Unit 3: Macroscopic Maxwell's Equations in Matter

In this unit we discuss the behavior of electric and magnetic fields in dielectric and magnetic materials. So that we do not have to explicitly treat all the charged particles that comprise the material, we will do an averaging on length scales large on the atomic scale, but small on the macroscopic scale, to arrive at an effective set of equations known as the Macroscopic Maxwell Equations. In this process we will introduce the polarization density $\mathbf{P}$ and the magnetization density $\mathbb{M}$ that characterize the average response of the material to electric and magnetic fields, and show that these describe the *bound* charges and currents that arise from the charged particles out of which the material is made. We will use those to define the electric displacement field $\mathbf{D}$ and the magnetic field $\mathbf{H}$, and then discuss *linear materials* in which $\mathbf{P}$ and $\mathbb{M}$ are linearly proportional to the electric and magnetic fields in the material.

Unit 3-1: Dielectric Materials: Polarization Density P, Electric Displacement Field D, Bound Charge

Maxwell's equations apply exactly to the true microscopic electric and magnetic fields that arise from *all* charges and currents in the system. In this unit we will use lower case letters $\mathbf{e}$ and $\mathbf{b}$ for these exact microscopic fields. The microscopic Maxwell's equation are:

$$\boldsymbol{\nabla} \cdot \mathbf{b} = 0 \qquad \boldsymbol{\nabla} \times \mathbf{e} + \frac{1}{c}\frac{\partial \mathbf{b}}{\partial t} = 0 \tag{3.1.1}$$

$$\boldsymbol{\nabla} \cdot \mathbf{e} = 4\pi \rho_0 \qquad \boldsymbol{\nabla} \times \mathbf{b} = \frac{4\pi}{c}\mathbf{j}_0 + \frac{1}{c}\frac{\partial \mathbf{e}}{\partial t} \tag{3.1.2}$$

where ρ_0 and $\mathbf{j}_0$ are the microscopic charge and current densities, that represent *all* charges in the system, including those in the atoms and molecules out of which the macroscopic material is made.
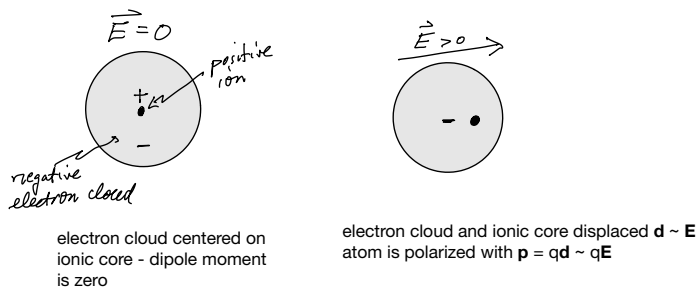
However, in most problems involving macroscopic materials (gases, liquids, solids), if we used the microscopic ρ_0 and $\mathbf{j}_0$, the resulting fields $\mathbf{e}$ and $\mathbf{b}$ would be enormously complicated functions, varying rapidly over atomic distances $\sim 10^{-8}$cm and atomic times $\sim 10^{-16}$sec.

In classical E&M we are generally concerned only with phenomena that vary slowly compared to these atomic scales. Rather than worry about the microscopic details of ρ_0 and $\mathbf{j}_0$ and the resulting $\mathbf{e}$ and $\mathbf{b}$, we want to describe phenomena in terms of averaged quantities that are smoothly varying at the atomic scale. This results in what are known as the *Macroscopic Maxwell Equations*.

Dielectric Materials

In the discussion here we will refer to the basic building blocks of the material as "atoms", although for some materials they would be better thought of as "molecules". A dielectric material is an insulator (can be solid, liquid, or gas), in which the valence electrons remain bound to the ionic cores of the atoms out of which the material is made. These atoms are in general charge neutral. When there is no electric field present, the ρ from these atoms, when averaged over an atomic length scale, therefore *vanishes*. One might therefore think that electrodynamics in such a dielectric material is just due to whatever "extra" or "free" charge is added to the material. However this is not the case due to the phenomena of *polarization*.

