

Polarization

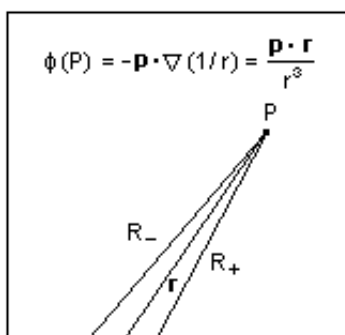
The influence of matter on the electric field

The electromagnetic field in the absence of matter, that is, in the "vacuum," is excellently described classically by Maxwell's theory, which is relativistically correct, in terms of the fundamental field vectors \mathbf{E} and \mathbf{B} . There is an equally successful quantum field theory. In both cases, however, we must introduce sources of the field, and these sources lie in matter, the rigorous description of which is extremely difficult. In Maxwell's theory, charge is introduced as the source of the electromagnetic field, and is idealized to point and continuous distributions. Matter is separated into conductors and dielectrics depending on whether the fields can penetrate into the matter. Conductors carry free charges that move to positions of equilibrium in response to the fields, but cannot leave the matter. Dielectrics are presumed to contain bound charges that cannot move freely, but can shift positions when in the presence of the field, which exerts forces upon them, producing polarization, and nonuniform polarization gives rise to new sources of the field. Simple laws are postulated to account for these effects, such as the dielectric constant κ that relates the \mathbf{D} and \mathbf{E} vectors: $\mathbf{D} = \kappa\mathbf{E}$ (we'll define these vectors later, but they are probably familiar to you). This theory is called *phenomenological* because all the parameters are empirical, and are not defined in terms of the constitution of the matter.

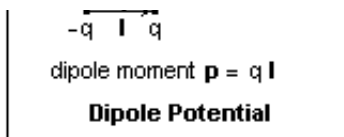
We will freely use vector calculus here, since it makes the description of vector fields convenient and easy. Since browsers do not support the symbol ∇ (inverted triangle), I'll use the older terms grad (del), div (del dot), curl (del cross) and div grad (del squared) instead in the text. The *divergence theorem* says that the volume integral of the divergence of a vector through a region is equal to the surface integral of its normal component over the boundary of the region. We will use the divergence theorem to "integrate by parts" and transform an integral into a different form.

The problem to be discussed here is the determination of these empirical parameters in terms of the molecular constitution of matter, especially the dielectric constant, historically the first such parameter to be studied, even before the appearance of Maxwellian electrodynamics. This is a huge area of study, and we will only discuss the first step in it, for the simple case of electrostatics, and its extension to electromagnetic waves. The general problem is so complicated that there is no comprehensive, relativistically correct description of the electromagnetic field in matter, although practically a great deal is known, especially in the nonrelativistic case.

The "real" electric field in vacuum is \mathbf{E} , giving the force on a point charge q in vacuum: $\mathbf{F} = q\mathbf{E}$. It is a vector field, obeying the differential laws $\text{div } \mathbf{E} = 4\pi\rho$ and $\text{curl } \mathbf{E} = 0$, where ρ is the charge density. This leads to the expressions $\mathbf{E} = -\text{grad } \phi$, $\phi = \int \rho dV/R$, where ϕ is the scalar potential, and R is the distance from the charge element ρdV to the point P where the potential is desired. If we know the charge distribution we can, in principle, find the electric field at any point in this way. A point charge q produces a potential $\phi = q/R$, and so the electric field is $\mathbf{E} = -q \text{grad}(1/R) = (q/R^3)\mathbf{R}$, in the direction of \mathbf{R} , a vector from the source point to the observation point.



