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A Survey of the Theory of Dielectrics

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Résumé.

On donne un résumé de la théorie générale de l'absorption diélectrique. Il est démontré qu'il existe quatre types d'absorption diélectrique dont un seul n'est pas encore bien compris. Le passage des théories générales aux théories particulières est discuté. Les considérations macroscopiques et microscopiques sont nettement distinguées.

1. GENERAL STATE OF THE THEORY.

The basic theory of the dielectric properties of materials is well understood. It would be sad otherwise for the theory makes use of principles which have been known for some fifty years. Plenty of scope remains, of course, for application of the basic theory to specific cases and models.

The main difficulties which inhibited an earlier development are connected with the long range of the forces between the (permanent or induced) electric dipoles of molecules. It is just this point, however, which makes it possible to treat this part of the interaction in a macroscopic way [1]. This is in step with a general trend in theoretical physics: introduction of collective coordinates which often make macro- and micro-treatments identical.

2. TYPES OF ABSORPTION.

Consider the complex dielectric constant $\varepsilon(\omega)$,

$$\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega); \quad \varepsilon_2(\omega) = 4\pi\sigma(\omega)/\omega, \quad (1)$$

where ε_1 and ε_2 are real, ω is the circular frequency and σ the conductivity. $\varepsilon_2(\omega)$ then measures the dielectric absorption of which we can distinguish four types:

- (i) due to free carriers;
- (ii) single absorption bands, well separated from others;

- (iii) overlapping absorption bands;
- (iv) very weak absorption which is nearly independent of frequency over a wide range.

Case (i) is governed by two parameters, the plasma frequency ω_p and the collision time τ_1 ,

$$\varepsilon_2(\omega) = \frac{\omega_p^2 \tau_1}{\omega} \frac{1}{1 + \omega^2 \tau_1^2}. \quad (2)$$

Only τ_1 is a microscopic quantity because

$$\omega_p^2 = \frac{4\pi (en)^2}{nm} \quad (3)$$

which depends on the macroscopic quantities, charge (en) and mass (nm) of the carriers per unit volume.

Case (ii) contains essentially three parameters: average position ω_0 , width $1/\tau_2$, and magnitude $\Delta\varepsilon$ of the band. The latter is defined by an integral over the band (cf. § 3),

$$\Delta\varepsilon = \frac{2}{\pi} \int_B \varepsilon_2(\omega) \frac{d\omega}{\omega}. \quad (4)$$

Two sub-types can now be distinguished:

- (a) ω_0 tends to zero as the temperature T tends to zero
- (b) ω_0 tends to a finite value.

The latter is characteristic for resonance absorption and poses all the problems connected with the shape of absorption lines. (a) represents Debye-type of absorption. It requires a degeneracy of energy levels such that at least two of them are connected with different dipole directions. In equilibrium this is prohibited at $T = 0$ as it would lead to a non vanishing entropy. Ice is an example which shows Debye absorption down to very low temperatures [2]. A phase transition should be expected but might be inhibited by extremely long relaxation times.

For another example we note that electrons attached to defects in crystals may show Debye loss at temperatures $T \gg T_0$ where kT_0 is of the order of the first excitation energy. Below this temperature a transition to resonance loss ($\hbar\omega_0 = kT_0$) takes place. In certain crystals in which the

electrons interact very strongly with neighbouring ions T_0 may be very small [3, 4].

Case (iii), the overlapping of a number of case (ii) absorption bands offers little general interest, though it may lead to great complications.

Case (iv), absorption of low magnitude ranging over a very large frequency region is often observed in non polar substances, or in polar substances outside the main absorption regions. Its origin is not quite clear yet. According to Garton [5], it is due to thermally excited defects. Another interesting possibility applicable to high polymers has been indicated by Pelzer [6] from an investigation of frequencies of networks. This suggestion may prove useful in conjecture with non-linear vibrational effects: they may lead to induced dipoles, and to absorption even in the case of non-polar substances [7].

3. DISPERSION RELATIONS.

These relations,

$$\epsilon_1(\omega) - 1 = \frac{2}{\pi} \int_0^\infty \frac{\epsilon_2(\mu) \mu d\mu}{\mu^2 - \omega^2}, \quad \epsilon_2(\omega) = \frac{2}{\pi} \int_0^\infty \frac{(\epsilon_1(\mu) - 1) \omega d\mu}{\omega^2 - \mu^2} \quad (5)$$

are valid quite generally under the conditions which are of interest here. They show in particular that the static dielectric constant $\epsilon_s = \epsilon_1(0)$ is uniquely obtained from contributions of various absorption regions as indicated in equation (4).

4. STATISTICAL MACRO-RELATIONS [1].

As is well known the electrostatic energy plays thermodynamically the role of a free energy. It follows then that a macroscopic sphere of radius a polarised homogenously with a dipole moment M has an M -dependent fraction of its free energy given by

$$\Delta F(M) = \frac{1}{2} \frac{\epsilon_s + 2}{\epsilon_s - 1} \frac{M^2}{a^3}, \quad (6)$$

This permits the calculation of the mean free energy due to fluctuations in M ,

$$\Delta F = \frac{3}{2} kT = \frac{1}{2} \frac{\epsilon_s + 2}{\epsilon_s - 1} \frac{\overline{M^2}}{a^3}, \quad (7)$$

where $\overline{M^2}$ is the mean square of M at temperature T . Expression (7) forms the basis of all micro theories of the static dielectric constant. It is useful to generalise (7) to the case that the sphere is surrounded by a macroscopic medium with dielectric constant ϵ_0 . Instead of (7) this leads to

$$\epsilon_s - 1 = \frac{\epsilon_s + 2\epsilon_0}{1 + 2\epsilon_0} \frac{\overline{M^2}(\epsilon_0)}{kTa^3} \quad (8)$$

which for $\epsilon_0 = 1$ is identical with (7). $\overline{M^2}(\epsilon_0)$ depends on ϵ_0 . It will be noticed that the factor $(\epsilon_s + 2)/3$ in the case $\epsilon_0 = 1$ is replaced by $3\epsilon_s/(2\epsilon_s + 1)$ when $\epsilon_0 = \epsilon_s$. These terms frequently introduced in terms of an internal field (Clausius-Mosotti or Onsager) can thus be obtained by purely macroscopic considerations. Which of the two (if any) persists in a microscopic theory depends entirely on the way in which $\overline{M^2}(\epsilon_0)$ can be expressed in terms of microscopic parameters.

A correct calculation will, of course, always lead to a result for ϵ_s which is independent of ϵ_0 . It is useful, however, to choose ϵ_0 in such a manner that calculation of $\overline{M^2}$ requires investigation of short range forces only. Thus, if we deal with a vibrating system (e.g. ionic crystal) then it is useful to choose $\epsilon_0 = 1$ because then M is given immediately in terms of the three normal modes with wave vector zero. If on the other hand we deal with an assembly of disoriented permanent dipoles then $\epsilon_0 = \epsilon_s$ is more useful because a single dipole does then not induce a homogeneous polarisation in the sphere as it would in the case $\epsilon_0 = 1$.

Finally, it should be pointed out that treatment of the region outside the sphere as a macroscopic dielectric automatically takes account of the effect of thermal fluctuations within this region.

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