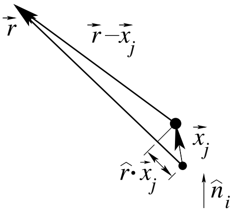
Lecture 13 March 7, 2011

Last time we discussed a small scatterer at origin. Interesting effects come from many small scatterers occupying a region of size d large compared to λ. The scatterer j at position $\vec{x}_j$ has an $\vec{E}_{\text{inc}}$ with an extra factor of $e^{ik\hat{n}_i\cdot\vec{x}_j}$, and in the scattered wave, $\vec{r}$ needs to be replaced by $\vec{r}-\vec{x}_j$. Assuming we are observing from far away, $|\vec{r}| \gg d$, the variations of the r in the denominator or the $\hat{r}$'s are not important, but the effect in the oscillating exponential is, and we should approximate



$$e^{ik|\vec{r}-\vec{x}_j|} \approx e^{ikr}e^{-ik\hat{r}\cdot\vec{x}_j}$$

So the amplitude for the scattered wave due to j has an extra factor of

$$e^{ik\hat{n}_i\cdot\vec{x}_j - ik\hat{r}\cdot\vec{x}_j} = e^{i\vec{q}\cdot\vec{x}_j}, \quad \text{with } \vec{q} = k(\hat{n}_i - \hat{r}).$$

The amplitudes for all the scatterers need to be added before squaring to find the flux, so we have

$$\frac{d\sigma}{d\Omega} = \frac{k^4}{(4\pi\epsilon_0 E_i)^2} \left| \sum_j \left[\vec{\epsilon}^* \cdot \vec{p}_j + (\hat{r} \times \vec{\epsilon}^*) \cdot \vec{m}_j / c \right] e^{i\vec{q}\cdot\vec{x}_j} \right|^2 .$$

If all the scatterers react the same way, p_j and m_j can be factored out of the sum, and we appear to have a single scatterer with a structure factor

$$\mathcal{F}(\vec{q}) = \left| \sum_j e^{i\vec{q}\cdot\vec{x}_j} \right|^2 = \sum_j \sum_{j'} e^{i\vec{q}\cdot(\vec{x}_j - \vec{x}_{j'})}.$$

The nature of $\mathcal{F}(\vec{q})$ depends on how the scatterers are distributed.

Structure Factor

- Large number of randomly positioned scatterers: phases random — superposition incoherent.
  Only the terms with $i = j$ contribute, $\mathcal{F}(\vec{q}) = N$, except for $\vec{q} = 0$. Coherent scattering $\approx N^2$, so incoherent scattering is very faint.
- Crystaline structure: with a regular array we can get even less scattering.
  Consider a one dimensional array of N scatterers each displaced by $\vec{a}$ from the previous.

$$\mathcal{F}(\vec{q}) = \left| \sum_{j=0}^{N-1} e^{ij\vec{q}\cdot\vec{a}} \right|^2 = \left| \frac{1 - e^{iN\vec{q}\cdot\vec{a}}}{1 - e^{i\vec{q}\cdot\vec{a}}} \right|^2 = N^2 \frac{\sin^2(N\vec{q}\cdot\vec{a}/2)}{(N\sin(\vec{q}\cdot\vec{a}/2))^2}.$$

For lattice spacings $a \ll \lambda$ but total extent $Na \gg \lambda$, the fraction is $(\sin x/x)^2$ for $x = N\vec{q}\cdot\vec{a}/2$. $x \gg 1$ and $(\sin x/x)^2 \ll 1$ unless $\vec{q}\cdot\vec{a}$ is comparable or smaller than $1/N$.