Equal and opposite charges $\pm q$ separated by a distance l directed from the negative charge to the positive charge make a finite dipole of dipole moment $\mathbf{p} = q\mathbf{l}$, as shown in the figure. The potential produced by this pair of charges is $\phi = q/R(+)$ - $q/R(-)$, where $R(\pm)$ are the distances from the charges to the observation point. The vector \mathbf{R} or \mathbf{r} points from the dipole to the observation point. We can approximate this difference by differentiating the potential of a point charge: $\phi = -\text{grad}(1/R) \cdot q \mathbf{l} = \mathbf{p} \cdot \mathbf{R}/R^3$. If we idealize the dipole to a point dipole by letting $q \rightarrow \infty$ and $l \rightarrow 0$ in such a way that \mathbf{p} remains constant, then this expression is exact. Such a point dipole is a very good approximation to a finite dipole if we consider observation



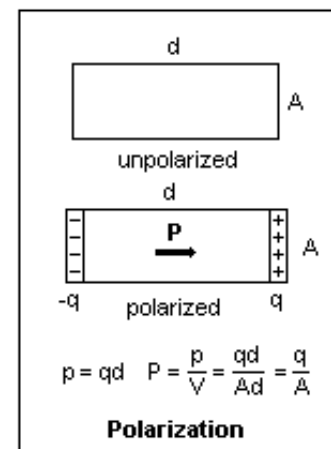
points at a distance much larger than the actual separation of the charges.

If a charge density ρ and a dipole density \mathbf{P} are considered as the sources of the field, then the potential is given by $\phi = \int [\rho/R + \mathbf{P} \cdot \text{grad}(1/R)] dV$. The second term can be cast into a different form by using the vector relation $\text{div}(\mathbf{P}/R) = \mathbf{P} \cdot \text{grad}(1/R) + \text{div}\mathbf{P}/R$ to integrate the dipole part of this expression by parts. Then $\phi = \int -\text{div}\mathbf{P} dV/R + \int \text{div}(\mathbf{P}/R) dV$. The second integral is equal to the surface integral (by the divergence theorem), which vanishes when all space is considered, since \mathbf{P} is zero at infinity. Now the potential is $\phi = \int [\rho - \text{div}\mathbf{P}] dV/R$, which shows that $-\text{div}\mathbf{P}$ is equivalent to charge density.

Therefore, we now find that $\text{div}\mathbf{E} = 4\pi\rho - 4\pi \text{div}\mathbf{P}$, so that $\text{div}(\mathbf{E} + 4\pi\mathbf{P}) = 4\pi\rho$. This shows that a new field, $\mathbf{D} = \mathbf{E} + 4\pi\mathbf{P}$, can be defined that has divergence only at "free" charge ρ , like the original \mathbf{E} without polarization. Polarization provides "bound" charge $\rho' = -\text{div}\mathbf{P}$. This new field, called the *displacement*, is found to have useful properties, usually involving different boundary conditions than those applying to \mathbf{E} . In free space, there is no polarization, so there $\mathbf{D} = \mathbf{E}$.

\mathbf{D} satisfies the equation $\text{div}\mathbf{D} = 4\pi\rho$. If there is no free charge, $\rho = 0$, then taking the divergence of \mathbf{D} we find $\text{div}\mathbf{E} = -4\pi\text{div}\mathbf{P} = 4\pi\rho'$, an easy way to remember the charge resulting from nonuniform polarization. At a boundary between two media where there is no free charge on the boundary, the normal component of \mathbf{D} is continuous, while the normal component of \mathbf{E} has a jump of 4π times the jump in polarization.

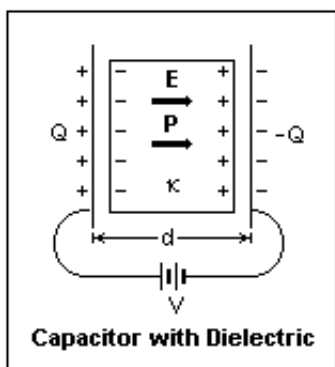
An illustration of these things is shown in the figure at the right. At the top there is a cylinder of length d and end area A , with superimposed equal uniform densities of positive and negative charge, so that there is no external field. This is the case in ordinary matter, where the positive and negative charges cancel, though the total amounts of each is very large, and the matter is said to be *unpolarized*. Now imagine the positive charge moved slightly with respect to the negative charge, so that positive charge of amount q is uncovered at the right, and negative charge of amount $-q$ at the left. The total dipole moment that results is qd (d is the length of the cylinder, not the displacement of the charge!). The polarization \mathbf{P} is the dipole moment per unit volume, $qd/V = q/A$. \mathbf{P} is uniform throughout the cylinder. It has a discontinuity in the normal component of $-\mathbf{P} = -q/A$ at the right face, which is accompanied by a surface bound charge density of q/A . The discontinuity of $+\mathbf{P}$ at the left face is accompanied by a bound charge density of $-q/A$. The normal component of \mathbf{P} is equivalent to a surface charge density, $P_n = \sigma'$. At the lateral surfaces, there is a discontinuity of the transverse component of \mathbf{P} , but this is accompanied by no surface charge density.



