

1 Scattering by an ensemble of small particles in the dipole approximation

Consider an ensemble of numerous small particles which have fixed locations in space and the scattering amplitudes of which can be expressed in the dipole approximation. Assume presently that the particles do not interact with each other. Since the induced dipole moments are proportional to the incident field, the moments will depend on the phase factor $e^{ik\hat{\mathbf{n}}_0 \cdot \mathbf{x}_j}$, where \mathbf{x}_j is the location of the j th scatterer. When the observer is located far away from the scatterer, the exponential part of the Green's function results in an additional phase factor for the j th scatterer, $e^{-ik\hat{\mathbf{n}} \cdot \mathbf{x}_j}$. In the dipole approximation, the ensemble of particles scatters as follows:

$$\frac{d\sigma}{d\Omega} = \frac{k^4}{(4\pi\epsilon_0 E_0)^2} \left| \sum_j \hat{\mathbf{e}}^* \cdot \mathbf{p}_j e^{i\mathbf{q} \cdot \mathbf{x}_j} \right|, \quad \mathbf{q} = k(\hat{\mathbf{n}}_0 - \hat{\mathbf{n}}) \quad (1)$$

Except for the forward-scattering direction ($\mathbf{q} = 0$), scattering will depend sensitively on how the small particles are located in space.

Assume now that all the particles are identical so that $\mathbf{p} = \mathbf{p}_j$ for all j and

$$\frac{d\sigma}{d\Omega} = \frac{k^4}{(4\pi\epsilon_0 E_0)^2} |\hat{\mathbf{e}}^* \cdot \mathbf{p}|^2 F(\mathbf{q}), \quad (2)$$

where $F(\mathbf{q})$ is the so-called structure factor,

$$F(\mathbf{q}) = \left| \sum_j e^{i\mathbf{q} \cdot \mathbf{x}_j} \right|^2 = \sum_{j,j'} e^{i\mathbf{q} \cdot (\mathbf{x}_j - \mathbf{x}_{j'})} \quad (3)$$

If the small particles are located in random positions, the terms $j \neq j'$ will cause a negligible contribution to the sum. Only the terms $j = j'$ are significant and $F(\mathbf{q}) = N$, where N is the number of scatterers. In this case, the total scattering is the incoherent superposition of the individual contributions.

If the small particles are regularly located in space, the structure factor disappears almost everywhere except for the proximity of the forward-scattering direction. Therefore, large regular arrays of small particles do not scatter (for example, individual transparent crystals of rock salt and quartz).

Consider scatterers located in a regular cubic lattice. The structure factor can be calculated analytically, since

$$\begin{aligned} \left| \sum_j e^{i\mathbf{q} \cdot \mathbf{x}_j} \right|^2 &= \left| \sum_{j_1=0}^{N_1-1} e^{iq_1 j_1 a} \sum_{j_2=0}^{N_2-1} e^{iq_2 j_2 a} \sum_{j_3=0}^{N_3-1} e^{iq_3 j_3 a} \right|^2 \\ &= \left| \left(\frac{1 - e^{iq_1 N_1 a}}{1 - e^{iq_1 a}} \right) \left(\frac{1 - e^{iq_2 N_2 a}}{1 - e^{iq_2 a}} \right) \left(\frac{1 - e^{iq_3 N_3 a}}{1 - e^{iq_3 a}} \right) \right|^2 \\ &= N^2 \left[\left(\frac{\sin^2 \frac{1}{2} N_1 q_1 a}{N_1^2 \sin^2 \frac{1}{2} q_1 a} \right) \left(\frac{\sin^2 \frac{1}{2} N_2 q_2 a}{N_2^2 \sin^2 \frac{1}{2} q_2 a} \right) \left(\frac{\sin^2 \frac{1}{2} N_3 q_3 a}{N_3^2 \sin^2 \frac{1}{2} q_3 a} \right) \right], \end{aligned} \quad (4)$$

where a is the lattice constant (distance between the lattice points) and where N_1 , N_2 , and N_3 are the numbers of lattice points in each direction hilapisteiden so that the total number of lattice points equals $N = N_1 N_2 N_3$ (this was utilized to obtain the final result above). The components of the vector \mathbf{q} in each direction are q_1 , q_2 , and q_3 .