So except for forward scattering, we have destructive interference.
In three dimensions, the same thing happens unless the Bragg condition holds for some pair of scatterers, $\vec{q} \cdot \vec{d} = 2n\pi$ for some $\vec{d}$ the separation between two scatterers, not too far apart. In that case there will be some fraction of N interfering constructively, and the structure factor will be proportional to N^2. But if the lattice spacing is much less than λ, this will happen only for forward scattering.
So a perfect crystal with $a \ll \lambda$ is $\approx$ uniform material with permittivity $\bar{\epsilon}$ and permeability $\bar{\mu}$, without scattering.
But suppose small fluctuations,

$$\begin{aligned} \epsilon &= \bar{\epsilon} + \delta\epsilon(\vec{x}), \\ \mu &= \bar{\mu} + \delta\mu(\vec{x}). \end{aligned}$$

Applying Maxwell

Maxwell in medium but without sources applies:
As $\vec{\nabla}\cdot\vec{D}=0$,

$$\begin{aligned}\nabla^2\vec{D} = &= \nabla^2\vec{D}-\vec{\nabla}\left(\vec{\nabla}\cdot\vec{D}\right) = -\vec{\nabla}\times\left(\vec{\nabla}\times\vec{D}\right)\\ &= -\vec{\nabla}\times\left(\vec{\nabla}\times(\vec{D}-\bar{\epsilon}E\right)-\bar{\epsilon}\vec{\nabla}\times\underbrace{\left(\vec{\nabla}\times\vec{E}\right)}_{-\frac{\partial\vec{B}}{\partial t}}.\end{aligned}$$

$$\text{last term: }\bar{\epsilon}\,\vec{\nabla}\times\frac{\partial\vec{B}}{\partial t} = \bar{\epsilon}\frac{\partial}{\partial t}\vec{\nabla}\times\left(\vec{B}-\bar{\mu}\vec{H}\right)+\bar{\epsilon}\bar{\mu}\frac{\partial}{\partial t}\underbrace{\vec{\nabla}\times\vec{H}}_{\frac{\partial\vec{D}}{\partial t}}$$

So altogether,

$$\nabla^2\vec{D}-\bar{\epsilon}\bar{\mu}\frac{\partial^2\vec{D}}{\partial t^2} = -\vec{\nabla}\times\left(\vec{\nabla}\times(\vec{D}-\bar{\epsilon}E\right)+\bar{\epsilon}\frac{\partial}{\partial t}\vec{\nabla}\times\left(\vec{B}-\bar{\mu}\vec{H}\right). \tag{1}$$

This equation is exact. Good approximations: $\delta\epsilon$, $\delta\mu$ small, treat to first order, as sources. Can treat full field $\vec{D}$ as harmonic, $\propto e^{-i\omega t}$ so $\vec{D}$ satisfies inhomogeneous Helmholtz equation with $k^2 := \bar{\mu}\bar{\epsilon}\omega^2$, and all fields perturbations on an incident plane wave

$$\begin{aligned}
\vec{D}_{\text{inc}}(\vec{x}) &= \vec{D}_i e^{ik\vec{n}_i\cdot\vec{x}} \\
\vec{B}_{\text{inc}}(\vec{x}) &= \sqrt{\frac{\bar{\mu}}{\bar{\epsilon}}}\,\vec{n}_i \times \vec{D}_{\text{inc}}(\vec{x}),
\end{aligned}$$

the fields in the source term, to first order in the variations, will be

$$\begin{aligned}
\vec{D} - \bar{\epsilon}E &= \frac{\delta\epsilon(\vec{x})}{\bar{\epsilon}}\vec{D}_{\text{inc}}(\vec{x}) \\
\vec{B} - \bar{\mu}H &= \frac{\delta\mu(\vec{x})}{\bar{\mu}}\vec{B}_{\text{inc}}(\vec{x})
\end{aligned}$$

the correction will then be the scattered wave given by the Green's function

$$\vec{D} - \vec{D}_{\rm inc} = \frac{1}{4\pi} \int d^3x' \frac{e^{ik|\vec{x} - \vec{x}'|}}{|\vec{x} - \vec{x}'|} \times \left\{ \frac{1}{\bar{\epsilon}} \vec{\nabla}' \times \vec{\nabla}' \times \left(\delta\epsilon(\vec{x}') \vec{D}_{\rm inc}(\vec{x}') \right) + \frac{i\bar{\epsilon}\omega}{\bar{\mu}} \vec{\nabla}' \times \left(\delta\mu(\vec{x}') \vec{B}_{\rm inc}(\vec{x}') \right) \right\}$$

