## LECTURE NOTES VI

In these notes, we will turn to *scattering*, discussing how light interacts with matter. As an application, we will look at the sky.

### 6.1 Scattering

In a typical scattering problem, the sources $(\mathbf{J}, \rho)$ will be localised in some region of space. At some early time we are given some (free) fields $\mathbf{A}_{in}, \Phi_{in}$ which propagate forward in time, and then interact with (i.e., scatter from) the sources. Considering $\mathbf{A}$ (a similar discussion applies to $\Phi$) we have ($\Box = \nabla^2 - \frac{1}{c^2}\frac{\partial^2}{\partial t^2}$)

$$\Box \mathbf{A}_{in} = 0,$$

since the incident fields are free, and

$$\Box \mathbf{A} = \mu_0 \mathbf{J},$$

in which the fields $\mathbf{A}$ are a superposition

$$\mathbf{A} = \mathbf{A}_{in} + \mathbf{A}_{sc}$$

of the incident fields and the scattered fields. The incident fields are in effect the complementary function for the inhomogeneous equation which is the field equation (i.e., a solution to the corresponding homogeneous equation), whilst the scattered fields are a particular integral, which physical considerations dictate should be the one with only *outgoing* waves, and so are determined by the retarded potentials

$$\mathbf{A}_{sc} = \frac{\mu_0}{4\pi} \int d^3x' \, \mathbf{J}(\mathbf{x}', t - r/c)\frac{1}{r},$$

giving

$$\mathbf{A} = \mathbf{A}_{in} + \frac{\mu_0}{4\pi} \int d^3x' \, \mathbf{J}(\mathbf{x}', t - r/c)\frac{1}{r}.$$

There is a similar equation for the scalar potential $\Phi$.

### 6.2 Scattering from a Small Scatterer

Let us consider the case when the incident field is a plane wave, with angular frequency $\omega$; the scattered wave will then have the same frequency (at least for the simple cases we will consider), and is generated by the charge and current distributions induced in the scatterer by the incident radiation – which will oscillate with the same frequency $\omega$ in this analysis. If the scatterer is small, we may use a multipole expansion, and then in the far zone, keeping only the dipole contributions,

$$\mathbf{E}_{sc} = \frac{k^2}{4\pi\epsilon_0} \frac{e^{ikr}}{r}[(\mathbf{n} \times \mathbf{p}) \times \mathbf{n} - \mathbf{n} \times \mathbf{m}/c]$$
$$\mathbf{B}_{sc} = \frac{1}{c}\mathbf{n} \times \mathbf{E}_{sc}$$

where $\mathbf{p}$ and $\mathbf{m}$ are the induced electric and magnetic dipole moments of the scatterer. If the incident plane-wave is in the direction of the unit vector $\mathbf{n}_0$, we have

$$\mathbf{E}_{in} = \mathbf{E}_0 e^{i\mathbf{k}_0 \cdot \mathbf{x}},$$
$$\mathbf{B}_{in} = \frac{1}{c}\mathbf{n}_0 \times \mathbf{E}_{in}.$$

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The wave vector is $\mathbf{k}_0 = k\mathbf{n}_0$, and the time-dependence is in the amplitude $\mathbf{E}_0$, which also specifies the polarisation of the incident radiation. The incident flux, the power per unit area normal to the incident wave, after taking the time average, is given by

$$\langle|\mathbf{S}_{\text{in}}|\rangle = \frac{1}{2\mu_0 c}|\mathbf{E}_{\text{in}}|^2 = \frac{1}{2\mu_0 c}E_0^2.$$

Similarly the flux of energy in the scattered wave is

$$\langle|\mathbf{S}_{\text{sc}}|\rangle = \frac{1}{2\mu_0 c}|\mathbf{E}_{\text{sc}}|^2.$$

This flux is radially outward, i.e., along the direction $\mathbf{n}$, and falls off as $\frac{1}{r^2}$. The polarisation of the scattered radiation is determined by the direction of $\mathbf{E}_{\text{sc}}$.

In real scattering experiments, one is interested in the *differential scattering cross-section*. This is defined to be the power radiated in a direction $\mathbf{n}$, per unit of incident flux (with direction $\mathbf{n}_0$). We can also take account of the polarisation state of the incident and scattered waves, by introducing unit vectors (which may be complex if for example the polarisation is circular) $\boldsymbol{\epsilon}_0$ and $\boldsymbol{\epsilon}$ respectively. Then

$$\begin{aligned}
\frac{d\sigma}{d\Omega}(\mathbf{n}, \boldsymbol{\epsilon}; \mathbf{n}_0, \boldsymbol{\epsilon}_0) &= \frac{r^2|\boldsymbol{\epsilon}^* \cdot \mathbf{E}_{\text{sc}}|^2}{|\boldsymbol{\epsilon}_0^* \cdot \mathbf{E}_{\text{in}}|^2} \\
&= \left(\frac{k^2}{4\pi\epsilon_0}\right)^2 \frac{1}{E_0^2}\left|\boldsymbol{\epsilon}^* \cdot [(\mathbf{n} \times \mathbf{p}) \times \mathbf{n} - \mathbf{n} \times \mathbf{m}/c]\right|^2 \\
&= \left(\frac{k^2}{4\pi\epsilon_0}\right)^2 \frac{1}{E_0^2}\left|\boldsymbol{\epsilon}^* \cdot \mathbf{p} - \boldsymbol{\epsilon}^* \cdot (\mathbf{n} \times \mathbf{m})/c\right|^2.
\end{aligned}$$

(We have used $\mathbf{n} \cdot \boldsymbol{\epsilon}^* = 0$ as the dipole electric field is perpendicular to $\mathbf{n}$ is the far zone.) Note that unless the dipole moments vanish the radiation scattered has a fourth power frequency dependence, as contained in the factor $k^4$ ($k = 2\pi\nu/c$). This is *Rayleigh's law*.

