DISPERSIVE MATTER

Previously we've assumed that the period of oscillation of fields is long compared to the response time of matter in establishing polarization and magnetisation. That is we've restricted ourselves to relatively low frequency fields — it's now time to relax this assumption.

The following equations still describe the fields:

$$\vec{\nabla}\cdot\vec{D} = 0 \qquad \vec{\nabla}\cdot\vec{B} = 0$$

$$\vec{\nabla}\times\vec{E} = -\frac{\partial\vec{B}}{\partial t} \qquad \vec{\nabla}\times\vec{H} = \frac{\partial\vec{D}}{\partial t}$$

but the precise relationship between e.g. $\vec{D}$ and $\vec{E}$ must be reconsidered, since in general now $\vec{D}(t)$ (or $\vec{P}(t)$ if you prefer) depends upon $\vec{E}$ at all previous times, since the material may take some time to adjust.

We can write $\underbrace{\vec{D}(t)}_{\varepsilon_0\vec{E}(t)+\vec{P}(t)} = \varepsilon_0\vec{E}(t) + \varepsilon_0\int_0^\infty d\tau\, f(\tau)\,\vec{E}(t-\tau)$

where $f(\tau)$ encodes the polarization behavior of the material.

We've implicitly assumed that the fields are weak enough that the polarization is linear in $\vec{E}$.

We can express this general relation in a simple form by considering the Fourier expansion into frequency modes

$$\vec{D}(t) = \frac{1}{2\pi}\int_{-\infty}^{\infty} d\omega\, \vec{D}(\omega)e^{-i\omega t}, \quad \vec{E}(t-\tau) = \frac{1}{2\pi}\int d\omega\, \vec{E}(\omega)\, e^{-i\omega(t-\tau)}$$

then $$\int d\omega\, \vec{D}(\omega)e^{-i\omega t} = \int d\omega\, \varepsilon_0\vec{E}(\omega)e^{-i\omega t} + \int d\omega\, \varepsilon_0\vec{E}(\omega)\int_0^\infty d\tau\, f(\tau)\, e^{-i\omega t}e^{i\omega\tau}$$

& thus $$\vec{D}(\omega) = \varepsilon_0\left[1 + \int_0^\infty d\tau\, f(\tau)e^{i\omega\tau}\right]\vec{E}(\omega)$$

Which we may write as $\vec{D} = \varepsilon(\omega)\vec{E}$ with $\varepsilon(\omega)$ a complex, frequency dependent permittivity

$$\boxed{\frac{\epsilon(\omega)}{\varepsilon_0} \equiv 1 + \int_0^\infty d\tau\, f(\tau)e^{i\omega\tau}}$$

notice that $\epsilon(-\omega) = \epsilon^*(\omega)$ so $\epsilon_r(\omega) = \epsilon_r(-\omega)$ "even"
& $\epsilon_i(\omega) = -\epsilon_i(-\omega)$ "odd"

in a Taylor series about $\omega=0$ $\rightarrow$ $\epsilon_r(\omega) = \bar{\epsilon} + O(\omega^2)$
$\epsilon_i(\omega) = A\omega + O(\omega^3)$

[see Zangwill or Landau & Lifshitz for an explanation of why we need only consider $\epsilon(\omega)$ and

At this stage it is useful to consider a simple classical model that illustrates how $\epsilon(\omega)$ can arise.

Consider an electron bound to a molecule by a force that can be approximated as harmonic ($V \sim r^2$), which also undergoes collisions, or other sources of "damping", when it is acted upon by an external electric field. Then the equation of motion is

$$m\left[\ddot{\vec{r}} + \gamma\dot{\vec{r}} + \omega_0^2\vec{r}\right] = -e\vec{E}(\vec{r},t)$$

For a field of small amplitude we can neglect the spatial variation in $\vec{E}(\vec{r},t)$, and considering a harmonic time variation $\vec{E} \sim e^{-i\omega t}$ we have

$$\ddot{\vec{r}} + \gamma\dot{\vec{r}} + \omega_0^2\vec{r} = \frac{-e}{m}\vec{E}e^{-i\omega t}$$

ignoring transient behaviour, a solution $\vec{r}(t) = Ae^{-i\omega t}$ can be found with

$$(-\omega^2 + \omega_0^2 - i\gamma\omega)\vec{A} = -\frac{e}{m}\vec{E}$$

and thus the electric dipole moment of this electron is

$$\vec{p} = -e\vec{r} = \frac{e^2}{m}\frac{1}{\omega_0^2 - \omega^2 - i\gamma\omega}\vec{E}$$

