Water Complex Dielectric and Polarization

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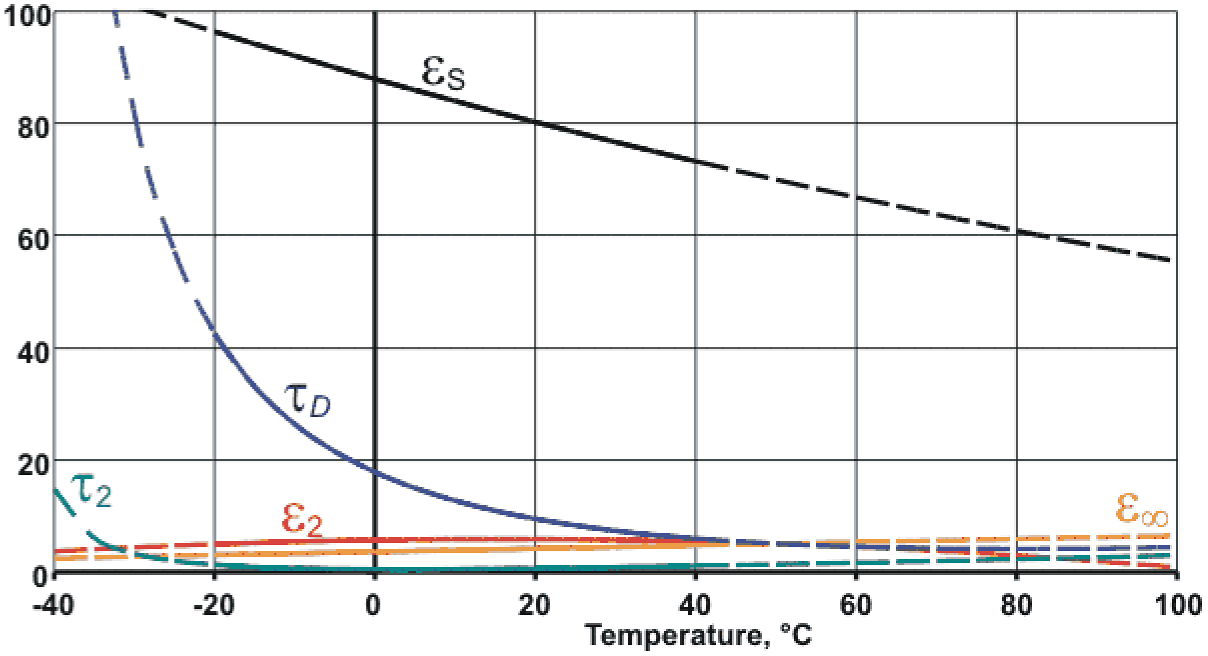
The complex dielectric permittivity

It has been suggested that a bimodal relaxation time expression is the most appropriate description of the dielectric properties of water [135].[b]

$$\varepsilon_r^* = \varepsilon_\infty + \frac{\varepsilon_S - \varepsilon_2}{1+i\omega\tau_D} + \frac{\varepsilon_2 - \varepsilon_\infty}{1+i\omega\tau_2} \qquad (1)$$

where ε_r* is the complex permittivity, ε_S is the relative permittivity at low frequencies (static region), ε_2 is the intermediate relative permittivity, ε_∞ is the relative permittivity at high frequencies (optical permittivity), ω is the angular frequency in radians.second^{-1}, τ_D and τ_2 are relaxation times and i = $\sqrt{-1}$. τ_D is relatively long (18 ps at 0 °C [135]), due primarily to the rotational relaxation within a hydrogen bonded cluster, but reduces considerably with temperature as hydrogen bonds are weakened and broken. τ_2 is small (~1 ps [135] or 0.2 ps [343])[a] and less temperature dependent being determined primarily by the translational vibrations (near 200 cm^{-1}) within the hydrogen bonded cluster [240].

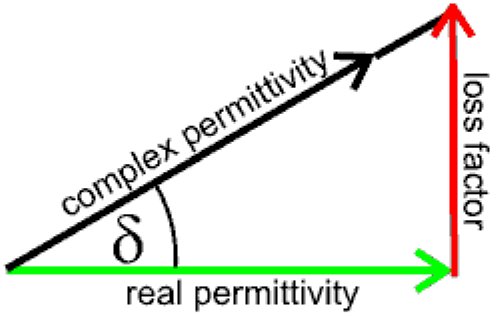


Plotted opposite are equations derived for pure water over the range for -20 °C ~ +40 °C [683], extrapolated (dashed lines) to indicate trends; relaxation times are in ps. Further data has been published [1185].