## 6.3 Many Scatterers

In the previous section, we had supposed that the scatterer was at the origin. Had it been at the point $\mathbf{x}_j$, the incident wave would have been modified by an additional factor $\exp[ik\mathbf{n}_0 \cdot \mathbf{x}_j]$ in $\mathbf{E}_0$, and the phase at the (distant) point at which the scattered wave is observed would likewise be modified by a phase $\exp[-ik\mathbf{n} \cdot \mathbf{x}_j]$. (Including the time dependence, the waves $e^{\pm ikx - i\omega t}$ are incoming to the origin for the plus sign (there is an "$x - vt$" dependence), and outgoing from the origin for the minus sign.)

The resultant phase change overall between the scattered and the incident wave, $\exp[i\mathbf{q} \cdot \mathbf{x}_j]$, where $\mathbf{q} = k(\mathbf{n}_0 - \mathbf{n})$, makes no difference to the resultant differential cross-section. However, if there are a number of scattering centres, located at different points, the phase differences between them will lead to interference effects. For a collection of dipole scatterers, we will now find that we first need to sum over the fields for the scattering sites, including the phase factors, before squaring to get the scattering cross section -

$$\frac{d\sigma}{d\Omega} = \left(\frac{k^2}{4\pi\epsilon_0}\right)^2 \frac{1}{E_0^2}\left|\sum_j \boldsymbol{\epsilon}^* \cdot \left[\mathbf{p}_j - \frac{1}{c}(\mathbf{n} \times \mathbf{m}_j)\right]e^{i\mathbf{q} \cdot \mathbf{x}_j}\right|^2 .$$

This clearly depends sensitively on the positions $\mathbf{x}_j$ of the scatterers. If all the scatterers are identical, the effect is to multiply the cross-section for a single scatterer by

$$\mathcal{F}(\mathbf{q}) = |\sum_j e^{i\mathbf{q} \cdot \mathbf{x}_j}|^2,$$

which is called the *structure factor*. In the forward direction, where $\mathbf{q} = 0$, we have $\mathcal{F} = N^2$ (where $N$ is the number of scatterers). In general,

$$\mathcal{F}(\mathbf{q}) = \sum_{ij} e^{i\mathbf{q} \cdot (\mathbf{x}_i - \mathbf{x}_j)} .$$

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When the distribution of scatterers is random, the phases of the off-diagonal terms in this sum cancel except very close to the forward direction, and the result for this case, called *incoherent* scattering, is that $\mathcal{F}(\mathbf{q}) = N$. (This assumes that $|\mathbf{q}| \gg a^{-1}$, $a$ being a typical distance between the scatterers. This implies that $|q||\mathbf{x}_i - \mathbf{x}_j| \gg 1$ so that $e^{i\mathbf{q}\cdot(\mathbf{x}_i - \mathbf{x}_j)}$ oscillates rapidly as one considers different pairs of sites.)

On the other hand, if the scatterers are arranged in a regular array, as for example in a crystal, the coherence of the contributions to the scattering leads to a characteristic pattern. For a simple cubic structure for example, with lattice spacing $a$, and $N_1, N_2, N_3$ lattice sites along the three axes of the crystal, and with $\mathbf{q} = (q_1, q_2, q_3)$ when referred to these axes, one finds the structure factor

$$\mathcal{F}(\mathbf{q}) = \left[ \frac{\sin^2\left(\frac{N_1 q_1 a}{2}\right)}{\sin^2\left(\frac{q_1 a}{2}\right)} \right] \cdot \left[ \frac{\sin^2\left(\frac{N_2 q_2 a}{2}\right)}{\sin^2\left(\frac{q_2 a}{2}\right)} \right] \cdot \left[ \frac{\sin^2\left(\frac{N_3 q_3 a}{2}\right)}{\sin^2\left(\frac{q_3 a}{2}\right)} \right].$$

(One may more quickly understand this result by considering a one-dimensional array of scatterers, at sites $\mathbf{x}_i = ((i-1)a, 0, 0)$, for $i = 1, 2, ..., N$. The sum over pairs of sites in $\mathcal{F}$ then gives rise to the factor $(1 + e^{iqa} + e^{2iqa} + ... + e^{iq(N-1)a})(1 + e^{-iqa} + e^{-2iqa} + ... + e^{-iq(N-1)a})$ which leads to one of the ratios of sines in the above.)

Each factor in the above expression for $\mathcal{F}$ peaks sharply around $qa = 0, 2\pi, 4\pi, ...$, *i.e.* whenever the Bragg condition is satisfied, and then, just as in the forward direction, $\mathcal{F} = N^2$. The number of peaks is limited by the maximum value which $qa$ can attain, $qa \leq 2ka$, so that at long wavelengths, only the forward peak occurs. This has a width determined by $q_i \leq 2\pi/N_i a$, corresponding to scattering angles less than or of order $\lambda/L$, where $L$ is the linear size of the crystal.

