3.3.3 Resonance for Ionic and Atomic Polarization

The frequency dependence of the electronic and ionic polarization mechanisms are mathematically identical - we have a driven oscillating system with a linear force law and some damping. In the simple classical approximation used so far, we may use the universal equation describing an oscillating system driven by a force with a **sin(ωt)** time dependence

$$m \cdot \frac{d^2x}{dt^2} + k_F \cdot m \cdot \frac{dx}{dt} + k_S \cdot x = q \cdot E_0 \cdot \exp(i \omega t)$$

- With **m =** mass, **k_F = friction** coefficient; describing damping, **k_S =** "spring" coefficient or constant; describing the restoring force, **$q \cdot E_0$ =** amplitude times charge to give a force , **$E = E_0 \cdot \exp(i \omega t)$** is the time dependence of electrical field in complex notation.

- This is of course a gross simplification: In the equation above we look at *one* mass **m** hooked up to *one* spring, whereas a crystal consists of a hell of a lot of masses (= atoms), all coupled by plenty of springs (= bonds). Nevertheless, the analysis of just one oscillating mass provides the basically correct answer to our quest for the frequency dependence of the ionic and atomic polarization. More to that in link.

We know the *"spring" coefficient* for the electronic and ionic polarization mechanism; however, we do not know from our simple consideration of these two mechanisms the *"friction" term*.

- So lets just consider the general solution to the differential equation given above in terms of the general constants **k_S** and **k_F** and see what kind of general conclusions we can draw.

From classical mechanics we know that the system has a resonance frequency ω_0, the frequency with the maximum amplitude of the oscillation, that is (for undamped oscillators) always given by

$$\omega_0 = \left(\frac{k_S}{m} \right)^{1/2}$$

- The general solution of the differential equation is

$$x(\omega, t) = x(\omega) \cdot \exp(i\omega t + \phi)$$

- The angle ϕ is necessary because there might be some phase shift. This phase shift, however, is automatically taken care of if we use a complex amplitude. The complex **$x(\omega)$** is given by

$$x(\omega) = \frac{q \cdot E_0}{m} \left(\left(\frac{\omega_0^2 - \omega^2}{(\omega_0^2 - \omega^2)^2 + k_F^2 \omega^2} \right) - i \cdot \left(\frac{k_F \omega}{(\omega_0^2 - \omega^2)^2 + k_F^2 \omega^2} \right) \right)$$

- **$x(\omega)$** indeed is a *complex function*, which means that the amplitude is not in phase with the driving force if the imaginary part is not zero.

Again, we are interested in a relation between the **sin** components of the polarization **$P(\omega)$** and the **sin** components of the driving field **$E = E_0 \cdot \exp(i\omega t)$** or the dielectric flux **$D(\omega)$** and the field. We have

$$P = N \cdot q \cdot x(\omega)$$

$$D = \epsilon_0 \cdot \epsilon_r \cdot E = \epsilon_0 \cdot E + P = \epsilon_0 \cdot E + N \cdot q \cdot x(\omega)$$

If we insert **$x(\omega)$** from the solution given above, we obtain a complex relationship between **D** and **E**

$$D = \left(\epsilon_0 + \frac{N \cdot q^2}{m} \left(\left(\frac{\omega_0^2 - \omega^2}{(\omega_0^2 - \omega^2)^2 + k_F^2 \omega^2} \right) - i \left(\frac{k_F \omega}{(\omega_0^2 - \omega^2)^2 + k_F^2 \omega^2} \right) \right) \right) \cdot E$$

- This looks pretty awful, but it encodes basic everyday knowledge!

This equation can be rewritten using the **dielectric function** defined before with the added generalization that we now define it for the permittivity, i.e, for

$$\epsilon(\omega) \ = \ \epsilon_r(\omega) \cdot \epsilon_0 = \ \epsilon'(\omega) \ - \ i \cdot \epsilon''(\omega)$$

🔵 For the dielectric flux **D**, which we prefer in this case to the polarization **P**, we have as always

$$D(\omega, t) \ = \ [\epsilon'(\omega) \ - \ i \cdot \epsilon''(\omega)] \cdot E_0 \cdot \exp{(i\omega\, t)}$$

🔵 The time dependence of **D** is simple given by **exp (i**ω **t)**, so the interesting part is only the ω - dependent factor.

Rewriting the equations for the real and imaginary part of ϵ we obtain the *general dielectric function for resonant polarization mechanisms*:

$$\epsilon' \ = \ \epsilon_0 \ + \ \frac{N \cdot q^2}{m} \left(\frac{\omega_0^2 - \omega^2}{(\omega_0^2 - \omega^2)^2 \ + \ k_F^2 \cdot \omega^2} \right)$$

$$\epsilon'' \ = \ \frac{N \cdot q^2}{m} \left(\frac{k_F \cdot \omega}{(\omega_0^2 - \omega^2)^2 \ + \ k_F^2 \cdot \omega^2} \right)$$

These formula describe the frequency dependence of the dielectric constant of *any* material where the polarization mechanism is given by separating charges with mass **m** by an electrical field against a *linear* restoring force.

🔵 For the *limiting cases* we obtain for the real and imaginary part

$$\epsilon'(\omega = 0) \ = \ \left(\epsilon_0 \ + \ \frac{N \cdot q^2}{m} \right) \frac{1}{\omega_0^2} \ = \ \left(\epsilon_0 \ + \ \frac{N \cdot q^2}{m} \right) \frac{m}{k_S}$$

$$\epsilon'(\omega = \infty) \ = \ \epsilon_0$$

🔵 For $\epsilon'(\omega = \infty)$ we thus have $\epsilon_r = \epsilon'/\epsilon_0 = 1$ as must be.

