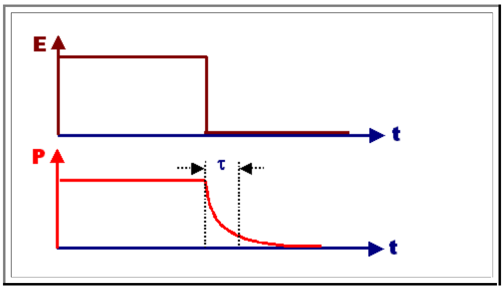
3.3.2 Dipole Relaxation

From Time Dependence to Frequency Dependence

- The easiest way to look at *relaxation phenomena* is to consider what happens if the driving force - the electrical field in our case - is suddenly switched off, after it has been constant for a sufficiently long time so that an equilibrium distribution of dipoles could be obtained.
  - We expect then that the dipoles will randomize, i.e. their dipole moment or their polarization will go to zero.
  - However, that cannot happen instantaneously. A specific dipole will have a certain orientation at the time the field will be switched off, and it will change that orientation only by some interaction with other dipoles (or, in a solid, with phonons), in other words upon collisions or other "violent" encounters. It will take a characteristic time, roughly the time between collisions, before the dipole moment will have disappeared.
  - Since we are discussing statistical events in this case, the individual characteristic time for a given dipole will be small for some, and large for others. But there will be an *average* value which we will call the **relaxation time** τ of the system. We thus expect a smooth change over from the polarization with field to zero within the relaxation time τ, or a behavior as shown below



- In formulas, we expect that ***P*** decays starting at the time of the switch-off according to

$$P(t) = P_0 \cdot \exp -\frac{t}{\tau}$$

- This simple equation describes the behavior of a simple system like our "ideal" dipoles very well. It is, however, not easy to derive from first principles, because we would have to look at the development of an ensemble of interacting particles in time, a classical task of non-classical, i.e. statistical mechanics, but beyond our ***ken*** at this point.
  - Nevertheless, we know that a relation like that comes up whenever we look at the decay of some ensemble of particles or objects, where some have more (or less) energy than required by equilibrium conditions, and the change-over from the excited state to the base state needs "help", i.e. has to overcome some energy barrier.
  - All we have to assume is that the number of particles or objects decaying from the excited to the base state is proportional to the number of excited objects. In other words, we have a relation as follows:

$$\frac{dn}{dt} \propto n = -\frac{1}{\tau} \cdot n$$

$$n = n_0 \cdot \exp -\frac{t}{\tau}$$

  - This covers for example radioactive decay, cooling of any material, and the decay of the foam or froth on top of your **beer**: Bubbles are an energetically excited state of beer because of the additional surface energy as compared to a droplet. If you measure the height of the head on your beer as a function of time, you will find the exponential law.
- When we turn on an electrical field, our dipole system with random distribution of orientations has too much energy relative to what it could have for a better orientation distribution.
  - The "decay" to the lower (free) energy state and the concomitant built-up of polarization when we switch on the field, will follow our universal law from above, and so will the decay of the polarization when we turn it off.

- We are, however, not so interested in the *time* dependence $P(t)$ of the polarization when we apply some disturbance or *input* to the system (the switching on or off of the electrical field). We rather would like to know its *frequency* dependence $P(\omega)$ with $\omega = 2\pi\nu$ = angular frequency, i.e. the output to a periodic harmonic input, i.e. to a field like $E = E_0 \cdot \sin\omega t$.
    - Since *any* signal can be expressed as a **Fourier series or Fourier integral** of sin functions as the one above, by knowing $P(\omega)$ we can express the response to *any* signal just as well.
- In other words: We can switch back and forth between $P(\tau)$ and $P(\omega)$ via a **Fourier transformation**.
    - We already know the time dependence $P(\tau)$ for a switch-on / switch-off signal, and from that we can - in principle - derive $P(\omega)$.
    - We thus have to consider the **Fourier transform** of $P(t)$. However, while clear in principle, details can become nasty. While some details are given in an advanced module, here it must suffice to say that our Fouriertransform is given by

$$P(\omega) \;=\; \int_0^{\infty} P_0 \cdot \exp - \frac{t}{\tau} \cdot \exp - (i\omega t) \cdot dt$$

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    - P_0 is the static polarization, i.e. the value of $P(\omega)$ for $\omega = 0$ Hz , and $i = (-1)^{1/2}$ is the imaginary unit (note that in electrical engineering usually the symbol **j** is used instead of **i**).
- This is an easy integral, we obtain

$$P(\omega) \;=\; \frac{P_0}{\omega_0 \;+\; i \cdot \omega}$$

$$\omega_0 \;=\; \frac{1}{\tau}$$

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    - Note that ω_0 is *not* $2\pi/\tau$, as usual, but just $1/\tau$. That does not mean anything except that it makes writing the formulas somewhat easier.
- The $P(\omega)$ then are the *Fourier coefficients* if you describe the $P(t)$ curve by a Fourier integral (or series, if you like that better, with infinitesimally closely spaced frequency intervals).
    - $P(\omega)$ thus is the polarization response of the system if you jiggle it with an electrical field given by $E = E_0 \cdot \exp(i\omega t)$ that contains just one frequency ω.
    - However, our Fourier coefficients are *complex numbers*, and we have to discuss what that means now.

