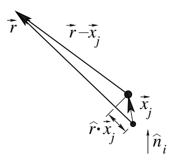
Lectu e 10 Feb ua y 25, 2010

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 λ. The scatterer j at position $\vec{x}_j$ has an $\vec{E}_{\rm inc}$ 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

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

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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

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- 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 $1/N$.

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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

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

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

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

So altogether,

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

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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

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

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

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

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

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

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

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

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

Again $f(\vec{x}')=e^{ik|\vec{x}'-\vec{x}|}/|\vec{x}'-\vec{x}|$ is the Green's function for ∇^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 $k^2\int_V d^3x'\vec{A}(\vec{x}')e^{ik|\vec{x}'-\vec{x}|}/|\vec{x}'-\vec{x}|$.

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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

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

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

$$\begin{aligned}\frac{d\sigma}{d\Omega}&=\frac{\left|\vec\epsilon^*\cdot\vec{A}_{\rm sc}\right|^2}{\left|\vec{D}_{\rm inc}\right|^2}\\ &=\left[\frac{k^2}{4\pi}\int d^3x' e^{i\vec{q}\cdot\vec{x}'}\right.\\ &\qquad\left.\left\{\vec\epsilon^*\cdot\vec\epsilon_i\frac{\delta\epsilon(\vec{x}')}{\bar\epsilon}-\frac{\delta\mu(\vec{x}')}{\bar\mu}\left(\vec\epsilon^*\times\hat{r}\right)\cdot\left(\hat{n}_i\times\vec\epsilon_i\right)\right\}\right]^2,\end{aligned}$$

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

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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.

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The total scattering cross section per molecule is then

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

The polarization factor is
$\sum_{\vec\epsilon}\left(\vec\epsilon_i{}^*\cdot\vec\epsilon\right)\left(\vec\epsilon^*\cdot\vec\epsilon_i\right)=1-|\hat{r}\cdot\vec\epsilon_i|^2$, 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 Ndz 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

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

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

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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

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

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?

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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*

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

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

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

[2]See Reif, p300

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

$$\begin{aligned} NV\left\langle\frac{d\sigma}{d\Omega}\right\rangle &= \frac{k^4}{16\pi^2}\left|\vec\epsilon^{\,*}\cdot\vec\epsilon_i\right|^2\left\langle\left|\int d^3x e^{i\vec q\cdot\vec x}\frac{\delta\epsilon(\vec x)}{\bar\epsilon}\right|^2\right\rangle \\ &= \frac{k^4}{16\pi^2}\left|\vec\epsilon^{\,*}\cdot\vec\epsilon_i\right|^2\left|\frac{\epsilon_r-1)(\epsilon_r+2)}{3N\epsilon_r}\right|^2 \\ &\quad\times\int d^3x\int d^3x' e^{i\vec q\cdot(\vec x-\vec x')}\langle\delta N(\vec x)\delta N(\vec x')\rangle. \end{aligned}$$

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 $V\langle(\delta N)^2\rangle = N^2 k_BT\beta_T$.

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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

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

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.