Light in complex dielectrics

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CHAPTER 2

Macroscopic dielectric response of microscopic particles

This chapter serves as a concise tutorial on the interaction of light with dielectrics. It contains the necessary theoretical aspects for describing the experiments performed. Emphasis is put on the microscopic origin of the macroscopic dielectric function; several non-standard derivations including local-field corrections are presented. An extension is made to mixtures of dielectrics, treating several effective medium theories for the average dielectric constant. Scattering of light by such mixtures is captured in the quasi-static dielectric function.

2.1 The microscopic polarizable dipole

Light is generated by the acceleration of charged particles. The interaction of light with dielectric material is therefore a subtle interplay between absorption of light and the subsequent emission of it by the atoms or molecules, i.e. the microscopic polarizable dipoles, that constitute the dielectric. The interaction is complicated as each dipole not only feels the external electro-magnetic field, but also the fields produced by all the other dipoles. In order to understand the full macroscopic response of a collection of microscopic polarizable dipoles, first the description of one such dipole is presented.

Note that many of the elementary ingredients used in this chapter can be found in the excellent book by J.D. Jackson [24]. Throughout this chapter Heaviside-Lorentz units are used, as discussed in table 2 in the appendix of the book by Jackson [24].

The microscopic polarizable dipole can be modeled by a damped harmonic oscillator, with mass \( m \) and charge \( -e \) that oscillates around a fixed charge \( +e \) [11]. It is assumed that the amplitude of oscillation is small, so that the spatial variation of the time varying electric field \( \mathbf{E}(t) \) can be neglected; the dipole approximation
is employed. The equation of motion for an oscillator with displacement \( x \) from its equilibrium position is

\[
m \left[ \frac{\partial^2 x}{\partial t^2} + \Gamma \frac{\partial x}{\partial t} + \omega_0^2 x \right] = -eE(t),
\]

(2.1)

where \( \omega_0 \) is the resonance frequency of the oscillator and \( \Gamma \) a to be determined damping rate. If the electric field varies harmonically in time with frequency \( \omega \) as \( e^{-i\omega t} \), i.e., monochromatic light with frequency \( \omega \), the induced dipole moment \( p \) of the oscillator is

\[
p = -ex = \frac{e^2/m}{\omega_0^2 - \omega^2 - i\omega \Gamma}E.
\]

(2.2)

As can be seen from Eq. 2.2, the discussion presented here is restricted to linear and isotropic dielectrics, as \( p \) is linear with \( E \). The (linear) dynamic polarizability \( \alpha(\omega) \) is defined as \( p = \alpha(\omega)E \), giving

\[
\alpha(\omega) = \alpha(0) \times \frac{\omega_0^2}{\omega_0^2 - \omega^2 - i\omega \Gamma},
\]

(2.3)

where \( \alpha(0) = e^2/(m\omega_0^2) \) is the static polarizability. The dynamic polarizability displays the resonant structure of an absorbing atom or molecule with resonance frequency \( \omega_0 \) and line width \( \Gamma \).

In an oscillating dipole the charge \( -e \) is accelerated sinusoidally, hence the dipole emits radiation. As a result, the amplitude of the oscillating dipole gradually decreases, since energy of motion is converted into radiant energy. This phenomenon is called radiation damping, and is the classical analogue of spontaneous emission in which an atom makes a transition from an excited state to a state of lower energy by emission of a photon. The decrease in amplitude is grasped in the damping rate \( \Gamma \). In order to conserve energy, the power taken by the dipole from the incident electric field should equal the reradiated power, i.e., the optical theorem [25] should hold. As a result, the set \( \{\Gamma, \alpha(0), \omega_0\} \) has only two independent parameters: \( \Gamma \) cannot be chosen independently. The optical theorem requires

\[
\Gamma = \frac{\alpha(0)\omega^2\omega_0^2}{6\pi c_0^3},
\]

(2.4)

where \( c_0 \) is the speed of light in vacuo. It is convenient to remove the functional dependence of \( \Gamma \) on \( \omega \) by introducing

\[
\Gamma_0 \equiv \Gamma(\omega_0^2/\omega^2) = \frac{\alpha(0)\omega_0^4}{6\pi c_0^3},
\]

(2.5)
the spontaneous emission rate or the Einstein A coefficient. The full mapping of our results on those of Fermi's golden rule [26] from quantum mechanics can be obtained by taking for the static polarizability \( \alpha(0) = 2|D|^2/(\varepsilon_0\omega_0) \) [16, 25], where \( D \) is the dipole matrix element of two atomic levels. In fact, this treatment of an atom is equivalent to the two-level atom approach in quantum mechanics, except that the induced dipole cannot be saturated. The full frequency dependency of the dynamic polarizability is thus given by

\[
\alpha(\omega) = \alpha(0) \times \frac{\omega^2_0}{\omega^2_0 - \omega^2 - i(\Gamma_0\omega^3/\omega_0^2)}. \tag{2.6}
\]