Inspired by our understanding from quantum mechanics, we will take as a simple model for an atom a positive point charge for the nucleus, and a spherical cloud of negative charge for the valence electron. When no electric field is present, the center of charge of the electron cloud sits on top of the nucleus. The atom therefore has no net charge and no net electric dipole moment. However, when an electric field $\mathbf{E}$ is applied to the atom, the nucleus and the electron cloud feel a force from the electric field that pushes them in opposite directions. The atom develops a non-zero electric dipole moment $\mathbf{p} \propto \mathbf{E}$. We say that the atom has been *polarized*.

electron cloud centered on
ionic core - dipole moment
is zero

electron cloud and ionic core displaced **d** ~ **E**
atom is polarized with **p** = q**d** ~ q**E**

We define the vector *polarization density* **P** as the density of electric dipole moments in the system,

$$\mathbf{P}(\mathbf{r}, t) = \sum_i \mathbf{p}_i \delta(\mathbf{r} - \mathbf{r}_i(t)) \tag{3.1.3}$$

where $\mathbf{p}_i$ is the dipole moment of atom i at position $\mathbf{r}_i$.

The polarization density **P** can give rise to regions of net charge in the material – this is called *bound charge* because it arises from the charges that are bound together in the atoms that make up the material. To see how this bound charge comes about from the polarization of atoms, consider the sketches below. In these sketches, the left column diagrams illustrate the charge configurations at the atomic scale, while the right column diagrams illustrate the macroscopic charge configurations obtained by averaging over the atomic scale.
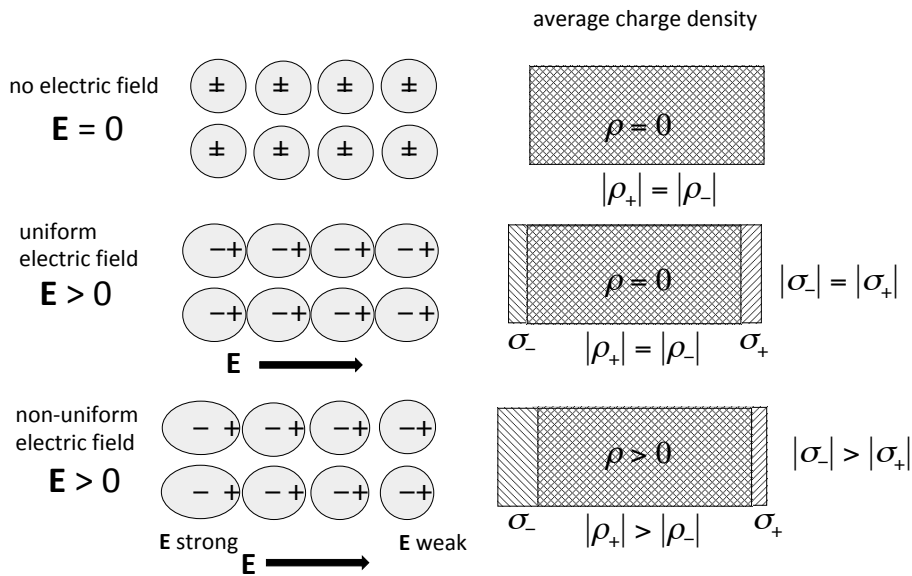
The top row corresponds to the case of zero electric field. Atoms are neutral and unpolarized. The average charge densities of the ions ρ_+ and the electronic clouds ρ_- are equal in magnitude but opposite in sign, and so cancel, and the resulting average net charge density $\rho = 0$ everywhere.

The middle row corresponds to the case of a uniform **E** field pointing in the horizontal direction. The atoms get polarized, with each atom acquiring the same dipole moment **p**. The ions are heavy and don't move much, while the electron clouds all shift to the left by the same amount. The result is the build up of a negative surface charge σ_- on the left side of the material, and a positive surface charge σ_+ on the right side of the material. Since the electron clouds all move the same amount, these surface charges are equal in magnitude $|\sigma_-| = |\sigma_+|$, and in between the average charge density remains neutral, $\rho = \rho_- + \rho_+ = 0$.

