

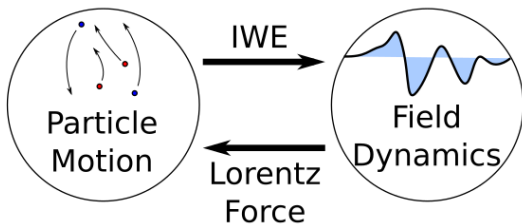
Macroscopic Electrodynamics

Mike Reppert

September 14, 2020

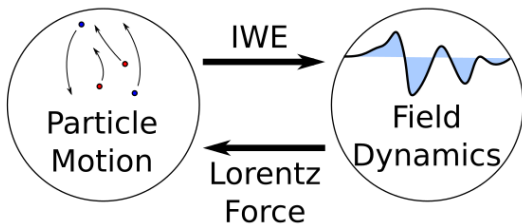
Previously on CHM676...

The Inhomogeneous Wave Equation (IEW – derived from Maxwell's equations) can be used to calculate the EM field *given* particle trajectories.



Previously on CHM676...

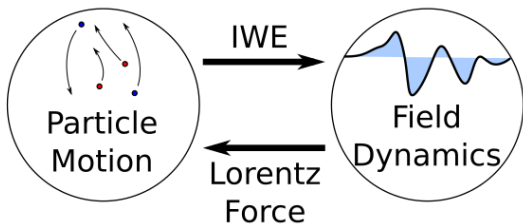
The Inhomogeneous Wave Equation (IEW – derived from Maxwell's equations) can be used to calculate the EM field *given* particle trajectories.



But in general, the particle trajectories are impossibly hard to calculate!

Previously on CHM676...

The Inhomogeneous Wave Equation (IEW – derived from Maxwell's equations) can be used to calculate the EM field *given* particle trajectories.



But in general, the particle trajectories are impossibly hard to calculate!

Today: How to simplify the equations by *coarse-graining*.

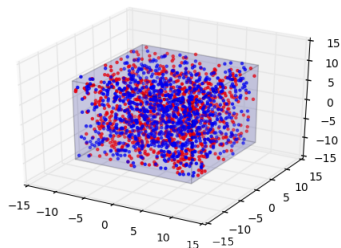
Outline for Today:

- 1 Ensemble Averages and Statistical Mechanics
- 2 Coarse-grained Densities
- 3 Molecular Spectroscopy and Material Polarization

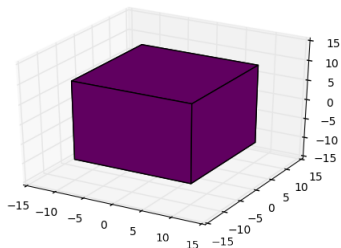
Ensemble Averages and Statistical Mechanics

Statistical Mechanics: Average Physics

Microstate

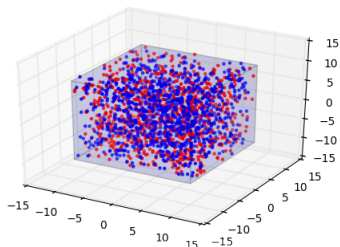


Macrostate

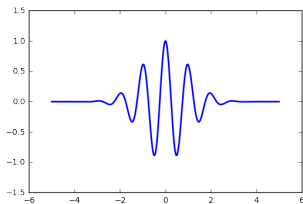
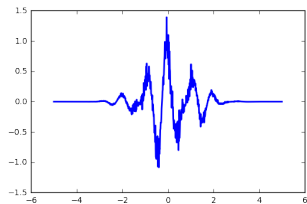
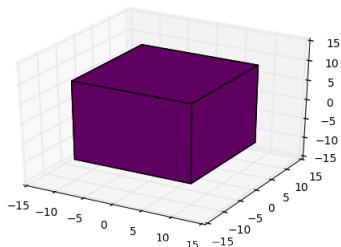


Statistical Mechanics: Average Physics

Microstate



Macrostate



Ensemble Averages

Formally, we define the ensemble average

$$\langle f \rangle_M = \sum_{\mu \in M} p_{\mu}^{(M)} f(\mu)$$

as the average value *over all microstates consistent with a specific macrostate* (temperature, volume, charge, etc.).

Ensemble Averages

Formally, we define the ensemble average

$$\langle f \rangle_M = \sum_{\mu \in M} p_{\mu}^{(M)} f(\mu)$$

as the average value *over all microstates consistent with a specific macrostate* (temperature, volume, charge, etc.).