The study and analysis of scattering from matter has had profound effects on our understanding of physics, chemistry and biology. For example, X-ray scattering has been extensively used to determine crystal and molecular structure. Probably the most far-reaching result was the understanding of the molecular basis to genetics − X-ray scattering experiments, notably those of Rosalind Franklin and Maurice Wilkins at Kings College London, were crucial to the discovery of the double helix structure of DNA.

## 6.4 Scattering from the Sky

The light scattered from a cloudless sky is blue. The explanation of this may be given at various levels of sophistication. It is already apparent from the Rayleigh formula that the $k^4$ dependence of dipole scattering will lead to a dominance of the shorter wavelengths in the scattered radiation from an originally white source. A more detailed description of the origin of this dipole scattering will now be given.

We will suppose that there are no free charges or currents in the sky. This means $\rho = \mathbf{j} = 0$, and our previous approach fails to give any scattering at all. The reason is that we have been considering sources *in vacuo*, but air is not a vacuum, so that $\epsilon \equiv \epsilon_0 \epsilon_r \neq \epsilon_0$ and $\mu \equiv \mu_0 \mu_r \neq \mu_0$. The relative permittivity $\epsilon_r$ and relative permeability $\mu_r$ are close to unity for air. Their deviation from unity is not in itself enough to give scattering: what is important is that there are local *fluctuations* in the values of these quantities.

From Maxwell's equations

$$\nabla \cdot \mathbf{D} = 0, \qquad \nabla \times \mathbf{H} = \frac{\partial \mathbf{D}}{\partial t},$$

$$\nabla \cdot \mathbf{B} = 0, \qquad \nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t},$$

it follows that

$$\nabla \times (\mathbf{D} - \epsilon_0 \mathbf{E}) = \nabla \times \mathbf{D} + \epsilon_0 \dot{\mathbf{B}},$$

so that

$$\nabla \times (\nabla \times (\mathbf{D} - \epsilon_0 \mathbf{E})) = \nabla \times (\nabla \times \mathbf{D}) + \epsilon_0 \frac{\partial}{\partial t}(\nabla \times \mathbf{B}).$$

We may recognise that the expression $\mathbf{D} - \epsilon_0 \mathbf{E} = \mathbf{P}$ is the polarisation, so that

$$\nabla \times (\nabla \times \mathbf{P}) = \nabla \times (\nabla \times \mathbf{D}) + \epsilon_0 \frac{\partial}{\partial t}(\nabla \times \mathbf{B}).$$

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Likewise, using $\mathbf{B} - \mu_0\mathbf{H} = \mu_0\mathbf{M}$, where $\mathbf{M}$ is the *magnetisation*, we have

$$\mu_0\frac{\partial}{\partial t}\boldsymbol{\nabla}\times\mathbf{M} = \frac{\partial}{\partial t}\Big[\boldsymbol{\nabla}\times\mathbf{B} - \mu_0\frac{\partial\mathbf{D}}{\partial t}\Big].$$

Subtracting the last two equations gives

$$\epsilon_0\mu_0\frac{\partial}{\partial t}\boldsymbol{\nabla}\times\mathbf{M} - \boldsymbol{\nabla}\times(\boldsymbol{\nabla}\times\mathbf{P}) = -\epsilon_0\mu_0\frac{\partial^2}{\partial t^2}\mathbf{D} - \boldsymbol{\nabla}\times(\boldsymbol{\nabla}\times\mathbf{D})$$

$$= \nabla^2\mathbf{D} - \frac{1}{c^2}\frac{\partial^2}{\partial t^2}\mathbf{D}.$$

For each frequency $\omega = kc$ we have time dependence $e^{-i\omega t}$, leading to

$$(\nabla^2 + k^2)\mathbf{D}(\mathbf{x}) = \mathbf{s}(\mathbf{x}),$$

where

$$\mathbf{s} = -\frac{i\omega}{c^2}\boldsymbol{\nabla}\times\mathbf{M} - \boldsymbol{\nabla}\times(\boldsymbol{\nabla}\times\mathbf{P}).$$

This is small, as we are considering small fluctuations away from the vacuum. We have solved this type of equation earlier using the method of Green's functions. In this case we then derive

$$\mathbf{D}(\mathbf{x}) = \mathbf{D}_0(\mathbf{x}) - \frac{1}{4\pi}\int d^3x'\frac{e^{ik|\mathbf{x}-\mathbf{x}'|}}{|\mathbf{x}-\mathbf{x}'|}\mathbf{s}(\mathbf{x}'),$$

where $\mathbf{D}_0$ is any solution to the homogeneous equation

$$(\nabla^2 + k^2)\mathbf{D}_0 = 0.$$

(Note that we have as usual imposed outgoing boundary conditions.) So if $\mathbf{D}_0$ represents the incident (plane-wave) radiation on some region where $\epsilon \neq \epsilon_0$, $\mu \neq \mu_0$, the integral represents the resultant scattered radiation from that region. In the far zone, where $|\mathbf{x}-\mathbf{x}'| \to r$ we have

$$\mathbf{D} \to \mathbf{D}_0 + \frac{e^{ikr}}{r}\boldsymbol{\mathcal{A}},$$

or, writing $\mathbf{x} = r\mathbf{n}$,

$$\boldsymbol{\mathcal{A}}(\mathbf{x}) = -\frac{1}{4\pi}\int d^3x'\,e^{-ik\mathbf{n}\cdot\mathbf{x}'}\mathbf{s}(\mathbf{x}').$$