Usimg Complex Numbers and Functions

- Using the powerful math of complex numbers, we end up with a *complex* polarization. That need not bother us since by convention we would only consider the *real part* of P when we are in need of real numbers.
    - Essentially, we are done. If we know the Amplitude ($= E_0$) and (circle) frequency ω of the electrical field in the material (taking into account possible "local field" effects), we know the polarization.
- However, there is a smarter way to describe that relationship than the equation above, with the added benefit that this "smart" way can be generalized to all frequency dependent polarization phenomena. Let's see how it is done:
- What we want to do, is to keep our basic equation that couples polarization and field strength for alternating fields, too. This requires that the susceptibility χ becomes frequency dependent. We then have

$$P(\omega) = \epsilon_0 \cdot \chi(\omega) \cdot E(\omega)$$

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    - and the decisive factor, giving the *amplitude* of $P(\omega)$, is $\chi(\omega)$.
    - The time dependence of $P(\omega)$ is trivial. It is either given by $\exp i(\omega t - \phi)$, with ϕ accounting for a possible phase shift, or simply by $\exp i(\omega t)$ if we include the phase shift in $\chi(\omega)$, which means it must be complex.
    - The second possibility is more powerful, so that is what we will do. If we then move from the polarization P to the more conventional electrical displacement D; the relation between $D(\omega)$ and $E(\omega)$ will require a *complex dielectric function* instead of a complex susceptibiltiy, and that is the quantity we will be after from now on.

  - It goes without saying that for more complex time dependencies of the electrical field, the equation above holds for every for every **sin** component of the Fourier series of an arbitrary periodic function.

- Extracting a *frequency dependent susceptibility* $\chi(\omega)$ from our equation for the polarization is fairly easy: Using the basic equation we have

$$\boxed{\epsilon_0 \cdot \chi(\omega) = \frac{P(\omega)}{E(\omega)} = \frac{P_0}{E_0} \cdot \frac{1}{\omega_0 + i \cdot \omega} = \chi_s \cdot \frac{1}{1 + i \cdot \omega/\omega_0}}$$

  - $\chi_s = P_0 / E_0$ is the *static susceptibility*, i.e. the value for zero frequency.

- Presently, we are only interested in the *real* part of the complex susceptibility thus obtained. As any complex number, we can decompose $\chi(\omega)$ in a real and a imaginary part, i.e. write it as

$$\boxed{\chi(\omega) = \chi'(\omega) + i \cdot \chi''(\omega)}$$

  - with χ' and χ'' being the real and the imaginary part of the complex susceptibility χ . *We drop the (ω) by now, because whenever we discuss real and imaginary parts it is clear that we discuss frequency dependence).*
  - All we have to do in order to obtain χ' and χ'' is to expand the fraction by $1 - i \cdot \omega/\omega_0$ which gives us

$$\boxed{\epsilon_0 \cdot \chi(\omega) = \frac{\chi_s}{1 + (\omega/\omega_0)^2} - i \cdot \frac{\chi_s \cdot (\omega/\omega_0)}{1 + (\omega/\omega_0)^2}}$$

  - We thus have for the real and imaginary part of $\epsilon_0 \cdot \chi(\omega)$, which is almost, but not yet quite the *dielectric function* that we are trying to establish:

$$\boxed{\begin{aligned} \epsilon_0 \cdot \chi' &= \frac{\chi_s}{1 + (\omega/\omega_0)^2} \\ - \epsilon_0 \cdot \chi'' &= \frac{\chi_s \cdot (\omega/\omega_0)}{1 + (\omega/\omega_0)^2} \end{aligned}}$$

- This is pretty good, because, as we will see, the real *and* imaginary part of the complex susceptibility contain an unexpected wealth of material properties. Not only the dielectric behavior, but also (almost) all optical properties and essentially also the conductivity of non-perfect dielectrics.

- Before we proceed to the *dielectric function* which is what we really want to obtain, we have to makes things a tiny bit more complicated - in three easy steps.
  - **1.** People in general like the dielectric constant ϵ_r as a material parameter far better than the susceptibility χ - history just cannot be ignored, even in physics. Everything we did above for the polarization ***P***, we could also have done for the dielectric flux density ***D*** - just replace the letter "***P***" by "***D***" and "χ" by "ϵ_r" and we obtain a complex frequency dependent dielectric constant $\epsilon_r(\omega) = \chi(\omega) + 1$ with, of course, ϵ_s instead of χ_s as the zero frequency static case.
  - **2.** So far we assumed that at very large frequencies the polarization is essentially zero - the dipole cannot follow and $\chi(\omega \to \infty) = 0$ That is not necessarily true in the most general case - there might be, after all, other mechanisms that still "work" at frequencies far larger than what orientation polarization can take. If we take that into account, we have to change our consideration of relaxation somewhat and introduce the new, but simple parameter $\chi(\omega >> \omega_0) = \chi_\infty$ or, as we prefer, the same thing for the dielectric "constant", i.e. we introduce $\epsilon_r(\omega >> \omega_0) = \epsilon_\infty$.
  - **3.** Since we always have either $\epsilon_0 \cdot \chi(\omega)$ or $\epsilon_0 \cdot \epsilon(\omega)$, and the ϵ_0 is becoming cumbersome, we may just include it in what we now call the **dielectric function** $\epsilon(\omega)$ of the material. This simply means that all the ϵ_i are what they are as the relative dielectric "constant" and multiplied with ϵ_0

