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## **Chapter 1**

## Capacitance

Capacitance is the ability of a body to store an electrical charge. Any object that can be electrically charged exhibits capacitance. A common form of energy storage device is a parallel-plate capacitor. In a parallel plate capacitor, capacitance is directly proportional to the surface area of the conductor plates and inversely proportional to the separation distance between the plates. If the charges on the plates are +q and -q respectively, and V gives the voltage between the plates, then the capacitance C is given by

$$C = \frac{q}{V}$$
.

which gives the voltage/current relationship

$$I(t) = C \frac{\mathrm{d}V(t)}{\mathrm{d}t}.$$

The capacitance is a function only of the geometry of the design (area of the plates and the distance between them) and the permittivity of the dielectric material between the plates of the capacitor. For many dielectric materials, the permittivity and thus the capacitance, is independent of the potential difference between the conductors and the total charge on them.

The SI unit of capacitance is the farad (symbol: F), named after the English physicist Michael Faraday. A 1 farad capacitor, when charged with 1 coulomb of electrical charge, has a potential difference of 1 volt between its plates. [1] Historically, a farad was regarded as an inconveniently large unit, both electrically and physically. Its subdivisions were invariably used, namely the microfarad, nanofarad and picofarad. More recently, technology has advanced such that capacitors of 1 farad and greater (so-called 'supercapacitors') can be constructed in a structure little larger than a coin battery. Such capacitors are principally used for energy storage replacing more traditional batteries.

The energy (measured in joules) stored in a capacitor is equal to the *work* required to push the charges into the capacitor, i.e. to charge it. Consider a capacitor of capacitance C, holding a charge +q on one plate and -q on the other. Moving a small element of charge dq from one

plate to the other against the potential difference V = q/C requires the work dW:

$$\mathrm{d}W = \frac{q}{C}\,\mathrm{d}q$$

where W is the work measured in joules, q is the charge measured in coulombs and C is the capacitance, measured in farads.

The energy stored in a capacitor is found by integrating this equation. Starting with an uncharged capacitance (q = 0) and moving charge from one plate to the other until the plates have charge +Q and -Q requires the work W:

$$W_{\text{charging}} = \int_0^Q \frac{q}{C} \, \mathrm{d}q = \frac{1}{2} \frac{Q^2}{C} = \frac{1}{2} QV = \frac{1}{2} CV^2 = W_{\text{stored}}.$$

## 1.1 Capacitors

Main article: Capacitor

The capacitance of the majority of capacitors used in electronic circuits is generally several orders of magnitude smaller than the farad. The most common subunits of capacitance in use today are the microfarad ( $\mu F$ ), nanofarad (n F), picofarad (n F), and, in microcircuits, femtofarad (n F). However, specially made supercapacitors can be much larger (as much as hundreds of farads), and parasitic capacitive elements can be less than a femtofarad.

Capacitance can be calculated if the geometry of the conductors and the dielectric properties of the insulator between the conductors are known. A qualitative explanation for this can be given as follows.

Once a positive charge is put unto a conductor, this charge creates an electrical field, repelling any other positive charge to be moved onto the conductor. I.e. increasing the necessary voltage. But if nearby there is another conductor with a negative charge on it, the electrical field of the positive conductor repelling the second positive charge is weakened (the second positive charge also feels

the attracting force of the negative charge). So due to the second conductor with a negative charge, it becomes easier to put a positive charge on the already positive charged first conductor, and vice versa. I.e. the necessary voltage is lowered.

As a quantitative example consider the capacitance of a capacitor constructed of two parallel plates both of area A separated by a distance d:

$$C = \varepsilon_r \varepsilon_0 \frac{A}{d}$$

where

C is the capacitance, in Farads;

A is the area of overlap of the two plates, in square meters;

 $\varepsilon_{\rm r}$  is the relative static permittivity (sometimes called the dielectric constant) of the material between the plates (for a vacuum,  $\varepsilon_{\rm r} = 1$ );

 $\varepsilon_0$  is the electric constant ( $\varepsilon_0 \approx 8.854 \times 10^{-12}$  F·m<sup>-1</sup>); and

d is the separation between the plates, in meters;

Capacitance is proportional to the area of overlap and inversely proportional to the separation between conducting sheets. The closer the sheets are to each other, the greater the capacitance. The equation is a good approximation if d is small compared to the other dimensions of the plates so that the electric field in the capacitor area is uniform, and the so-called *fringing field* around the periphery provides only a small contribution to the capacitance. In CGS units the equation has the form: [2]

$$C = \varepsilon_r \frac{A}{4\pi d}$$

where *C* in this case has the units of length. Combining the SI equation for capacitance with the above equation for the energy stored in a capacitance, for a flat-plate capacitor the energy stored is:

$$W_{\rm stored} = \frac{1}{2}CV^2 = \frac{1}{2}\varepsilon_r\varepsilon_0\frac{A}{d}V^2. \label{eq:wstored}$$

where W is the energy, in joules; C is the capacitance, in farads; and V is the voltage, in volts.

#### 1.1.1 Voltage-dependent capacitors

The dielectric constant for a number of very useful dielectrics changes as a function of the applied electrical field, for example ferroelectric materials, so the capacitance for these devices is more complex. For example, in charging such a capacitor the differential increase in voltage with charge is governed by:

$$dQ = C(V) dV$$

where the voltage dependence of capacitance, C(V), suggests that the capacitance is a function of the electric field strength, which in a large area parallel plate device is given by  $\varepsilon = V/d$ . This field polarizes the dielectric, which polarization, in the case of a ferroelectric, is a nonlinear S-shaped function of the electric field, which, in the case of a large area parallel plate device, translates into a capacitance that is a nonlinear function of the voltage. [3][4]

Corresponding to the voltage-dependent capacitance, to charge the capacitor to voltage V an integral relation is found:

$$Q = \int_0^V C(V) \, dV$$

which agrees with Q = CV only when C is not voltage independent.

By the same token, the energy stored in the capacitor now is given by

$$dW = Q dV = \left[ \int_0^V dV' C(V') \right] dV.$$

Integrating:

$$W = \int_0^V dV \int_0^V dV' C(V') = \int_0^V dV' \int_{V'}^V dV C(V') = \int_0^V dV'$$

where interchange of the order of integration is used.

The nonlinear capacitance of a microscope probe scanned along a ferroelectric surface is used to study the domain structure of ferroelectric materials.<sup>[5]</sup>

Another example of voltage dependent capacitance occurs in semiconductor devices such as semiconductor diodes, where the voltage dependence stems not from a change in dielectric constant but in a voltage dependence of the spacing between the charges on the two sides of the capacitor.<sup>[6]</sup> This effect is intentionally exploited in diode-like devices known as varicaps.

#### 1.1.2 Frequency-dependent capacitors

If a capacitor is driven with a time-varying voltage that changes rapidly enough, at some frequency the polarization of the dielectric cannot follow the voltage. As an example of the origin of this mechanism, the internal microscopic dipoles contributing to the dielectric constant cannot move instantly, and so as frequency of an applied alternating voltage increases, the dipole response is limited

and the dielectric constant diminishes. A changing dielectric constant with frequency is referred to as dielectric dispersion, and is governed by dielectric relaxation processes, such as Debye relaxation. Under transient conditions, the displacement field can be expressed as (see electric susceptibility):

$$\boldsymbol{D(t)} = \varepsilon_0 \int_{-\infty}^{t} \varepsilon_r(t - t') \boldsymbol{E}(t') dt',$$

indicating the lag in response by the time dependence of  $\varepsilon r$ , calculated in principle from an underlying microscopic analysis, for example, of the dipole behavior in the dielectric. See, for example, linear response function. [7][8] The integral extends over the entire past history up to the present time. A Fourier transform in time then results in:

$$\mathbf{D}(\omega) = \varepsilon_0 \varepsilon_r(\omega) \mathbf{E}(\omega) ,$$

where  $\varepsilon_r(\omega)$  is now a complex function, with an imaginary part related to absorption of energy from the field by the medium. See permittivity. The capacitance, being proportional to the dielectric constant, also exhibits this frequency behavior. Fourier transforming Gauss's law with this form for displacement field:

$$I(\omega) = j\omega Q(\omega) = j\omega \oint_{\Sigma} \boldsymbol{D}(\boldsymbol{r},\;\omega) \cdot d\boldsymbol{\Sigma}$$

$$= \left[ G(\omega) + j\omega C(\omega) \right] V(\omega) = \frac{V(\omega)}{Z(\omega)} \; ,$$

where j is the imaginary unit,  $V(\omega)$  is the voltage component at angular frequency  $\omega$ ,  $G(\omega)$  is the *real* part of the current, called the *conductance*, and  $C(\omega)$  determines the *imaginary* part of the current and is the *capacitance*.  $Z(\omega)$  is the complex impedance.

When a parallel-plate capacitor is filled with a dielectric, the measurement of dielectric properties of the medium is based upon the relation:

$$\varepsilon_r(\omega) = \varepsilon_r'(\omega) - j\varepsilon_r''(\omega) = \frac{1}{j\omega Z(\omega)C_0} = \frac{C_{\rm cmplx}(\omega)}{C_0} \; , \label{epsilon}$$

where a single *prime* denotes the real part and a double *prime* the imaginary part,  $Z(\omega)$  is the complex impedance with the dielectric present,  $C_{\rm cmplx}(\omega)$  is the so-called *complex* capacitance with the dielectric present, and  $C_0$  is the capacitance without the dielectric. [9][10] (Measurement "without the dielectric" in principle means measurement in free space, an unattainable goal inasmuch as even the quantum vacuum is predicted to exhibit nonideal behavior, such as dichroism. For practical purposes, when measurement errors are taken into account, often a measurement in terrestrial vacuum, or simply a calculation of  $C_0$ , is sufficiently accurate. [11])

Using this measurement method, the dielectric constant may exhibit a resonance at certain frequencies corresponding to characteristic response frequencies (excitation energies) of contributors to the dielectric constant. These resonances are the basis for a number of experimental techniques for detecting defects. The *conductance method* measures absorption as a function of frequency. Alternatively, the time response of the capacitance can be used directly, as in *deep-level transient spectroscopy*. [13]

Another example of frequency dependent capacitance occurs with MOS capacitors, where the slow generation of minority carriers means that at high frequencies the capacitance measures only the majority carrier response, while at low frequencies both types of carrier respond.<sup>[14][15]</sup>

At optical frequencies, in semiconductors the dielectric constant exhibits structure related to the band structure of the solid. Sophisticated modulation spectroscopy measurement methods based upon modulating the crystal structure by pressure or by other stresses and observing the related changes in absorption or reflection of light have advanced our knowledge of these materials.<sup>[16]</sup>

### 1.2 Capacitance matrix

The discussion above is limited to the case of two conducting plates, although of arbitrary size and shape. The definition C=Q/V still holds for a single plate given a charge, in which case the field lines produced by that charge terminate as if the plate were at the center of an oppositely charged sphere at infinity.