In fact the only dependence on $\mathbf{x}$ is through its direction $\mathbf{n}$. We then obtain for the differential cross-section for scattering of radiation with polarisation $\boldsymbol{\epsilon}$ from this region

$$\frac{d\sigma}{d\Omega} = \frac{|\boldsymbol{\epsilon}^*\cdot\boldsymbol{\mathcal{A}}|^2}{|\mathbf{D}_0|^2}.$$

To proceed further we need to be able to say something more about $\mathbf{s}(\mathbf{x})$. As remarked, it is *small*, and is expressed in terms of the polarisation $\mathbf{P} = \mathbf{D} - \epsilon_0\mathbf{E}$ and the magnetisation $\mathbf{M} = \frac{\mathbf{B}-\mu_0\mathbf{H}}{\mu_0}$ above. On integrating by parts

$$\boldsymbol{\mathcal{A}} = -\frac{1}{4\pi}\int d^3x'\,e^{-ik\mathbf{n}\cdot\mathbf{x}'}\mathbf{s}(\mathbf{x}')$$

$$= \frac{1}{4\pi}\int d^3x'\,e^{-ik\mathbf{n}\cdot\mathbf{x}'}\Big[\frac{i}{c^2}\omega\boldsymbol{\nabla}\times\mathbf{M} + \boldsymbol{\nabla}\times(\boldsymbol{\nabla}\times\mathbf{P})\Big]'$$

$$= -\frac{k^2}{4\pi}\int d^3x'\,e^{-ik\mathbf{n}\cdot\mathbf{x}'}[\mathbf{n}\times(\mathbf{n}\times\mathbf{P}') + \mathbf{n}\times\mathbf{M}'/c].$$

We now need to be able to say something about the (induced) polarisation and magnetisation $\mathbf{P}$ and $\mathbf{M}$.

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## 6.5 The Born Approximation

The induced polarisation and magnetisation will depend in detail on the medium—in this case air—and on the fields imposed. We don't know the fields, so need to know how to make some suitable approximation. We do know that

$$\mathbf{P} = \mathbf{D} - \epsilon_0 \mathbf{E} = \epsilon_0 (\epsilon_r - 1)\mathbf{E} = \epsilon_0 \delta\epsilon_r \mathbf{E},$$

where $\delta\epsilon_r = \epsilon_r - 1$; and similarly

$$\mathbf{M} = (\mu_r - 1)\mathbf{H} = \frac{\delta\mu_r}{\mu}\mathbf{B},$$

where $\delta\mu_r = \mu_r - 1$. Because the scattered wave has an amplitude which is small compared with the incident wave, we may to first order in the small quantities $\delta\epsilon_r$ and $\delta\mu_r$ replace the fields $\mathbf{E}$ and $\mathbf{B}$ by the contributions to them from the incident radiation, ignoring the small contribution from the scattered radiation itself. So to first order we may write

$$\mathbf{P} \approx \delta\epsilon_r \mathbf{D}_0$$
$$\mathbf{M} \approx \delta\mu_r c \mathbf{n}_0 \times \mathbf{D}_0,$$

where we have also used $\mathbf{B}_0 = \mathbf{n}_0 \times \mathbf{E}_0/c$ since the incident wave is taken to be a plane wave in the direction $\mathbf{n}_0$. This replacement of the full field by the contribution of the incident field alone, dropping the contribution of the scattered component, is the *Born approximation.*

Using it, we have for the Born approximation to the amplitude

$$\mathcal{A}_{\text{Born}} = -\frac{k^2}{4\pi} \int d^3x' \, e^{-ik\mathbf{n}\cdot\mathbf{x}'} [\mathbf{n} \times (\mathbf{n} \times \mathbf{D}_0')\delta\epsilon_r' + \mathbf{n} \times (\mathbf{n}_0 \times \mathbf{D}_0')\delta\mu_r'].$$

But if the incident wave is plane-polarised with polarisation vector $\boldsymbol{\epsilon}_0$ and is propagating in the direction $\mathbf{n}_0$, we have

$$\mathbf{D}_0' = \mathbf{D}_0(\mathbf{x}') = D_0 \boldsymbol{\epsilon}_0 e^{ik\mathbf{n}_0\cdot\mathbf{x}'},$$

and so obtain

$$\mathcal{A}_{\text{Born}} = -\frac{k^2}{4\pi} D_0 \int d^3x' e^{i\mathbf{q}\cdot\mathbf{x}'} [\mathbf{n} \times (\mathbf{n} \times \boldsymbol{\epsilon}_0)\delta\epsilon_r' + \mathbf{n} \times (\mathbf{n}_0 \times \boldsymbol{\epsilon}_0)\delta\mu_r'],$$

from which it follows that

$$\left(\frac{d\sigma}{d\Omega}\right)_{\text{Born}} = \left(\frac{k^2}{4\pi}\right)^2 \left| \int d^3x \, e^{i\mathbf{q}\cdot\mathbf{x}} \boldsymbol{\epsilon}^* \cdot [\mathbf{n} \times (\mathbf{n} \times \boldsymbol{\epsilon}_0)\delta\epsilon_r + \mathbf{n} \times (\mathbf{n}_0 \times \boldsymbol{\epsilon}_0)\delta\mu_r] \right|^2$$

$$= \left(\frac{k^2}{4\pi}\right)^2 \left| \int d^3x \, e^{i\mathbf{q}\cdot\mathbf{x}} [\boldsymbol{\epsilon}^* \cdot \boldsymbol{\epsilon}_0 \delta\epsilon_r + (\mathbf{n} \times \boldsymbol{\epsilon}^*) \cdot (\mathbf{n}_0 \times \boldsymbol{\epsilon}_0)\delta\mu_r] \right|^2.$$

