

Why quadrupole + higher order terms
can generally be ignored:

Let a_0 be the length scale that characterizes the size of a molecule in the dielectric

Let l be the typical spacing between molecules

Let L be the length scale of the spatial averaging function $f(\vec{r})$. $L \gg a_0$

dipole moment per a_0

$$\Rightarrow \text{polarization density } P \sim \frac{a_0}{l^3}$$

$$\vec{\nabla} \cdot \vec{P} \sim \left(\frac{a_0}{L}\right) \frac{1}{l^3}$$

since P cannot vary on length scale shorter than the averaging length L

quadrupole moment

$$Q \sim a_0^2$$

$$\text{quadrupole density } Q \sim \frac{a_0^2}{l^3}$$

$$\frac{\partial^2 Q}{\partial r_\alpha \partial r_\beta} \sim \left(\frac{a_0}{L}\right)^2 \frac{1}{l^3}$$

each higher moment gives extra factor a_0

each higher derivative gives extra factor $\frac{1}{L}$

so quadrupole is smaller than dipole term by factor $\left(\frac{a_0}{L}\right) \ll 1$. Higher terms smaller $\frac{1}{L}$ by additional factors of $\left(\frac{a_0}{L}\right)$

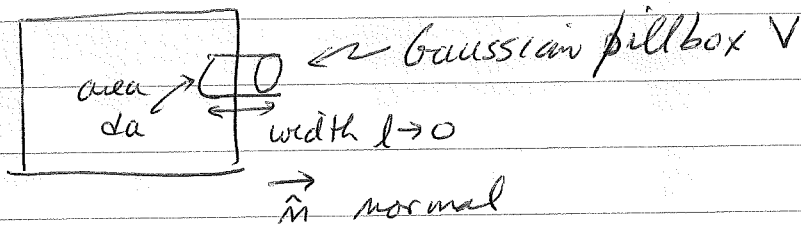
For insulators one generally has $\rho_n = 0$
 molecules are neutral.

In this case the macroscopic ρ is just the
 free charge $\rho = \langle \rho_{\text{free}} \rangle$.

And the bound charge is just

$$\langle \rho_{\text{bound}} \rangle = -\nabla \cdot \vec{P}$$

At a surface of a dielectric



$$-\int_V d^3r \nabla \cdot \vec{P} = -\int_S da \hat{n} \cdot \vec{P}$$

contrib from sides $\rightarrow 0$ as $l \rightarrow 0$
 contrib from outside surface $= 0$
 as $P=0$ outside

$$= \hat{n} \cdot \vec{P} da$$

only contrib is from inside surface
 (\hat{n} is outward normal)

$$= \int_V d^3r \rho_{\text{bound}}$$

as $l \rightarrow 0$, $\int_V d^3r \rho_{\text{bound}} \rightarrow \int da \sigma_{\text{bound}} = da \sigma_{\text{bound}}$ surface charge

$$\Rightarrow \boxed{\sigma_{\text{bound}} = \hat{n} \cdot \vec{P}} \text{ at surface of dielectric}$$

the

Center of mass vs center of charge?

When we wrote for the contribution of the molecules to the average charge density

$$\sum_n \langle \rho_n \rangle = \left\langle \sum_n q_n \delta(\vec{r} - \vec{r}_n) \right\rangle - \vec{P} \cdot \vec{P} \quad \text{with } \vec{P} = \left\langle \sum_n \vec{p}_n \delta(\vec{r} - \vec{r}_n) \right\rangle$$

The question arises what should one take for \vec{r}_n , the coordinate that defines where molecule n is located. If the molecules are charged, $q_n > 0$, then we know that we can choose \vec{r}_n to be the center of charge of the molecule $\sum_i e_n q_i \vec{r}_i / \sum_i q_i$ and then $\vec{p}_n = 0$ when computed about that origin, and so $\vec{P} = 0$ and there would be no polarization density. This might sound like it would be the "best choice" [when $q_n = 0$, then \vec{p}_n is ~~not~~ independent of what is chosen for \vec{r}_n]