C=Q/V does not apply when there are more than two charged plates, or when the net charge on the two plates is non-zero. To handle this case, Maxwell introduced his coefficients of potential. If three plates are given charges  $Q_1,Q_2,Q_3$ , then the voltage of plate 1 is given by

$$V_1 = P_{11}Q_1 + P_{12}Q_2 + P_{13}Q_3$$

and similarly for the other voltages. Hermann von Helmholtz and Sir William Thomson showed that the coefficients of potential are symmetric, so that  $P_{12}=P_{21}$ , etc. Thus the system can be described by a collection of coefficients known as the *elastance matrix* or *reciprocal capacitance matrix*, which is defined as:

$$P_{ij} = \frac{\partial V_i}{\partial Q_i}$$

From this, the mutual capacitance  $C_m$  between two objects can be defined<sup>[17]</sup> by solving for the total charge Q and using  $C_m=Q/V$ .

$$C_m = \frac{1}{(P_{11} + P_{22}) - (P_{12} + P_{21})}$$

Since no actual device holds perfectly equal and opposite charges on each of the two "plates", it is the mutual capacitance that is reported on capacitors.

The collection of coefficients  $C_{ij} = \frac{\partial Q_i}{\partial V_j}$  is known as the *capacitance matrix*, [18][19] and is the inverse of the elastance matrix.

## 1.3 Self-capacitance

In electrical circuits, the term *capacitance* is usually a shorthand for the *mutual capacitance* between two adjacent conductors, such as the two plates of a capacitor. However, for an isolated conductor there also exists a property called *self-capacitance*, which is the amount of electric charge that must be added to an isolated conductor to raise its electric potential by one unit (i.e. one volt, in most measurement systems). [20] The reference point for this potential is a theoretical hollow conducting sphere, of infinite radius, centered on the conductor. Using this method, the self-capacitance of a conducting sphere of radius R is given by: [21]

$$C = 4\pi\varepsilon_0 R$$

Example values of self-capacitance are:

- for the top "plate" of a van de Graaff generator, typically a sphere 20 cm in radius: 22.24 pF
- the planet Earth: about 710 μF<sup>[22]</sup>

The inter-winding capacitance of a coil, which changes its impedance at high frequencies and gives rise to parallel resonance, is variously called self-capacitance, [23] stray capacitance, or parasitic capacitance.

## 1.4 Stray capacitance

Main article: Parasitic capacitance

Any two adjacent conductors can function as a capacitor, though the capacitance is small unless the conductors are close together for long distances or over a large area. This (often unwanted) capacitance is called parasitic or "stray capacitance". Stray capacitance can allow signals to leak between otherwise isolated circuits (an effect called crosstalk), and it can be a limiting factor for proper functioning of circuits at high frequency.

Stray capacitance between the input and output in amplifier circuits can be troublesome because it can form a path for feedback, which can cause instability and parasitic oscillation in the amplifier. It is often convenient for analytical purposes to replace this capacitance with a combination of one input-to-ground capacitance and one output-to-ground capacitance; the original configuration — including the input-to-output capacitance — is often referred to as a pi-configuration. Miller's theorem can be used to effect this replacement: it states that, if the gain ratio of two nodes is 1/K, then an impedance of Z connecting the two nodes can be replaced with a Z/(1-k) impedance between the first node and ground and a KZ/(K-1) impedance between the second node and ground. Since impedance varies inversely with capacitance, the internode capacitance, C, is replaced by a capacitance of KC from input to ground and a capacitance of (K-1)C/K from output to ground. When the input-to-output gain is very large, the equivalent inputto-ground impedance is very small while the output-toground impedance is essentially equal to the original (input-to-output) impedance.

## 1.5 Capacitance of simple systems

Calculating the capacitance of a system amounts to solving the Laplace equation  $\nabla^2 \varphi = 0$  with a constant potential  $\varphi$  on the surface of the conductors. This is trivial in cases with high symmetry. There is no solution in terms of elementary functions in more complicated cases.

For quasi-two-dimensional situations analytic functions may be used to map different geometries to each other. See also Schwarz–Christoffel mapping.

# 1.6 Capacitance of nanoscale systems

The capacitance of nanoscale dielectric capacitors such as quantum dots may differ from conventional formulations of larger capacitors. In particular, the electrostatic potential difference experienced by electrons in conventional capacitors is spatially well-defined and fixed by the shape and size of metallic electrodes in addition to the statistically large number of electrons present in conventional capacitors. In nanoscale capacitors, however, the electrostatic potentials experienced by electrons are determined by the number and locations of all electrons that contribute to the electronic properties of the device. In such devices, the number of electrons may be very small, however, the resulting spatial distribution of equipotential surfaces within the device are exceedingly complex.

#### 1.6.1 Single-electron devices

The capacitance of a connected, or "closed", single-electron device is twice the capacitance of an unconnected, or "open", single-electron device. [32] This fact may be traced more fundamentally to the energy stored in the single-electron device whose "direct polarization" interaction energy may be equally divided into the interaction of the electron with the polarized charge on the device itself due to the presence of the electron and the amount of potential energy required to form the polarized charge on the device (the interaction of charges in the device's dielectric material with the potential due to the electron). [33]

#### 1.6.2 Few-electron devices

The derivation of a "quantum capacitance" of a fewelectron device involves the thermodynamic chemical potential of an *N*-particle system given by

$$\mu(N) = U(N) - U(N-1)$$

whose energy terms may be obtained as solutions of the Schrödinger equation. The definition of capacitance,

$$\frac{1}{C} \equiv \frac{\Delta\,V}{\Delta\,Q}$$

with the potential difference

$$\Delta V = \frac{\Delta \mu}{e} = \frac{\mu(N + \Delta N) - \mu(N)}{e}$$

may be applied to the device with the addition or removal of individual electrons,

$$\Delta N = 1$$
 and  $\Delta Q = e$ .

Then

$$C_Q(N) = \frac{e^2}{\mu(N+1) - \mu(N)} = \frac{e^2}{E(N)}$$

is the "quantum capacitance" of the device. [34]

This expression of "quantum capacitance" may be written as

$$C_Q(N) = \frac{e^2}{U(N)}$$

which differs from the conventional expression described in the introduction where  $W_{\rm stored}=U$ , the stored electrostatic potential energy,

$$C = \frac{Q^2}{2U}$$

by a factor of 1/2 with Q = Ne.

However, within the framework of purely classical electrostatic interactions, the appearance of the factor of 1/2 is the result of integration in the conventional formulation.

$$W_{ ext{charging}} = U = \int_0^Q rac{q}{C} \, \mathrm{d}q$$

which is appropriate since  $\mathrm{d}q=0$  for systems involving either many electrons or metallic electrodes, but in few-electron systems,  $\mathrm{d}q\to\Delta\,Q=e$ . The integral generally becomes a summation. One may trivially combine the expressions of capacitance and electrostatic interaction energy,

$$Q = CV$$
 and  $U = QV$ ,

respectively, to obtain,

$$C = Q\frac{1}{V} = Q\frac{Q}{U} = \frac{Q^2}{U}$$

which is similar to the quantum capacitance. A more rigorous derivation is reported in the literature.<sup>[35]</sup> In particular, to circumvent the mathematical challenges of the spatially complex equipotential surfaces within the device, an *average* electrostatic potential experiences by *each* electron is utilized in the derivation.

The reason for apparent mathematical differences is understood more fundamentally as the potential energy, U(N), of an isolated device (self-capacitance) is twice that stored in a "connected" device in the lower limit N=1. As N grows large,  $U(N) \rightarrow U$ . [33] Thus, the general expression of capacitance is

$$C(N) = \frac{(Ne)^2}{U(N)}$$

In nanoscale devices such as quantum dots, the "capacitor" is often an isolated, or partially isolated, component within the device. The primary differences between nanoscale capacitors and macroscopic (conventional) capacitors are the number of excess electrons (charge carriers, or electrons, that contribute to the device's electronic behavior) and the shape and size of metallic electrodes. In nanoscale devices, nanowires consisting of metal atoms typically do not exhibit the same conductive properties as their macroscopic, or bulk material, counterparts.

#### 1.7 See also

- Ampère's law
- Capacitor
- Capacitive Displacement Sensors
- Conductance
- Conductor
- Displacement current
- Electromagnetism
- Electricity
- Electronics
- · Gauss law
- Hydraulic analogy
- Inductor
- Inductance
- Orders of magnitude (capacitance)
- Quantum capacitance
- LCR meter

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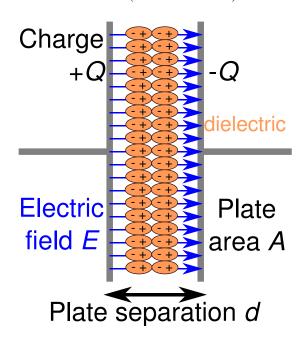
## **Chapter 2**

## **Dielectric**

This article is about the material. For the song by American industrial metal band Fear Factory, see Genexus (album).

Not to be confused with Dialectic.