We note that, at short wavelengths ($ka \geq \pi$), the structure factor has peaks when the Bragg condition is fulfilled: $q_i a = 0, 2\pi, 4\pi \dots$, where $i = 1, 2, 3 \dots$. This is typical in X-ray diffraction. At long wavelengths, only the peak $q_i a = 0$ is relevant, since $\max |q_i a| = 2ka \ll 1$. In this limit, the structure factor is a product of three $\sin^2 x_i/x_i^2$ -type factors ($x_i = \frac{1}{2}N_i q_i a$), and scattering is confined to the region $q_i \leq 2\pi/N_i a$, corresponding to the angles λ/L , where L is the size of the lattice.

2 Volume integral equation for scattering

In a uniform medium, the electromagnetic wave propagates undisturbed and without changing its direction of propagation. If there are fluctuations in the medium depending on space or time, the wave is scattered, and part of its energy is redirected. If the fluctuations in the medium are small, scattering is weak and one may utilize methods based on perturbation series.

Consider a uniform isotropic medium with electric permittivity ϵ_m and magnetic permeability equal to the permeability of vacuum, $\mu_m = \mu_0$. Fluctuations in the medium result in $\mathbf{D} \neq \epsilon_m \mathbf{E}$ in some constrained region. Let us start from Maxwell's equations in sourceless space:

$$\begin{aligned} \nabla \cdot \mathbf{B} = 0 \quad , \quad \nabla \times \mathbf{E} &= -\frac{\partial \mathbf{B}}{\partial t} \\ \nabla \cdot \mathbf{D} = 0 \quad , \quad \nabla \times \mathbf{H} &= \frac{\partial \mathbf{D}}{\partial t} \end{aligned}$$

Then

$$\nabla \times (\mathbf{D} - \epsilon_m \mathbf{E}) = -\epsilon_m \frac{\partial \mathbf{B}}{\partial t}, \quad (5)$$

so that

$$\nabla \times (\nabla \times \mathbf{D}) = \nabla \times [\nabla \times (\mathbf{D} - \epsilon_m \mathbf{E})] - \epsilon_m \frac{\partial}{\partial t} \mu_0 \nabla \times \mathbf{H}. \quad (6)$$

Moreover, after further manipulation,

$$-\nabla^2 \mathbf{D} = \nabla \times \nabla \times (\mathbf{D} - \epsilon_m \mathbf{E}) - \epsilon_m \mu_0 \frac{\partial^2}{\partial t^2} \mathbf{D}, \quad (7)$$

which can be written in the form

$$\nabla^2 \mathbf{D} - \epsilon_m \mu_0 \frac{\partial^2 \mathbf{D}}{\partial t^2} = -\nabla \times \nabla \times (\mathbf{D} - \epsilon_m \mathbf{E}), \quad (8)$$

that is the exact wave equation for the \mathbf{D} -field derived without any approximations. Later, the right-hand side of the equation is treated as a small perturbation.

If the right-hand side of the equation were known, the solution of the wave equation could be written as a suitable integral of it. Although the right-hand side is usually unknown, the integral form is useful, since it allows the derivation of important approximations.

Assume again harmonic time dependence $e^{-i\omega t}$, in which case

$$\begin{aligned}(\nabla^2 + k^2)\mathbf{D} &= -\nabla \times \nabla \times (\mathbf{D} - \epsilon_m \mathbf{E}) \\ k^2 &= \mu_0 \epsilon_m \omega^2,\end{aligned}\tag{9}$$

where ϵ_m is the permittivity corresponding to the angular frequency ω . The solution of the undisturbed problem is obtained by setting the right-hand side equal to zero; denote this solution by $\mathbf{D}^{(0)}$. The formal complete solution is then, in an exact way,

$$\mathbf{D}(\mathbf{x}) = \mathbf{D}^{(0)}(\mathbf{x}) + \frac{1}{4\pi} \int d^3 \mathbf{x}' \frac{e^{ik|\mathbf{x}-\mathbf{x}'|}}{|\mathbf{x}-\mathbf{x}'|} \nabla' \times \nabla' \times (\mathbf{D}(\mathbf{x}') - \epsilon_m \mathbf{E}(\mathbf{x}'))\tag{10}$$

In a scattering problem, the integral on the right-hand side is taken over a constrained region of space and $\mathbf{D}^{(0)}$ describes the incident field. Then, in the far zone,

$$\mathbf{D}(\mathbf{x}) \rightarrow \mathbf{D}^{(0)}(\mathbf{x}) + \frac{e^{ikr}}{r} \mathbf{A}_s,\tag{11}$$

where the scattering amplitude \mathbf{A}_s is

$$\mathbf{A}_s = \frac{1}{4\pi} \int d^3 \mathbf{x}' e^{-ik\hat{\mathbf{n}} \cdot \mathbf{x}'} \nabla' \times \nabla' \times (\mathbf{D}(\mathbf{x}') - \epsilon_m \mathbf{E}(\mathbf{x}')).\tag{12}$$