A useful check with previous results is to apply this Born approximation to the scattering from a small dielectric sphere of radius $a$. This gives

$$\left(\frac{d\sigma}{d\Omega}\right)_{\text{Born}} = \left(\frac{k^2}{4\pi}\right)^2 \left| \int_{\text{sphere}} d^3x \, e^{i\mathbf{q}\cdot\mathbf{x}} \boldsymbol{\epsilon}^* \cdot \boldsymbol{\epsilon}_0 \delta\epsilon_r \right|^2$$

$$= \left(\frac{k^2}{4\pi}\right)^2 |\boldsymbol{\epsilon}^* \cdot \boldsymbol{\epsilon}_0|^2 (\delta\epsilon_r)^2 \left| \int_0^a r^2 \, dr \int_{-1}^{+1} d(\cos\theta) \int_0^{2\pi} d\phi \, e^{iqr\cos\theta} \right|^2$$

$$= k^4 |\boldsymbol{\epsilon}^* \cdot \boldsymbol{\epsilon}_0|^2 (\delta\epsilon_r)^2 \left(\frac{\sin qa - qa\cos qa}{q^3}\right)^2$$

$$\rightarrow k^4 a^6 |\boldsymbol{\epsilon}^* \cdot \boldsymbol{\epsilon}_0|^2 \left(\frac{\delta\epsilon_r}{3}\right)^2 \qquad \text{as } qa \rightarrow 0.$$

The result for the long wave-length scattering from a small dielectric scatterer is

$$\left(\frac{k^2}{4\pi\epsilon_0}\right)^2 \frac{1}{E_0^2} |\boldsymbol{\epsilon}^* \cdot \mathbf{p}|^2.$$

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But we also have for a sphere with relative permittivity $\epsilon_r$ that the induced dipole moment $\mathbf{p}$ is given by

$$\mathbf{p} = 4\pi\epsilon_0 a^3 \left(\frac{\epsilon_r - 1}{\epsilon_r + 2}\right)\mathbf{E}_0.$$

Thus the two calculations agree when $\delta\epsilon_r$ is small.

## 6.6 Rayleigh's Explanation for the Blue Sky

The quantity $\delta\epsilon_r$ which appears in the considerations above is the *electric susceptibility* $\chi_e = \epsilon_r - 1$ of a medium. Since at optical frequencies $\delta\mu_r$ is extremely small, we may relate $\chi_e$ to the refractive index $n$ by

$$n^2 = \epsilon_r \mu_r \approx \epsilon_r = \chi_e + 1.$$

This is not yet enough to allow us to use the previous discussion to give an explanation for the scattering of sunlight in the atmosphere if the air is considered as a homogeneous medium. As already indicated, it is best explained through density fluctuations, but we give first another, somewhat simpler explanation due to Rayleigh. The basis of the discussion is to recognise that the air is not homogeneous, because it is constituted from molecules, and what we should do is to consider the scattering from the random distribution of molecules, each of which may be thought of as an electrically polarisable dipole. This model gives for the electric susceptibility

$$\chi_e(\mathbf{x}) = \frac{1}{\epsilon_0}\sum_j \gamma_{\mathrm{mol}}\delta^{(3)}(\mathbf{x} - \mathbf{x}_j)$$

where the *molecular polarisability* $\gamma_{\mathrm{mol}}$ is defined so that each molecule has an induced dipole moment

$$\mathbf{p}_j = \gamma_{\mathrm{mol}}\mathbf{E}(\mathbf{x}_j)$$

determined by the field $\mathbf{E}(\mathbf{x}_j)$ it experiences. This field is of course affected by the presence of other polarised molecules, and we will return to its determination below. But what we can already do is to obtain

$$\left(\frac{d\sigma}{d\Omega}\right) = \left(\frac{k^2}{4\pi}\right)^2 \left| \int d^3x\, e^{i\mathbf{q}\cdot\mathbf{x}}\boldsymbol{\epsilon}^* \cdot \boldsymbol{\epsilon}_0 \frac{1}{\epsilon_0}\sum_j \gamma_{\mathrm{mol}}\delta^{(3)}(\mathbf{x} - \mathbf{x}_j)\right|^2$$

$$= \left(\frac{k^2}{4\pi\epsilon_0}\right)^2 |\boldsymbol{\epsilon}^* \cdot \boldsymbol{\epsilon}_0|^2 \gamma_{\mathrm{mol}}^2 \left|\sum_j e^{i\mathbf{q}\cdot\mathbf{x}_j}\right|^2$$

$$= \left(\frac{k^2}{4\pi\epsilon_0}\right)^2 |\boldsymbol{\epsilon}^* \cdot \boldsymbol{\epsilon}_0|^2 \gamma_{\mathrm{mol}}^2 N,$$

from previous results, using the Born approximation, since the molecules are randomly distributed, and the resultant scattering is incoherent. $N$ is the number of molecules, and for simplicity they have all been taken to have the same polarisability. Thus the differential scattering cross-section per molecule is

$$k^4 |\boldsymbol{\epsilon}^* \cdot \boldsymbol{\epsilon}_0|^2 \left(\frac{\gamma_{\mathrm{mol}}}{4\pi\epsilon_0}\right)^2.$$