Integration by parts: Note[1] $\int_V \vec{\nabla} \times \vec{A} = \int_S \vec{n} \times \vec{A} \to 0$ if $\vec{A}$ vanishes sufficiently at infinity, and therefore $\int_V d^3x' f(\vec{x}') \vec{\nabla}' \times \vec{A}(\vec{x}') \sim -\int_V d^3x' \left(\vec{\nabla}' f(\vec{x}') \right) \times \vec{A}(\vec{x}')$.
For the $\vec{B}_{\rm inc}$ term, $f(\vec{x}')$ is the Green function,

$$\vec{\nabla}' \frac{e^{ik|\vec{x}' - \vec{x}|}}{|\vec{x}' - \vec{x}|} = -\vec{R} \frac{e^{ikR}}{R^3} \left[ikR - 1 \right], \quad \text{with } \vec{R} = \vec{x} - \vec{x}'$$

[1] See lecture notes

For the $\vec{D}_{\rm inc}$ term, we also need

$$\begin{aligned}
&\int_V d^3x' f(\vec{x}\,')\vec{\nabla}\,' \times \vec{\nabla}\,' \times \vec{A}(\vec{x}\,') \\
&\quad = \int_V d^3x' f(\vec{x}\,') \left(\vec{\nabla}\,' \left[\vec{\nabla}\,' \cdot \vec{A}(\vec{x}\,')\right] - \nabla'^2 \vec{A}\right) \\
&\quad \sim - \int_V d^3x' \left(\vec{\nabla}\,' f(\vec{x}\,')\right) \vec{\nabla}\,' \cdot \vec{A}(\vec{x}\,') \\
&\qquad\qquad - \int_V d^3x' \vec{A}(\vec{x}\,')\nabla'^2 f(\vec{x}\,') \\
&\quad \sim + \int_V d^3x' \vec{A}(\vec{x}\,') \cdot \vec{\nabla}\,' \left(\vec{\nabla}\,' f(\vec{x}\,')\right) \\
&\qquad\qquad - \int_V d^3x' \vec{A}(\vec{x}\,')\nabla'^2 f(\vec{x}\,').
\end{aligned}$$

Again $f(\vec{x}\,') = e^{ik|\vec{x}\,'-\vec{x}|}/|\vec{x}\,' - \vec{x}|$ is the Green's function for $\nabla^2 + k^2$, so for the second term, outside the region of scattering (where we can ignore the $\delta(\vec{x} - \vec{x}\,')$ term) we have $k^2 \int_V d^3x' \vec{A}(\vec{x}\,')e^{ik|\vec{x}\,'-\vec{x}|}/|\vec{x}\,' - \vec{x}|$.

For large r, we have

$$\begin{aligned} e^{ik|\vec{x}\,'-\vec{x}|} &= e^{ikr}e^{-ik\hat{r}\cdot\vec{x}\,'}, \\ \frac{1}{|\vec{x}\,'-\vec{x}|} &\approx 1/r, \\ \vec{\nabla}\,' f &= -\frac{ik}{r}\hat{r}e^{ikr}e^{-ik\hat{r}\cdot\vec{x}\,'}, \text{ and} \\ \left(\vec{A}\cdot\vec{\nabla}\,'\right)\left(\vec{\nabla}\,' f\right) &= -\frac{k^2}{r}\hat{r}\cdot\vec{A}\hat{r}e^{ikr}e^{-ik\hat{r}\cdot\vec{x}\,'}. \end{aligned}$$

So altogether

$$\vec{D} = \vec{D}_{\rm inc} + \frac{e^{ikr}}{r}\vec{A}_{\rm sc},$$

where

$$\begin{aligned} \vec{A}_{\rm sc} = \frac{k^2}{4\pi}\int d^3x' e^{-ik\hat{r}\cdot\vec{x}\,'}\left\{\frac{\delta\epsilon(\vec{x}\,')}{\bar{\epsilon}}\left(\hat{r}\times\vec{D}_{\rm inc}(\vec{x}\,')\right)\times\hat{r}\right. \\ \left. -\frac{\bar{\epsilon}\omega}{k}\frac{\delta\mu(\vec{x}\,')}{\bar{\mu}}\,\hat{r}\times\vec{B}_{\rm inc}(\vec{x}\,')\right\}. \end{aligned}$$