In spectroscopy, we work almost exclusively with the *macroscopic fields*

$$\mathbf{E}(\mathbf{x}, t) \equiv \langle \mathbf{e}(\mathbf{x}, t) \rangle_M$$

$$\mathbf{B}(\mathbf{x}, t) \equiv \langle \mathbf{b}(\mathbf{x}, t) \rangle_M.$$

Macroscopic Fields

What equations determine \mathbf{E} and \mathbf{B} ?

Macroscopic Fields

What equations determine \mathbf{E} and \mathbf{B} ?

Since Maxwell's equations are linear in \mathbf{b} and \mathbf{e} :

$$\begin{aligned}\nabla \cdot \mathbf{E} &= 4\pi \langle \rho(\mathbf{x}, t) \rangle_M \\ \nabla \cdot \mathbf{B} &= 0 \\ \nabla \times \mathbf{E} + \frac{1}{c} \frac{\partial \mathbf{B}}{\partial t} &= 0 \\ \nabla \times \mathbf{B} - \frac{1}{c} \frac{\partial \mathbf{E}}{\partial t} &= \frac{4\pi}{c} \langle \mathbf{j}(\mathbf{x}, t) \rangle_M\end{aligned}$$

But how do we get rid of the explicit ensemble average?

Wait for it...

Take-Home Points

In statistical mechanics, an *ensemble-averaged* quantity is the average value over all *microstates* consistent with a given *macrostate*.

In spectroscopy, we primarily deal with the *macroscopic fields* \mathbf{E} and \mathbf{B} – the ensemble averages of the *microscopic fields* \mathbf{e} and \mathbf{b} .

Since Maxwell's equations are linear, their form is unchanged by ensemble-averaging. The key question is how to handle $\langle \rho \rangle$ and $\langle \mathbf{j} \rangle$.

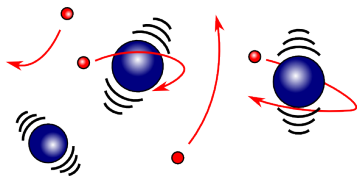
Coarse-grained Densities

Coarse-graining the Densities

A two-step process:

(1) Distinguish between *free* and *bound* charges:

“bound” \approx “stuck to a nucleus”

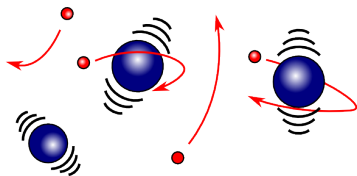


Coarse-graining the Densities

A two-step process:

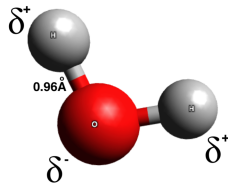
(1) Distinguish between *free* and *bound* charges:

“bound” \approx “stuck to a nucleus”



(2) Multipole expansion in molecular size

- 1 Monopole: Total charge
- 2 Dipole: Polarization



[https://en.wikipedia.org/wiki/File:](https://en.wikipedia.org/wiki/File:Ball_and_stick_model_of_a_water_molecule.png)

[Ball_and_stick_model_of_a_water_molecule.png](https://en.wikipedia.org/wiki/File:Ball_and_stick_model_of_a_water_molecule.png)

Macroscopic Densities

The result (after great suffering) is:

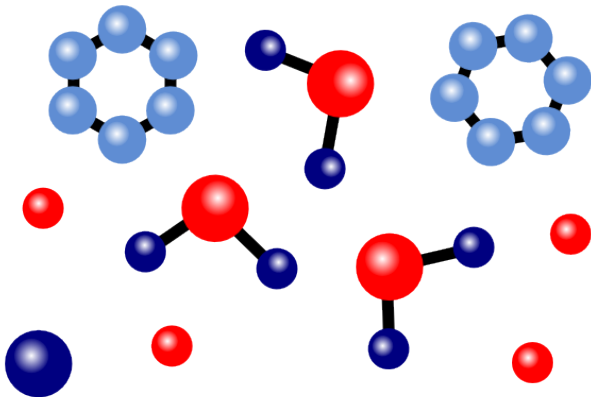
$$\begin{aligned}\langle \rho(\mathbf{x}, t) \rangle_M &\approx \rho(\mathbf{x}, t) - \nabla \cdot \mathbf{P}(\mathbf{x}, t) + \dots \\ \langle \mathbf{j}(\mathbf{x}, t) \rangle_M &\approx \mathbf{J}(\mathbf{x}, t) + \frac{\partial \mathbf{P}(\mathbf{x}, t)}{\partial t} + \dots\end{aligned}$$

where

- ρ is the *free charge* density
- \mathbf{P} is the *polarization* density
- \mathbf{J} is the *free current* density

