Lecture 10  Feb 14, 2010

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 \( \lambda \). The scatterer \( j \) at position \( \vec{x}_j \) has an \( E_{\text{inc}} \) with an extra factor of \( e^{ik\vec{r} \cdot \vec{x}_j} \), 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

\[ e^{ik|\vec{r} - \vec{x}_j|} \approx e^{ik\vec{r} \cdot \vec{x}_j} \]

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

\[ e^{ik\vec{r} \cdot \vec{x}_j} = e^{i\vec{q} \cdot \vec{x}_j} \], with \( \vec{q} = k(\hat{r}_j - \hat{r}) \).

### 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.

- Crystalline 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.

\[ \mathcal{F}(\vec{q}) = \left( \sum_{j=0}^{N-1} e^{i\vec{q} \cdot \vec{x}_j} \right)^2 = \frac{1}{N} \frac{\sin^2(N\vec{q} \cdot \vec{a}/2)}{\sin^2(\vec{q} \cdot \vec{a}/2)} \]

For lattice spacings \( a \ll \lambda \) but total extent \( N \vec{a} \gg \lambda \), the fraction is \( (\sin x/x)^2 \) for \( x = N\vec{a}/\lambda \). \( 1 \gg x \gg 1 \).

### Applying Maxwell

Maxwell in medium but without sources applies:

\[ \nabla \cdot \vec{D} = 0, \]

\[ \nabla \times \vec{E} = \frac{\partial \vec{B}}{\partial t} \]

\[ \nabla \times \vec{B} = \vec{0}, \]

\[ \nabla \cdot \vec{B} = 0. \]

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

\[ \frac{ds}{dt} = \frac{k^4}{4\pi \epsilon_0 c^4} \left( \sum_j |\vec{E}_j + \vec{E}'_j| \cdot |\vec{E}_j| e^{i\vec{q} \cdot \vec{x}_j} \right)^2. \]

If all the scatterers react the same way, \( p_j \) and \( n_j \) 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.

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, \( \vec{q} \cdot \vec{d} = 2\pi n \), and all fields perturbations on an incident plane wave

\[ \vec{B}_{\text{inc}}(\vec{x}) = \vec{B}_0 e^{ik\vec{q} \cdot \vec{x}} \]

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

\[ \vec{B} - \vec{E} = \frac{\delta \vec{q}(\vec{x})}{\vec{q}} \vec{B}_{\text{inc}}(\vec{x}), \]

\[ \vec{B} - \vec{\mu}_0 \vec{H} = \frac{\delta \mu(\vec{x})}{\vec{q}} \vec{B}_{\text{inc}}(\vec{x}), \]

This equation is exact. Good approximations: \( \delta \epsilon, \delta \mu \) small, \( \epsilon, \mu \) treat to first order, as sources. Can treat full field \( \vec{B} \) as harmonic, \( e^{-i\vec{q} \cdot \vec{x}} \) so \( \vec{B} \) satisfies inhomogeneous Helmholtz equation with \( k^2 = \mu_0 \mu \epsilon \), and all fields perturbations on an incident plane wave

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\[ \vec{B} - \vec{\mu}_0 \vec{H} = \frac{\delta \mu(\vec{x})}{\vec{q}} \vec{B}_{\text{inc}}(\vec{x}) \]
the correction will then be the scattered wave given by the Green’s function
\[ \vec{D} - \vec{D}_{\text{inc}} = \frac{1}{4\pi} \int d^3x' e^{ik[\vec{x} - \vec{x}']} \left\{ \frac{1}{\vec{x} - \vec{x}'} x \times \left( \delta(\vec{x}') \vec{B}_{\text{inc}}(\vec{x}') \right) + \frac{i\overline{\mu}}{\mu} \vec{x} \times \left( \delta(\vec{x}') \vec{B}_{\text{inc}}(\vec{x}') \right) \right\} \]
Integration by parts: Note 1. See lecture notes