The next step is to relate this molecular polarisability to the bulk polarisablity, and hence to the susceptibility and the refractive index. Here we turn to the Clausius-Mossotti relation we discussed in an earlier lecture. This is

$$\gamma_{\mathrm{mol}} = \frac{3\epsilon_0}{\rho_N}\frac{(\epsilon_r - 1)}{(\epsilon_r + 2)},$$

where here we introduce the volume $V$ explicitly and define $\rho_N = N/V$. Using the previously given relation between $\epsilon_r$ and the refractive index, one obtains

$$\frac{\gamma_{\mathrm{mol}}}{4\pi\epsilon_0} = \frac{3}{4\pi\rho_N}\frac{n^2 - 1}{n^2 + 2},$$

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known as the Lorentz-Lorenz equation (1880), which can then be used to express the differential scattering of light from the air in the sky as

$$\left(\frac{d\sigma}{d\Omega}\right)_{\text{per mol}} = k^4 |\boldsymbol{\epsilon}^* \cdot \boldsymbol{\epsilon}_0|^2 \left(\frac{3}{4\pi\rho_N}\frac{n^2-1}{n^2+2}\right)^2$$

$$\approx k^4 |\boldsymbol{\epsilon}^* \cdot \boldsymbol{\epsilon}_0|^2 \left(\frac{1}{2\pi\rho_N}\right)^2 (n-1)^2$$

where at the last step we have used $(n-1) << 1$.

So far in this long calculation, we have considered the scattering of incident sunlight which has been taken to be polarised, with polarisation vector $\boldsymbol{\epsilon}_0$. Since sunlight is unpolarised, we should really take an average over the two independent directions normal to $\mathbf{n}_0$. This then gives for the differential cross-section for scattering leading to a polarisation parallel to the scattering plane defined by the vectors $\mathbf{n}$ and $\mathbf{n}_0$

$$\left(\frac{d\sigma}{d\Omega}\right)_{\parallel} = \frac{1}{2}k^4 \left(\frac{1}{2\pi\rho_N}\right)^2 (n-1)^2 \cos^2\theta,$$

and for scattering leading to a polarisation perpendicular to the scattering plane

$$\left(\frac{d\sigma}{d\Omega}\right)_{\perp} = \frac{1}{2}k^4 \left(\frac{1}{2\pi\rho_N}\right)^2 (n-1)^2.$$

The scattered light is thus *polarised* on average, with a polarisation given by the difference between the perpendicular and parallel cross-sections divided by their sum, i.e.,

$$\Pi(\theta) = \frac{1-\cos^2\theta}{1+\cos^2\theta} = \frac{\sin^2\theta}{1+\cos^2\theta}.$$

As usual $\theta$ is the angle of scattering, i.e., the angle between the incident direction $\mathbf{n}_0$ and the scattered direction $\mathbf{n}$.

The total differential cross-section is the sum of the two possible final polarisations, and so is

$$\left(\frac{d\sigma}{d\Omega}\right)_T = \frac{1}{2}k^4 \left(\frac{1}{2\pi\rho_N}\right)^2 (n-1)^2 (1+\cos^2\theta).$$

On integrating this over angles, one obtains for the total cross-section per molecule

$$\sigma = \frac{2}{3\pi}\frac{k^4}{\rho_N^2}(n-1)^2.$$

This is the power scattered out of the incident sunlight per molecule per unit incident flux. Then if $I$ is the incident intensity, in traversing a thickness $dx$ of the atmosphere, the intensity is reduced by $dI = -I\rho_N\sigma\,dx$ so that after traversing a thickness $x$ the intensity is given by

$$I = I_0 e^{-\alpha x}$$

where $\alpha$, the *attenuation coefficient* is given by

$$\alpha = \rho_N \sigma = \frac{2}{3\pi}\frac{k^4}{\rho_N}(n-1)^2,$$

with a corresponding expression for its inverse $\Lambda$, the *attenuation length*. This expression for the attenuation length is due to Rayleigh. Note especially that the attenuation length is proportional to $\rho_N$, the number of molecules per unit volume. If there were no atomicity, there would be no attenuation, and the sky would not be blue! Note also the $k^4$ factor, which leads to very substantial differences in $\Lambda$ across the spectrum of visible wavelengths. There is also a wavelength dependence in the refractive index $n$.

## 6.7 Critical Opalescence

The discussion above is not appropriate to dense media, where the scattering is primarily caused by fluctuations in density. To deal with this situation, consider a division of the volume $V$ from which the scattering occurs into small cells of volume $v$. The cells, although small, with linear dimension much less than a wavelength, are to be large enough each to contain many molecules. The number of molecules in each cell will on average be $\rho_N v$, where $\rho_N$ is, as before, the (average) number of molecules per unit volume. The fluctuations in density will result in the number of molecules in the $j$th cell being different from the average number $\rho_N v$; let this difference be $\Delta_j$, i.e., there are $\rho_N v + \Delta_j$ molecules in the $j$th cell. The small difference in density of the $j$th cell produces a corresponding difference

$$\delta\epsilon_{rj} = \frac{\partial \epsilon_r}{\partial \rho_N} \frac{\Delta_j}{v}$$

in the relative permittivity of the $j$th cell. But by differentiating the logarithm of the Clausius-Mossotti equation,

$$\frac{\epsilon_r - 1}{\epsilon_r + 2} = \frac{4\pi \rho_N}{3} \frac{\gamma_{\text{mol}}}{4\pi\epsilon_0}$$

one obtains

$$\frac{\partial \epsilon_r}{\partial \rho_N} = \frac{(\epsilon_r - 1)(\epsilon_r + 2)}{3\rho_N}.$$

