Relaxation models

In polar materials containing permanent dipoles, in thermal equilibrium, the dipoles are randomly oriented. A partial alignment of the dipoles by any electric field is usually disrupted by thermal agitation, and once the field is withdrawn, the thermal agitation tries to relax a polarized region to the unpolarized equilibrium state of random orientation. This is conceptually very different from the Lorentz oscillator model. This kind of relaxation of polarization is usually associated with Debye (1929), and therefore sometimes called Debye relaxation. For polar liquids, Debye relaxation by molecular rotations determine the optical constants at low frequencies (usually in the microwave range). Many solids also show Debye relaxations. To distinguish Lorentz model from the relaxation model, note that for Lorentz oscillators, once the electric field is withdrawn, the charges equilibrate by executing damped oscillations about their equilibrium positions, i.e., for a single oscillator,

\[ x_\omega = x_\omega e^{-i\omega_c t}, \]

implying a decay of initial polarization as

\[ P(t) = P(t_0)e^{-\gamma t}, \]

where \( \gamma \) is the decay rate.

In contrast, a Debye oscillator (i.e., permanent dipole), if initially polarized, returns to equilibrium as

\[ P(t) = P(t_0)e^{-\tau D t}, \]

without any oscillation. The relaxation time \( \tau_D \) is usually much larger than \( 1/\gamma \), determined mainly by the diffusive rotational motion of the dipoles.

Debye relaxation model:

To describe a polar system within the Debye model, consider an ensemble of Debye oscillators (dipoles), subject to a constant electric field \( E_0 \) applied at \( t = t_0 \). The response of the oscillators are usually slow (because the dipole are heavy) compared with the polarizations of free electrons, lattice ions, and internal transitions (including vibrational) in the dipoles, and these may be regarded as instantaneous. This means, when the field is applied at \( t_0 \), the polarization \( P(t_0) = \varepsilon_\omega \chi_\omega E_0 \), is instantly induced; here \( \chi_\omega \) is the dielectric susceptibility at frequencies low compared with vibrational frequencies. As time increases, the polarization approaches a limiting value \( \lim_{t \to \infty} P(t) = \varepsilon_\omega \chi_\omega d E_0 \), where \( \chi_\omega d \) is the static or dc dielectric susceptibility. Thus one can write

\[ P(t) = P(\infty) - [P(\infty) - P(t_0)] e^{-\tau_D t}, \]

which can be rewritten as

\[ P(t) = \varepsilon_\omega \chi_\omega d E_0 + \varepsilon_\omega (\chi_\omega d - \chi_\omega) \left( 1 - e^{-\tau_D t} \right) E_0. \]

Since the electric field has the form \( E(t) = E_0 \Theta(t - t_0) \), where \( \Theta \) is the step function, one may write this as

\[ P(t) = \varepsilon_\omega \chi_\omega d E_0 + \varepsilon_\omega \int_{-\infty}^{t} \Theta(t') f(t-t') dt', \]

where the function \( f(t) \) is called Debye relaxation function defined as

\[ f(t) = \frac{\Delta}{\tau_D} e^{-t/\tau_D}, \]

with \( \Delta = \chi_\omega d - \chi_\omega = \varepsilon_\omega d - \varepsilon_\omega \) (a notation traditionally used by dielectricians).

For a time harmonic field of the form \( E(t) = E_0 e^{-i\omega t} \), the Eqn.(24) then leads a dielectric function of the form
\[ \varepsilon(\omega) = \varepsilon_{ov} + \frac{\Delta}{1 - i\omega\tau_D}, \]  

so that

\[ \varepsilon' = \varepsilon_{ov} + \frac{\Delta}{1 + \omega^2\tau_D^2}, \quad \text{and} \quad \varepsilon'' = \frac{\omega\tau_D\Delta}{1 + \omega^2\tau_D^2}. \]

Note that like the Lorentz oscillator, where \( \varepsilon'' \) has a maximum at \( \omega = \gamma_0 = 1/\tau_0 \), here too \( \varepsilon'' \) has a maximum at \( \omega = 1/\tau_D \), with \( \varepsilon''_{\text{max}} = \Delta/2 \). However \( \varepsilon' \) is very different now, having neither maxima nor minima, decreasing monotonically from \( \varepsilon_{od} \) at low frequency to \( \varepsilon_{ov} \) at high frequency. For a typical polar liquid such as water, the Debye model works fairly well, and the measured dielectric function of water at microwave frequencies can be fit very well with \( \tau_D = 8 \times 10^{-12} \text{sec} \), \( \varepsilon_{od} = 77.5 \) and \( \varepsilon_{ov} = 5.27 \) as shown in Fig. 3.10.

![Fig. 3.10: \( \varepsilon' \) and \( \varepsilon'' \) vs \( \omega \tau_D \) for water.](image)

On physical grounds, relaxation of permanent dipoles is expected to be highly temperature dependent. Debye showed that the relaxation time for a sphere of radius \( a \) in a fluid of viscosity \( \eta \) is

\[ \tau_D = \frac{4\pi \eta a^2}{k_BT}. \]  

At room temperature, taking \( \eta = 0.01 \text{g/ml(cm.sec)} \) and \( a = 10^{-8} \text{cm} \), gives \( \tau_D \approx 3 \times 10^{-12} \text{sec} \), which is close to the simple Debye model.

The experimental measurements on \( \varepsilon \) in the dipolar frequency range are often displayed as a plot of \( \varepsilon'' \) vs \( \varepsilon' \), called the Cole-Cole plot. A glance at such a plot tells one whether or not a single relaxation time is sufficient to determine the frequency dependence of \( \varepsilon \). For a single Debye oscillator, one has

\[ \left[ \varepsilon' - (\varepsilon_{od} + \varepsilon_{ov})/2 \right]^2 + [\varepsilon'']^2 = \left[ (\varepsilon_{od} - \varepsilon_{ov})/2 \right]^2. \]
which gives a Cole-Cole plot as a semicircle centered on $\varepsilon'$ axis at $(\varepsilon_{od} + \varepsilon_{ov})/2$ and with radius $(\varepsilon_{od} - \varepsilon_{ov})/2$, as illustrated in Fig. 3.11.

**Fig. 3.11:** A typical Cole-Cole plot.