The bottom row corresponds to the case of a non-uniform **E** in the horizontal direction, with the magnitude of **E** being larger on the left side of the material than on the right side. Again, the ions are heavy and don't move much, while the electron clouds all shift to the left. But now the electron clouds on the left side of the material, where **E** is

stronger, shift a greater distance than those on the right side, where $\mathbf{E}$ is weaker. The atoms on the left side of the material therefore acquire a larger dipole moment $\mathbf{p}$ than those on the right side. Moreover, since the electron clouds move a greater distance the further one goes to the left in the material, the average negative electron charge gets stretched out over a larger volume than is the average positive ion charge. Thus the average negative charge density inside the material is smaller in magnitude than the average positive charge density, $|\rho_-| < |\rho_+|$, and the material develops a net positive charge density in its interior, $\rho = \rho - +\rho_+ > 0$. The sides of the material develop surface charges, similar to the case of a uniform electric field, but now the magnitude of the negative surface charge on the left side must be greater than the magnitude of the positive surface charge on the right side, $|\sigma_-| > |\sigma_+|$. This is because there is now less negative charge in the interior, so that missing charge piles up on the left side.

What we see is the following. When the atoms polarize, there develops a polarization density $\mathbf{P} \propto \mathbf{E}$ in the material. This $\mathbf{P}$ results in a surface charge density σ building up on the boundaries of the material. If $\mathbf{P}$ is non-uniform, there may also develop a net volume charge density ρ within the material. We call these surface and volume charge densities that arise from $\mathbf{P}$ the *bound charge*, and denote them as σ_b and ρ_b.

The above picture was for sufficiently symmetric atoms or molecules which do not have an electric dipole moment unless an applied electric field polarizes them. There are other materials in which the constituent molecules do have an intrinsic electric dipole molecule even when $\mathbf{E} = 0$. An example is the water molecule H_2O, where the dipole moment points from the oxygen atom towards the hydrogen atoms. But in these materials the molecules are usually oriented with their dipole moments in random directions, so when $\mathbf{E} = 0$, the net dipole moment when averaged over many atomic length scales will vanish. However when a finite $\mathbf{E}$ is applied, it tends to orient the electric dipoles in a parallel direction, so again one finds a net $\mathbf{P} \propto \mathbf{E}$. The exception to this scenario is for materials called ferroelectrics, in which the constituent particles have a net electric dipole moment *and* those dipole moments tend to orient in a common direction even when $\mathbf{E} = 0$; this is similar to a ferromagnetic in which intrinsic magnetic moments orient in a common direction even when $\mathbf{B} = 0$.

Spatial Averaging over Atomic Length Scales

We now want to carry out mathematically the procedure of spatially averaging the microscopic fields $\mathbf{e}$ and $\mathbf{b}$, and microscopic charge and current densities ρ_0 and $\mathbf{j}_0$, over atomic length scales, to arrive at the average macroscopic quantities that will be used in the Macroscopic Maxwell's Equations.

We define spatially averaged quantities by,

$$\langle F(\mathbf{r}, t) \rangle = \int d^3r' \, f(\mathbf{r}') \, F(\mathbf{r} - \mathbf{r}', t) \qquad (3.1.4)$$

where $f(\mathbf{r})$ is the averaging function that vanishes when $|\mathbf{r}|$ is large on microscopic length scales, but is finite when $|\mathbf{r}|$ is small on macroscopic length scales. The averaging function is normalized so that $\int d^3r \, f(\mathbf{r}) = 1$. Other specific details of $f(\mathbf{r})$ are unimportant, as long as $f(\mathbf{r})$ is a smooth function of $\mathbf{r}$. We can imagine that $f(\mathbf{r})$ has the qualitative form as sketched below, where R is a length large on the microscopic scale, but small on the macroscopic scale.