A dielectric material (dielectric for short) is an electri-



A polarized dielectric material

cal insulator that can be polarized by an applied electric field. When a dielectric is placed in an electric field, electric charges do not flow through the material as they do in a conductor, but only slightly shift from their average equilibrium positions causing **dielectric polarization**. Because of dielectric polarization, positive charges are displaced toward the field and negative charges shift in the opposite direction. This creates an internal electric field that reduces the overall field within the dielectric itself.<sup>[1]</sup> If a dielectric is composed of weakly bonded molecules, those molecules not only become polarized, but also reorient so that their symmetry axes align to the field.<sup>[1]</sup>

The study of dielectric properties concerns storage and dissipation of electric and magnetic energy in materials.<sup>[2]</sup> Dielectrics are important for explaining various phenomena in electronics, optics, and solid-state

physics.

### 2.1 Terminology

While the term *insulator* implies low electrical conduction, *dielectric* typically means materials with a high polarizability. The latter is expressed by a number called the relative permittivity (also known in older texts as dielectric constant). The term insulator is generally used to indicate electrical obstruction while the term dielectric is used to indicate the energy storing capacity of the material (by means of polarization). A common example of a dielectric is the electrically insulating material between the metallic plates of a capacitor. The polarization of the dielectric by the applied electric field increases the capacitor's surface charge for the given electric field strength. [1]

The term "dielectric" was coined by William Whewell (from "dia-electric") in response to a request from Michael Faraday.<sup>[3][4]</sup> A *perfect dielectric* is a material with zero electrical conductivity (cf. perfect conductor),<sup>[5]</sup> thus exhibiting only a displacement current; therefore it stores and returns electrical energy as if it were an ideal capacitor.

## 2.2 Electric susceptibility

Main article: permittivity

The **electric susceptibility**  $\chi e$  of a dielectric material is a measure of how easily it polarizes in response to an electric field. This, in turn, determines the electric permittivity of the material and thus influences many other phenomena in that medium, from the capacitance of capacitors to the speed of light.

It is defined as the constant of proportionality (which may be a tensor) relating an electric field  ${\bf E}$  to the induced dielectric polarization density  ${\bf P}$  such that

 $\mathbf{P}=\varepsilon_0\chi_e\mathbf{E},$ 

where  $\varepsilon_0$  is the electric permittivity of free space.

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The susceptibility of a medium is related to its relative permittivity  $\varepsilon r$  by

$$\chi_e = \varepsilon_r - 1.$$

So in the case of a vacuum,

$$\chi_e = 0.$$

The electric displacement  $\mathbf{D}$  is related to the polarization density  $\mathbf{P}$  by

$$\mathbf{D} = \varepsilon_0 \mathbf{E} + \mathbf{P} = \varepsilon_0 (1 + \chi_e) \mathbf{E} = \varepsilon_r \varepsilon_0 \mathbf{E}.$$

### 2.2.1 Dispersion and causality

In general, a material cannot polarize instantaneously in response to an applied field. The more general formulation as a function of time is

$$\mathbf{P}(t) = \varepsilon_0 \int_{-\infty}^t \chi_e(t - t') \mathbf{E}(t') dt'.$$

That is, the polarization is a convolution of the electric field at previous times with time-dependent susceptibility given by  $\chi e(\Delta t)$ . The upper limit of this integral can be extended to infinity as well if one defines  $\chi e(\Delta t) = 0$  for  $\Delta t < 0$ . An instantaneous response corresponds to Dirac delta function susceptibility  $\chi e(\Delta t) = \chi e\delta(\Delta t)$ .

It is more convenient in a linear system to take the Fourier transform and write this relationship as a function of frequency. Due to the convolution theorem, the integral becomes a simple product,

$$\mathbf{P}(\omega) = \varepsilon_0 \chi_e(\omega) \mathbf{E}(\omega).$$

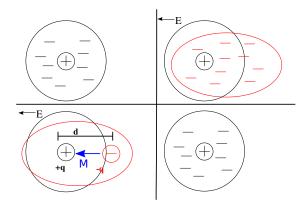
Note the simple frequency dependence of the susceptibility, or equivalently the permittivity. The shape of the susceptibility with respect to frequency characterizes the dispersion properties of the material.

Moreover, the fact that the polarization can only depend on the electric field at previous times (i.e.,  $\chi e(\Delta t) = 0$  for  $\Delta t < 0$ , a consequence of causality, imposes Kramers–Kronig constraints on the real and imaginary parts of the susceptibility  $\chi e(\omega)$ .

## 2.3 Dielectric polarization

#### 2.3.1 Basic atomic model

In the classical approach to the dielectric model, a material is made up of atoms. Each atom consists of a cloud



Electric field interaction with an atom under the classical dielectric model.

of negative charge (electrons) bound to and surrounding a positive point charge at its center. In the presence of an electric field the charge cloud is distorted, as shown in the top right of the figure.

This can be reduced to a simple dipole using the superposition principle. A dipole is characterized by its dipole moment, a vector quantity shown in the figure as the blue arrow labeled M. It is the relationship between the electric field and the dipole moment that gives rise to the behavior of the dielectric. (Note that the dipole moment points in the same direction as the electric field in the figure. This isn't always the case, and is a major simplification, but is true for many materials.)

When the electric field is removed the atom returns to its original state. The time required to do so is the so-called relaxation time; an exponential decay.

This is the essence of the model in physics. The behavior of the dielectric now depends on the situation. The more complicated the situation, the richer the model must be to accurately describe the behavior. Important questions are:

- Is the electric field constant or does it vary with time?
   At what rate?
- Does the response depend on the direction of the applied field (isotropy of the material)?
- Is the response the same everywhere (homogeneity of the material)?
- Do any boundaries or interfaces have to be taken into account?
- Is the response linear with respect to the field, or are there nonlinearities?

The relationship between the electric field  ${\bf E}$  and the dipole moment  ${\bf M}$  gives rise to the behavior of the dielectric, which, for a given material, can be characterized by the function  ${\bf F}$  defined by the equation:

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 $\mathbf{M} = \mathbf{F}(\mathbf{E})$ 

When both the type of electric field and the type of material have been defined, one then chooses the simplest function F that correctly predicts the phenomena of interest. Examples of phenomena that can be so modeled include:

- Refractive index
- Group velocity dispersion
- Birefringence
- Self-focusing
- Harmonic generation

#### 2.3.2 Dipolar polarization

Dipolar polarization is a polarization that is either inherent to polar molecules (**orientation polarization**), or can be induced in any molecule in which the asymmetric distortion of the nuclei is possible (**distortion polarization**). Orientation polarization results from a permanent dipole, e.g., that arising from the 104.45° angle between the asymmetric bonds between oxygen and hydrogen atoms in the water molecule, which retains polarization in the absence of an external electric field. The assembly of these dipoles forms a macroscopic polarization.

When an external electric field is applied, the distance between charges within each permanent dipole, which is related to chemical bonding, remains constant in orientation polarization; however, the direction of polarization itself rotates. This rotation occurs on a timescale that depends on the torque and surrounding local viscosity of the molecules. Because the rotation is not instantaneous, dipolar polarizations lose the response to electric fields at the highest frequencies. A molecule rotates about 1 radian per picosecond in a fluid, thus this loss occurs at about  $10^{11}$  Hz (in the microwave region). The delay of the response to the change of the electric field causes friction and heat.

When an external electric field is applied at infrared frequencies or less, the molecules are bent and stretched by the field and the molecular dipole moment changes. The molecular vibration frequency is roughly the inverse of the time it takes for the molecules to bend, and this **distortion polarization** disappears above the infrared.

#### 2.3.3 Ionic polarization

Ionic polarization is polarization caused by relative displacements between positive and negative ions in ionic crystals (for example, NaCl).

If a crystal or molecule consists of atoms of more than one kind, the distribution of charges around an atom in the crystal or molecule leans to positive or negative. As a result, when lattice vibrations or molecular vibrations induce relative displacements of the atoms, the centers of positive and negative charges are also displaced. The locations of these centers are affected by the symmetry of the displacements. When the centers don't correspond, polarizations arise in molecules or crystals. This polarization is called **ionic polarization**.

Ionic polarization causes the ferroelectric effect as well as dipolar polarization. The ferroelectric transition, which is caused by the lining up of the orientations of permanent dipoles along a particular direction, is called an **order-disorder phase transition**. The transition caused by ionic polarizations in crystals is called a **displacive phase transition**.

### 2.4 Dielectric dispersion

In physics, **dielectric dispersion** is the dependence of the permittivity of a dielectric material on the frequency of an applied electric field. Because there is a lag between changes in polarization and changes in the electric field, the permittivity of the dielectric is a complicated function of frequency of the electric field. Dielectric dispersion is very important for the applications of dielectric materials and for the analysis of polarization systems.

This is one instance of a general phenomenon known as material dispersion: a frequency-dependent response of a medium for wave propagation.

When the frequency becomes higher:

- 1. dipolar polarization can no longer follow the oscillations of the electric field in the microwave region around  $10^{10}$  Hz;
- ionic polarization and molecular distortion polarization can no longer track the electric field past the infrared or far-infrared region around 10<sup>13</sup> Hz,;
- 3. electronic polarization loses its response in the ultraviolet region around  $10^{15}$  Hz.

In the frequency region above ultraviolet, permittivity approaches the constant  $\varepsilon_0$  in every substance, where  $\varepsilon_0$  is the permittivity of the free space. Because permittivity indicates the strength of the relation between an electric field and polarization, if a polarization process loses its response, permittivity decreases.

#### 2.5 Dielectric relaxation

**Dielectric relaxation** is the momentary delay (or lag) in the dielectric constant of a material. This is usually

2.6. PARAELECTRICITY 11

caused by the delay in molecular polarization with respect to a changing electric field in a dielectric medium (e.g., inside capacitors or between two large conducting surfaces). Dielectric relaxation in changing electric fields could be considered analogous to hysteresis in changing magnetic fields (for inductors or transformers). Relaxation in general is a delay or lag in the response of a linear system, and therefore dielectric relaxation is measured relative to the expected linear steady state (equilibrium) dielectric values. The time lag between electrical field and polarization implies an irreversible degradation of Gibbs free energy.