For large \( r \), we have
\[ e^{ik[\vec{r}' - \vec{r}]} = e^{ik|\vec{r}' - \vec{r}|}, \]
\[ \frac{1}{|\vec{r}' - \vec{r}|} \approx \frac{1}{r}, \]
\[ \vec{\nabla}' f = -\frac{ik}{r} e^{ik\vec{r}' \cdot \vec{r}}, \]
\[ \left( \vec{A} \cdot \vec{\nabla}' \right) \left( \vec{\nabla}' f \right) = -\frac{k^2}{r} \vec{A} e^{ik\vec{r}' \cdot \vec{r}}. \]
So altogether
\[ \vec{D} = \vec{D}_{\text{inc}} + \frac{e\hbar r}{\epsilon} \vec{A}_{\text{sc}}, \]
where
\[ \vec{A}_{\text{sc}} = \frac{k^2}{4\pi} \int d^3x' e^{-i\vec{k}\vec{r}'} \left\{ \frac{\delta(\vec{r}')}{\epsilon} \left( \hat{r} \times \vec{D}_{\text{inc}}(\vec{r}') \right) \cdot \hat{r} - \frac{\overline{\mu}}{\epsilon} \frac{\delta(\vec{r}')}{\mu} \left( \hat{r} \times \vec{A}_{\text{inc}}(\vec{r}') \right) \right\}. \]

Blue Sky
Our first application is to consider molecules in a dilute gas as a fluctuation in \( \epsilon \) from the vacuum at a point. With an induced dipole moment \( \vec{p}_j = e_0 \mu_0 \vec{E}(\vec{x}_j) \) we have
\[ \delta \epsilon = \epsilon_0 \sum \gamma_{\text{mol}} \delta(\vec{x} - \vec{x}_j) \]
and we assume no magnetic moments, so \( \delta \mu = 0 \). Then
\[ \frac{d\sigma}{d\Omega} = \frac{k^4}{16\pi^2} |\epsilon| \cdot |\epsilon| |\vec{c}| \vec{c} \cdot \vec{c} | \mathcal{F}(\vec{q}) |^2 \]
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 \( \epsilon_0 = \epsilon/\epsilon_0 = 1 + N\gamma_{\text{mol}} \), where \( N \) is the number density of molecules.

For the \( \vec{D}_{\text{inc}} \) term, we also need
\[ \int d^3x f(\vec{x}') \vec{\nabla}' \times \vec{A}(\vec{x}') \]
\[ = \int \left( \frac{d^3x f(\vec{x}')}{|\vec{x}'|} \left( \vec{\nabla}' \cdot \vec{A}(\vec{x}') \right) - \vec{\nabla}'^2 \vec{A}(\vec{x}') \right) \]
\[ \approx - \int d^3x f(\vec{x}') \left( \vec{\nabla}' \cdot \vec{A}(\vec{x}') \right) \vec{\nabla}' \vec{A}(\vec{x}') \]
\[ \sim - \int d^3x f(\vec{x}') \left( \vec{\nabla}' \vec{A}(\vec{x}') \right) \vec{\nabla}'^2 f(\vec{x}') \]
\[ \sim - \int d^3x f(\vec{x}') \vec{\nabla}'^2 f(\vec{x}') \]
Again \( f(\vec{x}') = e^{i|\vec{r}' - \vec{r}|}/|\vec{r}' - \vec{r}| \) is the Green’s function for \( \vec{\nabla}'^2 + k^2 \), so for the second term, outside the region of scattering (where we can ignore the \( \delta(\vec{x} - \vec{x}') \) term) we have
\[ k^2 \int d^3x f(\vec{x}') e^{i|\vec{r}' - \vec{r}|}/|\vec{r}' - \vec{r}| \]

The differential cross section for light with polarization \( \vec{\epsilon} \) is
\[ \frac{d\sigma}{d\Omega} = \frac{|\vec{\epsilon} \cdot \vec{A}_{\text{inc}}|^2}{|\vec{D}_{\text{inc}}|^2} \]
\[ = \left[ \frac{k^2}{4\pi} \int d^3x f(\vec{r}) \left( \vec{\nabla} \cdot \vec{A}_{\text{inc}}(\vec{r}) \right) \left( \vec{\nabla} \times \vec{A}_{\text{inc}}(\vec{r}) \right) \right]^2, \]
with \( \vec{q} = k(\hat{n} - \hat{r}) \).