A body such as this with a permanent polarization \mathbf{P} is called an *electret*, by analogy with "magnet." Actual electrets, left exposed, will attract stray charges from the surroundings, which will soon neutralize the surface charges. Magnets do not have this problem, since there are no free magnetic charges. Some crystals have this property of retaining polarization, as permanent magnets retain magnetism. Most materials do not, however, and polarization is produced only by an electric field in the material. Such materials are called *dielectrics*, since electric fields pass through them, in distinction to conductors. There are no free charges in a dielectric that move when an electric field is applied, to a good approximation.

The charge in a dielectric is in its molecules, where strong electric forces hold the light electrons and the heavy nuclei closely together. An external field moves these charges slightly, separating the positive and negative charges to produce polarization. The usual external fields are much smaller than the molecular fields, so to a good approximation the charge separation is proportional to the applied external field. This is expressed by $\mathbf{P} = \chi\mathbf{E}$, where the constant χ is the *susceptibility*. The relation between polarization and applied field can be much more complicated than this, even involving the time, but this simplest case covers most applications. Then, $\mathbf{D} = \mathbf{E} + 4\pi\chi\mathbf{E} = \kappa\mathbf{E}$, where κ is the *dielectric constant*. It is clear that κ expresses properties of matter in relation to the

electric field, and is not fundamental.

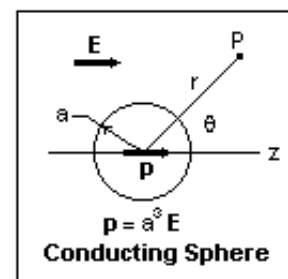


The capacitor with dielectric shown in the diagram at the left is a familiar example. The space between the plates and the dielectric is exaggerated; they should both be considered a distance d apart, and of area A . The applied voltage V produces an electric field of magnitude $E = V/d$ between the plates, whether the dielectric is present or absent. This means that the net surface charge density on the plates is $E/4\pi$. If there is no dielectric, this is the actual free charge density on the plates, supplied by the battery. In the presence of the dielectric, $D = \kappa E$ (since all the vectors are parallel, we work with the magnitudes only), and $P = \chi E$. The free charge density on the plates is $D/4\pi$ or $\kappa E/4\pi$, κ times what it was in the absence of the dielectric. The total charge on the plates is $Q = \kappa AV/4\pi d = (\kappa A/4\pi d)V = CV$, where the *capacitance* is $C = \kappa A/4\pi d$.

We can look at this another way. The bound charge density is $\sigma' = P_n = \chi E$, while the net charge density is $\sigma'' = E/4\pi$. Hence, the free charge density on the plates is $\sigma = E/4\pi + \chi E = (1 + 4\pi\chi)E/4\pi = \kappa E/4\pi$, the same as we found above using D . Note that the field used in χE is the actual field in the dielectric, produced by both free and bound charge, not just the field produced by the free charge. The electric field in the narrow region between the plate and the dielectric is larger than E ; in fact, it is $\kappa E = D$.

The polarization P is the sum of the polarizations of the individual molecules in unit volume: $P = Np$, where N is the number of molecules per unit volume, and p is the dipole moment of each molecule. For simplicity, we consider that there is only one kind of molecule, and that p is induced by the field that the molecule finds itself in. Molecules with permanent dipole moments, like water, are excluded here, because they require special treatment. If E' is the field at the molecule, then $p = \alpha E'$, where α is the *molecular polarizability*. We will consider only the simplest case when α is a scalar, so that p and E' are in the same direction, and further that α is independent of frequency.