- This reasoning follows **Debye**, who by doing this expanded our knowledge of materials in a major way. Going through the points **1. - 3.** (which we will not do here), produces the final result for the frequency dependence of the *orientation polarization*, the so-called **Debye equations**:
  - In general notation we have pretty much the same equation as for the susceptibility χ; the only real difference is the introduction of ϵ_∞ for the high frequency limit:

$$D(\omega) = \epsilon(\omega) \cdot E(\omega) = \left(\frac{\epsilon_s - \epsilon_\infty}{1 + i\,(\omega/\omega_0)} + \epsilon_\infty \right) \cdot E(\omega)$$

- The complex function ϵ **(ω)** is the **dielectric function**. In the equation above it is given in a closed form for the dipole relaxation mechanism.

- Again, we write the complex function as a sum of a real part and a complex part, i.e. as **ϵ(ω) = ϵ'(ω) – i · ϵ"(ω)**. We use a "**–**" sign, as a matter of taste; it makes some follow-up equations easier. But you may just as well define it with a **+** sign and in some books that is what you will find. For the dielectric function from above we now obtain

$$\epsilon' = \epsilon_\infty + \frac{\epsilon_s - \epsilon_\infty}{1 + (\omega/\omega_0)^2}$$

$$\epsilon'' = \frac{(\omega/\omega_0)(\epsilon_s - \epsilon_\infty)}{1 + (\omega/\omega_0)^2}$$

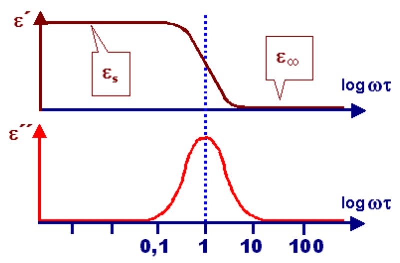
  - As it *must* be, we have

$$\epsilon'(\omega = 0) = \epsilon_s \qquad \epsilon'(\omega = 0) = 0$$

$$\epsilon'(\omega \to \infty) = \epsilon_\infty$$

- From working with the complex notation for sin- and cosin-functions we also know that
  - **ϵ'**, the *real part* of a complex amplitude, gives the amplitude of the response that is *in phase* with the driving force, **ϵ"**, the *imaginary part*, gives the amplitude of the response that is *phase-shifted by 90^o*.

- Finally, we can ask ourselves: What does it look like? What are the graphs of **ϵ'** and **ϵ"**?
  - Relatively simple curves, actually, They always look like the graphs shown below, the three numbers that define a particular material (ϵ_s, ϵ_∞, and **τ = 2π /ω$_0$**) only change the numbers on the scales.



  - Note that ω for curves like this one is always on a *logarithmic scale!*

- What the dielectric function for orientation polarization looks like for real systems can be tried out with the JAVA applet below - compare that with the measured curves for water. We have a theory for the frequency dependence which is *pretty good*!

- Since ϵ_∞ must be **= 1** (or some value determined by some *other* mechanism that also exists) if we go to frequencies high enough, the essential parameters that characterize a material with orientation polarization are ϵ_s and **τ** (or ω$_0$).
  - ϵ_s we can get from the polarization mechanism for the materials being considered. If we know the dipole moments of the particles and their density, the Langevin function gives the (static) polarization and thus ϵ_s.
  - We will *not*, however, obtain **τ** from the theory of the polarization considered so far. Here we have to know more about the system; for liquids, e.g., the mean time before two dipoles collide and "loose" all their memory about their previous orientation. This will be expressed in some kind of diffusion terminology, and we have to know something about the random walk of the dipoles in the liquid. This, however, will go far beyond the scope of this course.

- Suffice it to say that typical relaxation times are around **10^{-11} s**; this corresponds to *frequencies in the **GHz** range* , i.e. "**cm** -waves". We must therefore expect that typical materials exhibiting orientation polarization (e.g. water), will show some peculiar behavior in the microwave range of the electromagnetic spectrum.
  - In mixtures of materials, or in complicated materials with several different dipoles and several different relaxation times, things get more complicated. The smooth curves shown above may be no longer smooth, because they now result from a superposition of several smooth curves.
  - Finally, it is also clear that **τ** may vary quite a bit, depending on the material and the temperature. If heavy atoms are involved, **τ** tends to be larger and ***vice versa***. If movements speed up because of temperature, **τ** will get smaller.