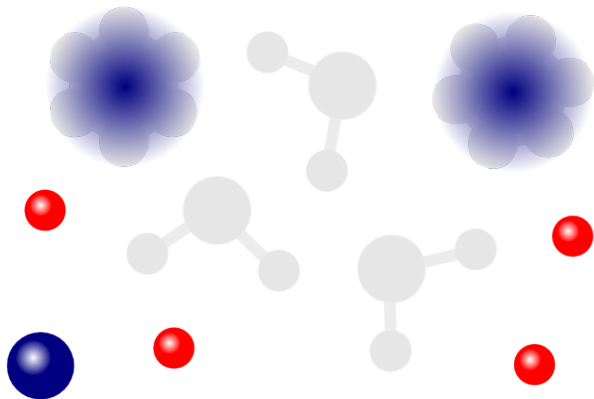
Microscopic Charge Density: ρ

How much total charge?



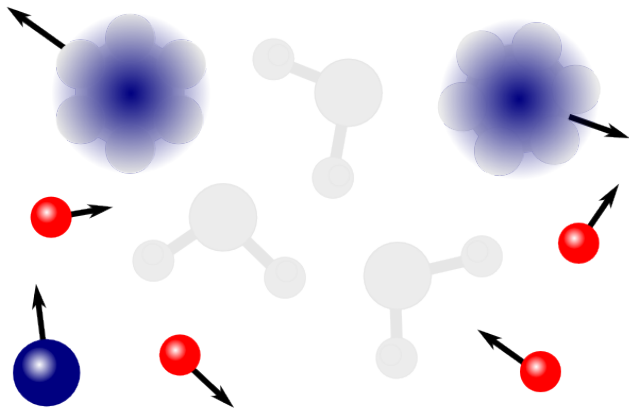
Free Charge Density: ρ

How much mobile charge?



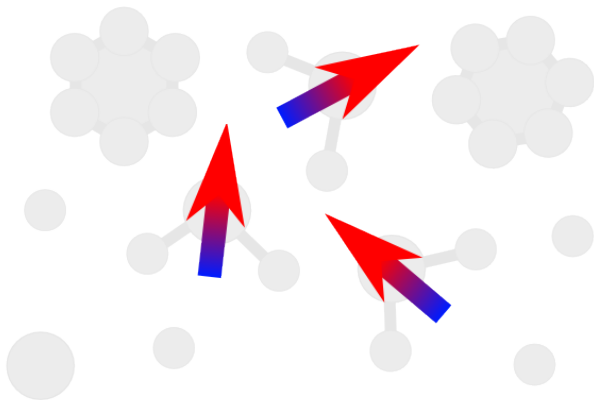
Free Current Density: J

How much mobile charge movement?



Polarization Density: \mathbf{P}

How much polarization?



$\mathbf{P}(\mathbf{x}, t)$ is the average molecular dipole at \mathbf{x} :

$$\mathbf{P}(\mathbf{x}, t) \equiv \langle \mu^{\text{mol}} \delta(\mathbf{x} - \mathbf{r}^{\text{mol}}) \rangle_M$$

Read the Signs

	Microscopic	Macroscopic
Electric Field	e	\mathbf{E}
Magnetic Field	b	\mathbf{B}
Charge Density	ϱ	ρ
Current Density	j	\mathbf{J}

Read the Signs

	Microscopic	Macroscopic
Electric Field	e	E
Magnetic Field	b	B
Charge Density	q	ρ
Current Density	j	J

But watch out!

$$E = \langle e \rangle$$

$$\rho \neq \langle q \rangle$$

$$B = \langle b \rangle$$

$$J \neq \langle j \rangle$$

Read the Signs

	Microscopic	Macroscopic
Electric Field	e	\mathbf{E}
Magnetic Field	b	\mathbf{B}
Charge Density	q	ρ
Current Density	j	\mathbf{J}

But watch out!

$$\mathbf{E} = \langle e \rangle \quad \rho \neq \langle q \rangle$$

$$\mathbf{B} = \langle b \rangle \quad \mathbf{J} \neq \langle j \rangle$$

$$\begin{aligned} \langle q(\mathbf{x}, t) \rangle_M &\approx \rho(\mathbf{x}, t) - \nabla \cdot \mathbf{P}(\mathbf{x}, t) + \dots \\ \langle \mathbf{j}(\mathbf{x}, t) \rangle_M &\approx \mathbf{J}(\mathbf{x}, t) + \frac{\partial \mathbf{P}(\mathbf{x}, t)}{\partial t} + \dots \end{aligned}$$