$$f \approx \text{constant for } r < R$$
$$f \approx 0 \quad \text{for } \quad r \gg R$$
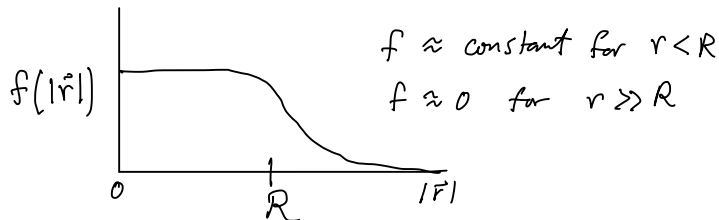
We then have for spatial and temporal derivatives,

$$\frac{\partial}{\partial r_i} \langle F(\mathbf{r}, t) \rangle = \int d^3r' \, f(\mathbf{r}') \, \frac{\partial F(\mathbf{r} - \mathbf{r}', t)}{\partial r_i} = \left\langle \frac{\partial F}{\partial r_i} \right\rangle \qquad (3.1.5)$$

$$\frac{\partial}{\partial t} \langle F(\mathbf{r}, t) \rangle = \left\langle \frac{\partial F}{\partial t} \right\rangle \qquad (3.1.6)$$

Macroscopic Fields

We now define the macroscopic electric and magnetic fields,

$$\mathbf{E}(\mathbf{r}, t) \equiv \langle \mathbf{e}(\mathbf{r}, t) \rangle, \qquad \mathbf{B}(\mathbf{r}, t) \equiv \langle \mathbf{b}(\mathbf{r}, t) \rangle \tag{3.1.7}$$

We can then write for the homogeneous Maxwell equations (the ones without any source terms),

$$\boldsymbol{\nabla} \cdot \mathbf{b} = 0 \quad \Rightarrow \quad \langle \boldsymbol{\nabla} \cdot \mathbf{b} \rangle = 0 \quad \Rightarrow \quad \boldsymbol{\nabla} \cdot \langle \mathbf{b} \rangle = 0 \quad \Rightarrow \quad \boldsymbol{\nabla} \cdot \mathbf{B} = 0 \tag{3.1.8}$$

$$\boldsymbol{\nabla} \times \mathbf{e} + \frac{1}{c} \frac{\partial \mathbf{b}}{\partial t} = 0 \quad \Rightarrow \quad \left\langle \boldsymbol{\nabla} \times \mathbf{e} + \frac{1}{c} \frac{\partial \mathbf{b}}{\partial t} \right\rangle = 0 \quad \Rightarrow \quad \boldsymbol{\nabla} \times \langle \mathbf{e} \rangle + \frac{1}{c} \frac{\partial \langle \mathbf{b} \rangle}{\partial t} = 0 \quad \Rightarrow \quad \boldsymbol{\nabla} \times \mathbf{E} + \frac{1}{c} \frac{\partial B}{\partial t} = 0 \tag{3.1.9}$$

So the homogeneous Macroscopic Maxwell Equations look just like the microscopic ones, except we replace the microscopic $\mathbf{e}$ and $\mathbf{b}$ with the macroscopic $\mathbf{E}$ and $\mathbf{B}$.

The inhomogeneous Maxwell equations become,

$$\boldsymbol{\nabla} \cdot \mathbf{E} = 4\pi \langle \rho_0 \rangle, \qquad \boldsymbol{\nabla} \times \mathbf{B} = \frac{4\pi}{c} \langle \mathbf{j}_0 \rangle + \frac{1}{c} \frac{\partial \mathbf{E}}{\partial t} \tag{3.1.10}$$

All the work in deriving the Macroscopic Maxwell Equations will now go into determining the average charge density $\langle \rho_0 \rangle$ and the average current density $\langle \mathbf{j}_0 \rangle$. In this section we will focus on computing $\langle \rho_0 \rangle$.