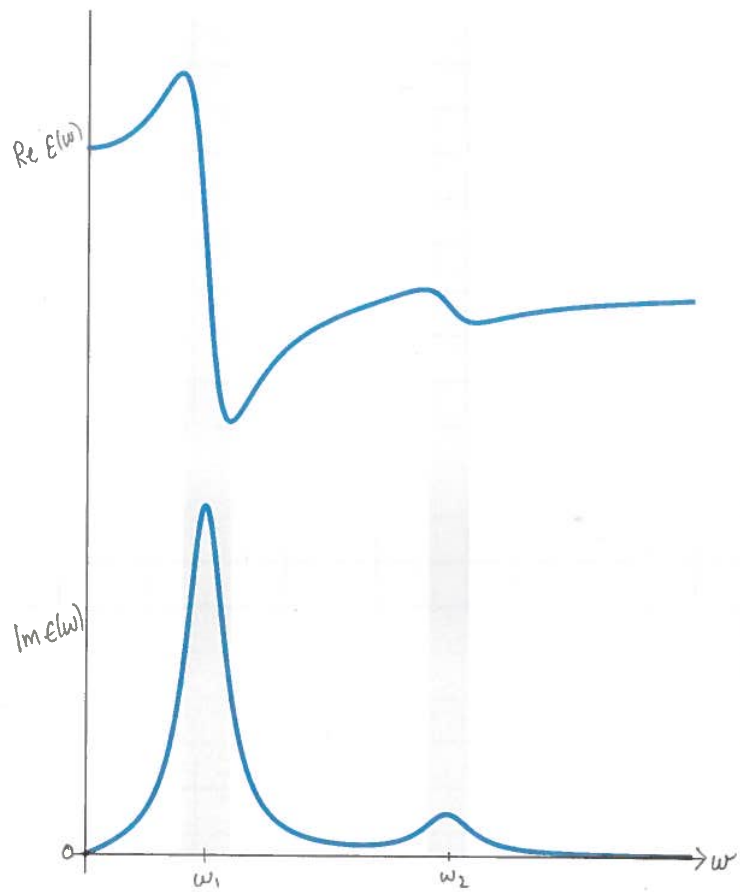
with N molecules per unit volume and allowing multiple electrons per molecule with different binding frequencies & dampings we have, for the polarization

$$\vec{P} = \vec{E}\cdot\frac{Ne^2}{m}\sum_i\frac{f_i}{\omega_i^2 - \omega^2 - i\gamma_i\omega}$$

where $\sum_i f_i = Z$ = number of electrons per molecule

$$\Rightarrow \boxed{\epsilon(\omega) = \epsilon_0 + \frac{Ne^2}{m}\sum_i\frac{f_i}{\omega_i^2 - \omega^2 - i\gamma_i\omega}} \quad [L]$$

notice that $\epsilon(-\omega) = \epsilon^*(\omega)$ as we'd expect.



e.g. a two-resonance case

When $\frac{d}{d\omega} \epsilon_r(\omega) > 0$ "normal dispersion"

$\frac{d}{d\omega} \epsilon_r(\omega) < 0$ "anomalous dispersion"

note that anomalous dispersion occurs in the region of the resonance peak page 29

In our previous consideration of waves in conductors, we found that the conductivity could be included in the imaginary part of $\epsilon(\omega)$

→ in order to account for ohms law in $\vec{\nabla}\times\vec{H} = \frac{\partial \vec{D}}{\partial t}$

we must have that $\frac{\partial \vec{D}}{\partial t} \to \sigma \vec{E}$ for small ω, & since $\vec{D}(t) = \frac{1}{2\pi}\int d\omega\, \epsilon(\omega)\vec{E}(\omega)e^{-i\omega t}$

$$\frac{\partial \vec{D}}{\partial t} \to \frac{1}{2\pi}\int d\omega\, (-i\omega\epsilon)\vec{E}(\omega)e^{-i\omega t}$$ & thus $\epsilon(\omega) \to \frac{i\sigma}{\omega}$ for small ω

Which is indeed what we found on page 29.