Equation (1) may be simplified:

$$\varepsilon_r^* = \varepsilon_\infty + \frac{\varepsilon_S - \varepsilon_2}{1+i\omega\tau_D}\times\frac{1-i\omega\tau_D}{1-i\omega\tau_D} + \frac{\varepsilon_2-\varepsilon_\infty}{1+i\omega\tau_2}\times\frac{1-i\omega\tau_2}{1-i\omega\tau_2}$$

$$\varepsilon_r^* = \varepsilon_\infty + \frac{\varepsilon_S-\varepsilon_2}{1+\omega^2\tau_D{}^2}\times\left(1-i\omega\tau_D\right)+\frac{\varepsilon_2-\varepsilon_\infty}{1+\omega^2\tau_2{}^2}\times\left(1-i\omega\tau_2\right)$$



and the complex permittivity rearranged to give real permittivity and imaginary (the loss factor) parts:

$$\varepsilon_r^* = \varepsilon_\infty + \frac{\varepsilon_S-\varepsilon_2}{1+\omega^2\tau_D{}^2}+\frac{\varepsilon_2-\varepsilon_\infty}{1+\omega^2\tau_2{}^2}+i\left\{\frac{\omega\tau_D\left(\varepsilon_S-\varepsilon_2\right)}{1+\omega^2\tau_D{}^2}+\frac{\omega\tau_2\left(\varepsilon_2-\varepsilon_\infty\right)}{1+\omega^2\tau_2{}^2}\right\}$$

The real part corresponds to the dielectric constant:

$$\varepsilon_r' = \varepsilon_\infty + \frac{\varepsilon_S-\varepsilon_2}{1+\omega^2\tau_D{}^2}+\frac{\varepsilon_2-\varepsilon_\infty}{1+\omega^2\tau_2{}^2}$$

and the imaginary part corresponds to the loss factor (**Lf**):

$$\mathrm{Lf} = \frac{\omega\tau_D\left(\varepsilon_S-\varepsilon_2\right)}{1+\omega^2\tau_D{}^2}+\frac{\omega\tau_2\left(\varepsilon_2-\varepsilon_\infty\right)}{1+\omega^2\tau_2{}^2}$$

As $(\varepsilon_S - \varepsilon_2) >> (\varepsilon_S - \varepsilon_\infty)$ the permittivity may be approximated to within the accuracy of current instrumentation by:

$$\varepsilon_r' = \varepsilon_\infty + \frac{\varepsilon_S-\varepsilon_\infty}{1+\omega^2\tau^2} \qquad (2)$$

As $\tau_D >> \tau_2$ and $(\varepsilon_S - \varepsilon_2) >> (\varepsilon_S - \varepsilon_\infty)$ the permittivity may be approximated by:

$$\mathbf{Lf} = \frac{\omega\tau\,(\varepsilon_S - \varepsilon_\infty)}{1+\omega^2\tau^2}$$

which shows small deviations between about 100 - 1000 GHz which reduce with temperature increase.

Polarization

The polarization (P) of a substance is its electric dipole moment density (see also). It varies with the applied field ($E = E_{max}e^{-i\omega t}$) and the permittivity. It is given by the real part of the expression:

$$P = E\,\varepsilon_r{}^*\varepsilon_0$$

As $E = E_{max}\{\cos(\omega t) - i.\sin(\omega t)\}$ and $\varepsilon_r{}^* = \varepsilon_r' - i.\mathbf{Lf}$

$$P = E_{max}.\varepsilon_0(\varepsilon_r' - i.\mathbf{Lf})\{\cos(\omega t) - i.\sin(\omega\, t)\}$$

Therefore, taking only the real part:

$$P = E_{max}.\varepsilon_0\{(\varepsilon_r'\cos(\omega t) - \mathbf{Lf}\,\sin(\omega t)\}$$