Average Charge Density, Polarization Density, Electric Displacement Field

The microscopic charge density is

$$\rho_0 = \sum_i q_i \delta(\mathbf{r} - \mathbf{r}_i(t)) \tag{3.1.11}$$

Consider dividing the charges into "free" charges and "bound" charges, where the latter are associated with the atoms or molecules that make up the dielectric.

$$\rho_f = \sum_{i \in \text{free}} q_i \delta(\mathbf{r} - \mathbf{r}_i(t)), \qquad \rho_b = \sum_n \rho_n(\mathbf{r}, t) \tag{3.1.12}$$

Here q_i are the free charges (i.e., the external charges added to the system) at positions $\mathbf{r}_i$, and $\rho_n(\mathbf{r}, t)$ is the charge distribution associated with atom or molecule n of the dielectric. We can write ρ_n in terms of the individual charges that make up atom or molecule n,

$$\rho_n(\mathbf{r}, t) = \sum_{i \in n} q_i \delta(\mathbf{r} - \mathbf{r}_i(t)) \qquad \text{where the sum is over all charges } q_i \text{ at positions } \mathbf{r}_i \text{ in atom } n \tag{3.1.13}$$

Now we will do the spatial averaging.

$$\langle \rho_n(\mathbf{r}, t) \rangle = \int d^3 r' \, f(\mathbf{r}') \, \rho_n(\mathbf{r} - \mathbf{r}', t) = \sum_{i \in n} q_i \int d^3 r' \, f(\mathbf{r}') \, \delta(\mathbf{r} - \mathbf{r}' - \mathbf{r}_i(t)) = \sum_{i \in n} q_i f(\mathbf{r} - \mathbf{r}_i(t)) \tag{3.1.14}$$

Now we write the position $\mathbf{r}_i$ of charge i in atom n in terms of the center of mass position of the atom $\mathbf{r}_n$, and the relative displacement $\mathbf{r}_{ni}$ of i from the center of mass,

$$\mathbf{r}_i = \mathbf{r}_n(t) + \mathbf{r}_{ni}(t) \tag{3.1.15}$$

Then

$$\langle \rho_n(\mathbf{r}, t) \rangle = \sum_{i \in n} q_i f(\mathbf{r} - \mathbf{r}_n - \mathbf{r}_{ni}) \tag{3.1.16}$$

Since the $|\mathbf{r}_{ni}|$ are all on the atomic length scale, and $f(\mathbf{r})$ is slowly varying on this atomic length scale, we can expand the above to write to second order in $\mathbf{r}_{ni}$,

$$\langle \rho_n(\mathbf{r},t)\rangle = \sum_{i\in n} q_i \left[f(\mathbf{r}-\mathbf{r}_n) - [\boldsymbol{\nabla} f(\mathbf{r}-\mathbf{r}_n)]\cdot \mathbf{r}_{ni} + \frac{1}{2}\sum_{\alpha,\beta=1}^{3}\frac{\partial^2 f(\mathbf{r}-\mathbf{r}_n)}{\partial r_\alpha \partial r_\beta}(\mathbf{r}_{ni})_\alpha(\mathbf{r}_{ni})_\beta + \ldots \right] \tag{3.1.17}$$

where r_α denotes the $\alpha=1,2,3$ or x,y,z component of the position vector $\mathbf{r}$. Factoring out the terms that do not depend on q_i, we get,

$$\langle \rho_n(\mathbf{r},t)\rangle = f(\mathbf{r}-\mathbf{r}_n)\left[\sum_{i\in n}q_i\right] - [\boldsymbol{\nabla} f(\mathbf{r}-\mathbf{r}_n)]\cdot \left[\sum_{i\in n}q_i\mathbf{r}_{ni}\right] + \sum_{\alpha,\beta=1}^{3}\frac{1}{6}\frac{\partial^2 f(\mathbf{r}-\mathbf{r}_n)}{\partial r_\alpha \partial r_\beta}\left[\sum_{i\in n}3q_i(\mathbf{r}_{ni})_\alpha(\mathbf{r}_{ni})_\beta\right] + \ldots \tag{3.1.18}$$

We now define

$$q_n \equiv \sum_{i\in n}q_i \qquad\qquad \text{the total charge on atom/molecule } n \tag{3.1.19}$$

$$\mathbf{p}_n \equiv \sum_{i\in n}q_i\mathbf{r}_{ni} \qquad\qquad \text{the dipole moment about the center of mass of atom/molecule } n \tag{3.1.20}$$

$$\overset{\leftrightarrow}{\mathbf{Q}}'_n \equiv \sum_{i\in n}3q_i\mathbf{r}_{ni}\mathbf{r}_{ni} \qquad \text{the quadrupole moment about the center of mass of atom/molecule } n \tag{3.1.21}$$