If the material is conducting then, the behavior for small ω is modified to

$$\epsilon(\omega) = \frac{i\sigma}{\omega} + \bar{\epsilon} + iA\omega + O(\omega^2)$$

Our classical model is capable of describing this behavior. Equation [L] on pg 34 reads,

$$\epsilon(\omega) = \epsilon_0 + \frac{Ne^2}{m}\sum_i \frac{f_i}{\omega_i^2 - \omega^2 - i\gamma_i\omega},$$

and let's suppose there are some electrons $(i=0)$ which are "free", that is not harmonically bound, so $\omega_0 = 0$. They still undergo collisions so $\gamma_0 \neq 0$.

Thus

$$\epsilon(\omega) = -\frac{Ne^2}{m}\frac{f_0}{\omega^2 + i\gamma_0\omega} + \underbrace{\left[\epsilon_0 + \frac{Ne^2}{m}\sum_{i>0}\frac{f_i}{\omega_i^2-\omega^2-i\gamma_i\omega}\right]}_{\epsilon_b(\omega)}$$

$\epsilon_b(\omega)$ ← behavior of "bound" electrons

$$= +i\left[\frac{Ne^2}{m}f_0\frac{1}{\gamma_0 - i\omega}\right]\cdot\frac{1}{\omega} + \epsilon_b(\omega)$$

and we observe the imaginary $\frac{1}{\omega}$ behavior expected for conduction.

In this model $\sigma = \frac{Ne^2 f_0}{m\gamma_0}$ as $\omega \to 0$, which corresponds to the Drude model.

energy considerations

the rate of change of electromagnetic energy per unit volume is

$$-\left(\vec{E}\cdot\frac{\partial\vec{D}}{\partial t} + \vec{H}\cdot\frac{\partial\vec{B}}{\partial t}\right)$$

~~we~~ we recall that we must take the real parts of $\vec{E}$, $\frac{\partial\vec{D}}{\partial t}$, $\vec{H}$ and $\frac{\partial\vec{B}}{\partial t}$

$$Re(\vec{E}) = \frac{1}{2}(\vec{E}+\vec{E}^*)$$

for a monochromatic field $\frac{\partial\vec{D}}{\partial t} = -i\omega\epsilon(\omega)\vec{E}$ & $Re\left(\frac{\partial\vec{D}}{\partial t}\right) = \frac{1}{2}\left(-i\omega\epsilon(\omega)\vec{E} + (-i\omega\epsilon(\omega)\vec{E})^*\right)$

$$= \frac{1}{2}i\omega\left(-\epsilon\vec{E} + \epsilon^*\vec{E}^*\right)$$

& similarly for the magnetic terms

thus the rate of loss of electric field energy per unit volume is

$$\frac{1}{2}(\vec{E}+\vec{E}^*)\cdot\frac{1}{2}i\omega\left(-\epsilon\vec{E}+\epsilon^*\vec{E}^*\right) = \frac{i\omega}{4}\left(-\epsilon\vec{E}\cdot\vec{E} + \epsilon^*\vec{E}^*\cdot\vec{E}^* + (\epsilon^*-\epsilon)\vec{E}\cdot\vec{E}^*\right)$$

averaged over a complete oscillation $\langle\vec{E}\cdot\vec{E}\rangle = \langle\vec{E}^*\cdot\vec{E}^*\rangle = 0$ so the material loses energy at a rate

$$\frac{i\omega}{4}(-2i\epsilon_i)\langle\vec{E}\cdot\vec{E}^*\rangle = \frac{1}{2}\omega\epsilon_i\langle\vec{E}\cdot\vec{E}^*\rangle$$

and we see that the presence of any imaginary part in the complex permittivity means that energy is absorbed by the material.

It also follows that $\epsilon_i > 0$ always to have energy loss.

[see Zangwill for a more rigorous consideration of the realistic case where the fields aren't monochromatic]

causality & the relationship between ϵ_r and ϵ_i

Let's return to our original expression for $\vec{D}(t)$ in terms of the current and previous $\vec{E}(t)$:

$$\vec{D}(t) = \epsilon_0 \vec{E}(t) + \epsilon_0 \int_0^\infty d\tau\, f(\tau)\, \vec{E}(t-\tau).$$

It should be obvious that in the case of a dielectric $f(\tau\to\infty)\to 0$, as electric fields very far in the past cannot have an impact on the current polarization.