Take-Home Points

Free charges can move over large distances

Bound charges are *mostly* stuck in place

The multipole expansion allows us to write $\langle \rho \rangle_M$ and $\langle \mathbf{j} \rangle_M$ in terms of *macroscopic quantities*:

- The free charge density ρ
- The polarization density \mathbf{P}
- The free current density \mathbf{J}

Molecular Spectroscopy and Material Polarization

Going Forward: Dielectric Materials

In this course we'll work with *dielectrics*: materials without free charges. *Whole molecules don't move very fast!*

Going Forward: Dielectric Materials

In this course we'll work with *dielectrics*: materials without free charges. *Whole molecules don't move very fast!*

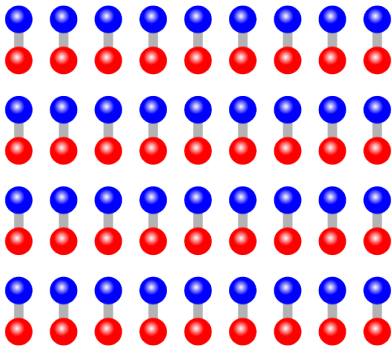
In dielectrics, both ρ and \mathbf{J} vanish:

$$\begin{aligned}\nabla \cdot \mathbf{E} &= -4\pi \nabla \cdot \mathbf{P}(\mathbf{x}, t) \\ \nabla \cdot \mathbf{B} &= 0 \\ \nabla \times \mathbf{E} + \frac{1}{c} \frac{\partial \mathbf{B}}{\partial t} &= 0 \\ \nabla \times \mathbf{B} - \frac{1}{c} \frac{\partial \mathbf{E}}{\partial t} &= \frac{4\pi}{c} \frac{\partial \mathbf{P}(\mathbf{x}, t)}{\partial t}\end{aligned}$$

For molecular spectroscopy, the *polarization density* is key.

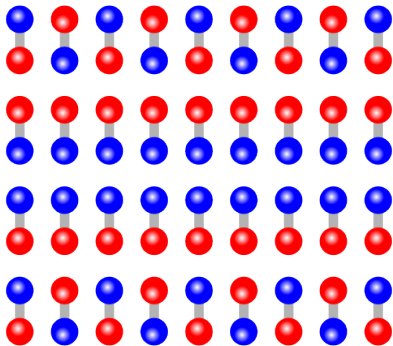
Think about it!

Q: How does polarization contribute to $\langle \rho \rangle_M$?



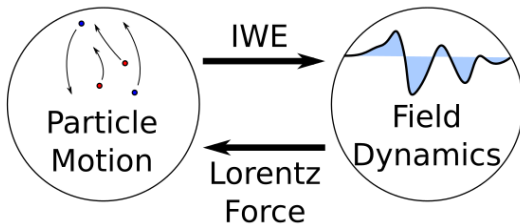
Think about it!

Q: How does polarization contribute to $\langle \rho \rangle_M$?

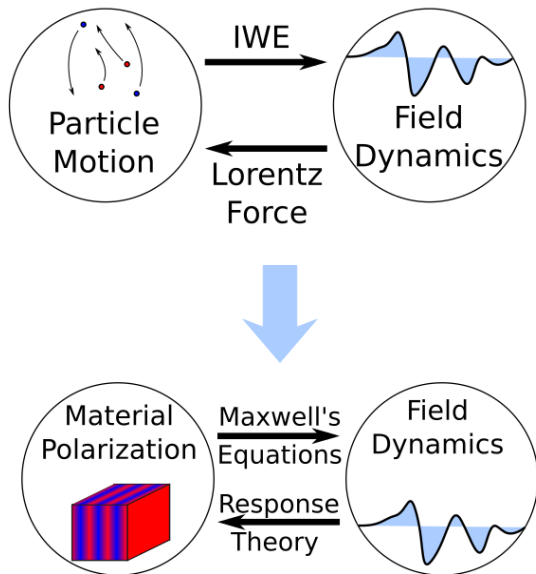


A: It doesn't! It's $\nabla \cdot \mathbf{P}$!

Next up: Response Theory



Next up: Response Theory



Take-Home Points

\mathbf{P} doesn't contribute directly to $\langle \rho \rangle_M$ or $\langle \mathbf{j} \rangle_M$:
It's $\nabla \cdot \mathbf{P}$ and $\frac{\partial \mathbf{P}}{\partial t}$ that contribute.

In macroscopic electrodynamics, *response theory* replaces the Lorentz force law in describing how materials respond to the EM field.