The meaning of the molecular polarizability can be made clearer by considering the dipole moment induced in a conducting sphere of radius a by an applied field E , as illustrated at the right. This is a standard potential problem, in which the potential satisfies $\text{div grad } \phi = 0$ (this is the Laplacian, del squared), since there is no free charge or polarization in the space where we desire the potential. We know the solutions for this simple geometry, and try the function $\phi = -Ar \cos\theta + B \cos\theta/r^2$. If it satisfies the boundary conditions, then it is the solution. First, we see that $A = E$, so at large distances the potential is $-Ez$, where $z = r \cos\theta$, appropriate for the uniform applied field. Next, ϕ must be constant (independent of θ) when $r = a$, which means that $-Ea + B/a^2 = 0$, or $B = Ea^3$. Finally, $\phi = -Ez + p \cos\theta/r^2$, which is just the superimposed field of a uniform applied field and a dipole field from a dipole of magnitude $p = Ea^3$. The polarizability of a conducting sphere is, therefore, a^3 . This gives us an idea of what the size of the molecular polarizability will be, about the cube of the molecular dimensions.



Now we wish to relate the molecular polarizability to the susceptibility and dielectric constant, which are experimentally measurable. If we consider a molecule in the dielectric of the capacitor discussed above, we might assume that the field E' experienced by a molecule is the field E . However, this is not a valid assumption. E is the average field in the dielectric, which can be related to the applied voltage, but it does not reflect the possibly large variations in the field produced by the discrete molecules. The molecule we have under consideration is surrounded by many others which may change the local field. In a gas the molecules are moving at random, and in a crystal they occupy the lattice sites. Liquids are an intermediate case. In both these cases, it can be shown that the average fields produced by the neighbors of the molecule under consideration are zero. This is not always true, but is true for most substances.

We can, therefore, imagine a spherical region surrounding the molecule to be removed from the dielectric without affecting the local field. This region must be spherical to retain the symmetry. Its size is indefinite, but can be chosen large enough that the rest of the dielectric can be considered as a continuum, if the result does not depend on the size of the sphere. When this region is removed, the polarization now has a discontinuity on the remaining surface of the dielectric, and the resulting bound charge creates a field that represents the net effect of the other molecules of the dielectric on the one in question. This field must be added to the average field to find the effective field E' .

This is a standard potential problem, which we could solve in the same way that we did the problem of the conducting sphere in a uniform field. We assume a dipole field outside the cavity, and a uniform field inside the cavity, and then apply the boundary conditions. However, we will follow a somewhat different method suggested by Born and Wolf (and not too well explained there). Let the potential in the problem of the field produced by the removed sphere be ϕ' , and the potential we are seeking ϕ . If we superimpose these solutions, we find the solution for the undisturbed dielectric, $\phi = 0$. Therefore, $\phi = -\phi' = -\int \mathbf{P} \cdot \text{grad}'(1/R) dV'$, where we are integrating over the primed coordinates. Now, $\text{grad}'(1/R) = -\text{grad}(1/R)$ (since the coordinates appear as $x - x'$, etc., in R), and we can take the gradient outside the integral sign to get $\phi = \mathbf{P} \cdot \int dV'/R = -\mathbf{P} \cdot \text{grad} \phi''$, where ϕ'' is the potential of a sphere of uniform charge density -1 , a problem we can easily solve by direct integration or Gauss's Law.

By Gauss's Law, we find that the radial field inside the sphere is $-(4\pi/3)r$, so that $\phi = \mathbf{P} \cdot \mathbf{E}'' = -P(4\pi/3)z$, and the field is $-(d/dz)\phi = 4\pi P/3$, where we have taken the z -direction in the direction of \mathbf{P} . Therefore, the effective field is $\mathbf{E}' = \mathbf{E} + (4\pi/3)\mathbf{P}$. The result is independent of the size of the removed sphere, as it should be. Now we have $\mathbf{p} = \alpha \mathbf{E}'$, or $\mathbf{P} = N\alpha(\mathbf{E} + 4\pi\mathbf{P}/3)$. If we solve for \mathbf{P} , then $\mathbf{P} = [N\alpha/(1 - 4\pi N\alpha/3)]\mathbf{E}$, and we have found the susceptibility in terms of the molecular polarizability.