In physics, **dielectric relaxation** refers to the relaxation response of a dielectric medium to an external, oscillating electric field. This relaxation is often described in terms of permittivity as a function of frequency, which can, for ideal systems, be described by the Debye equation. On the other hand, the distortion related to ionic and electronic polarization shows behavior of the resonance or oscillator type. The character of the distortion process depends on the structure, composition, and surroundings of the sample.

#### 2.5.1 Debye relaxation

**Debye relaxation** is the dielectric relaxation response of an ideal, noninteracting population of dipoles to an alternating external electric field. It is usually expressed in the complex permittivity  $\varepsilon$  of a medium as a function of the field's frequency  $\omega$ :

$$\hat{\varepsilon}(\omega) = \varepsilon_{\infty} + \frac{\Delta \varepsilon}{1 + i\omega \tau},$$

where  $\varepsilon \infty$  is the permittivity at the high frequency limit,  $\Delta \varepsilon = \varepsilon s - \varepsilon \infty$  where  $\varepsilon s$  is the static, low frequency permittivity, and  $\tau$  is the characteristic relaxation time of the medium.

This relaxation model was introduced by and named after the physicist Peter Debye (1913).<sup>[6]</sup>

#### 2.5.2 Variants of the Debye equation

• Cole-Cole equation

This equation is used when the dilectric loss peak shows symmetric broadening

• Cole-Davidson equation

This equation is used when the dilectric loss peak shows asymmetric broadening

• Havriliak-Negami relaxation

This equation considers both symmetric and asymmetric broadenig

• Kohlrausch–Williams–Watts function (Fourier transform of stretched exponential function)

#### 2.6 Paraelectricity

Paraelectricity is the ability of many materials (specifically ceramics) to become polarized under an applied electric field. Unlike ferroelectricity, this can happen even if there is no permanent electric dipole that exists in the material, and removal of the fields results in the polarization in the material returning to zero. <sup>[7]</sup> The mechanisms that cause **paraelectric** behaviour are the distortion of individual ions (displacement of the electron cloud from the nucleus) and polarization of molecules or combinations of ions or defects.

Paraelectricity can occur in crystal phases where electric dipoles are unaligned and thus have the potential to align in an external electric field and weaken it.

An example of a paraelectric material of high dielectric constant is strontium titanate.

The LiNbO<sub>3</sub> crystal is ferroelectric below 1430 K, and above this temperature it transforms into a disordered paraelectric phase. Similarly, other perovskites also exhibit paraelectricity at high temperatures.

Paraelectricity has been explored as a possible refrigeration mechanism; polarizing a paraelectric by applying an electric field under adiabatic process conditions raises the temperature, while removing the field lowers the temperature. [8] A heat pump that operates by polarizing the paraelectric, allowing it to return to ambient temperature (by dissipating the extra heat), bringing it into contact with the object to be cooled, and finally depolarizing it, would result in refrigeration.

## 2.7 Tunability

*Tunable dielectrics* are insulators whose ability to store electrical charge changes when a voltage is applied. <sup>[9][10]</sup>

Generally, strontium titanate (SrTiO

3) is used for devices operating at low temperatures, while barium strontium titanate (Ba

1-xSr

xTiO

3) substitutes for room temperature devices. Other potential materials include microwave dielectrics and carbon nanotube (CNT) composites. [9][11][12]

In 2013 multi-sheet layers of strontium titanate interleaved with single layers of strontium oxide produced a dielectric capable of operating at up to 125 GHz. The material was created via molecular beam epitaxy. The 12 CHAPTER 2. DIELECTRIC

two have mismatched crystal spacing that produces strain within the strontium titanate layer that makes it less stable and tunable. [9]

Systems such as Ba

1-xSr

xTiO

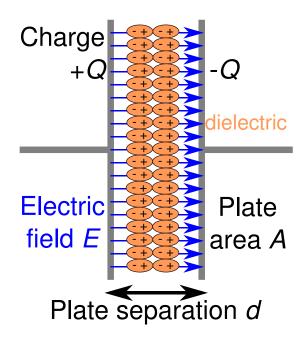
3 have a paraelectric–ferroelectric transition just below ambient temperature, providing high tunability. Such films suffer significant losses arising from defects.

## 2.8 Applications

#### 2.8.1 Capacitors

Main article: Capacitor

Commercially manufactured capacitors typically use a



Charge separation in a parallel-plate capacitor causes an internal electric field. A dielectric (orange) reduces the field and increases the capacitance.

solid dielectric material with high permittivity as the intervening medium between the stored positive and negative charges. This material is often referred to in technical contexts as the *capacitor dielectric*.<sup>[13]</sup>

The most obvious advantage to using such a dielectric material is that it prevents the conducting plates, on which the charges are stored, from coming into direct electrical contact. More significantly, however, a high permittivity allows a greater stored charge at a given voltage. This can be seen by treating the case of a linear dielectric with permittivity  $\varepsilon$  and thickness d between two conducting plates with uniform charge density  $\sigma \varepsilon$ . In this case the charge density is given by

$$\sigma_{\varepsilon} = \varepsilon \frac{V}{d}$$

and the capacitance per unit area by

$$c = \frac{\sigma_{\varepsilon}}{V} = \frac{\varepsilon}{d}$$

From this, it can easily be seen that a larger  $\varepsilon$  leads to greater charge stored and thus greater capacitance.

Dielectric materials used for capacitors are also chosen such that they are resistant to ionization. This allows the capacitor to operate at higher voltages before the insulating dielectric ionizes and begins to allow undesirable current.

#### 2.8.2 Dielectric resonator

Main article: dielectric resonator

A dielectric resonator oscillator (DRO) is an electronic component that exhibits resonance of the polarization response for a narrow range of frequencies, generally in the microwave band. It consists of a "puck" of ceramic that has a large dielectric constant and a low dissipation factor. Such resonators are often used to provide a frequency reference in an oscillator circuit. An unshielded dielectric resonator can be used as a Dielectric Resonator Antenna (DRA).

## 2.9 Some practical dielectrics

Dielectric materials can be solids, liquids, or gases. In addition, a high vacuum can also be a useful, nearly lossless dielectric even though its relative dielectric constant is only unity.

Solid dielectrics are perhaps the most commonly used dielectrics in electrical engineering, and many solids are very good insulators. Some examples include porcelain, glass, and most plastics. Air, nitrogen and sulfur hexafluoride are the three most commonly used gaseous dielectrics.

- Industrial coatings such as parylene provide a dielectric barrier between the substrate and its environment.
- Mineral oil is used extensively inside electrical transformers as a fluid dielectric and to assist in cooling. Dielectric fluids with higher dielectric constants, such as electrical grade castor oil, are often used in high voltage capacitors to help prevent corona discharge and increase capacitance.

- Because dielectrics resist the flow of electricity, the surface of a dielectric may retain *stranded* excess electrical charges. This may occur accidentally when the dielectric is rubbed (the triboelectric effect). This can be useful, as in a Van de Graaff generator or electrophorus, or it can be potentially destructive as in the case of electrostatic discharge.
- Specially processed dielectrics, called electrets (which should not be confused with ferroelectrics), may retain excess internal charge or "frozen in" polarization. Electrets have a semipermanent electric field, and are the electrostatic equivalent to magnets. Electrets have numerous practical applications in the home and industry.
- Some dielectrics can generate a potential difference when subjected to mechanical stress, or (equivalently) change physical shape if an external voltage is applied across the material. This property is called piezoelectricity. Piezoelectric materials are another class of very useful dielectrics.
- Some ionic crystals and polymer dielectrics exhibit a spontaneous dipole moment, which can be reversed by an externally applied electric field. This behavior is called the ferroelectric effect. These materials are analogous to the way ferromagnetic materials behave within an externally applied magnetic field. Ferroelectric materials often have very high dielectric constants, making them quite useful for capacitors.

#### 2.10 See also

- Classification of materials based on permittivity
- Paramagnetism
- Ferroelectricity
- Clausius-Mossotti relation
- Dielectric losses
- Dielectric strength
- Dielectric spectroscopy
- EIA Class 1 dielectric
- EIA Class 2 dielectric
- High-k dielectric
- Low-k dielectric
- leakage
- Linear response function
- Metamaterial
- RC delay
- Rotational Brownian motion

#### 2.11 References

- [1] Quote from Encyclopædia Britannica: "Dielectric, insulating material or a very poor conductor of electric current. When dielectrics are placed in an electric field, practically no current flows in them because, unlike metals, they have no loosely bound, or free, electrons that may drift through the material."
  - "Dielectrics (physics)". *Britannica*. 2009. p. 1. Retrieved 2009-08-12.
- [2] Arthur R. von Hippel, in his seminal work, *Dielectric Materials and Applications*, stated: "*Dielectrics...* are not a narrow class of so-called insulators, but the broad expanse of *nonmetals* considered from the standpoint of their interaction with electric, magnetic, or electromagnetic fields. Thus we are concerned with gases as well as with liquids and solids, and with the storage of electric and magnetic energy as well as its dissipation." (Technology Press of MIT and John Wiley, NY, 1954).
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- [11] "Electrically tunable dielectric materials and strategies to improve their performances". Progress in Materials Science 55: 840–893. 2010-11-30. doi:10.1016/j.pmatsci.2010.04.004. Retrieved 2013-11-08

- [12] Giere, A.; Zheng, Y.; Maune, H.; Sazegar, M.; Paul, F.; Zhou, X.; Binder, J. R.; Muller, S.; Jakoby, R. (2008). "Tunable dielectrics for microwave applications". 2008 17th IEEE International Symposium on the Applications of Ferroelectrics. p. 1. doi:10.1109/ISAF.2008.4693753. ISBN 978-1-4244-2744-4.
- [13] Mussig & Hans-Joachim, Semiconductor capacitor with praseodymium oxide as dielectric, U.S. Patent 7,113,388 published 2003-11-06, issued 2004-10-18, assigned to IHP GmbH- Innovations for High Performance Microelectronics/Institute Fur Innovative Mikroelektronik

## 2.12 Further reading

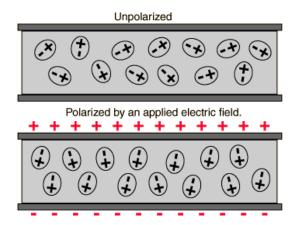
- Jackson, John David (August 10, 1998). Classical Electrodynamics (3 rd ed.). John Wiley & Sons. ISBN 978-0-471-30932-1. 808 or 832 pages.
- Scaife, Brendan (September 3, 1998). *Principles of Dielectrics (Monographs on the Physics & Chemistry of Materials)* (2 nd ed.). Oxford University Press. ISBN 978-0198565574.