However, if one used \vec{r}_n as the center of charge, then one would have to know how \vec{r}_n moved in response to \vec{E} fields or other forces that act on the molecule in order to correctly compute the contribution of the first term $\left\langle \sum_n q_n \delta(\vec{r} - \vec{r}_n) \right\rangle$ to the average charge density. Doing that ~~is~~ often not generally not the simplest thing to do. If one is talking about polarization in a crystal, the positions of the molecules (or atoms) should generally be considered as stationary, while the center of charge is not - heavy nuclei stay still but electrons can shift in applied \vec{E} . So if one used \vec{r}_n as the center of charge, one would need

to consider the shift when computing the first term.

But if we took \vec{r}_n as the center of mass, then the first term does not change (since the heavy ~~nuclei~~ nuclei do not move). The \vec{F}_n about the center of mass then becomes finite and the change in average charge density will come from the second $-\vec{\nabla} \cdot \vec{P}$ term rather than from the first $(\sum_n q_n \delta(\vec{r} - \vec{r}_n))$ term. It is generally easier to do it this way - from both conceptual and calculational point of view.

Similarly, if one is talking about the polarization of a charged molecular gas, where molecules are randomly moving about, then too it is the center of mass not the center of charge for which it is easiest to compute the molecule's motion. Thus again it is more convenient to take \vec{r}_n as the center of mass, and use a finite \vec{P}_n when computed about the center of mass.

Magnetic Materials

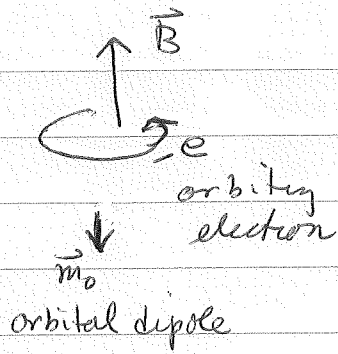
Circulating currents on atomic scale give rise to local magnetic dipole moments, which create local magnetic fields in the material.

Sources of circulating atomic currents:

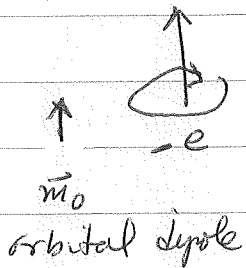
- 1) intrinsic angular momentum of electrons, i.e. "electron spin" - can add up and give a net angular momentum to atom
- 2) orbital angular momentum of electrons - can add up to give net angular momentum of atom.

(1) + (2) \Rightarrow atoms can have a net magnetic dipole moment. When $\vec{B} = 0$, these atomic moments are generally in random orientations ^{and average to zero} (exception is a ferromagnet where moments can align even if $\vec{B} = 0$)
When apply $\vec{B} \neq 0$, the moments tend to align parallel to \vec{B} giving a net magnetization density $\vec{M} \propto \vec{B}$. This is a paramagnetic effect.

But there is also a diamagnetic effect from orbital angular momentum (exists even if total angular momentum of electrons is zero, i.e. exists for atoms with zero net dipole moment)



← applying \vec{B} to orbiting electron speeds up its orbital velocity. Increased angular momentum of negatively charged electron gives change in dipole moment $\Delta \vec{m} \propto -\vec{B}$



← applying \vec{B} to orbiting electron slows down its orbital velocity. Net result is again that $\Delta \vec{m} \propto -\vec{B}$

see Griffiths
chpt 6 + prob
7.17 2nd ed
for details

No matter which way electron orbits with respect to \vec{B} , result is a decrease in magnetic moment, so $\Delta \vec{m} \propto -\vec{B}$

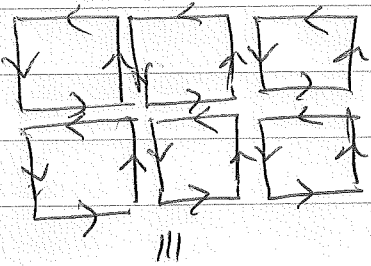
That $\Delta \vec{m}$ is opposite to \vec{B} is called diamagnetism