Note, the quadrupole moment defined above is not quite the same as the quadrupole moment we defined in the electric multipole expansion, because it is lacking the term $-\sum_{i\in n}q_i|\mathbf{r}_{ni}|^2\overset{\leftrightarrow}{\mathbf{I}}$ that is needed to make the quadrupole tensor traceless. Hence we call this $\overset{\leftrightarrow}{\mathbf{Q}}'_n$ rather than $\overset{\leftrightarrow}{\mathbf{Q}}_n$, but still it is a second moment of the charge distribution of the atom/molecule. With these we have

$$\langle \rho_n(\mathbf{r},t)\rangle = q_n f(\mathbf{r}-\mathbf{r}_n) - \mathbf{p}_n\cdot\boldsymbol{\nabla} f(\mathbf{r}-\mathbf{r}_n) + \frac{1}{6}\sum_{\alpha,\beta}\left[\overset{\leftrightarrow}{\mathbf{Q}}'_n\right]_{\alpha\beta}\frac{\partial^2 f(\mathbf{r}-\mathbf{r}_n)}{\partial r_\alpha \partial r_\beta} + \ldots \tag{3.1.22}$$

Now we use $\langle \delta(\mathbf{r}-\mathbf{r}_n)\rangle = f(\mathbf{r}-\mathbf{r}_n)$, which follows by our definition of spatial averaging in Eq. (3.1.4), to write,

$$\langle \rho_n(\mathbf{r},t)\rangle = \langle q_n\delta(\mathbf{r}-\mathbf{r}_n)\rangle - \boldsymbol{\nabla}\cdot\langle \mathbf{p}_n\delta(\mathbf{r}-\mathbf{r}_n)\rangle + \frac{1}{6}\sum_{\alpha,\beta}\frac{\partial^2}{\partial r_\alpha \partial r_\beta}\left\langle \left[\overset{\leftrightarrow}{\mathbf{Q}}'_n\right]_{\alpha\beta}\delta(\mathbf{r}-\mathbf{r}')\right\rangle + \ldots \tag{3.1.23}$$

where the middle term follows from $\boldsymbol{\nabla}\cdot(\mathbf{p}\delta) = \mathbf{p}\cdot\boldsymbol{\nabla}\delta$, since $\mathbf{p}$ is a constant.

Adding up over all atoms/molecules n, we then get for the total average bound charge,

$$\langle \rho_b(\mathbf{r},t)\rangle = \sum_n\langle \rho_n(\mathbf{r},t)\rangle = \left\langle \sum_n q_n\delta(\mathbf{r}-\mathbf{r}_n)\right\rangle - \boldsymbol{\nabla}\cdot\left\langle \sum_n \mathbf{p}_n\delta(\mathbf{r}-\mathbf{r}_n)\right\rangle + \frac{1}{6}\sum_{\alpha,\beta}\frac{\partial^2}{\partial r_\alpha \partial r_\beta}\left\langle \sum_n\left[\overset{\leftrightarrow}{\mathbf{Q}}'_n\right]_{\alpha\beta}\delta(\mathbf{r}-\mathbf{r}')\right\rangle + \ldots \tag{3.1.24}$$

We can now define the average polarization density and the average quadrupole density,

$$\mathbf{P}(\mathbf{r},t) \equiv \left\langle \sum_n \mathbf{p}_n\delta(\mathbf{r}-\mathbf{r}_n(t))\right\rangle, \qquad\qquad \overset{\leftrightarrow}{\mathbf{Q}}'(\mathbf{r},t) \equiv \frac{1}{6}\left\langle \sum_n \overset{\leftrightarrow}{\mathbf{Q}}'_n\delta(\mathbf{r}-\mathbf{r}_n(t))\right\rangle \tag{3.1.25}$$

and so the bound charge can be written as,

$$\langle \rho_b(\mathbf{r},t)\rangle = \left\langle \sum_n q_n\delta(\mathbf{r}-\mathbf{r}_n(t))\right\rangle - \boldsymbol{\nabla}\cdot\mathbf{P}(\mathbf{r},t) + \sum_{\alpha,\beta}\frac{\partial^2}{\partial r_\alpha \partial r_\beta}Q'_{\alpha\beta}(\mathbf{r},t) + \ldots \tag{3.1.26}$$