#### 2.13 External links

- Electromagnetism A chapter from an online textbook
- Dielectric Sphere in an Electric Field
- DoITPoMS Teaching and Learning Package "Dielectric Materials"
- Texts on Wikisource:
  - "Dielectric". Encyclopedia Americana. 1920.
  - "Dielectric". *Encyclopædia Britannica* (11th ed.). 1911.

## **Chapter 3**

## **Permittivity**



A dielectric medium showing orientation of charged particles creating polarization effects. Such a medium can have a higher ratio of electric flux to charge (permittivity) than empty space

In electromagnetism, **absolute permittivity** is the measure of the resistance that is encountered when forming an electric field in a medium. In other words, permittivity is a measure of how an electric field affects, and is affected by, a dielectric medium. The permittivity of a medium describes how much electric field (more correctly, flux) is 'generated' per unit charge in that medium. More electric flux exists in a medium with a low permittivity (per unit charge) because of polarization effects. Permittivity is directly related to electric susceptibility, which is a measure of how easily a dielectric polarizes in response to an electric field. Thus, permittivity relates to a material's ability to **resist** an electric field (while unfortunately the word stem "permit" suggests the inverse quantity).

In SI units, permittivity  $\varepsilon$  is measured in farads per meter (F/m); electric susceptibility  $\chi$  is dimensionless. They are related to each other through

$$\varepsilon = \varepsilon_{\rm r} \varepsilon_0 = (1 + \chi) \varepsilon_0$$

where  $\varepsilon_r$  is the relative permittivity of the material, and  $\varepsilon_0 = 8.8541878176.. \times 10^{-12}$  F/m is the vacuum permittivity.

## 3.1 Explanation

In electromagnetism, the electric displacement field **D** represents how an electric field **E** influences the organization of electric charges in a given medium, including charge migration and electric dipole reorientation. Its relation to permittivity in the very simple case of *linear*, homogeneous, isotropic materials with "instantaneous" response to changes in electric field is

$$\mathbf{D} = \varepsilon \mathbf{E}$$

where the permittivity  $\varepsilon$  is a scalar. If the medium is anisotropic, the permittivity is a second rank tensor.

In general, permittivity is not a constant, as it can vary with the position in the medium, the frequency of the field applied, humidity, temperature, and other parameters. In a nonlinear medium, the permittivity can depend on the strength of the electric field. Permittivity as a function of frequency can take on real or complex values.

In SI units, permittivity is measured in farads per meter (F/m or  $A^2 \cdot s^4 \cdot kg^{-1} \cdot m^{-3}$ ). The displacement field **D** is measured in units of coulombs per square meter (C/m<sup>2</sup>), while the electric field **E** is measured in volts per meter (V/m). **D** and **E** describe the interaction between charged objects. **D** is related to the *charge densities* associated with this interaction, while **E** is related to the *forces* and *potential differences*.

## 3.2 Vacuum permittivity

Main article: Vacuum permittivity

The vacuum permittivity  $\varepsilon_0$  (also called **permittivity of free space** or the **electric constant**) is the ratio **D/E** in free space. It also appears in the Coulomb force constant,  $k_e = 1/(4\pi\varepsilon_0)$ .

Its value is<sup>[1]</sup>

$$\varepsilon_0 \! \stackrel{\mathrm{def}}{=} \frac{1}{c_0^2 \mu_0} = \frac{1}{35950207149.4727056\pi} \, \frac{\mathrm{F}}{\mathrm{m}} \approx 8.8541878176\ldots \times 10^{-12} \, \mathrm{F}_0 + 10^{-1$$

where

 $c_0$  is the speed of light in free space,<sup>[2]</sup>  $\mu_0$  is the vacuum permeability.

Constants  $c_0$  and  $\mu_0$  are defined in SI units to have exact numerical values, shifting responsibility of experiment to the determination of the meter and the ampere. [3] (The approximation in the second value of  $\varepsilon_0$  above stems from  $\pi$  being an irrational number.)

## 3.3 Relative permittivity

Main article: Relative permittivity

The linear permittivity of a homogeneous material is usually given relative to that of free space, as a relative permittivity  $\varepsilon_{\rm r}$  (also called dielectric constant, although this sometimes only refers to the static, zero-frequency relative permittivity). In an anisotropic material, the relative permittivity may be a tensor, causing birefringence. The actual permittivity is then calculated by multiplying the relative permittivity by  $\varepsilon_0$ :

$$\varepsilon = \varepsilon_{\rm r} \varepsilon_0 = (1 + \chi) \varepsilon_0,$$

where  $\chi$  (frequently written  $\chi_e$ ) is the electric susceptibility of the material.

The susceptibility is defined as the constant of proportionality (which may be a tensor) relating an electric field  ${\bf E}$  to the induced dielectric polarization density  ${\bf P}$  such that

$$\mathbf{P} = \varepsilon_0 \chi \mathbf{E},$$

where  $\varepsilon_0$  is the electric permittivity of free space.

The susceptibility of a medium is related to its relative permittivity  $\varepsilon_{\rm r}$  by

$$\chi = \varepsilon_{\rm r} - 1$$
.

So in the case of a vacuum.

$$\chi = 0.$$

The susceptibility is also related to the polarizability of individual particles in the medium by the Clausius-Mossotti relation.

The electric displacement  $\mathbf{D}$  is related to the polarization density  $\mathbf{P}$  by

$$\mathbf{D} = \varepsilon_0 \mathbf{E} + \mathbf{P} = \varepsilon_0 (1 + \chi) \mathbf{E} = \varepsilon_r \varepsilon_0 \mathbf{E}.$$

The permittivity  $\varepsilon$  and permeability  $\mu$  of a medium together determine the phase velocity v = c/n of electromagnetic radiation through that medium:

$$\varepsilon\mu = \frac{1}{v^2}.$$

## 3.4 Dispersion and causality

In general, a material cannot polarize instantaneously in response to an applied field, and so the more general formulation as a function of time is

$$\mathbf{P}(t) = \varepsilon_0 \int_{-\infty}^{t} \chi(t - t') \mathbf{E}(t') dt'.$$

That is, the polarization is a convolution of the electric field at previous times with time-dependent susceptibility given by  $\chi(\Delta t)$ . The upper limit of this integral can be extended to infinity as well if one defines  $\chi(\Delta t) = 0$  for  $\Delta t < 0$ . An instantaneous response would correspond to a Dirac delta function susceptibility  $\chi(\Delta t) = \chi \ \delta(\Delta t)$ .

It is convenient to take the Fourier transform with respect to time and write this relationship as a function of frequency. Because of the convolution theorem, the integral becomes a simple product,

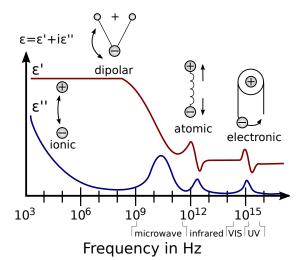
$$\mathbf{P}(\omega) = \varepsilon_0 \chi(\omega) \mathbf{E}(\omega).$$

This frequency dependence of the susceptibility leads to frequency dependence of the permittivity. The shape of the susceptibility with respect to frequency characterizes the dispersion properties of the material.

Moreover, the fact that the polarization can only depend on the electric field at previous times (i.e. effectively  $\chi(\Delta t) = 0$  for  $\Delta t < 0$ ), a consequence of causality, imposes Kramers–Kronig constraints on the susceptibility  $\chi(0)$ .

#### 3.4.1 Complex permittivity

As opposed to the response of a vacuum, the response of normal materials to external fields generally depends on the frequency of the field. This frequency dependence reflects the fact that a material's polarization does not respond instantaneously to an applied field. The response must always be *causal* (arising after the applied field) which can be represented by a phase difference. For this reason, permittivity is often treated as a complex function of the (angular) frequency of the applied field  $\omega$ :  $\varepsilon \to \widehat{\varepsilon}(\omega)$  (since complex numbers allow specification of magnitude and phase). The definition of permittivity therefore becomes



A dielectric permittivity spectrum over a wide range of frequencies.  $\varepsilon'$  and  $\varepsilon''$  denote the real and the imaginary part of the permittivity, respectively. Various processes are labeled on the image: ionic and dipolar relaxation, and atomic and electronic resonances at higher energies.<sup>[4]</sup>

$$D_0 e^{-i\omega t} = \widehat{\varepsilon}(\omega) E_0 e^{-i\omega t},$$

where

 $D_0$  and  $E_0$  are the amplitudes of the displacement and electric fields, respectively,

*i* is the imaginary unit,  $i^2 = -1$ .

The response of a medium to static electric fields is described by the low-frequency limit of permittivity, also called the static permittivity  $\varepsilon_s$  (also  $\varepsilon DC$ ):

$$\varepsilon_s = \lim_{\omega \to 0} \widehat{\varepsilon}(\omega).$$

At the high-frequency limit, the complex permittivity is commonly referred to as  $\varepsilon\infty$ . At the plasma frequency and above, dielectrics behave as ideal metals, with electron gas behavior. The static permittivity is a good approximation for alternating fields of low frequencies, and as the frequency increases a measurable phase difference  $\delta$  emerges between **D** and **E**. The frequency at which the phase shift becomes noticeable depends on temperature and the details of the medium. For moderate fields strength  $(E_0)$ , **D** and **E** remain proportional, and

$$\widehat{\varepsilon} = \frac{D_0}{E_0} = |\varepsilon| e^{i\delta}.$$

Since the response of materials to alternating fields is characterized by a complex permittivity, it is natural to separate its real and imaginary parts, which is done by convention in the following way:

$$\widehat{\varepsilon}(\omega) = \varepsilon'(\omega) + i\varepsilon''(\omega) = \frac{D_0}{E_0} (\cos \delta + i \sin \delta).$$

where

 $\varepsilon$ ' is the real part of the permittivity, which is related to the stored energy within the medium;

 $\varepsilon$ " is the imaginary part of the permittivity, which is related to the dissipation (or loss) of energy within the medium;

 $\delta$  is the loss angle.

