

SUSCEPTIBILITY OF A POLAR DIELECTRIC

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The Clausius-Mossotti formula gives the atomic polarizability in terms of the dielectric constant for a linear dielectric. This formula assumes that the entire polarization is caused by an external electric field, and that the atoms of the dielectric possess no intrinsic polarization. Many substances, such as water, do possess an intrinsic polarization, so we need a different formula for them.

The energy of a dipole in an external electric field is

$$u = -\mathbf{p} \cdot \mathbf{E} \quad (1)$$

From statistical mechanics, we know that for a material in thermal equilibrium at temperature T , the probability of a molecule having energy u is proportional to $e^{-u/kT}$, where k is the Boltzmann constant. The average energy of molecules in such a system is then

$$\langle u \rangle = \frac{\int u e^{-u/kT} du}{\int e^{-u/kT} du} \quad (2)$$

where both integrals are taken over all possible energies in the system.

In the case of a dipole in a field, the energy can range from $-pE$ to $+pE$, so these are the limits on the integrals. If we write the energy in terms of the angle θ between \mathbf{p} and \mathbf{E} , we have $u = -pE \cos \theta$ and

$$du = pE \sin \theta d\theta \quad (3)$$

Making this substitution, the limits on the integral become 0 to π and we have

$$\langle u \rangle = \frac{-p^2 E^2 \int_0^\pi e^{pE \cos \theta / kT} \cos \theta \sin \theta d\theta}{pE \int_0^\pi e^{pE \cos \theta / kT} \sin \theta d\theta} \quad (4)$$

The bottom integral is easily done straight away, and the top integral can be done by parts (integrate $e^{pE \cos \theta / kT} \sin \theta$ and differentiate $\cos \theta$) or with Maple, so we get

$$\langle u \rangle = -\frac{\left(1 + e^{2pE/kT}\right)pE + \left(1 - e^{2pE/kT}\right)kT}{e^{2pE/kT} - 1} \quad (5)$$

Multiplying top and bottom by $e^{-pE/kT}$ and converting to hyperbolic functions, we get

$$\langle u \rangle = kT - pE \coth\left(\frac{pE}{kT}\right) \quad (6)$$

If there are N molecules per unit volume, then the polarization density is

$$\mathbf{P} = N \langle \mathbf{p} \rangle \quad (7)$$

The only component of \mathbf{p} that contributes to the energy is the component that is parallel to \mathbf{E} . Suppose we look only at dipoles that make an angle θ with \mathbf{E} , so that the energy of such a dipole is $u = -pE \cos \theta$. Now consider the projection of one of these dipoles into the plane perpendicular to \mathbf{E} . If we take \mathbf{E} to be along the z axis, this projection lies in the xy plane, has a magnitude $pE \sin \theta$ and makes an angle ϕ with the x axis. Since ϕ has no effect on the energy, all values of ϕ are equally likely for each particular value of θ . As a result, we would expect $\langle \mathbf{p} \rangle$ to be parallel to \mathbf{E} , since all perpendicular components average out to zero. Therefore, since the net polarization density is $N \langle \mathbf{p} \rangle$, it is parallel to \mathbf{E} , so we have

$$N \langle u \rangle = -N \langle \mathbf{p} \cdot \mathbf{E} \rangle \quad (8)$$