We now define the *macroscopic charge density* ρ as the sum of the pieces coming from the free charge and from the net charge of the atoms/molecules that comprise the dielectric material,

$$\rho(\mathbf{r}, t) \equiv \left\langle \sum_{i \in \text{free}} q_i \delta(\mathbf{r} - \mathbf{r}_i(t)) \right\rangle + \left\langle \sum_n q_n \delta(\mathbf{r} - \mathbf{r}_n(t)) \right\rangle \tag{3.1.27}$$

Note, in most cases we will have in mind materials in which the constituent atoms/molecules are charge neutral, so $q_n = 0$ and the second term vanishes. In this case the macroscopic charge density is the same as the free charge density.

With the above definitions we can now write for the Macroscopic Gauss' Law,

$$\boldsymbol{\nabla} \cdot \mathbf{E} = 4\pi \langle \rho_0 \rangle = 4\pi \left[\rho - \boldsymbol{\nabla} \cdot \mathbf{P} + \sum_{\alpha, \beta} \frac{\partial^2}{\partial r_\alpha \partial r_\beta} Q'_{\alpha\beta}(\mathbf{r}, t) + \dots \right] \tag{3.1.28}$$

or, rearranging terms,

$$\sum_\alpha \frac{\partial}{\partial r_\alpha} \left[E_\alpha + 4\pi P_\alpha - 4\pi \sum_\beta \frac{\partial}{\partial \beta} Q'_{\alpha\beta} + \dots \right] = 4\pi \rho \tag{3.1.29}$$

This leads to the definition of the *electric displacement vector* $\mathbf{D}$,

$$D_\alpha \equiv E_\alpha + 4\pi P_\alpha - 4\pi \sum_\beta \frac{\partial}{\partial \beta} Q'_{\alpha\beta} + \dots \tag{3.1.30}$$

In terms of $\mathbf{D}$, the Macroscopic Gauss' Law is then,

$$\boxed{\boldsymbol{\nabla} \cdot \mathbf{D} = 4\pi \rho} \tag{3.1.31}$$

In most matrials the quadrupole and higher terms are negligible, and so we can write,

$$\boxed{\mathbf{D} = \mathbf{E} + 4\pi \mathbf{P}} \tag{3.1.32}$$

To see why the quadrupole terms and higher can usually be ignored, consider the following.

Let a_0 be the length scale that characterizes the size of an atom or molecule in the material. Let ℓ be the typical spacing between the atoms or molecules in the material. Let L be the length scale that characterizes the spatial averaging function $f(\mathbf{r})$; so $L \gg a_0$, but L is small on the macroscopic scale.

The dipole moment of an atom is determined by the distance over which the charge in the atom can be separated, so at most $p_n \sim a_0$. Since the volume per atom is roughly $1/\ell^3$, this leads to a polarization density of magnitude $P \sim a_0/\ell^3$. The contribution of $\mathbf{P}$ to the average charge $\langle \rho_0 \rangle$ is then $\boldsymbol{\nabla} \cdot \mathbf{P} \sim (a_0/\ell^3)(1/L) = (a_0/L)(1/\ell^3)$, since by our spatial averaging procedure $\mathbf{P}(\mathbf{r}, t)$ cannot vary on a length scale smaller than L.

In comparison, the quadrupole moment of an atom is at most $Q_n \sim a_0^2$, and so the quadrupole density has a magnitude $Q \sim a_0^2/\ell^3$. The contribution of the quadrupole term to the average $\langle \rho_0 \rangle$ is then $\partial^2 Q/\partial r_\alpha \partial r_\beta \sim (a_0^2/\ell^3)(1/L^2) = (a_0/L)^2(1/\ell^3)$. So compared with the contribution to $\langle \rho_0 \rangle$ from the dipole term, the contribution from the quadrupole term is a factor $(a_0/L) \ll 1$ smaller, and thus can usually be ignored. A similar argument shows that higher order terms are smaller by additional factors of (a_0/L).