The choice of sign for time-dependence,  $\exp(-i\omega t)$ , dictates the sign convention for the imaginary part of permittivity. The signs used here correspond to those commonly used in physics, whereas for the engineering convention one should reverse all imaginary quantities.

The complex permittivity is usually a complicated function of frequency  $\omega$ , since it is a superimposed description of dispersion phenomena occurring at multiple frequencies. The dielectric function  $\varepsilon(\omega)$  must have poles only for frequencies with positive imaginary parts, and therefore satisfies the Kramers–Kronig relations. However, in the narrow frequency ranges that are often studied in practice, the permittivity can be approximated as frequency-independent or by model functions.

At a given frequency, the imaginary part of  $\hat{\varepsilon}$  leads to absorption loss if it is positive (in the above sign convention) and gain if it is negative. More generally, the imaginary parts of the eigenvalues of the anisotropic dielectric tensor should be considered.

In the case of solids, the complex dielectric function is intimately connected to band structure. The primary quantity that characterizes the electronic structure of any crystalline material is the probability of photon absorption, which is directly related to the imaginary part of the optical dielectric function  $\varepsilon(\omega)$ . The optical dielectric function is given by the fundamental expression:<sup>[5]</sup>

$$\varepsilon(\omega) = 1 + \frac{8\pi^2 e^2}{m^2} \sum_{c,v} \int W_{c,v}(E) \left[ \varphi(\hbar\omega - E) - \varphi(\hbar\omega + E) \right] dx.$$

In this expression, Wc, v(E) represents the product of the Brillouin zone-averaged transition probability at the energy E with the joint density of states,  $^{[6][7]}$  Jc, v(E);  $\varphi$  is a broadening function, representing the role of scattering in smearing out the energy levels.  $^{[8]}$  In general, the broadening is intermediate between Lorentzian and Gaussian;  $^{[9][10]}$  for an alloy it is somewhat closer to Gaussian because of strong scattering from statistical fluctuations in the local composition on a nanometer scale.

#### 3.4.2 Tensorial permittivity

According to the Drude model of magnetized plasma, a more general expression which takes into account the interaction of the carriers with an alternating electric field at millimeter and microwave frequencies in an axially magnetized semiconductor requires the expression of the permittivity as a non-diagonal tensor.<sup>[11]</sup> (see also Electrogyration).

$$\mathbf{D}(\omega) = \begin{vmatrix} \varepsilon_1 & -i\varepsilon_2 & 0 \\ i\varepsilon_2 & \varepsilon_1 & 0 \\ 0 & 0 & \varepsilon_z \end{vmatrix} \mathbf{E}(\omega)$$

If  $\varepsilon_2$  vanishes, then the tensor is diagonal but not proportional to the identity and the medium is said to be a uniaxial medium, which has similar properties to a uniaxial crystal.

#### 3.4.3 Classification of materials

Materials can be classified according to their complexvalued permittivity  $\varepsilon$ , upon comparison of its real  $\varepsilon$ ' and imaginary  $\varepsilon$ " components (or, equivalently, conductivity, σ, when it's accounted for in the latter). A perfect conductor has infinite conductivity,  $\sigma=\infty$ , while a perfect di*electric* is a material that has no conductivity at all,  $\sigma$ =0; this latter case, of real-valued permittivity (or complexvalued permittivity with zero imaginary component) is also associated with the name lossless media. [12] Generally, when  $\sigma/(\omega \varepsilon) \ll 1$  we consider the material to be a low-loss dielectric (nearly though not exactly lossless), whereas  $\sigma/(\omega \varepsilon') \gg 1$  is associated with a good conductor; such materials with non-negligible conductivity yield a large amount of loss that inhibit the propagation of electromagnetic waves, thus are also said to be lossy media. Those materials that do not fall under either limit are considered to be general media.

#### 3.4.4 Lossy medium

In the case of lossy medium, i.e. when the conduction current is not negligible, the total current density flowing is:

$$J_{\rm tot} = J_{\rm c} + J_{\rm d} = \sigma E - i\omega \varepsilon' E = -i\omega \widehat{\varepsilon} E$$
 where

 $\sigma$  is the conductivity of the medium;  $\varepsilon$ ' is the real part of the permittivity.  $\widehat{\varepsilon}$  is the complex permittivity

The size of the displacement current is dependent on the frequency  $\omega$  of the applied field E; there is no displacement current in a constant field.

In this formalism, the complex permittivity is defined as:<sup>[13]</sup>

$$\widehat{\varepsilon} = \varepsilon' + i \frac{\sigma}{\omega}$$

In general, the absorption of electromagnetic energy by dielectrics is covered by a few different mechanisms that influence the shape of the permittivity as a function of frequency:

- First, are the relaxation effects associated with permanent and induced molecular dipoles. At low frequencies the field changes slowly enough to allow dipoles to reach equilibrium before the field has measurably changed. For frequencies at which dipole orientations cannot follow the applied field because of the viscosity of the medium, absorption of the field's energy leads to energy dissipation. The mechanism of dipoles relaxing is called dielectric relaxation and for ideal dipoles is described by classic Debye relaxation.
- Second are the resonance effects, which arise from the rotations or vibrations of atoms, ions, or electrons. These processes are observed in the neighborhood of their characteristic absorption frequencies.

The above effects often combine to cause non-linear effects within capacitors. For example, dielectric absorption refers to the inability of a capacitor that has been charged for a long time to completely discharge when briefly discharged. Although an ideal capacitor would remain at zero volts after being discharged, real capacitors will develop a small voltage, a phenomenon that is also called *soakage* or *battery action*. For some dielectrics, such as many polymer films, the resulting voltage may be less than 1-2% of the original voltage. However, it can be as much as 15 - 25% in the case of electrolytic capacitors or supercapacitors.

#### 3.4.5 Quantum-mechanical interpretation

In terms of quantum mechanics, permittivity is explained by atomic and molecular interactions.

At low frequencies, molecules in polar dielectrics are polarized by an applied electric field, which induces periodic rotations. For example, at the microwave frequency, the microwave field causes the periodic rotation of water molecules, sufficient to break hydrogen bonds. The field does work against the bonds and the energy is absorbed by the material as heat. This is why microwave ovens work very well for materials containing water. There are two maxima of the imaginary component (the absorptive index) of water, one at the microwave frequency, and the

other at far ultraviolet (UV) frequency. Both of these resonances are at higher frequencies than the operating frequency of microwave ovens.

At moderate frequencies, the energy is too high to cause rotation, yet too low to affect electrons directly, and is absorbed in the form of resonant molecular vibrations. In water, this is where the absorptive index starts to drop sharply, and the minimum of the imaginary permittivity is at the frequency of blue light (optical regime).

At high frequencies (such as UV and above), molecules cannot relax, and the energy is purely absorbed by atoms, exciting electron energy levels. Thus, these frequencies are classified as ionizing radiation.

While carrying out a complete *ab initio* (that is, first-principles) modelling is now computationally possible, it has not been widely applied yet. Thus, a phenomenological model is accepted as being an adequate method of capturing experimental behaviors. The Debye model and the Lorentz model use a 1st-order and 2nd-order (respectively) lumped system parameter linear representation (such as an RC and an LRC resonant circuit).

#### 3.5 Measurement

Main article: dielectric spectroscopy

The dielectric constant of a material can be found by a variety of static electrical measurements. The complex permittivity is evaluated over a wide range of frequencies by using different variants of dielectric spectroscopy, covering nearly 21 orders of magnitude from  $10^{-6}$  to  $10^{15}$  Hz. Also, by using cryostats and ovens, the dielectric properties of a medium can be characterized over an array of temperatures. In order to study systems for such diverse excitation fields, a number of measurement setups are used, each adequate for a special frequency range.

Various microwave measurement techniques are outlined in Chen *et al.*.<sup>[14]</sup> Typical errors for the Hakki-Coleman method employing a puck of material between conducting planes are about 0.3%.<sup>[15]</sup>

- Low-frequency time domain measurements  $(10^{-6}-10^3 \text{ Hz})$
- Low-frequency frequency domain measurements (10<sup>-5</sup>-10<sup>6</sup> Hz)
- Reflective coaxial methods (10<sup>6</sup> 10<sup>10</sup> Hz)
- Transmission coaxial method (10<sup>8</sup>-10<sup>11</sup> Hz)
- Quasi-optical methods (10<sup>9</sup> 10<sup>10</sup> Hz)
- Terahertz time-domain spectroscopy (10<sup>11</sup>-10<sup>13</sup> Hz)
- Fourier-transform methods (10<sup>11</sup>-10<sup>15</sup> Hz)

At infrared and optical frequencies, a common technique is ellipsometry. Dual polarisation interferometry is also used to measure the complex refractive index for very thin films at optical frequencies.

#### 3.6 See also

- Acoustic attenuation
- Density functional theory
- Electric-field screening
- · Green-Kubo relations
- Green's function (many-body theory)
- Linear response function
- Rotational Brownian motion
- Electromagnetic permeability

#### 3.7 References

- [1] electric constant
- [2] Current practice of standards organizations such as NIST and BIPM is to use  $c_0$ , rather than c, to denote the speed of light in vacuum according to ISO 31. In the original Recommendation of 1983, the symbol c was used for this purpose. See NIST *Special Publication 330*, Appendix 2, p. 45.
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- [13] John S. Seybold (2005) Introduction to RF propagation. 330 pp, eq.(2.6), p.22.
- [14] Linfeng Chen, V. V. Varadan, C. K. Ong, Chye Poh Neo (2004). "Microwave theory and techniques for materials characterization". *Microwave electronics*. Wiley. p. 37. ISBN 0-470-84492-2.
- [15] Mailadil T. Sebastian (2008). Dielectric Materials for Wireless Communication. Elsevier. p. 19. ISBN 0-08-045330-9.