$$= -\langle \mathbf{P} \cdot \mathbf{E} \rangle \quad (9)$$

$$= -PE \quad (10)$$

$$P = -\frac{N \langle u \rangle}{E} \quad (11)$$

$$= Np \coth\left(\frac{pE}{kT}\right) - \frac{NkT}{E} \quad (12)$$

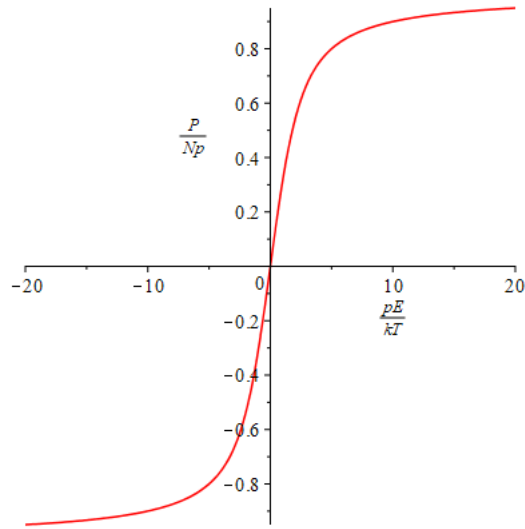
$$= Np \left[\coth\left(\frac{pE}{kT}\right) - \frac{kT}{pE} \right] \quad (13)$$

$$\frac{P}{Np} = \coth\left(\frac{pE}{kT}\right) - \frac{kT}{pE} \quad (14)$$

This is known as the Langevin formula.

A plot of P/Np against pE/kT is shown in Fig. 1.

The curve is sigmoidal (S-shaped) and tends to ± 1 for large fields and/or low temperatures (the sign being determined by the sign of p), indicating

FIGURE 1. Plot of P/Np vs pE/kT .

that polarization tends to become complete in these cases as you might expect.

In the region where pE/kT is small, we can approximate the RHS of the formula 14 by expanding it in a series. The series for $\coth x$ can be looked up (or you can work it out from the series for $\sinh x$ and $\cosh x$) and is

$$\coth x = \frac{1}{x} + \frac{x}{3} - \frac{x^3}{45} + \dots \quad (15)$$

From this we get, to first order in pE/kT :

$$P \simeq Np \left(\frac{pE}{3kT} \right) \quad (16)$$

$$= \frac{NEp^2}{3kT} \quad (17)$$

In this region, the material behaves like a linear dielectric (since $P \propto E$), so we can derive an expression for the susceptibility:

$$P = \epsilon_0 \chi_e E \quad (18)$$

$$\chi_e = \frac{Np^2}{3\epsilon_0 kT} \quad (19)$$

For water, we can work out estimates for the dielectric constant. We need

$$\epsilon_0 = 8.85418782 \times 10^{-12} \text{Farads m}^{-1} \quad (20)$$

$$k = 1.3806503 \times 10^{-23} \text{ m}^2 \text{kg s}^{-2} \text{K}^{-1} \quad (21)$$

$$p_{H_2O} = 6.1 \times 10^{-30} \text{C m} \quad (22)$$

For water at $20^\circ\text{C} = 293 \text{ K}$, we need the molecular density N . Water's mass is 18.0153 g/mole and 1 m^3 of water weighs 1000 kg , so contains 55508 moles. To get the molecular density, we multiply by Avogadro's number 6.0221415×10^{23} , so we have from 19

$$N = 3.343 \times 10^{28} \quad (23)$$

$$\epsilon_r = \chi_e + 1 \quad (24)$$

$$= 12.58 \quad (25)$$

The measured value is 80.4 , so this isn't a particularly accurate estimate.

For water vapour at $100^\circ\text{C} = 373 \text{ K}$ and 1 atm pressure we can use the ideal gas law $PV = nRT$ to find the number of molecules in a cubic metre. Using $R = 8.205746 \times 10^{-5} \text{ m}^3 \text{atm K}^{-1} \text{mol}^{-1}$ and $V = 1 \text{ m}^3$, we get

$$n = \frac{PV}{RT} \quad (26)$$

$$= \frac{1}{373 \times 8.205746 \times 10^{-5}} \quad (27)$$

$$= 32.672 \text{ moles/m}^3 \quad (28)$$

$$N = 1.968 \times 10^{25} \text{ molecules/m}^3 \quad (29)$$

$$\epsilon_r = 1.00535 \quad (30)$$

This time, the measured value is 1.00587 , so the answer isn't too far off.