Bound Charge

For typical dielectric insulators, the atoms or molecules out of which the material is comprised are usually charge neutral, so $q_n = 0$. In this case the macroscopic charge density ρ is just the same as the average free charge density, $\rho = \langle \rho_f \rangle$, and the average bound charge density is just,

$$\boxed{\langle \rho_b \rangle = -\boldsymbol{\nabla} \cdot \mathbf{P}} \tag{3.1.33}$$

This agrees with what we saw in the sketches at the beginning of this section – for there to be a net bound volume charge density ρ_b inside the material, the polarization density $\mathbf{P}$ must be non-uniform. We now want to show how $\mathbf{P}$ leads to bound surface charge σ_b on the surfaces of the material, like we also saw in those sketches.
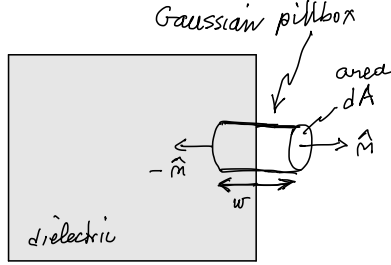
Consider a small Gaussian pillbox piercing the surface of the material, as in the sketch above. The right and left areas of the pillbox are dA, while the side has length w. Integrating over the pillbox we have,

$$-\int_V d^3r\, \boldsymbol{\nabla} \cdot \mathbf{P} = -\oint_S da\,\hat{\mathbf{n}} \cdot \mathbf{P} = -\left[\int_{\text{right}} + \int_{\text{left}} + \int_{\text{side}} da\,\hat{\mathbf{n}} \cdot \mathbf{P}\right] = dA\,\hat{\mathbf{n}} \cdot \mathbf{P} \tag{3.1.34}$$

where only the integral over the left area is non-zero, and in the last result $\hat{\mathbf{n}}$ is the outward pointing normal at the surface of the material. The last result is because (i) the integral over the right surface vanishes because it is outside the material, and so $\mathbf{P} = 0$ there, and (ii) the integral over the side surface vanishes as we take the length $w \to 0$. Using the result that $\rho_b = -\boldsymbol{\nabla} \cdot \mathbf{P}$ we then have,

$$\int_V d^3r\, \rho_b = -\int_V d^3r\, \boldsymbol{\nabla} \cdot \mathbf{P} = dA\hat{\mathbf{n}} \cdot \mathbf{P} \tag{3.1.35}$$

Now as the length $w \to 0$, the left hand side of the above will vanish *unless* there is a bound surface charge σ_b on the surface of the material. In that case,

$$\int_V d^3r\, \rho_b = dA\sigma_b = dA\,\hat{\mathbf{n}} \cdot \mathbf{P} \tag{3.1.36}$$

from which we conclude that the bound surface charge density is,

$$\boxed{\sigma_b = \hat{\mathbf{n}} \cdot \mathbf{P}} \tag{3.1.37}$$

Discussion Question 3.1

In the above discussion we computed the dipole moment $\mathbf{p}_n$ of atom n about the center of mass position $\mathbf{r}_n$ of that atom. If the atom is neutral with $q_n = 0$, then we know from our discussion of the multipole expansion that $\mathbf{p}_n$ is independent of what we choose as the origin of the coordinates. But suppose $q_n \neq 0$. If we then computed the dipole moment $\mathbf{p}_n$ about the *center of charge* of atom n, rather than the center of mass, we would find $\mathbf{p}_n = 0$, which would then give a vanishing polarization density $\mathbf{P} = 0$. Would that be a good thing to do? Why, or why not?

Note, this is not just an academic question. Later, when we consider the behavior of electromagnetic waves in a conductor, we will regard the conduction electrons as "free" charges, while the remaining electrons remain bound to the ionic cores of the atoms. We will then want to consider the polarization of those ionic cores, which are therefore not charge neutral objects.