## 3.8 Further reading

- Theory of Electric Polarization: Dielectric Polarization, C.J.F. Böttcher, ISBN 0-444-41579-3
- *Dielectrics and Waves* edited by von Hippel, Arthur R., ISBN 0-89006-803-8
- *Dielectric Materials and Applications* edited by Arthur von Hippel, ISBN 0-89006-805-4.

#### 3.9 External links

- Electromagnetism, a chapter from an online textbook
- What's all this trapped charge stuff . . ., A different approach to some capacitor problems
- Complex Permittivites of Metals, Plots of the complex permittivity and refractive index for many different metals.

## **Chapter 4**

## **Electric susceptibility**

In electromagnetism, the **electric susceptibility**  $\chi_e$  (latin: *susceptibilis* "receptive") is a dimensionless proportionality constant that indicates the degree of polarization of a dielectric material in response to an applied electric field. The greater the electric susceptibility, the greater the ability of a material to polarize in response to the field, and thereby reduce the total electric field inside the material (and store energy). It is in this way that the electric susceptibility influences the electric permittivity of the material and thus influences many other phenomena in that medium, from the capacitance of capacitors to the speed of light. [1][2]

# 4.1 Definition of volume susceptibility

Electric susceptibility is defined as the constant of proportionality (which may be a tensor) relating an electric field **E** to the induced dielectric polarization density **P** such that:

$$\mathbf{P} = \varepsilon_0 \chi_{\rm e} \mathbf{E},$$

where

- **P** is the polarization density;
- $\varepsilon_0$  is the electric permittivity of free space;
- $\chi_e$  is the electric susceptibility;
- E is the electric field.

The susceptibility is also related to the polarizability of individual particles in the medium by the Clausius-Mossotti relation. The susceptibility is related to its relative permittivity  $\varepsilon_{\rm r}$  by:

$$\chi_{\rm e} = \varepsilon_{\rm r} - 1$$

So in the case of a vacuum:

$$\chi_{\rm e} = 0$$

At the same time, the electric displacement  $\mathbf{D}$  is related to the polarization density  $\mathbf{P}$  by:

$$\mathbf{D} = \varepsilon_0 \mathbf{E} + \mathbf{P} = \varepsilon_0 (1 + \gamma_e) \mathbf{E} = \varepsilon_r \varepsilon_0 \mathbf{E}.$$

## 4.2 Molecular polarizability

A similar parameter exists to relate the magnitude of the induced dipole moment  $\mathbf{p}$  of an individual molecule to the local electric field  $\mathbf{E}$  that induced the dipole. This parameter is the *molecular polarizability*  $(\alpha)$ , and the dipole moment resulting from the local electric field  $\mathbf{E}_{local}$  is given by:

$$\mathbf{p} = \varepsilon_0 \alpha \mathbf{E}_{local}$$

This introduces a complication however, as locally the field can differ significantly from the overall applied field. We have:

$$\mathbf{P} = N\mathbf{p} = N\varepsilon_0 \alpha \mathbf{E}_{local}$$

where  $\mathbf{P}$  is the polarization per unit volume, and N is the number of molecules per unit volume contributing to the polarization. Thus, if the local electric field is parallel to the ambient electric field, we have:

$$\chi_{\rm e}\mathbf{E} = N\alpha\mathbf{E}_{\rm local}$$

Thus only if the local field equals the ambient field can we write:

$$\chi_{\rm e} = N\alpha$$

## 4.3 Nonlinear susceptibility

In many materials the polarizability starts to saturate at high values of electric field. This saturation can be modelled by a **nonlinear susceptibility**. These susceptibilities are important in nonlinear optics and lead to effects such as second harmonic generation (such as used to convert infrared light into visible light, in green laser pointers).

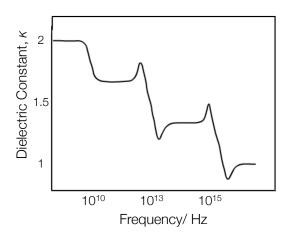
The standard definition of nonlinear susceptibilities in SI units is via a Taylor expansion of the polarization's reaction to electric field:<sup>[3]</sup>

$$P = P_0 + \varepsilon_0 \chi^{(1)} E + \varepsilon_0 \chi^{(2)} E^2 + \varepsilon_0 \chi^{(3)} E^3 + \cdots$$

(Except in ferroelectric materials, the built-in polarization is zero,  $P_0=0$ .) The first susceptibility term,  $\chi^{(1)}$ , corresponds to the linear susceptibility described above. While this first term is dimensionless, the subsequent nonlinear susceptibilities  $\chi^{(n)}$  have units of  $(\text{m/V})^{n-1}$ .

The nonlinear susceptibilities can be generalized to anisotropic materials (where each susceptibility  $\chi^{(n)}$  becomes an n+1-rank tensor).

## 4.4 Dispersion and causality



Schematic plot of the dielectric constant as a function of light frequency showing several resonances and plateaus indicating the activation of certain processes which can respond to the perturbation on the timescales of the frequency of the light. This demonstrates that thinking of the susceptibility in terms of its Fourier transform is useful, as light is a constant-frequency perturbation to a material

In general, a material cannot polarize instantaneously in response to an applied field, and so the more general formulation as a function of time is

$$\mathbf{P}(t) = \varepsilon_0 \int_{-\infty}^{t} \chi_{\mathbf{e}}(t - t') \mathbf{E}(t') dt'.$$

That is, the polarization is a convolution of the electric field at previous times with time-dependent susceptibility given by  $\chi_{\rm e}(\Delta t)$ . The upper limit of this integral can be extended to infinity as well if one defines  $\chi_{\rm e}(\Delta t)=0$  for  $\Delta t<0$ . An instantaneous response corresponds to Dirac delta function susceptibility  $\chi_{\rm e}(\Delta t)=\chi_{\rm e}\delta(\Delta t)$ .

It is more convenient in a linear system to take the Fourier transform and write this relationship as a function of frequency. Due to the convolution theorem, the integral becomes a simple product,

$$\mathbf{P}(\omega) = \varepsilon_0 \chi_{\mathbf{e}}(\omega) \mathbf{E}(\omega).$$

This frequency dependence of the susceptibility leads to frequency dependence of the permittivity. The shape of the susceptibility with respect to frequency characterizes the dispersion properties of the material.

Moreover, the fact that the polarization can only depend on the electric field at previous times (i.e.  $\chi_{\rm e}(\Delta t)=0$  for  $\Delta t<0$ ), a consequence of causality, imposes Kramers–Kronig constraints on the susceptibility  $\chi_{\rm e}(0)$ .

#### 4.5 See also

- Application of tensor theory in physics
- Magnetic susceptibility
- · Maxwell's equations
- Permittivity
- Clausius-Mossotti relation
- Linear response function
- · Green-Kubo relations

#### 4.6 References

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- [3] Paul N. Butcher, David Cotter, *The Elements of Nonlinear Optics*

## **Chapter 5**

## **Polarization density**

In classical electromagnetism, **polarization density** (or **electric polarization**, or simply **polarization**) is the vector field that expresses the density of permanent or induced electric dipole moments in a dielectric material. When a dielectric is placed in an external electric field, its molecules gain electric dipole moment and the dielectric is said to be polarized. The electric dipole moment induced per unit volume of the dielectric material is called the electric polarization of the dielectric. [1][2]

Polarization density also describes how a material responds to an applied electric field as well as the way the material changes the electric field, and can be used to calculate the forces that result from those interactions. It can be compared to magnetization, which is the measure of the corresponding response of a material to a magnetic field in magnetism. The SI unit of measure is coulombs per square meter, and polarization density is represented by a vector **P**.<sup>[2]</sup>

#### 5.1 Definition

An external electric field that is applied to a dielectric material, causes a displacement of bound charged elements. These are elements which are bound to molecules and are not free to move around the material. Positive charged elements are displaced in the direction of the field, and negative charged elements are displaced opposite to the direction of the field. The molecules may remain neutral in charge, yet an electric dipole moment forms. [3][4]

For a certain volume element in the material  $\Delta V$ , which carries a dipole moment  $\Delta \mathbf{p}$ , we define the polarization vector  $\mathbf{P}$ :

$$\mathbf{P} = \frac{\Delta \mathbf{p}}{\Delta V}$$

In general, the dipole moment  $\Delta \mathbf{p}$  changes from point to point within the dielectric. Hence, the polarization density  $\mathbf{P}$  of an infinitesimal change d $\mathbf{p}$  in the dipole moment for a given change dV in the volume is:

$$\mathbf{P} = \frac{\mathrm{d}\mathbf{p}}{\mathrm{d}V} \qquad (1)$$

The net charge appearing as a result of polarization is called bound charge and denoted  $Q_b$ .

### **5.2** Other Expressions

Let a volume  $\mathrm{d}V$  be isolated inside the dielectric. Due to polarization the positive bound charge  $\mathrm{d}q_b^+$  will be displaced a distance  $\mathrm{d}$  relative to the negative bound charge  $\mathrm{d}q_b^-$ , giving rise to a dipole moment  $\mathrm{d}\mathbf{p}=\mathrm{d}q_b\mathrm{d}$ . Replacing this expression into (1) we get:

$$\mathbf{P} = \frac{\mathrm{d}q_b}{\mathrm{d}V}\mathbf{d}$$

Since the charge  $dq_b$  bounded in the volume dV is equal to  $\rho_b dV$  the equation for **P** becomes:<sup>[3]</sup>

$$\mathbf{P} = \rho_b \mathbf{d} \tag{2}$$

where  $\rho_b$  is the density of the bound charge in the volume under consideration.

#### 5.3 Gauss's Law for the Field of P

For a given volume V enclosed by a surface S, the bound charge  $Q_b$  inside it is equal to the flux of  $\mathbf{P}$  through S taken with the negative sign, or

$$-Q_b = \iint_S \mathbf{P} \cdot d\mathbf{A} \qquad (3)$$

#### **5.3.1** Differential Form

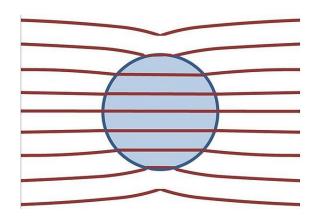
By the divergence theorem, Gauss's law for the field **P** can be stated in *differential form* as:

$$-\rho_b = \nabla \cdot \mathbf{P}$$

where  $\nabla \cdot \mathbf{P}$  is the divergence of the field  $\mathbf{P}$  through a given surface containing the bound charge density  $\rho_b$ .