Thus we have

$$\delta\epsilon_{rj} = \frac{(\epsilon_r - 1)(\epsilon_r + 2)}{3\rho_N} \frac{\Delta_j}{v}.$$

Recall that (setting $\delta\mu_r = 0$, as is appropriate at optical frequencies) for a single scatterer

$$\frac{d\sigma}{d\Omega} = \left(\frac{k^2}{4\pi}\right)^2 \left| \int d^3x\, e^{i\mathbf{q}\cdot\mathbf{x}} \boldsymbol{\epsilon}^* \cdot \boldsymbol{\epsilon}_0\, \delta\epsilon_r \right|^2.$$

Treating each cell as a single scatterer, and including the contributions from all $V/v$ cells in the volume $V$, which contains a total of $\rho_N V$ molecules, we have

$$\frac{d\sigma}{d\Omega} = \left(\frac{k^2}{4\pi}\right)^2 \left| \sum_j \int_{v_j} d^3x\, e^{i\mathbf{q}\cdot\mathbf{x}_j} \boldsymbol{\epsilon}^* \cdot \boldsymbol{\epsilon}_0\, \delta\epsilon_{rj} \right|^2$$

$$= \left(\frac{k^2}{4\pi}\right)^2 \left| \sum_j v\, \boldsymbol{\epsilon}^* \cdot \boldsymbol{\epsilon}_0\, \delta\epsilon_{rj} \right|^2$$

$$= \left(\frac{k^2}{4\pi}\right)^2 |\boldsymbol{\epsilon}^* \cdot \boldsymbol{\epsilon}_0|^2 \left| \sum_j v \frac{(\epsilon_r - 1)(\epsilon_r + 2)}{3\rho_N v} \Delta_j \right|^2$$

$$= \left(\frac{k^2}{4\pi}\right)^2 |\boldsymbol{\epsilon}^* \cdot \boldsymbol{\epsilon}_0|^2 \left[ \frac{(\epsilon_r - 1)(\epsilon_r + 2)}{3\rho_N} \right]^2 \left| \sum_j \Delta_j \right|^2.$$

In going from the first to the second line, we have assumed that the correlation between fluctuations from one cell to the next extends only over distances small compared with the wavelength, so that the exponential can be set to unity. Summing over the initial polarisations $\boldsymbol{\epsilon}_0$, averaging over the final polarisations $\boldsymbol{\epsilon}$, and integrating over $d\Omega$, we obtain for the total cross-section for scattering from the $\rho_N V$ molecules in the volume $V$:

$$\sigma = \left(\frac{k^2}{4\pi}\right)^2 \left(\frac{8\pi}{3}\right) \left[ \frac{(\epsilon_r - 1)(\epsilon_r + 2)}{3\rho_N} \right]^2 \left| \sum_j \Delta_j \right|^2.$$

The cross-section per molecule is then obtained by dividing by $\rho_N V$, and the attenuation coefficient $\alpha$, which is $\rho_N$ times the cross-section per molecule is

$$\alpha = \left(\frac{k^2}{4\pi}\right)^2 \left(\frac{8\pi}{3}\right) \left[ \frac{(\epsilon_r - 1)(\epsilon_r + 2)}{3\rho_N} \right]^2 \frac{|\sum_j \Delta_j|^2}{V}.$$

Now the quantity $|\sum_j \Delta_j|^2 \equiv \Delta_V^2$ is the square of the sum of the fluctuation in the number of molecules in each cell taken over all the cells in the volume $V$, i.e., it is the square of the fluctuation in the number of molecules in the volume $V$ from the average number $\rho_N V$ of molecules in that volume. That is in turn given by statistical mechanics arguments as

$$\frac{\Delta_V^2}{\rho_N V} = \rho_N \, k_B T \, \beta_T$$

where $k_B$ is the Boltzmann constant, and $\beta_T$ is the isothermal compressibility, $\beta_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$. From this it follows that

$$\alpha = \left(\frac{k^2}{4\pi}\right)^2 \left(\frac{8\pi}{3}\right)\left[\frac{(\epsilon_r - 1)(\epsilon_r + 2)}{3\rho_N}\right]^2 \rho_N^2 \, k_B T \beta_T$$
$$= k^4 \frac{2}{3\pi\rho_N}\left[\frac{(\epsilon_r - 1)(\epsilon_r + 2)}{6}\right]^2 (\rho_N \, k_B T \, \beta_T).$$

This is the Einstein-Smoluchowski equation (Smoluchowski obtained an incomplete version in 1904, which was completed by Einstein in 1910). The factor $|(\epsilon_r - 1)(\epsilon_r + 2)/6|$ is well approximated by $n - 1$ when $|\epsilon_r - 1| << 1$, and for an ideal gas, $\rho_N k_B T \beta_T = 1$, so that we recover the earlier result $\alpha = k^4 \frac{2}{3\pi\rho_N}(n-1)^2$ of Rayleigh. But we also learn that as the temperature approaches a critical temperature at which $\beta_T$ becomes infinite, the attenuation length diverges, and this leads to the phenomenon of *critical opalescence*. This isn't quite the end of the story, since the approximations we have made break down near the critical point. For as the critical point is approached, the correlation length for density fluctuations diverges, and so exceeds the wavelength; and we assumed no correlation from one cell to the other. The more detailed consideration needed to complete the argument was given in 1914 by Ornstein and Zernicke; but that is outside the scope of this course.

## 6.8 The Optical Theorem

A general result which was first encountered in the context of optics, which is a consequence of causality (like the Kramers-Krönig relations) is the *optical theorem*. This relates the total cross-section to the scattering amplitude in the forward direction.