The differential cross section for light with polarization $\vec{\epsilon}$ is

$$\frac{d\sigma}{d\Omega} = \frac{\left|\vec{\epsilon}^* \cdot \vec{A}_{\rm sc}\right|^2}{\left|\vec{D}_{\rm inc}\right|^2}$$

$$= \left[\frac{k^2}{4\pi}\int d^3x' e^{i\vec{q}\cdot\vec{x}'} \left\{\vec{\epsilon}^* \cdot \vec{\epsilon}_i \frac{\delta\epsilon(\vec{x}')}{\bar{\epsilon}} - \frac{\delta\mu(\vec{x}')}{\bar{\mu}} \, (\vec{\epsilon}^* \times \hat{r}) \cdot (\hat{n}_i \times \vec{\epsilon}_i)\right\}\right]^2,$$

with $\vec{q} = k(\hat{n}_i - \hat{r})$.

Blue Sky

Our first application is to consider molecules in a dilute gas as a fluctuation in ϵ from the vacuum at a point. With an induced dipole moment $\vec{p}_j = \epsilon_0 \gamma_{\rm mol} \vec{E}(\vec{x}_j)$ we have

$$\delta\epsilon = \epsilon_0 \sum_j \gamma_{\rm mol} \delta(\vec{x} - \vec{x}_j)$$

and we assume no magnetic moments, so $\delta\mu = 0$. Then

$$\frac{d\sigma}{d\Omega} = \frac{k^4}{16\pi^2} \left|\gamma_{\rm mol}\right|^2 \left|\vec{\epsilon}^* \cdot \vec{\epsilon}_i\right|^2 \mathcal{F}(\vec{q})$$

where for a dilute gas we have an incoherent sum and $\mathcal{F}(\vec{q})$ is the number of scattering molecules, except for $\vec{q} = 0$, the forward direction.
For the dilute gas as a whole the dielectric constant $\epsilon_r = \epsilon/\epsilon_0 = 1 + N\gamma_{\rm mol}$, where N is the number density of molecules.

The total scattering cross section per molecule is then

$$\sigma = \frac{k^4}{16\pi^2 N^2} \left|\epsilon_r - 1\right|^2 \sum_{\vec{\epsilon}} \int d\Omega \left|\vec{\epsilon}^{\,*} \times \vec{\epsilon}_i\right|^2$$

The polarization factor is
$\sum_{\vec{\epsilon}} (\vec{\epsilon}_i{}^* \cdot \vec{\epsilon}) \, (\vec{\epsilon}^{\,*} \cdot \vec{\epsilon}_i) = 1 - |\hat{r} \cdot \vec{\epsilon}_i|^2$, as $\sum_{\vec{\epsilon}} \vec{\epsilon}_j \vec{\epsilon}^{\,*}_k + \hat{r}_j \hat{r}_k = \delta_{jk}$.

Consider light incident in the z direction with $\vec{\epsilon}_i = \hat{x}$, so $\hat{r} \cdot \vec{\epsilon} = \sin\theta \cos\phi$, and the integral

$$\int d\Omega \left|\vec{\epsilon}^{\,*} \times \vec{\epsilon}_i\right|^2 = \int_0^\pi \sin\theta d\theta \int_0^{2\pi} d\phi (1 - \sin^2\theta \cos^2\phi) = 8\pi/3,$$

and

$$\sigma = \frac{k^4}{6\pi N^2} \left|\epsilon_r - 1\right|^2 = \frac{k^4}{6\pi N^2} \left|n^2 - 1\right|^2 \approx \frac{2k^4}{3\pi N^2} \left|n - 1\right|^2$$

where $n = \sqrt{\epsilon_r}$ is assumed to deviate only slightly from 1.