The total scattering cross section per molecule is then
\[ \sigma = \frac{k^4}{16\pi^2} (\epsilon_0 - 1)^2 \int d\Omega |\vec{c} \times \vec{c}|^2 \]
The polarization factor is
\[ \sum_\epsilon (\hat{c}_\epsilon \cdot \vec{\epsilon}) (\hat{c}_\epsilon \cdot \vec{\epsilon}) = 1 - |\vec{\epsilon}|^2, \]
as \( \sum_\epsilon \hat{c}_\epsilon \times \hat{c}_\epsilon + \hat{c}_\epsilon \hat{c}_\epsilon = \delta_{jk} \).
Consider light incident in the z direction with \( \hat{c}_z \), so \( \vec{\epsilon} \cdot \hat{c}_z = \sin \theta \cos \phi \), and the integral
\[ \int d\Omega |\vec{c} \times \vec{c}|^2 = \int_0^\infty \sin \theta d\theta \int_0^{2\pi} d\phi (1 - \sin^2 \theta \cos^2 \phi) = 8\pi/3, \]
and
\[ \sigma = \frac{k^4}{6\pi} (\epsilon_0 - 1)^2 = \frac{k^4}{6\pi^2 N^2} |\vec{c} - 1|^2 \approx \frac{2k^4}{3\pi N^2} |\vec{c} - 1|^2, \]
where \( n = \sqrt{\nu} \) 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 \( \alpha \) due to the scattering. In a slice of width \( dz \), there are \( Ndz \) scatterers per unit area, each scattering an area \( \sigma \) of the beam, so there is a fractional loss of \( N\sigma dz \) in distance \( dz \), and
\[
\alpha = N\sigma \approx \frac{2k^4}{3\pi N} |\epsilon - 1|^2.
\]
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.

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 \( \exp -G(V)/k_BT \), where \( G \) is the Gibbs free energy and \( k_B \) is Boltzmann’s constant.

In terms of the \( ^2 \) isothermal compressibility
\[
\beta_T = \frac{1}{V} \left( \frac{\partial^2 G}{\partial V^2} \right)_T = \left( \frac{V^2 \epsilon}{3} \right)^{-1},
\]
the mean square deviation of \( \langle (\Delta V)^2 \rangle = k_BT(\langle V \rangle)/\beta_T \), and
\[
\langle (\Delta N)^2 \rangle = k_BT\langle N^2/(\langle V \rangle) \rangle\beta_T.
\]

\( \epsilon \) is the mean permittivity of the fluid but to be the mean permittivity of the fluid but take into account density fluctuations. From the Clausius-Mossotti relation (J4.70) we have
\[
\epsilon_r = \frac{3+2N\epsilon_{\text{mol}}}{3-N\epsilon_{\text{mol}}} \Rightarrow \frac{d\epsilon}{dN} = 9N\epsilon_{\text{mol}} \frac{(\epsilon_r-1)(\epsilon_r+2)}{3N},
\]
so the variation of \( \epsilon \) 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 \( \delta N \)?

As for the blue sky, the attenuation coefficient is just \( \alpha = N\sigma \) and the angular integral is
\[
\int d\Omega \sum_i |\vec{e}_i \cdot \vec{e}|^2 = 8\pi / 3, \text{ so}
\]
\[
\alpha = \frac{k^4}{6\pi N} \left( \frac{(\epsilon_r-1)(\epsilon_r+2)}{3\epsilon_r} \right)^2 Nk_BT\beta_T
\]
\[
= \frac{\omega^4}{6\pi N^3} \left( \frac{(\epsilon_r-1)(\epsilon_r+2)}{3} \right) Nk_BT\beta_T.
\]
The most important feature of this is that at the critical point the compressibility \( \beta_T \) 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.

### Critical Opalescence

In the previous discussion we assumed no correlation in the positions of the scatterers. This is not a good approximation in denser fluids. A better approximation is to consider \( \vec{r} \) to be the mean permittivity of the fluid but take into account density fluctuations. From the Clausius-Mossotti relation (J4.70) we have
\[
\epsilon_r = \frac{3+2N\epsilon_{\text{mol}}}{3-N\epsilon_{\text{mol}}} \Rightarrow \frac{d\epsilon}{dN} = 9N\epsilon_{\text{mol}} \frac{(\epsilon_r-1)(\epsilon_r+2)}{3N},
\]
so the variation of \( \epsilon \) 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 \( \delta N \)?

So the total (for all the particles in the volume) differential cross section is
\[
NV \left( \frac{d\sigma}{d\Omega} \right) = \frac{k^4}{16\pi^2} \left( \frac{|\vec{e} \cdot \vec{e}'|^2}{\epsilon} \right) \left( \int d^3x \int d^3x' \delta(\vec{r} - \vec{r}') \right) \left( \int d^3x \int d^3x' \epsilon(\vec{r} - \vec{r}') \delta(N(\vec{r})dN(\vec{r}')) \right).
\]
If we assume the correlation length for density fluctuations is much less than the wavelength, we may take \( \epsilon(\vec{r} - \vec{r}') \approx 1 \) and the integrals give
\[
V \langle (\Delta N)^2 \rangle = N^2k_BT\beta_T.
\]