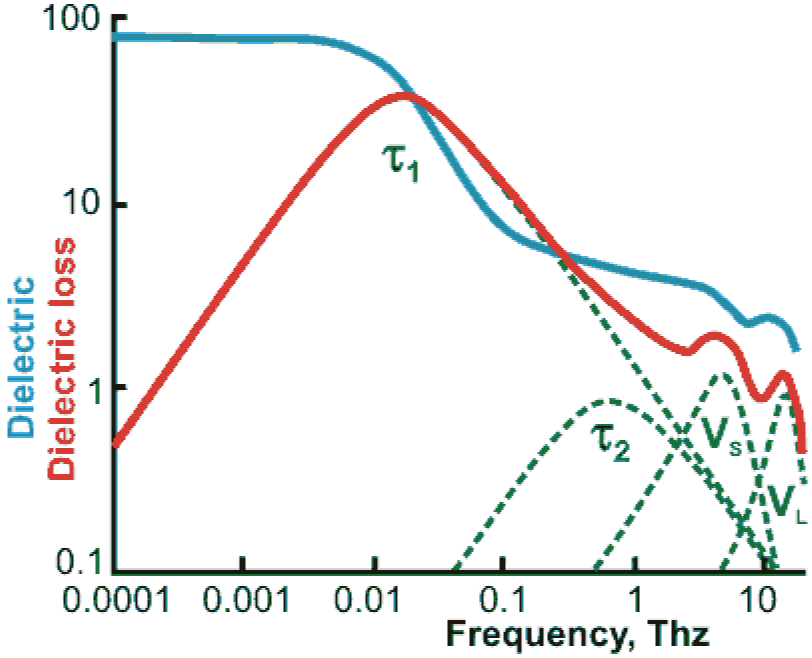
where ε_r' varies with frequency as equation (2) above. This equation is equivalent to:

$$P = P_{max}.\cos(\omega t - \delta)$$

where $\delta = \text{atan}(\mathbf{Lf}/\varepsilon_r')$ and P_{max} increases by a factor **secant(δ)**.

Footnotes

[a] It has been shown that the different values for τ_2 correspond to different frequency ranges and the most appropriate relaxation time expression is trimodal [1247]. This analysis gives relaxation times τ_D, τ_2 and τ_3 at 25 °C of 8.26 ps (19.3 GHz, corresponding to cooperative relaxation of long range H-bond-mediated dipole–dipole interactions), 1.05 ps (150 GHz, possibly associated with dipole–dipole interactions due to the free rotation of water molecules having no more than one hydrogen bond) and 0.135 ps (1.18 THz, possibly associated with dipole–dipole interactions due to the free rotation of water molecules having no hydrogen bonds) respectively; $\varepsilon_S = 78.4$, $\varepsilon_2 = 5.85$, $\varepsilon_3 = 3.65$, $\varepsilon_\infty = 2.4$ (compared with the bimodal relaxation times τ_D and τ_2 at 25 °C of 8.21 ps (19.3 GHz, corresponding to cooperative relaxation of long range H-bond-mediated dipole–dipole interactions) and 0.392 ps (406 GHz, possibly associated with dipole–dipole interactions due to the free rotation of water molecules having broken hydrogen bonds) respectively; $\varepsilon_S = 78.4$, $\varepsilon_2 = 5.54$, $\varepsilon_\infty = 3.04$) [1247].



[b] For use at higher frequencies up to 100 THz (that is, into the far infra-red) two extra terms, representing the intermolecular stretch (V_S) and intermolecular librations (V_L), may be added [1497]. When the intermolecular stretching vibration is included, the following equation has been used [1563]

$$\varepsilon_r^* = \varepsilon_\infty + \frac{\Delta\varepsilon_1}{1 - i\omega\tau_1} + \frac{\Delta\varepsilon_2}{1 - i\omega\tau_2} + \frac{A_S}{\omega_S^2 - \omega^2 - i\omega\gamma_S}$$

with the following values determined [1563]

	A_S, THz^2	ω_S, THz	λ_S, THz	ε_∞
H_2O	1386	33.3	33.9	2.34
D_2O	1248	33.7	31.8	2.29
$H_2{}^{18}O$	1184	31.1	26.7	2.28

Source: http://www1.lsbu.ac.uk/water/microwav3.html