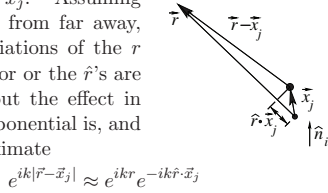


Last time we discussed a small scatterer at origin. Interesting effects come from many small scatterers occupying a region of size  $d$  large compared to  $\lambda$ . The scatterer  $j$  at position  $\vec{x}_j$  has an  $\vec{E}_{\text{inc}}$  with an extra factor of  $e^{ik\hat{n}_i \cdot \vec{x}_j}$ , 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

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

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.
- 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.

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

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  $\lambda$ , 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  $\vec{\nabla} \cdot \vec{D} = 0$ ,

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

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

So altogether,

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

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

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

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

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

Integration by parts: Note<sup>1</sup>  $\int_V \vec{\nabla} \times \vec{A} = \int_S \vec{n} \times \vec{A} \rightarrow 0$  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  $\vec{B}_{\text{inc}}$  term,  $f(\vec{x}')$  is the Green function,

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

<sup>1</sup>See lecture notes

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

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

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

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

So altogether

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

where

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

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

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

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  $\epsilon$  from the vacuum at a point. With an induced dipole moment  $\vec{p}_j = \epsilon_0 \gamma_{\text{mol}} \vec{E}(\vec{x}_j)$  we have

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

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

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

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  $\epsilon_r = \epsilon/\epsilon_0 = 1 + N\gamma_{\text{mol}}$ , where  $N$  is the number density of molecules.

The total scattering cross section per molecule is then

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

The polarization factor is

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

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

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

and

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

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*  $\alpha$  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

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

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 correlation 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

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

so the variation of  $\epsilon$  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  $\delta N$ ?

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 *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  $\langle (\Delta V)^2 \rangle = k_B T (V) \beta_T$ , and

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

<sup>2</sup>See Reif, p300

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

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

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

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