Center of mass or center of charge?

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

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

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, $q_n \geq 0$, then we know that we can choose $\vec{r}_n$ to be the center of charge of the molecule $\sum_{i \in n} q_i \vec{r}_i / \sum_i q_i$ 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 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 $\langle \sum_n q_n \delta(\vec{r}-\vec{r}_n) \rangle$ to the average charge density. Doing that would 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 this shift when computing the first term.
But if one 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 $\vec{r}_n$ 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 $\langle \sum_n q_n \delta(\vec{r}-\vec{r}_n)\rangle$ 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
molecules motion. Thus again it is more convenient
to take $\vec{r}_n$ as the center of mass, and use a
finite $\vec{r}_n$ 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, ie "electron spin" - can add up ad 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) ⇒ 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, ie exists for atoms with zero net dipole moment)

$\vec{B}$

orbiting electron

$\vec{m}_0$ orbital dipole
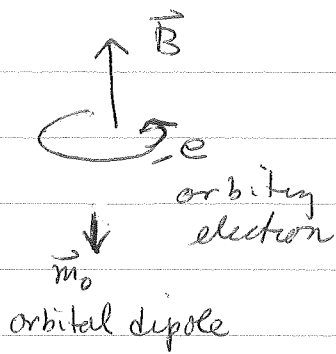
← applying $\vec{B}$ to orbiting electron speeds up its orbital velocity. Increased angular momentum of <u>negatively</u> charged electron gives change in dipole moment $\Delta \vec{m} \alpha - \vec{B}$

$\vec{m}_0$ orbital dipole
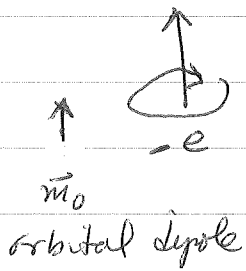
← applying $\vec{B}$ to orbiting electron slows down its orbital velocity. Net result is again that $\Delta \vec{m} \alpha - \vec{B}$

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 $\Delta \vec{m} \alpha - \vec{B}$. That $\Delta \vec{m}$ is opposite to $\vec{B}$ is called <u>diamagnetism</u>
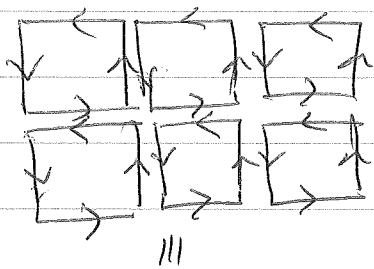
Model atomic magnetic moments as small current loops. When loops get oriented, ie there is non zero average magnetization density

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

then net effect is to have a current flowing around the system. This current gives rise to magnetic fields
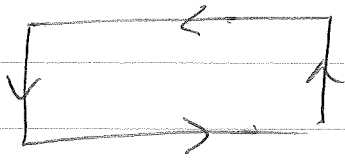
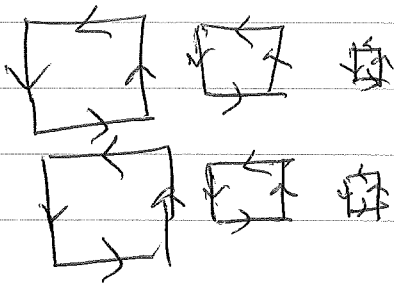# aligned atomic moments in a uniform applied $\vec{B}$

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

$\vec{B}$ out of page

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

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

K

$\vec{M}_{strong}$ $\vec{M}_{weak}$
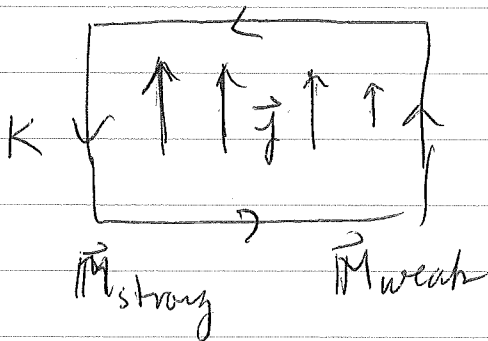
$\vec{B}$ out of page $\Rightarrow \vec{M}$ out of page
~~M varies along page~~
$\vec{M}$ varies in direction $\perp$ direction of $\vec{M}$
$\Rightarrow \vec{\nabla} \times \vec{M} \neq 0$ gives $\vec{J}_{bound}$

Average current

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

$$\underset{\underset{\text{charges}}{\text{current from free}}}{\uparrow} \qquad \underset{\underset{\underset{\text{the dielectric}}{\text{molecule } n \text{ of}}}{\text{current from}}}{\overset{\underset{\text{molec}}{}}{\uparrow}}$$

$$\langle \vec{j}_n(\vec{r}, t) \rangle = \sum_{i \in n} q_i \, (\overset{\overset{\text{center of mass}}{\text{velocity}}}{\vec{v}_n} + \overset{\overset{\text{relative}}{\text{velocity}}}{\vec{v}_{ni}}) \, \langle \delta(\vec{r} - \vec{r}_n(t) - \vec{r}_{ni}(t)) \rangle$$

$$= \sum_{i \in n} q_i \, (\vec{v}_n + \vec{v}_{ni}) \, f(\vec{r} - \vec{r}_n(t) - \vec{r}_{ni}(t))$$

$$\underset{\vec{v}_n = \dfrac{d\vec{r}_n}{dt}}{\uparrow} \quad \underset{\vec{v}_{ni} = \dfrac{d\vec{r}_{ni}}{dt}}{\uparrow} \quad \underset{\underset{\text{CM of molec } n}{\text{position of}}}{\uparrow} \quad \underset{\underset{\underset{\text{wrt CM}}{\text{charge } i}}{\text{position of}}}{\uparrow}$$

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

$$\langle \vec{j}_n \rangle = \sum_{i \in n} q_i \, (\vec{v}_n + \vec{v}_{ni}) \Big\{ f(\vec{r} - \vec{r}_n) - \vec{r}_{ni} \cdot \vec{\nabla} f(\vec{r} - \vec{r}_n)$$

$$+ \frac{1}{2} \sum_{\alpha\beta} (r_{ni})_\alpha (r_{ni})_\beta \frac{\partial^2 f(\vec{r} - \vec{r}_n)}{\partial r_\alpha \partial r_\beta}$$

$$+ \cdots \Big\}$$

we will keep only the first two terms in the expansion

The various terms we have to consider are

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

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

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

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

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

$\qquad\qquad\qquad\qquad = \langle q_n \vec{v}_n f(\vec{r} - \vec{r}_n) \rangle$

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.