The most important material parameters for dielectric constants at the low frequency limit, i.e. $\omega \Rightarrow$ **0**, are therefore the *masses* **m** of the oscillating charges, their *"spring" constants* k_S, their *density N*, and the *charge q* on the ion considered.

🔵 We have no big problem with these parameters, and that includes the *"spring" constants*. It is a direct property of the bonding situation and in principle we know how to calculate its value.

🔵 The friction constant k_F does not appear in the limit values of ϵ. As we will see below, it is only important for frequencies around the resonance frequency.

For this intermediate case k_F is the difficult parameter. On the atomic level, "friction" in a classical sense is *not defined*, instead we have to resort to *energy dispersion mechanisms*. While it is easy to see how this works, it is difficult to calculate numbers for k_F.

🔵 Imagine a single oscillating dipole in an ionic crystal. Since the vibrating ions are coupled to their neighbours via binding forces, they will induce this atoms to vibrate, too - in time the whole crystal vibrates. The ordered energy originally contained in the vibration of *one* dipole (ordered, because it vibrated in field direction) is now dispersed as *unordered* thermal energy throughout the crystal.

🔵 Since the energy contained in the original vibration is constant, the net effect on the single oscillating dipole is that of *damping* because its original energy is now spread out over many atoms. Formally, damping or energy dispersion can be described by some fictional "friction" force.

🔵 Keeping that in mind it is easy to see that all mechanisms, especially interaction with phonons, that convert the energy in an *ordered vibration in field direction* to *unordered thermal energy* always appears as a kind of friction force on a particular oscillator. Putting a number on this fictional friction force, however, is clearly a different (and difficult) business.

🔵 However, as soon as you realize that the dimension of k_F is **1/s** and that **1/**k_F simply is about the time that it takes for an oscillation to "die", you can start to have some ideas - or you check the link.

Now lets look at some characteristic behavior and some numbers as far as we can derive them in full generality.

- For the electronic polarization mechanism, we know the force constant, it is

$$k_S = \frac{(ze)^2}{4\pi \cdot \epsilon_0 \cdot R^3}$$
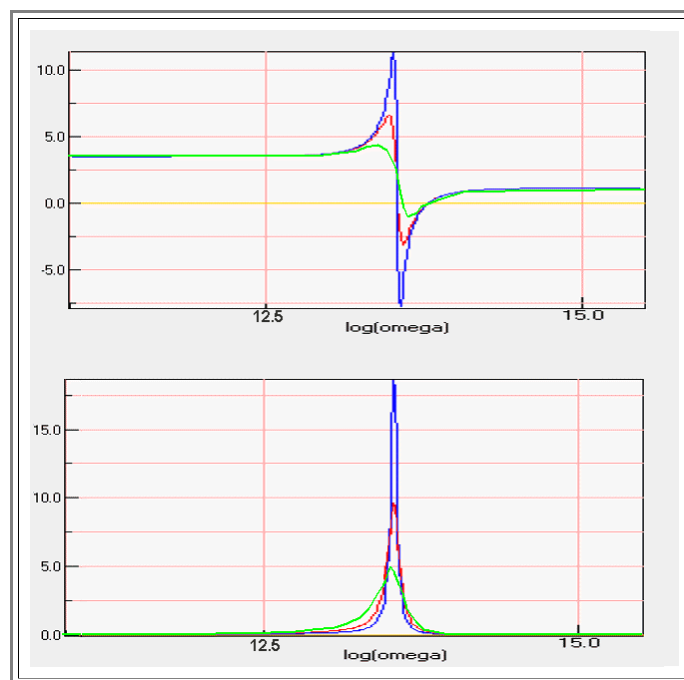
- With the proper numbers for a hydrogen atom we obtain

$$\omega_0 \approx 5 \cdot 10^{16} \text{ Hz}$$

- This is in the *ultraviolet region of electromagnetic radiation*. For all other materials we would expect similar values because the larger force constants (**(ze)^2** overcompensates the increasing size **R**) is balanced to some extent by the larger mass.
- For the *ionic polarization mechanism*, the masses are several thousand times higher, the resonance frequency thus will be considerably lower. It is, of course simply the frequency of the general lattice vibrations which, as we know, is in the **10^{13} Hz** range

This has an important consequence:

- The dielectric constant at frequencies higher than about the frequency corresponding to the **UV** part of the spectrum is always **1**. And since the optical index of refraction **n** is directly given by the DK (**n = ϵ $^{1/2}$**), there are no optical lenses beyond the **UV** part of the spectrum.
- In other words: You can not built a deep-**UV** or **X**-ray microscope with lenses, nor - unfortunately - lithography machines for chips with smallest dimension below about **0,2 µm**. For the exception to this rule see the footnote from before.

If we now look at the characteristic behavior of ω **'** and ω **''** we obtain quantitatively the following curves (by using the JAVA module provided for in the link):

- Note that ω is again on a *logarithmic scale!*
- Note also that it is perfectly possible that ϵ' and therefore ϵ_r becomes **negative**. We won't go into what that means. however.

The colors denote different friction coefficients **k$_F$**. If **k$_F$** would be zero, the amplitude and therefore ϵ' would be ∞ at the resonance point, and ϵ'' would be zero everywhere, and infinity at the resonance frequency; i.e. ϵ'' is the Delta function.

- While this can never happen in reality, we still may expect significantly larger ϵ values around the resonance frequency than in any other frequency region.

That the maximum value of ϵ'' *decreases* with increasing damping might be a bit counter-intuitive at first (in fact it was shown the wrong way in earlier versions of this Hyperscript), but for that it extends over ever increasing regions in frequency.