The dielectric constant $\kappa = 1 + 4\pi\chi = (1 + 8\pi N\alpha/3)/(1 - 4\pi N\alpha/3)$, from which $(4\pi/3)N\alpha = (\kappa - 1)/(\kappa + 2)$. A relation like this was first obtained by Mossotti in 1850, then by Lorenz in 1869, and refined by Clausius in 1879, and which is usually called the Clausius-Mossotti equation. Polarizable matter was modeled as an assembly of small conducting spheres (we found the polarizability of such bodies above) in the early studies. Maxwell's theory showed that the index of refraction of light, n , was related to κ by $n^2 = \kappa$, so that the formula could be applied to light as well as to static fields. H. A. Lorentz, in 1878, and L. V. Lorenz (1829-1891), in 1881, derived a similar formula on the basis of the electron theory in which n^2 replaced κ . This formula is called the Lorentz-Lorenz formula. It was a very important step in relating Maxwell's phenomenological theory to the molecular structure of matter. Lorenz was a Danish physicist with a name strikingly similar to Lorentz's.

We note that the presence of polarization encourages further polarization, cooperatively, since the effective field $\mathbf{E}' = \mathbf{E} + (4\pi/3)\mathbf{P}$ increases with \mathbf{P} . In fact, if the quantity $4\pi N\alpha/3$ approaches 1, κ increases without limit. The material then "locks in" to a state of permanent polarization (as in an electret). This actually happens for some crystals, called ferroelectrics, and is analogous to permanent magnetic polarization in ferromagnetic substances. For $n = 1.5$, $4\pi N\alpha/3$ is about 0.3, so significant cooperation is a normal thing.

The quantity $A = (4\pi/3)N_A\alpha$, where N_A is Avogadro's Number, 6.02×10^{23} , is called the *molar refractivity*. The factor $(4\pi/3)$ is included just to take it out of subsequent relations. Aside from this, it is simply the polarizability per mole. We have $A = (N/N_A$

$\chi)(n^2 - 1)/(n^2 + 2)]$, where N is the number of molecules per unit volume. The factor (N/N_A) can be written M/d , where M is the molecular weight and d is the density, or, for ideal gases, as RT/p . It is simply the volume in cm^3 occupied by a gram-mole of the substance (22,400 cc at STP). For p in atmospheres, $R = 82.057 \text{ atm-cc/K}$ is convenient. The molar refractivity remains remarkably constant as the density or

pressure is varied, even when there is a change of state. It even works for water (a polar molecule), for which $M = 18$ g, $d = 1.0$ g/cc, and $n = 1.334$. This gives $A = 3.71$, and the same value is found for water vapor. It holds as well for mixtures, when the separate values of A are weighted by the relative number of molecules. It is possible to assign atomic refractivities for various atoms, and then add them up to find the molar refractivity. For example, the atomic refractivity of oxygen is 2.01, and that of hydrogen 1.02, so the molar refractivity of water is predicted to be $2.01 + 2 \times 1.02 = 4.05$, surprisingly close to the actual value of 3.71. The atomic refractivity of carbon is 2.11, sulphur 8.23 and chlorine 5.72, so the molar refractivities of many organic compounds can be estimated.

As a random example, the substance octane, $(\text{CH}_3)(\text{CH}_2)_6(\text{CH}_3)$, was chosen in the Handbook of Chemistry and Physics, where $M = 114.23$ g, $d = 0.7025$ g/cc and $n = 1.3974$ for NaD light at 20° C were found. These figures give $A = 39.19$. This reference gives the atomic refractivities as $C = 2.591$ and $H = 1.028$. From these we find that $8 \times 2.591 + 18 \times 1.028 = 39.23$, which is remarkably close agreement.

For gases, where $n \approx 1$, $\alpha = (n^2 - 1)/4N$ and $A = (RT/p)(n^2 - 1)/3$, approximately. For air at 0°C and 1 atm, $n = 1.0002926$ (Handbook of Chemistry and Physics, p. E-224). This gives $A = 4.37$. The relatively large value is due to the N-N triple bond.