After some partial integration and noticing that the substitution terms disappear, one obtains

$$\mathbf{A}_s = \frac{k^2}{4\pi} \int d^3 \mathbf{x}' e^{-ik\hat{\mathbf{n}} \cdot \mathbf{x}'} \{[\hat{\mathbf{n}} \times (\mathbf{D}(\mathbf{x}') - \epsilon_m \mathbf{E}(\mathbf{x}'))] \times \hat{\mathbf{n}}\}.\tag{13}$$

The vector characteristics of the integrand can be compared with the field scattered by an electric dipole: the contribution from the term $\mathbf{D} - \epsilon_m \mathbf{E}$ is precisely the field of the electric dipole so that the scattering amplitude is a vector sum from all induced electric dipole moments. The differential cross section is

$$\frac{d\sigma}{d\Omega} = \frac{|\hat{\mathbf{e}}^* \cdot \mathbf{A}_s|}{|\mathbf{D}^{(0)}|^2},\tag{14}$$

where $\hat{\mathbf{e}}$ is the polarization vector of scattered radiation. In principle, we have solved the scattering problem for an arbitrary scatterer in an exact way. The caveat is that we do not know the field inside the scatterer.

1 Rayleigh-Gansin or Born approximation

The integral equation derived above allows for a solution via perturbation series, where the internal field of the scatterer is first approximated by the incident field. What follows is the so-called Rayleigh-Gans approximation or the first Born approximation based on the corresponding integral equation in quantum mechanics.

Consider purely spatial fluctuations from an otherwise uniform medium and assume, in addition, that the fluctuations are linear, $\mathbf{D}(\mathbf{x}) = [\epsilon_m + \delta\epsilon(\mathbf{x})]\mathbf{E}(\mathbf{x})$, where $\delta\epsilon(\mathbf{x})$ is small compared to ϵ_m . The difference $\mathbf{D} - \epsilon_m\mathbf{E}$ showing up in the integral equation is proportional to $\delta\epsilon(\mathbf{x})$. In the lowest order,

$$\mathbf{D} - \epsilon_m\mathbf{E} \approx \frac{\delta\epsilon(\mathbf{x})}{\epsilon_m}\mathbf{D}^{(0)}. \quad (1)$$

Let the incident field be a plane wave so that $\mathbf{D}^{(0)}(\mathbf{x}) = \hat{\epsilon}_0 D_0 e^{ik\hat{n}_0 \cdot \mathbf{x}}$. Then

$$\begin{aligned} \frac{\hat{\epsilon}^* \cdot \mathbf{A}_s^{(0)}}{D_0} &= \frac{k^2}{4\pi} \int d^3\mathbf{x}' e^{i\mathbf{q} \cdot \mathbf{x}} \hat{\epsilon}^* \cdot \hat{\epsilon}_0 \frac{\delta\epsilon(\mathbf{x})}{\epsilon_m} \\ \mathbf{q} &= k(\hat{n}_0 - \hat{n}), \end{aligned} \quad (2)$$

the square of which, in absolute terms, gives the differential cross section. If the wavelength is much larger than the size of the region where $\delta\epsilon \neq 0$, the exponent in the integral can be set to unity. This results in the dipole approximation that was treated before for a small spherical particle.

Let us study the situation where the particle continues to be spherical and is located in free space. Thus, $\delta\epsilon \neq 0$ inside a sphere of radius a . We obtain

$$\begin{aligned} \frac{\hat{\epsilon}^* \cdot \mathbf{A}_s^{(1)}}{D_0} &= \frac{k^2}{4\pi} (\hat{\epsilon}^* \cdot \hat{\epsilon}_0) \frac{\delta\epsilon}{\epsilon_0} \int d^3\mathbf{x}' e^{i\mathbf{q} \cdot \mathbf{x}'} \\ &= \frac{k^2}{4\pi} (\hat{\epsilon}^* \cdot \hat{\epsilon}_0) \frac{\delta\epsilon}{\epsilon_0} \int_0^{2\pi} d\varphi' \int_0^\pi d\theta' \sin\theta' \int_0^a dr' r'^2 e^{iqr' \cos\theta'} \\ &= \frac{k^2}{2} (\hat{\epsilon}^* \cdot \hat{\epsilon}_0) \frac{\delta\epsilon}{\epsilon_0} \int_0^a dr' r'^2 \int_{-1}^1 \frac{1}{iqr'} e^{iqr'\mu'} d\mu', \quad \mu' = \cos\theta' \\ &= \frac{k^2}{4\pi} (\hat{\epsilon}^* \cdot \hat{\epsilon}_0) \frac{\delta\epsilon}{\epsilon_0} \frac{1}{iq} \left\{ \int_0^a r' \frac{1}{iq} (e^{iqr'} + e^{-iqr'}) - \int_0^a dr' \frac{1}{iq} (e^{iqr'} + e^{-iqr'}) \right\} \\ &= k^2 \frac{\delta\epsilon}{\epsilon_0} (\hat{\epsilon}^* \cdot \hat{\epsilon}_0) \left(\frac{\sin qa - qa \cos qa}{q^3} \right), \quad q = |\mathbf{q}| = \sqrt{2}k\sqrt{1 - \hat{n} \cdot \hat{n}_0}. \end{aligned}$$