We saw above that when an incident electromagnetic wave of frequency $\omega$ is scattered from a localised scatterer, at large distances from the scatterer we may write

$$\mathbf{D} \to \mathbf{D}_0 + \frac{e^{ikr}}{r}\mathcal{A},$$

and the differential cross-section for scattering is then given by

$$\frac{d\sigma}{d\Omega} = \frac{|\boldsymbol{\epsilon}^* \cdot \mathcal{A}|^2}{|\mathbf{D}_0|^2}.$$

It can be shown (Kirchoff) that

$$F(\mathbf{k}, \boldsymbol{\epsilon}; \mathbf{k}_0, \boldsymbol{\epsilon}_0) \equiv \boldsymbol{\epsilon}^* \cdot \mathcal{A} \frac{1}{|\mathbf{D}_0|},$$

which is the scattering amplitude for scattering from an initial wave vector and polarisation $\mathbf{k}_0, \boldsymbol{\epsilon}_0$ to a final wave vector and polarisation $\mathbf{k}, \boldsymbol{\epsilon}$ (the square modulus of which gives the corresponding differential cross-section), may also be expressed as

$$F = \frac{1}{|\mathbf{E}_0|}\frac{i}{4\pi}\int_S e^{-i\mathbf{k}\cdot\mathbf{x}}[\omega\boldsymbol{\epsilon}^* \cdot (\mathbf{n} \times \mathbf{B}_s) + \boldsymbol{\epsilon}^* \cdot (\mathbf{k} \times (\mathbf{n} \times \mathbf{E}_s))]\,dS$$

where $\mathbf{B}_s, \mathbf{E}_s$ describe the scattered wave, and the integration is over any closed surface $S$ which encloses the scatterer, the outward normal from which is written $\mathbf{n}$. The derivation of this formula makes use of Green's theorem, and although not difficult will be omitted.

The total field in the presence of the scatterer is described by

$$\mathbf{E} = \mathbf{E}_0 + \mathbf{E}_s$$
$$\mathbf{B} = \mathbf{B}_0 + \mathbf{B}_s.$$

The scatterer will absorb radiation, as well as scatter it, and the time-averaged absorption power, $P_{\text{abs}}$, is given from the inward flow of energy as

$$P_{\text{abs}} = -\frac{1}{2\mu_0} \int_S \Re[(\mathbf{E} \times \mathbf{B}^*) \cdot \mathbf{n}] \, dS,$$

(the minus sign because we want the inward flux of energy, and the factor of a half because of the time averaging). On the other hand the time averaged scattered power is

$$P_{\text{scattd}} = \frac{1}{2\mu_0} \int \Re[(\mathbf{E}_s \times \mathbf{B}_s^*) \cdot \mathbf{n}] \, dS,$$

so that the total power removed from the incident wave, either by absorption or by scattering is

$$P = -\frac{1}{2\mu_0} \int \Re[(\mathbf{E}_s \times \mathbf{B}_0^* + \mathbf{E}_0^* \times \mathbf{B}_s) \cdot \mathbf{n}] \, dS.$$

Setting $\mathbf{E}_0 = E_0 \boldsymbol{\epsilon}_0 e^{i\mathbf{k}_0 \cdot \mathbf{x}}$, $\mathbf{B}_0 = \frac{c}{k}\mathbf{k}_0 \times \mathbf{E}_0$ gives

$$P = \frac{1}{2\mu_0} \Re\{E_0^* \int e^{-i\mathbf{k}_0 \cdot \mathbf{x}} \boldsymbol{\epsilon}_0^* \cdot [\mathbf{n} \times \mathbf{B}_s + \mathbf{k}_0 \times (\mathbf{n} \times \mathbf{E}_s)/ck] \, dS\}.$$

We have previously determined the differential cross-section for scattering, and by integrating this over solid angles have obtained the scattering cross-section $\sigma$. What we are now interested in is the total cross-section $\sigma_{\text{tot}}$, which also takes into account the absorption as well as the scattering of radiation. This is defined as the power removed from the incident radiation divided by the incident power crossing a unit area, i.e., divided by the incident flux. So

$$\sigma_{\text{tot}} = \frac{P}{\epsilon_0 |E_0|^2 c/2}$$
$$= \Re\{E_0^{-1} c \int e^{-i\mathbf{k}_0 \cdot \mathbf{x}} \boldsymbol{\epsilon}_0^* \cdot [\mathbf{n} \times \mathbf{B}_s + \mathbf{k}_0 \times (\mathbf{n} \times \mathbf{E}_s)/ck] \, dS\}.$$

Now compare this with the scattering amplitude in the forward direction, for unaltered polarisation (elastic scattering)

$$F(\mathbf{k}_0, \boldsymbol{\epsilon}_0; \mathbf{k}_0, \boldsymbol{\epsilon}_0) = \frac{1}{E_0} \frac{i}{4\pi} \int e^{-i\mathbf{k}_0 \cdot \mathbf{x}} \boldsymbol{\epsilon}_0^* \cdot [\omega \mathbf{n} \times \mathbf{B}_s + \mathbf{k}_0 \times (\mathbf{n} \times \mathbf{E}_s)] \, dS,$$

and conclude that

$$\sigma_{\text{tot}} = \frac{4\pi}{k} \Im F(\text{forward elastic}).$$

This is the optical theorem. A review and a more complete derivation can be found in the Supplementary Notes.

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