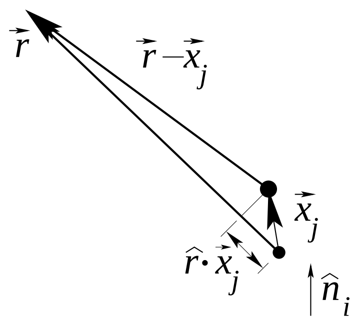
Physics 504, Lecture 13
March 7, 2011

1 Collections of Scatterers

As we have seen, the response of a single small scatterer is pretty much determined, except for strength, simply by its being small, size $\ll \lambda$. But the response of a collection of small scatterers at fixed but diverse locations $\vec{x}_j$ is more interesting. Suppose these occupy a region of size roughly d, with $d \gg \lambda$, but d small compared to the distance from which we are observing, $d \ll |\vec{r}|$. 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 $e^{ik|\vec{r}-\vec{x}_j|} \approx e^{ikr}e^{-ik\hat{r}\cdot\vec{x}_j}$, as $r \gg |x_j|$. Thus the j'th scatterer will contribute an amplitude with an additional phase factor $e^{i\vec{q}\cdot\vec{x}_j}$, with $\vec{q} = k(\hat{n}_i - \hat{r})$, and



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

If all the scatterers have the same reaction to fields, the reaction terms factor out of the sum, and the collection of scatterers behaves like a single scatterer multiplied by a structure factor

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

Although all the scatterers are being coherently excited, the phases of the scattered wave will depend on the positions of the many scatterers, and if they are randomly situated, as in a gas, with many atoms contributing various random phase factors $\vec{q}\cdot\vec{x}_j$, we may consider the scattering as incoherent, with only the terms with $j = j'$ contributing, and $\mathcal{F}(\vec{q}) = N$, except when $\vec{q} = 0$, for forward scattering. Note that a coherent effect would be proportional to N^2, so this incoherent scattering is small. If the scatterers are not randomly situated, but, for example, in a crystal, whether we get coherent scattering or not depends on whether the $\vec{q} \cdot \Delta x_j$ is an integer multiple of 2π for large sets of atoms, as in Bragg scattering. In that case $\mathcal{F}$ will have a factor of N^2, much larger than the N which comes from incoherent scattering of individual scatterers. But this large value is only for specific values of $\vec{q}$, giving angles of scattering that satisfy the Bragg condition. For other $\vec{q}$'s in a large perfect crystal, there is no scattering at all, just as for a diffraction grating, there is no appreciable amplitude for angles which violate $d \sin\theta = n\lambda$ by more than $\Delta\theta \approx 1/N$. Crystal lattice spacings are much smaller than optical wavelengths, so we will only get Bragg scattering for X-rays, not optical frequencies. There is coherent scattering in the forward direction, for all frequencies, but this is not exactly scattering but rather is experienced as an index of refraction. So a uniform medium medium with $a \ll \lambda$, there is effectively no scattering.

Real media, however, are not perfect crystals and are not perfectly uniform. In particular, gases have variation both because of the randomness in the location of molecules and because interactions between the molecules can form fluctuations.

Let us consider a medium without free charges or currents, but with permittivity ϵ and permeability μ which fluctuate by small amounts from the average values $\bar\epsilon$ and $\bar\mu$ in the medium. Maxwell's equations apply without sources but with ϵ and μ that vary from point to point. As $\vec\nabla \cdot \vec D = 0$,

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

As $\vec\nabla \times \vec E = \partial B/\partial t$, the last term is

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

and the last term of this is

$$\bar\epsilon\bar\mu \frac{\partial}{\partial t} \vec\nabla \times \vec H = \bar\epsilon\bar\mu \frac{\partial}{\partial t}\frac{\partial \vec D}{\partial t} = \bar\epsilon\bar\mu \frac{\partial^2 \vec D}{\partial t^2}.$$

So all together,

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

This equation is exact but it is most useful if we make approximations to the right hand side. If we assume the fluctuations $\delta\epsilon := \epsilon - \bar{\epsilon}$ and $\delta\mu := \mu - \bar{\mu}$ are small, and we are interested only in first order effects, we can consider one frequency at a time, assume all fields are $\propto e^{-i\omega t}$ and note that $\vec{D}$ satisfies an inhomogeneous Helmholtz equation with $k^2 := \bar{\mu}\bar{\epsilon}\omega^2$, and with the right hand side of (1) as the source. If the unperturbed field is an incident plane wave