The intensity of the beam $I(z) = I(0)e^{-\alpha z}$ falls exponentially with distance with the *attenuation coefficient* α due to the scattering. In a slice of width dz, there are $N dz$ scatterers per unit area, each scattering an area σ of the beam, so there is a fractional loss of $N\sigma dz$ in distance dz, and

$$\alpha = N\sigma \approx \frac{2k^4}{3\pi N} |n-1|^2 .$$

This is Rayleigh scattering. Note that it is a method of determining the number of molecules, so an approach which was used historically to determine Avagadro's number.

Critical Opalescence

In the previous discussion we assumed no corrolation in the positions of the scatterers. This is not a good approximation in denser fluids. A better approximation is to consider $\bar{\epsilon}$ to be the mean permittivity of the fluid but take into account density fluctuations. From the Clausius-Mossotti relation (J4.70) we have

$$\epsilon_r = \frac{3 + 2N\gamma_{\text{mol}}}{3 - N\gamma_{\text{mol}}} \Longrightarrow \frac{d\epsilon_r}{dN} = \frac{9\gamma_{\text{mol}}}{(3-N\gamma_{\text{mol}})^2} = \frac{(\epsilon_r-1)(\epsilon_r+2)}{3N},$$

so the variation of ϵ in a region of fluid with varying density is

$$\frac{\delta\epsilon}{\epsilon_0} = \frac{(\epsilon_r - 1)(\epsilon_r + 2)}{3N}\delta N.$$

How do we evaluate δN?

In a fluid in equilibrium with a reservoir at constant pressure and temperature, the probability that a given piece of fluid occupies a volume V is $\exp -G(V)/k_B T$, where G is the Gibbs free energy and k_B is Boltzmann's constant.

In terms of the[2] *isothermal compressibility*

$$\beta_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T = \left(V\frac{\partial^2 G}{\partial V^2}\right)^{-1},$$

the mean square deviation of $\langle(\Delta V)^2\rangle = k_B T\langle V\rangle\beta_T$, and

$$\langle(\Delta N)^2\rangle = k_B T\langle N^2/V\rangle\beta_T.$$

[2]See Reif, p300

So the total (for all the particles in the volume) differential cross section is

$$NV\left\langle \frac{d\sigma}{d\Omega}\right\rangle = \frac{k^4}{16\pi^2}\left|\vec{\epsilon}^{\,*}\cdot\vec{\epsilon}_i\right|^2\left\langle\left|\int d^3x e^{i\vec{q}\cdot\vec{x}}\frac{\delta\epsilon(\vec{x})}{\bar{\epsilon}}\right|^2\right\rangle$$

$$= \frac{k^4}{16\pi^2}\left|\vec{\epsilon}^{\,*}\cdot\vec{\epsilon}_i\right|^2\left|\frac{\epsilon_r-1)(\epsilon_r+2)}{3N\epsilon_r}\right|^2$$

$$\times\int d^3x\int d^3x' e^{i\vec{q}\cdot(\vec{x}-\vec{x}\,')}\langle\delta N(\vec{x})\delta N(\vec{x}\,')\rangle.$$

If we assume the correlation length for density fluctuations is much less than the wavelength, we may take $e^{i\vec{q}\cdot(\vec{x}-\vec{x}\,')}\approx 1$ and the integrals give $V\langle(\delta N)^2\rangle = N^2 k_B T\beta_T$.

As for the blue sky, the attenuation coefficient is just $\alpha = N\sigma$ and the angular integral is $\int d\Omega \sum_{\vec\epsilon} |\vec\epsilon^{\,*} \cdot \vec\epsilon_i|^2 = 8\pi/3$, so

$$\begin{aligned} \alpha &= \frac{k^4}{6\pi N} \left| \frac{(\epsilon_r - 1)(\epsilon_r + 2)}{3\epsilon_r} \right|^2 N k_B T \beta_T \\ &= \frac{\omega^4}{6\pi N c^4} \left| \frac{(\epsilon_r - 1)(\epsilon_r + 2)}{3} \right|^2 N k_B T \beta_T . \end{aligned}$$

The most important feature of this is that at the critical point the compressibility β_T blows up, so the fluid becomes opalescent.

I am going to skip the sections on diffraction. This has been or is covered in our optics courses.