Model atomic magnetic moments as small current loops. When loops get oriented, i.e. there is non zero average magnetization density

$$\vec{M}(\vec{r}) = \sum_i \vec{m}_i \delta(\vec{r} - \vec{r}_i)$$

then net effect is to have a current flowing around the system. This current gives rise to magnetic fields

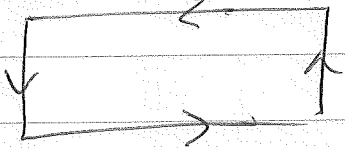
aligned atomic moments in a uniform applied \vec{B}



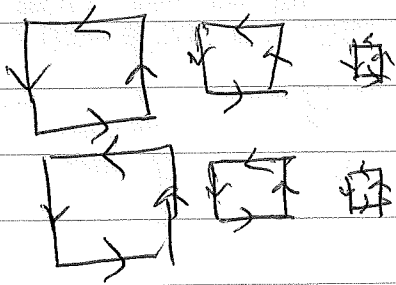
in interior, currents in opposite directions cancel also $\vec{j} = 0$ inside

but is net circulation of current around boundary of material
 \Rightarrow surface current \vec{K}_{bound}

⊙ \vec{B} out of page



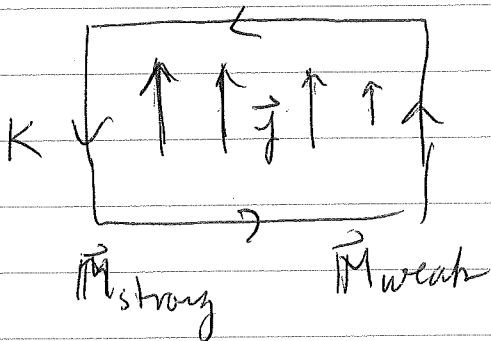
If \vec{B} is not uniform, then \vec{M} is not uniform
 Can create finite current density \vec{j} in interior, as well as surface currents



Now currents in interior do not cancel. Net current \vec{j}_{bound} in interior

\vec{B} strong

\vec{B} weak



\vec{B} out of page $\Rightarrow \vec{M}$ out of page
 μ varies along page
 \vec{M} varies in direction \perp direction of \vec{M}
 $\Rightarrow \nabla \times \vec{M} \neq 0$ gives \vec{j}_{bound}

Average current

$$\langle \vec{j}_0 \rangle = \left\langle \sum_{i \in \text{free}} q_i \vec{v}_i \delta(\vec{r} - \vec{r}_i) \right\rangle + \sum_n \langle \vec{j}_n \rangle$$

↑
current from free charges

↑
current from molecule n of the dielectric

$$\begin{aligned} \langle \vec{j}_n(\vec{r}, t) \rangle &= \sum_{i \in n} q_i (\vec{v}_n + \vec{v}_{ni}) \langle \delta(\vec{r} - \vec{r}_n(t) - \vec{r}_{ni}(t)) \rangle \\ &= \sum_{i \in n} q_i (\vec{v}_n + \vec{v}_{ni}) f(\vec{r} - \vec{r}_n(t) - \vec{r}_{ni}(t)) \end{aligned}$$

↑ center of mass velocity
↑ relative velocity

↑ $\vec{v}_n = \frac{d\vec{r}_n}{dt}$
↑ $\vec{v}_{ni} = \frac{d\vec{r}_{ni}}{dt}$
↑ position of CM of molec n
↑ position of charge i wrt CM

as with $\langle j_0 \rangle$, we can expand in \vec{r}_{ni}

$$\begin{aligned} \langle \vec{j}_n \rangle &= \sum_{i \in n} q_i (\vec{v}_n + \vec{v}_{ni}) \left\{ f(\vec{r} - \vec{r}_n) - \vec{r}_{ni} \cdot \vec{\nabla} f(\vec{r} - \vec{r}_n) \right. \\ &\quad \left. + \frac{1}{2} \sum_{\alpha\beta} (r_{ni})_\alpha (r_{ni})_\beta \frac{\partial^2 f(\vec{r} - \vec{r}_n)}{\partial r_\alpha \partial r_\beta} \right. \\ &\quad \left. + \dots \right\} \end{aligned}$$