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

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

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

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

$\qquad\qquad = \dfrac{\partial}{\partial t} \langle \vec{p}_n f(\vec{r} - \vec{r}_n) \rangle$

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

So

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

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

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

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

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

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

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

is current density with respect to center of mass of molecule

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

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

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

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

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

although this is not zero, it is a quadrapole term of the same order as the terms we dropped when we truncated expansion to *linear order*

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

So $\quad \int d^3r \; \vec{r}\,\vec{j} \simeq -\int d^3r \; \vec{j}\,\vec{r} \qquad$ ignoring the quadrupole term

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

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

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

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

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

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

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

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

$\qquad\qquad\qquad\qquad\qquad$ is magnetic dipole moment of molecule n

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

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

Adding all the pieces

$$\langle \vec{j}_n \rangle = \underbrace{\langle q_n \vec{v}_n \, \delta(\vec{r}-\vec{r}_n) \rangle}_{①} + \underbrace{c\, \vec{\nabla} \times \langle \vec{m}_n \, \delta(\vec{r}-\vec{r}_n) \rangle}_{④}$$

$$+ \underbrace{\frac{\partial}{\partial t} \langle \vec{p}_n \, \delta(\vec{r}-\vec{r}_n) \rangle}_{②} + \underbrace{(\vec{v}_n \cdot \vec{\nabla}) \langle \vec{p}_n \, \delta(\vec{r}-\vec{r}_n) \rangle}_{②}$$

$$- \underbrace{\vec{v}_n \, \vec{\nabla}_0 \langle \vec{p}_n \, \delta(\vec{r}-\vec{r}_n) \rangle}_{③}$$

Define $\vec{M}(\vec{r}) \equiv \sum\limits_n \langle \vec{m}_n \, \delta(\vec{r}-\vec{r}_n) \rangle$ average magnetization density

$\vec{P}(\vec{r}) \equiv \sum\limits_n \langle \vec{p}_n \, \delta(\vec{r}-\vec{r}_n) \rangle$ polarization density, as before

$$\sum_n \langle \vec{j}_n \rangle = \sum_n \langle q_n \vec{v}_n \, \delta(\vec{r}-\vec{r}_n) \rangle + c \, \vec{\nabla} \times \vec{M} + \frac{\partial \vec{P}}{\partial t}$$

$$+ \sum_n \left[(\vec{v}_n \cdot \vec{\nabla}) \langle \vec{p}_n \, \delta(\vec{r}-\vec{r}_n) \rangle - \vec{v}_n \, \vec{\nabla}_0 \langle \vec{p}_n \, \delta(\vec{r}-\vec{r}_n) \rangle \right]$$

See Jackson (6.96) for additional
electric quadrupole terms

The last term on the right hand side is
usually small and ignored. This is because
the molecular velocities $\vec{v}_n$ are usually small,
and randomly oriented, so that they average to zero.
(see Jackson (6.100) for case of net translation of
dielectric, $\vec{v}_n = $ const all n)

Define macroscopic current density

$$\vec{J}(\vec{r},t) = \left\langle \sum_{i \in \text{free}} q_i \vec{v}_i \, \delta(\vec{r}-\vec{r}_i) \right\rangle + \left\langle \sum_{n} q_n \vec{v}_n \, \delta(\vec{r}-\vec{r}_n) \right\rangle$$

current of free charges   current of molecular drifting
                                 if molecules are charged

Then $\langle \vec{j_o} \rangle = \vec{J} + c \, \vec{\nabla} \times \vec{M} + \dfrac{\partial \vec{P}}{\partial t}$

Ampere's law becomes upon averaging

$$\vec{\nabla} \times \vec{B} = \frac{4\pi}{c} \langle \vec{J_o} \rangle + \frac{1}{c} \frac{\partial \vec{E}}{\partial t}$$

$$= \frac{4\pi}{c} \vec{J} + 4\pi \vec{\nabla} \times \vec{M} + \frac{4\pi}{c} \frac{\partial \vec{P}}{\partial t} + \frac{1}{c} \frac{\partial \vec{E}}{\partial t}$$

$$\vec{\nabla} \times \left(\vec{B} - 4\pi \vec{M} \right) = \frac{4\pi}{c} \vec{J} + \frac{1}{c} \frac{\partial}{\partial t} \left(\vec{E} + 4\pi \vec{P} \right)$$

define $\boxed{\vec{H} \equiv \vec{B} - 4\pi \vec{M}}$ to get

$$\boxed{\vec{\nabla} \times \vec{H} = \frac{4\pi}{c} \vec{J} + \frac{1}{c} \frac{\partial \vec{D}}{\partial t}}$$ $\boxed{\vec{D} = \vec{E} + 4\pi \vec{P}}$ as before

official nomenclature: $\vec{B}$ is the magnetic <u>induction</u>

$\vec{H}$ is the magnetic <u>field</u>

common usage: both $\vec{H}$ and $\vec{B}$ are called magnetic field