Note on Units

I have used cgs (Gaussian) units here, as do the principal references. Although the units used are immaterial, Gaussian units do not involve arbitrary changes of units without physical significance. Conversion to practical units is easily made when necessary. The Giorgi (MKS) units used in engineering are only the cgs absolute magnetic units with assorted factors of 10, with the confusing unit changes brought about by the constants ϵ_0 and μ_0 , which are merely composed of factors of 4π , 10 and the speed of light c .

To work with Gaussian units, a few defining equations such as $E = q/r^2$, $\phi = q/r$ and $F = qE$ help to keep units straight. Charge q is in statcoulomb, usually called e.s.u., and one e.s.u. is $10/c$ coulomb. Here, $c = 3 \times 10^{10}$ cm/s (approximately). The charge q is divided by c in all matters concerned with current in the Gaussian system. The force F is in dyne = $\text{gm-cm/s}^2 = 10^{-5}$ N, and energy is in erg = dyne-cm. 1 erg is 10^{-7} J. The unit of ϕ , the statvolt, or e.s.u., is 1 erg/statcoulomb or $300 (c/10^7)$ volts. The unit of capacity, the statfarad, is 1 statcoulomb/statvolt, or $10^9/c^2$ F. This makes an e.s.u. of capacity equal to about 1.11 μF , so this unit is a very practical size, unlike the farad. With the help of these factors, all quantities discussed above can be converted to practical units.

Our equation $D = E + 4\pi P$ implies that D , E and P all have the same units. This is easy to check, since Coulomb's law gives $[E] = \text{statcoulomb/cm}^2$, which should be the same as dyne/statcoulomb, as $F = qE$ shows. $[P] = \text{statcoulomb-cm/cm}^3$, from its definition, and this likewise is statcoulomb/cm^2 . Finally, the normal component of D is a surface charge density, which again is statcoulomb/cm^2 . From $F = qE = q^2/r^2$, we can find the dimensions of statcoulomb in terms of the centimeter (L), gram (M) and second (T). $[q^2] = (\text{gm-cm/s}^2)(\text{cm}^2)$, or $[q] = \text{M}^{1/2}\text{L}^{3/2}\text{T}^{-1}$. Now the dimensions of any quantity can be found, and conversions to any system of units carried out. Be aware, though, that different definitions in Gaussian and Giorgi units introduce some hazards.

Since D , E and P all have the same units, equations like $P = \chi E$ are easy to interpret, and χ is dimensionless. In magnetism, Giorgi units make H the basic magnetic vector, by analogy with E , but this is a very unfortunate choice, since B and E are actually analogous, and H and D . This has created such great confusion that many

workers have reverted to e.m.u. for magnetic problems. There is no substantive difference, of course, just confusion. No such confusion arises when we write $B = H + 4\pi M$ in Gaussian units, since it is the same as writing $H = B - 4\pi M$ to define H, by analogy to the definition of D electrically. Now B has all the sources, while those arising from magnetization are subtracted to get H. In $D = E + 4\pi P$, E has all the sources, and those arising from polarization are subtracted to get D (remember that bound charge is $-\text{div } P$). There is more to be said about magnetism, but this shows the analogy with electricity.

References

M. Born and E. Wolf, *Principles of Optics* (London: Pergamon Press, 1959). Chapter 2.

J. D. Jackson, *Classical Electrodynamics*, 2nd ed. (New York: John Wiley & Sons, 1975). Chapter 4. The third edition, I understand, uses Giorgi units, a regrettable concession to fashion.

M. Abraham and R. Becker, *Classical Electricity and Magnetism* 2nd ed. (New York: Hafner, 1949). This classic text, also reprinted by Dover, is still the best concise introduction to vector fields and electromagnetism, on an intermediate undergraduate level, beginning with an introduction to vectors and vector fields. Many more recent texts contain too much material, some of which is not even correct.

Handbook of Chemistry and Physics, 56th ed. (Cleveland, OH: Chemical Rubber Press, 1975). Page E-223, E-224.

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