we will keep only the first two terms in the expansion

The various terms we have to consider are

$$\textcircled{1} \quad \sum_{i \in n} q_i \vec{v}_n f(\vec{r}-\vec{r}_n)$$

$$\textcircled{2} \quad \sum_{i \in n} q_i \vec{v}_{ni} f(\vec{r}-\vec{r}_n)$$

$$\textcircled{3} \quad - \sum_{i \in n} q_i \vec{v}_n \left[\vec{r}_{ni} \cdot \vec{\nabla} f(\vec{r}-\vec{r}_n) \right]$$

$$\textcircled{4} \quad - \sum_{i \in n} q_i \vec{v}_{ni} \left[\vec{r}_{ni} \cdot \vec{\nabla} f(\vec{r}-\vec{r}_n) \right]$$

$$\textcircled{1} = \vec{v}_n f(\vec{r}-\vec{r}_n) \sum_{i \in n} q_i = q_n \vec{v}_n f(r-r_n) = \langle q_n \vec{v}_n \delta(\vec{r}-\vec{r}_n) \rangle$$

this is just current of molecule as if it were a point charge q_n . For a neutral molecule $q_n=0$ and this term vanishes.

$$\textcircled{2} \quad \text{Note: } \frac{\partial}{\partial t} \langle \vec{p}_n \delta(\vec{r}-\vec{r}_n) \rangle = \frac{\partial}{\partial t} \left(\sum_{i \in n} q_i \vec{r}_{ni} f(\vec{r}-\vec{r}_n) \right) = \sum_{i \in n} q_i \vec{v}_{ni} f(\vec{r}-\vec{r}_n)$$

$$+ \sum_{i \in n} q_i \vec{r}_{ni} \left[-\vec{\nabla} f(\vec{r}-\vec{r}_n) \cdot \vec{v}_n \right] = \frac{\partial f(\vec{r}-\vec{r}_n)}{\partial t}$$

$$\text{So for } \textcircled{2}, \quad \sum_{i \in n} q_i \vec{v}_{ni} f(\vec{r}-\vec{r}_n)$$

$$= \frac{\partial}{\partial t} \langle \vec{p}_n \delta(\vec{r}-\vec{r}_n) \rangle$$

$$+ \left[\vec{v}_n \cdot \vec{\nabla} f(\vec{r}-\vec{r}_n) \right] \vec{p}_n$$

So

$$\textcircled{2} = \sum_{i \in n} q_i \vec{v}_{ni} f(\vec{r} - \vec{r}_n) = \frac{\partial}{\partial t} \langle \vec{p}_n \delta(\vec{r} - \vec{r}_n) \rangle + (\vec{v}_n \cdot \vec{\nabla}) \langle \vec{p}_n \delta(\vec{r} - \vec{r}_n) \rangle$$

2nd term is $\sum_{\alpha} v_{n\alpha} \frac{\partial}{\partial r_{\alpha}} \langle \vec{p}_n \delta(\vec{r} - \vec{r}_n) \rangle$

$$\textcircled{3} = -\vec{v}_n \left(\sum_{i \in n} q_i \vec{r}_{ni} \right) \cdot \vec{\nabla} f(\vec{r} - \vec{r}_n) = -\vec{v}_n (\vec{p}_n \cdot \vec{\nabla} f(\vec{r} - \vec{r}_n))$$

$$= -\vec{v}_n \cdot \vec{\nabla} \langle \vec{p}_n \delta(\vec{r} - \vec{r}_n) \rangle = \sum_{\alpha} \vec{v}_n \frac{\partial}{\partial r_{\alpha}} \langle p_{n\alpha} \delta(\vec{r} - \vec{r}_n) \rangle$$

$$\textcircled{4} = -\vec{\nabla} f(\vec{r} - \vec{r}_n) \cdot \sum_{i \in n} q_i \vec{r}_{ni} \vec{v}_{ni}$$