Somewhat less obvious is the fact that $f(\tau\to\infty) \to \sigma/\epsilon_0$ in the case that the material has some conductivity, σ, but this follows from the need for

$\frac{\partial \vec{D}}{\partial t}$ to become $\sigma \vec{E}$ $\Rightarrow$ $\vec{D}(t) = \int_{-\infty}^{t} d\tau\, \sigma \vec{E}(\tau)$ $\quad \tau = t - \tau'$

$$\vec{D}(t) = \sigma \int_0^\infty d\tau'\, \vec{E}(t-\tau')$$

The complex permittivity is defined by

$$\frac{\epsilon(\omega)}{\epsilon_0} \equiv 1 + \int_0^\infty d\tau\, f(\tau) e^{i\omega\tau}$$

and we can derive some general relations featuring $\epsilon(\omega)$ by using the theory of functions of a complex variable.

consider $\frac{\epsilon(z)}{\epsilon_0} \equiv 1 + \int_0^\infty d\tau\, f(\tau) e^{iz\tau}$ [Z] for complex $z = x+iy$

which is what we had if z is taken real

it follows that $\frac{\epsilon}{\epsilon_0}(z=x+iy) = 1 + \int_0^\infty d\tau\, f(\tau) e^{ix\tau} e^{-y\tau}$

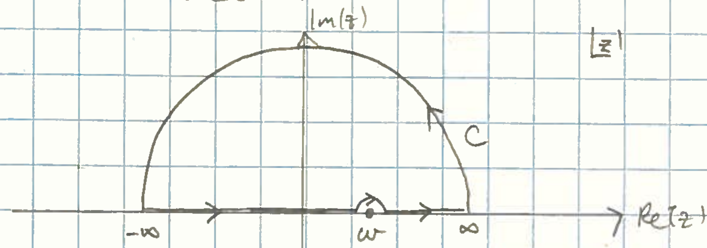
and thus, since $f(\tau)$ does not diverge as $\tau\to\infty$, this integral converges for $y>0$, ie in the upper half-plane of z.

$\epsilon(z)$ is regular in the upper half-plane, and this follows ultimately from CAUSALITY – we considered only times <u>before</u> t, which limited τ to positive values – because of this the integral converged.

from [Z] we note that $\epsilon(-z^*) = \epsilon^*(z)$

and $\epsilon(z\to\infty) \to 1$ for any direction in the upper half plane because $\epsilon(z)$ has no singularities in the upper half-plane, the following integral round the contour C shown is zero:

$$0 = \oint_C dz\, \frac{\epsilon(z) - \epsilon_0}{z - \omega}$$



the semicircle at infinity contributes nothing so

$$0 = \int_{-\infty}^{\omega-\delta} dx\, \frac{\epsilon(x) - \epsilon_0}{x - \omega} + \int_{S} dz\, \frac{\epsilon(z) - \epsilon_0}{z - \omega} + \int_{\omega+\delta}^{\infty} dx\, \frac{\epsilon(x) - \epsilon_0}{x - \omega} \quad \text{in the limit } \delta \to 0$$

semicircle of radius δ at ω

the second integral can easily be evaluated: $z = \omega + \delta e^{i\phi}$ $\Rightarrow dz = i\delta e^{i\phi} d\phi$

$$i\delta \int_{\pi}^{0} d\phi\, \frac{\epsilon(\omega) - \epsilon_0}{\delta e^{i\phi}} = i\left(\epsilon(\omega) - \epsilon_0\right)(-\pi)$$

and the first and third integrals combine to give the PRINCIPAL VALUE integral

$$0 = P\int_{-\infty}^{\infty} dx\, \frac{\epsilon(x)/\epsilon_0 - 1}{x - \omega} - i\pi\left[\epsilon(\omega)/\epsilon_0 - 1\right]$$

taking the real & imaginary parts we have

$$\boxed{\begin{aligned} \epsilon_r(\omega)/\epsilon_0 &= 1 + \frac{1}{\pi} P\int_{-\infty}^{\infty} dx\, \frac{\epsilon_i(x)/\epsilon_0}{x - \omega} \\ \epsilon_i(\omega)/\epsilon_0 &= -\frac{1}{\pi} P\int_{-\infty}^{\infty} dx\, \frac{\epsilon_r(x)/\epsilon_0 - 1}{x - \omega} \end{aligned}}$$