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

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

$$\begin{aligned} \vec{D} - \vec{D}_{\rm inc} &= \frac{1}{4\pi}\int d^3x' \frac{e^{ik|\vec{x}-\vec{x}\,'|}}{|\vec{x}-\vec{x}\,'|}\left\{\frac{1}{\bar{\epsilon}}\vec{\nabla}\,' \times \vec{\nabla}\,' \times \left(\delta\epsilon(\vec{x}\,')\vec{D}_{\rm inc}(\vec{x}\,')\right)\right. \\ &\qquad \left. + \frac{i\bar{\epsilon}\omega}{\bar{\mu}}\vec{\nabla}\,' \times \left(\delta\mu(\vec{x}\,')\vec{B}_{\rm inc}(\vec{x}\,')\right)\right\} \end{aligned} \tag{2}$$

We can do various integration by parts. Note[1] that for any vector field $\vec{A}$ $\int_V \vec{\nabla} \times \vec{A} = \int_S \vec{n} \times \vec{A} \to 0$ 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]For any constant vector $\vec{C}$, by (10) from the front cover,

$$\vec{C} \cdot \int_V \vec{\nabla} \times \vec{A} = \int_V \vec{\nabla} \cdot \left(\vec{A} \times \vec{C}\right) = \int_S \vec{n} \cdot \left(\vec{A} \times \vec{C}\right) = \vec{C} \cdot \int_S \vec{n} \times \vec{A}.$$

and if we only need the leading order in $1/r$, this is $ike^{ik|\vec{x}'-\vec{x}|}\hat{r}/r$. Thus the $\vec{B}_{\rm inc}$ term's contribution to $\vec{D}-\vec{D}_{\rm inc}$ in (2) is

$$-\frac{\omega k}{4\pi}\int d^3x' \frac{e^{ik|\vec{x}'-\vec{x}|}}{r}\frac{\delta\mu(\vec{r}')}{\bar{\mu}}\hat{r}\times\vec{B}_{\rm inc}(\vec{x}').$$

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

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

where the $\sim$ means throwing away surface terms. Note that the two terms in the last line do not cancel, as the left ∇ is contracted into $\vec{A}$ in the first term but into the other ∇ in the second. 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 $k^2\int_V d^3x'\vec{A}(\vec{x}')e^{ik|\vec{x}'-\vec{x}|}/|\vec{x}'-\vec{x}|$. For large r, we have

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

The $\vec{D}_{\rm inc}$ contribution in (2), to leading order, is therefore

$$\frac{1}{4\pi}\int d^3x'\frac{\delta\epsilon(\vec{x}')}{\bar{\epsilon}}\frac{k^2}{r}\left[-\left(\hat{r}\cdot\vec{D}_{\rm inc}\right)\hat{r}+\vec{D}_{\rm inc}\right]e^{ikr}e^{-ik\hat{r}\cdot\vec{x}'},$$

and the term in brackets is $(\hat{r}\times D_{\rm inc})\times\hat{r}$. So altogether

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

where

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

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

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

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

1.1 Blue Sky

Our first application is to consider molecules in a dilute gas as a fluctuation in ϵ from the vacuum at a point. The induced dipole moment is $\vec{p}_j = \epsilon_0\gamma_{\rm mol}\vec{E}(\vec{x}_j)$ from Jackson 4.67, so 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 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 $\sum_{\vec{\epsilon}}\left(\vec{\epsilon}_i^{\,*}\cdot\vec{\epsilon}\right)\left(\vec{\epsilon}^{\,*}\cdot\vec{\epsilon}_i\right) = 1 - \left|\hat{r}\cdot\vec{\epsilon}_i\right|^2$, because the two polarizations plus $\hat{r}$ form an orthonormal basis.

Consider light incident in the z direction with $\vec{\epsilon}_i = \hat{x}$, so $\hat{r}\cdot\vec{\epsilon}_i = \sin\theta\cos\phi$, 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, with a fractional loss of $N\sigma dz$ in distance dz, so

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

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.

1.2 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

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

so the variation of a region of fluid is

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

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

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

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

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

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 $\int d\Omega \sum_{\vec{\epsilon}} \left|\vec{\epsilon}^* \cdot \vec{\epsilon}_i\right|^2 = 8\pi/3$, so

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

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.