We have seen the tensor $\sum_{i \in n} q_i \vec{r}_{ni} \vec{v}_{ni}$ before when we considered the magnetic dipole moment

$$\sum_{i \in n} q_i \vec{r}_{ni} \vec{v}_{ni} = \int d^3r \vec{r} \vec{j} \quad \text{where } \vec{j}(\vec{r}) \equiv \sum_{i \in n} q_i \vec{v}_{ni} \delta(\vec{r} - \vec{r}_{ni})$$

is current density with respect to center of mass of molecule

We had $\int d^3r \vec{r} \vec{j} = -\int d^3r \vec{j} \vec{r} - \int d^3r (\vec{\nabla} \cdot \vec{j}) \vec{r} \vec{r}$

\uparrow
in statics, $\vec{\nabla} \cdot \vec{j} = 0$

in general $\vec{\nabla} \cdot \vec{j} = -\frac{\partial \rho}{\partial t}$

$$\int d^3r \vec{r} \vec{j} = -\int d^3r \vec{j} \vec{r} + \int d^3r \frac{\partial \rho}{\partial t} \vec{r} \vec{r}$$

$$= -\int d^3r \vec{j} \vec{r} + \frac{\partial}{\partial t} \left[\int d^3r \rho \vec{r} \vec{r} \right]$$

\uparrow

although this is not zero,

it is a quadrupole term

of the same order as the terms we dropped when we truncated our sum to linear order

$$\sim O\left(\frac{a_0}{L}\right)^2$$

So $\int d^3r \vec{r} \vec{j} \approx - \int d^3r \vec{j} \vec{r}$ ignoring the quadrupole term

$$= \frac{1}{2} \int d^3r [\vec{r} \vec{j} - \vec{j} \vec{r}]$$

$$\sum_{i \in n} q_i \vec{r}_{ni} \vec{v}_{ni} = \frac{1}{2} \sum_{i \in n} q_i [\vec{r}_{ni} \vec{v}_{ni} - \vec{v}_{ni} \vec{r}_{ni}]$$

$$- \vec{\nabla} f(\vec{r} - \vec{r}_n) \cdot \sum_{i \in n} q_i \vec{r}_{ni} \vec{v}_{ni} = - \vec{\nabla} f(\vec{r} - \vec{r}_n) \cdot \frac{1}{2} \sum_i q_i [\vec{r}_{ni} \vec{v}_{ni} - \vec{v}_{ni} \vec{r}_{ni}]$$

$$= -\frac{1}{2} \sum_{i \in n} q_i [(\vec{\nabla} f \cdot \vec{r}_{ni}) \vec{v}_{ni} - (\vec{\nabla} f \cdot \vec{v}_{ni}) \vec{r}_{ni}]$$

$$= -\frac{1}{2} \sum_{i \in n} q_i \vec{\nabla} f \times (\vec{v}_{ni} \times \vec{r}_{ni}) \quad \text{triple product rule}$$

$$= \vec{\nabla} f(\vec{r} - \vec{r}_n) \times \frac{1}{2} \sum_{i \in n} \vec{r}_{ni} \times \vec{v}_{ni} q_i$$

$$= \vec{\nabla} f(\vec{r} - \vec{r}_n) \times \frac{1}{2} \int d^3r \vec{r} \times \vec{j}$$

$$= \vec{\nabla} f(\vec{r} - \vec{r}_n) \times c \vec{m}_n \quad \text{where } \vec{m}_n = \frac{1}{2e} \sum_{i \in n} \vec{r}_{ni} \times \vec{v}_{ni} q_i$$

is magnetic dipole moment of molecule n

$$= \vec{\nabla} \times f(\vec{r} - \vec{r}_n) c \vec{m}_n$$

$$= \vec{\nabla} \times \langle c \vec{m}_n \delta(\vec{r} - \vec{r}_n) \rangle$$