- Consistency: check, if both dispersion and absorption are known
- Correction: absolute values hard to measure
- Calculation: complex n for multilayers with complex response
- Modelling: additional consistency check for fit

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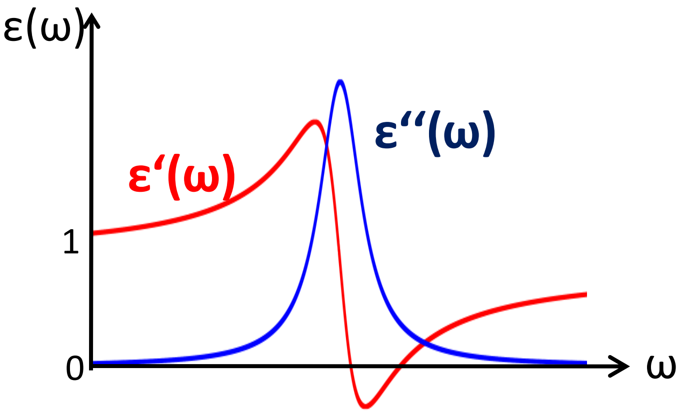
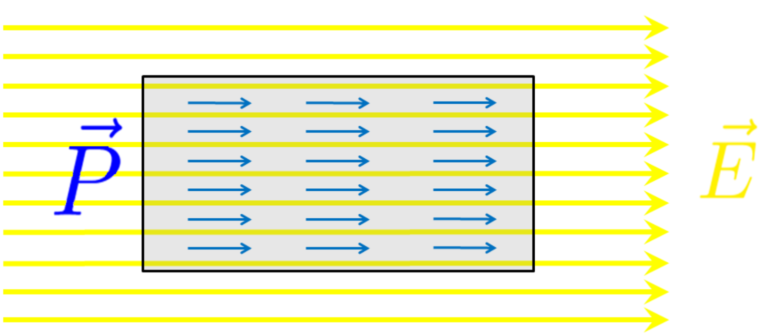




What to remember

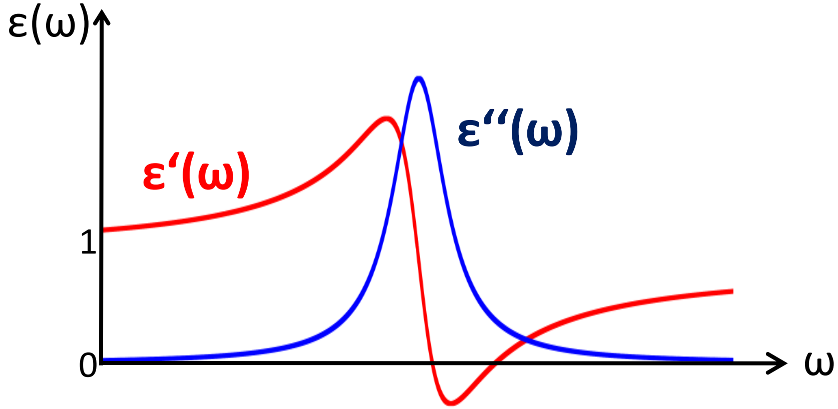
Kramers-Kronig relations

- connecting dispersion with dissipation (real and imaginary part of response)
- for linear response and causality, so rather universal
- but note that in principle the integral runs from + ∞ to - ∞

Useful from IR to magnetic resonance to optical spectroscopy to X-rays to …

- if one part is known, the other can be calculated
- helps with consistency checks of experiment and also theory

$$\boxed{\begin{aligned} \epsilon_1(\omega) - 1 &= +\frac{2}{\pi}\,\mathrm{CH}\int_{-\infty}^{\infty} \frac{\epsilon_2(\omega')\,\omega'}{\omega'^2 - \omega^2}\,d\omega' \\ \epsilon_2(\omega) &= -\frac{2\omega}{\pi}\,\mathrm{CH}\int_{-\infty}^{\infty} \frac{\epsilon_1(\omega') - 1}{\omega'^2 - \omega^2}\,d\omega' \end{aligned}}$$



Sources

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- Wikipedia-Artikel: Kramers-Kronig-Relationen (de, en)

  https://en.wikipedia.org/wiki/Kramers%E2%80%93Kronig_relations
- Wikipedia-Artikel: Lorentzoszillator (de)

  https://de.wikipedia.org/wiki/Lorentzoszillator

Images

• *http://resources.huygens.knaw.nl/bwn1880-2000/lemmata/bwn1/kramers*	Hans Kramers
• *http://www.tau.ac.il/~tsirel/dump/Static/knowino.org/wiki/Ralph_Kronig.html*	Ralph Kronig
• *http://www.radartutorial.eu/10.processing/pic/fourier2.print.png*	Rechteck-Fouriertransformierte
• *M. Kytka, L. Gisslen, A. Gerlach, U. Heinemeyer, J. Kováč, R. Scholz, F. Schreiber;*	Diagramme und Bilder zu Rubren
J. Chem. Phys. 130, 214507 (2009)	gesamtes Absorptionsspektrum
• *https://de.wikipedia.org/wiki/Permittivit%C3%A4t*	Frequenzabhängige Permittivität