# 5.4 Relationship between the fields of *P* and *E*

#### 5.4.1 Homogeneous, Isotropic Dielectrics



Field lines of the **D**-field in a dielectric sphere with greater susceptibility than its surroundings, placed in a previously-uniform field.<sup>[5]</sup> The field lines of the **E**-field are not shown: These point in the same directions, but many field lines start and end on the surface of the sphere, where there is bound charge. As a result, the density of E-field lines is lower inside the sphere than outside, which corresponds to the fact that the E-field is weaker inside the sphere than outside.

In a homogeneous linear and isotropic dielectric medium, the **polarization** is aligned with and proportional to the electric field  $\mathbf{E}$ :<sup>[6]</sup>

$$\mathbf{P} = \chi \varepsilon_0 \mathbf{E}$$
.

where  $\varepsilon_0$  is the electric constant, and  $\chi$  is the electric susceptibility of the medium. Note that  $\chi$  is just a scalar. This is a particular case due to the *isotropy* of the dielectric.

Taking into account this relation between  $\mathbf{P}$  and  $\mathbf{E}$ , equation (3) becomes:<sup>[3]</sup>

$$-Q_b = \chi \varepsilon_0 \iint_S \mathbf{E} \cdot d\mathbf{A}$$

The expression in the integral is Gauss's law for the field  ${\bf E}$  which yields the total charge, both free  $(Q_f)$  and bound  $(Q_b)$ , in the volume V enclosed by  $S.^{[3]}$  Therefore

$$\begin{aligned} -Q_b &= \chi Q_{\text{total}} \\ &= \chi (Q_f + Q_b) \\ Q_b &= -\frac{\chi}{1+\chi} Q_f, \end{aligned}$$

which can be written in terms of free charge and bound charge densities (by considering the relationship between the charges, their volume charge densities and the given volume):

$$\rho_b = -\frac{\chi}{1+\chi}\rho_f$$

Since within a homogeneous dielectric there can be no free charges  $(\rho_f=0)$ , by the last equation it follows that there is no bulk bound charge in the material  $(\rho_b=0)$ . And since free charges can get as close to the dielectric as to its topmost surface, it follows that polarization only gives rise to surface bound charge density (denoted  $\sigma_b$  to avoid ambiguity with the volume bound charge density  $\rho_b$ ).  $^{[3]}$ 

 $\sigma_b$  may be related to **P** by the following equation:<sup>[7]</sup>

$$\sigma_b = \mathbf{P} \cdot \mathbf{\hat{n}_{out}}$$

where  $\mathbf{h}_{out}$  is the normal vector to the surface S pointing outwards.

#### **5.4.2** Anisotropic Dielectrics

The class of dielectrics where the polarization density and the electric field are not in the same direction are known as *anisotropic* materials.

In such materials, the  $i^{th}$  component of the polarization is related to the  $j^{th}$  component of the electric field according to: $^{[6]}$ 

$$P_i = \sum_j \epsilon_0 \chi_{ij} E_j,$$

This relation shows, for example, that a material can polarize in the x direction by applying a field in the z direction, and so on. The case of an anisotropic dielectric medium is described by the field of crystal optics.

As in most electromagnetism, this relation deals with macroscopic averages of the fields and dipole density, so that one has a continuum approximation of the dielectric materials that neglects atomic-scale behaviors. The polarizability of individual particles in the medium can be related to the average susceptibility and polarization density by the Clausius-Mossotti relation.

In general, the susceptibility is a function of the frequency  $\omega$  of the applied field. When the field is an arbitrary function of time t, the polarization is a convolution of the

25

Fourier transform of  $\chi(\omega)$  with the  $\mathbf{E}(t)$ . This reflects the fact that the dipoles in the material cannot respond instantaneously to the applied field, and causality considerations lead to the Kramers-Kronig relations.

If the polarization **P** is not linearly proportional to the electric field E, the medium is termed nonlinear and is described by the field of nonlinear optics. To a good approximation (for sufficiently weak fields, assuming no permanent dipole moments are present), P is usually given by a Taylor series in E whose coefficients are the nonlinear susceptibilities:

$$\mathbf{J}_{p} = \frac{\partial \mathbf{P}}{\partial t}$$

$$\frac{P_{i}}{\epsilon_{0}} = \sum_{j} \chi_{ij}^{(1)} E_{j} + \sum_{jk} \chi_{ijk}^{(2)} E_{j} E_{k} + \sum_{jk\ell} \chi_{ijk\ell}^{(3)} E_{j} E_{k} E_{\ell} + \cdots$$
so that the equations

where  $\chi^{(1)}$  is the linear susceptibility,  $\chi^{(2)}$  is the secondorder susceptibility (describing phenomena such as the Pockels effect, optical rectification and second-harmonic generation), and  $\chi^{(3)}$  is the third-order susceptibility (describing third-order effects such as the Kerr effect and electric field-induced optical rectification).

In ferroelectric materials, there is no one-to-one correspondence between P and E at all because of hysteresis.

on the medium, as described later in the article. In many problems, it is more convenient to work with **D** and the free charges than with **E** and the total charge.<sup>[1]</sup>

#### 5.5.2 **Time-varying Polarization Density**

When the polarization density changes with time, the time-dependent bound-charge density creates a polarization current density of

$$\mathbf{J}_p = \frac{\partial \mathbf{P}}{\partial t}$$

so that the total current density that enters Maxwell's equations is given by

$$\mathbf{J} = \mathbf{J}_f + \nabla \times \mathbf{M} + \frac{\partial \mathbf{P}}{\partial t}$$

where  $J_f$  is the free-charge current density, and the second term is the magnetization current density (also called the bound current density), a contribution from atomic-scale magnetic dipoles (when they are present).

#### 5.5 **Polarization** density in Maxwell's equations

The behavior of electric fields (E and D), magnetic fields  $(\mathbf{B}, \mathbf{H})$ , charge density  $(\rho)$  and current density  $(\mathbf{J})$  are described by Maxwell's equations in matter.

#### 5.5.1 Relations between E, D and P

In terms of volume charge densities, the free charge density  $\rho_f$  is given by

$$\rho_f = \rho - \rho_b$$

where  $\rho$  is the total charge density. By considering the relationship of each of the terms of the above equation to the divergence of their corresponding fields (of the electric displacement field **D**, **E** and **P** in that order), this can be written as:[8]

$$\mathbf{D} = \varepsilon_0 \mathbf{E} + \mathbf{P}.$$

Here  $\varepsilon_0$  is the electric permittivity of empty space. In this equation, P is the (negative of the) field induced in the material when the "fixed" charges, the dipoles, shift in response to the total underlying field  ${\bf E}$ , whereas  ${\bf D}$  is the field due to the remaining charges, known as "free" charges. In general, P varies as a function of E depending

## Polarization ambiguity

Example of how the polarization density in a bulk crystal is ambiguous. (a) A solid crystal. (b) By pairing the positive and negative charges in a certain way, the crystal appears to have an upward polarization. (c) By pairing the charges differently, the crystal appears to have a downward polarization.

The polarization inside a solid is not, in general, uniquely defined: It depends on which electrons are paired up with which nuclei.<sup>[9]</sup> (See figure.) In other words, two people, Alice and Bob, looking at the same solid, may calculate different values of P, and neither of them will be wrong. Alice and Bob will agree on the microscopic electric field E in the solid, but disagree on the value of the displacement field  $\mathbf{D} = \varepsilon_0 \mathbf{E} + \mathbf{P}$ . They will both find that Gauss's law is correct (  $\nabla \cdot \mathbf{D} = \rho_f$  ), but they will disagree on the value of  $\rho_f$  at the surfaces of the crystal. For example, if Alice interprets the bulk solid to consist of dipoles with positive ions above and negative ions below, but the real crystal has negative ions as the topmost surface, then Alice will say that there is a negative free charge at the topmost surface. (She might view this as a type of surface reconstruction).

On the other hand, even though the value of **P** is not uniquely defined in a bulk solid, *variations* in **P** *are* uniquely defined. [9] If the crystal is gradually changed from one structure to another, there will be a current inside each unit cell, due to the motion of nuclei and electrons. This current results in a macroscopic transfer of charge from one side of the crystal to the other, and therefore it can be measured with an ammeter (like any other current) when wires are attached to the opposite sides of the crystal. The time-integral of the current is proportional to the change in **P**. The current can be calculated in computer simulations (such as density functional theory); the formula for the integrated current turns out to be a type of Berry's phase. [9]

The non-uniqueness of **P** is not problematic, because every measurable consequence of **P** is in fact a consequence of a continuous change in **P**.<sup>[9]</sup> For example, when a material is put in an electric field **E**, which ramps up from zero to a finite value, the material's electronic and ionic positions slightly shift. This changes **P**, and the result is electric susceptibility (and hence permittivity). As another example, when some crystals are heated, their electronic and ionic positions slightly shift, changing **P**. The result is pyroelectricity. In all cases, the properties of interest are associated with a *change* in **P**.

Even though the polarization is *in principle* non-unique, in practice it is often (not always) defined by convention in a specific, unique way. For example, in a perfectly centrosymmetric crystal, **P** is usually defined by convention to be exactly zero. As another example, in a ferroelectric crystal, there is typically a centrosymmetric configuration above the Curie temperature, and **P** is defined there by convention to be zero. As the crystal is cooled below the Curie temperature, it shifts gradually into a more and more non-centrosymmetric configuration. Since gradual changes in **P** are uniquely defined, this convention gives a unique value of **P** for the ferroelectric crystal, even below its Curie temperature.

#### 5.7 See also

- Crystal structure
- Electret
- Polarization (disambiguation)

#### 5.8 References and notes

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