"Kramers-Kronig equations"

(we've assumed here that $\sigma = 0$ so there is no pole at $\omega = 0$ - if this is not the case the second equation is modified to be

$$\frac{\epsilon_i(\omega)}{\epsilon_0} = \frac{\sigma}{\epsilon_0 \omega} - \frac{1}{\pi} P\int_{-\infty}^{\infty} dx\, \frac{\epsilon_r(x)/\epsilon_0 - 1}{x - \omega}$$)

these equations can be recast into a form that includes only positive frequencies using the symmetry properties derived earlier: $\epsilon_r(-\omega) = \epsilon_r(\omega)$

$\epsilon_i(-\omega) = -\epsilon_i(\omega)$

$$\int_{-\infty}^{\infty} dx \, \frac{\epsilon_i(x)}{x-\omega} = \int_{-\infty}^{0} dx \, \frac{\epsilon_i(x)}{x-\omega} + \int_{0}^{\infty} dx \, \frac{\epsilon_i(x)}{x-\omega}$$

$$= \int_{0}^{\infty} dx \, \frac{\epsilon_i(-x)}{-x-\omega} + \int_{0}^{\infty} dx \, \frac{\epsilon_i(x)}{x-\omega}$$

$$= \int_{0}^{\infty} dx \, \frac{\epsilon_i(x)}{x+\omega} + \int_{0}^{\infty} dx \, \frac{\epsilon_i(x)}{x+\omega} = 2\int_{0}^{\infty} dx \, \frac{x\,\epsilon_i(x)}{x^2-\omega^2}$$

$$\int_{-\infty}^{\infty} dx \, \frac{\epsilon_r(x)/\epsilon_0 - 1}{x-\omega} = \int_{0}^{\infty} dx \, \left(\epsilon_r(x)/\epsilon_0 - 1\right)\left(\frac{-1}{x+\omega} + \frac{1}{x-\omega}\right) = 2\omega \int_{0}^{\infty} dx \, \frac{\epsilon_r(x)/\epsilon_0 - 1}{x^2-\omega^2}$$

$$\mathrm{Re}\left[\epsilon(\omega)/\epsilon_0\right] = 1 + \frac{2}{\pi} P \int_{0}^{\infty} dx \, \frac{x \, \mathrm{Im}\left[\epsilon(x)/\epsilon_0\right]}{x^2-\omega^2}$$

$$\mathrm{Im}\left[\epsilon(\omega)/\epsilon_0\right] = -\frac{2\omega}{\pi} P \int_{0}^{\infty} dx \, \frac{\mathrm{Re}\left[\epsilon(x)/\epsilon_0\right] - 1}{x^2-\omega^2}$$

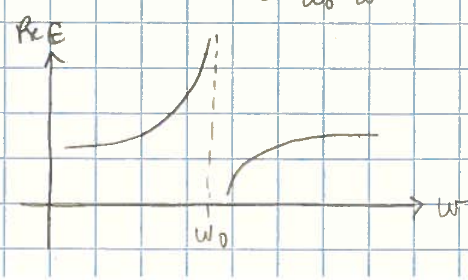
One use of "dispersion relations" of this type is to find the real part of $\epsilon(\omega)$ when only the imaginary part is known (eg. the absorption has been measured).

A very simple example is if a single narrow resonance dominates $\mathrm{Im}\,\epsilon(\omega)$ so that it is approximately

$$\mathrm{Im}\, \epsilon(z)/\epsilon_0 = K \cdot \frac{\pi}{2\omega_0} \delta(z-\omega_0) + \ldots$$

then the first relation above gives $\mathrm{Re}\left[\epsilon(\omega)/\epsilon_0\right] = \frac{K}{\omega_0} \cdot \frac{\omega_0}{\omega_0^2-\omega^2} + \ldots$

$$\mathrm{Re}\left[\epsilon(\omega \neq \omega_0)/\epsilon_0\right] \simeq \frac{K}{\omega_0^2-\omega^2} + \ldots$$



notice anomalous region is vanishingly small because the resonance is vanishingly wide.