In the limit $a \rightarrow 0$, the term inside the parentheses approaches $a^3/3$ so that, for scatterers much smaller than the wavelength or for q approaching zero,

$$\lim_{q \rightarrow 0} \left(\frac{d\sigma}{d\Omega} \right)_{R-G} = k^4 a^6 \left| \frac{\delta\epsilon}{3\epsilon_0} \right|^2 |\hat{\epsilon}^* \cdot \hat{\epsilon}_0|^2. \quad (3)$$

This is in agreement with the long-wavelength limit studied earlier. The integral $\int_S d^3\mathbf{x}' e^{i\mathbf{q}\cdot\mathbf{x}'}$ is commonly called the form factor.

2 Why is the sky blue?

In the present context, we can consider the blueness of the sky and redness of the sunrises and sunsets. Assume that the atmosphere is composed of individual molecules with locations \mathbf{x}_j and that have the dipole moment $\mathbf{p}_j = \hat{\epsilon}_0 \gamma_{\text{mol}} \mathbf{E}(\mathbf{x}_j)$, where γ_{mol} is the molecular polarizability. Then, the fluctuations of the electric permittivity can be described with the sum

$$\delta\epsilon(\mathbf{x}) = \epsilon_0 \sum_j \gamma_{\text{mol}} \delta(\mathbf{x} - \mathbf{x}_j) \quad (4)$$

The differential scattering cross section is of the form

$$\frac{d\sigma}{d\Omega} = \frac{k^4}{16\pi^2} |\gamma_{\text{mol}}|^2 |\hat{\epsilon}^* \cdot \hat{\epsilon}_0|^2 F(\mathbf{q}), \quad (5)$$

where F is the structure factor treated before. For randomly distributed scatterers, $F(\mathbf{q})$ is directly the number of the molecules. For low-density gas, the relative permittivity is $\epsilon_r = \epsilon/\epsilon_0 = 1 + N\gamma_{\text{mol}}$, where N is now the number of molecules in unit volume. The total scattering cross section as per molecule is

$$\sigma_s \approx \frac{k^4}{6\pi N^2} |\epsilon_r - 1|^2 \cong \frac{2k^4}{3\pi N^2} |m - 1|^2, \quad (6)$$

where m is the refractive index and $|m - 1| \ll 1$.

When the radiation propagates a distance dx in the atmosphere, the relative change in its intensity is $N\sigma dx$ and $I(x) = I_0 e^{-k_e x}$, where k_e is the so-called extinction coefficient:

$$k_e = N\sigma_s \cong \frac{2k^4}{3\pi N} |m - 1|^2 \quad (7)$$

This is called Rayleigh scattering that is incoherent scattering by gas molecules and other dipole scatterers, where each scatterer scatters radiation based on Rayleigh's $1/\lambda^4$ -law.

The $1/\lambda^4$ -law means that blue light is scattered much more efficiently than red light. In practice, this shows up so that blue color predominates when looking in directions other than the light source whereas, in the direction of the light source, red color predominates.

For visible light, $\lambda = 0.41 - 0.65 \mu\text{m}$ and, under normal conditions, $m - 1 \approx 2.78 \cdot 10^{-4}$. When $N = 2.69 \cdot 10^{19}$ molecules/cm³, we obtain for the mean free path $1/k_e = 30, 77, \text{ and } 188$ km at wavelengths $0.41 \mu\text{m}$ (violet), $0.52 \mu\text{m}$ (green), and $0.65 \mu\text{m}$ (red), respectively.

Polarization reaches its maximum of 75 % at the wavelength of $0.55 \mu\text{m}$. The deviation from 100 % derives from multiple scattering (6 %), the anisotropy of the molecules (6 %), reflection from the surface (5 %, in particular, for green light in the case of vegetation), and aerosols (8 %).