As mentioned above, the oscillating dipole radiates. The field felt by a dipole inside a dielectric is a summation of all fields from the other dipoles and the incident exciting field. In order to be able to perform such a summation, one needs to know the field of one such point dipole. This field \( \mathbf{E}_{\text{dip}}(\mathbf{r}) \) at position \( \mathbf{r} \) produced by an oscillating dipole positioned at the origin is given by

\[
\mathbf{E}_{\text{dip}}(\mathbf{p}, k, \mathbf{r}) = k^2 (\mathbf{n} \times \mathbf{p}) \times \mathbf{n} \frac{e^{ikr}}{4\pi r} - \frac{1}{3} \mathbf{p} \delta^3(\mathbf{r})
\]

\[
+ \frac{1}{4\pi} [3\mathbf{n}(\mathbf{n} \cdot \mathbf{p}) - \mathbf{p}] \left( \frac{1}{r^3} - \frac{ik}{r^2} \right) e^{ikr}. \tag{2.7}
\]

Here \( k = \omega/c_0 \) is the wavevector, \( r = |\mathbf{r}| \) the distance from the dipole, and \( \mathbf{n} = \mathbf{r}/r \) the unit vector pointing from the dipole towards \( \mathbf{r} \). Note that when the dipole is position at \( \mathbf{r}_0 \), \( \mathbf{r} \) should be replaced by \( (\mathbf{r} - \mathbf{r}_0) \). As can be guessed from Eq. 2.7, the summation of the contributions of all the dipoles at different positions is quite cumbersome. However, this complicated form can in some limits be simplified. In the far field, or radiation zone \( (kr \to \infty) \), this equation reduces to

\[
\mathbf{E}_{\text{dip}}^{\text{rf}}(\mathbf{p}, k, \mathbf{r}) = k^2 (\mathbf{n} \times \mathbf{p}) \times \mathbf{n} \frac{e^{ikr}}{4\pi r}. \tag{2.8}
\]

Whereas in the near field, or static zone \( (kr \downarrow 0) \), the field approaches

\[
\mathbf{E}_{\text{dip}}^{\text{nf}}(\mathbf{p}, \mathbf{r}) = \frac{1}{4\pi} [3\mathbf{n}(\mathbf{n} \cdot \mathbf{p}) - \mathbf{p}] \frac{1}{r^3} - \frac{1}{3} \mathbf{p} \delta^3(\mathbf{r}), \tag{2.9}
\]

which is, apart from its oscillations in time, just the static electric dipole field. Equation 2.9 will be used for dense dielectrics in which the dipoles are in each others near field.

The delta function term in Eqs. 2.7 and 2.9 only contributes to the dipole field at the position of the point dipole. Nevertheless, the delta function is essential to
fulfill a general theorem by Maxwell: the volume integral of the static electric field over a sphere with radius $R$ is

$$\int_{r<R} E(r) \, d^3r = -\frac{1}{3} \mathbf{p}. \quad (2.10)$$

Here $E$ is the electric field produced by the charges, which are assumed to be all inside the sphere, and $\mathbf{p}$ the electric dipole moment of the charge distribution with respect to the center of the sphere, see Fig. 2.1. Note that this volume integral is independent of the size of the spherical region of integration provided that all the charge is inside. For a set of point dipoles $\{\mathbf{p}_i\}$, the total electric dipole moment with respect to the center of the sphere resides to a simple summation of all the individual dipole moments $\sum_i \mathbf{p}_i$, independent of the positional distribution of these dipoles. In fact, the delta function term in Eqs. 2.7 and 2.9 carries the essential information about the actual finite charge distribution of the dipole. The role of the delta function will be rediscussed when treating the small dielectric sphere, or point scatterer. Complementary, when all the charges are outside the sphere, see Fig. 2.1, the volume integral of $E$ is

$$\int_{r<R} E(r) \, d^3r = \frac{4\pi}{3} R^3 E(0). \quad (2.11)$$

In other words, the average value of the electric field over a spherical volume containing no charge is the value of the field at center of the sphere $E(0)$. It should be stressed that Eqs. 2.10 and 2.11 only hold for static charge distributions.
2.2 Macroscopic quantities; spatial averaging

The fields introduced so far are microscopic electric fields produced by a microscopic charge distribution. However, for many macroscopic properties of dielectrics it is not essential, and actually far to complicated, to know the exact microscopic electric field. For any dielectric, except for extremely dilute gases, the number of microscopic polarizable dipoles within the optical volume \( \rho \lambda^3 \) is very large, where \( \rho \) is the number density of the dipoles and \( \lambda \) the wavelength of (visible) light. As a result, the microscopic fields produced by these dipoles vary extremely rapidly in space and time. On length scales \( \Lambda \), with \( \lambda \gg \Lambda \gg \rho^{-1/3} \), these microscopic fluctuations average out, giving relatively smooth and slowly varying macroscopic quantities.

To obtain such macroscopic quantities, it is necessary to perform a spatial averaging procedure. The spatial average of a microscopic quantity \( S(r, t) \) with respect to a test function \( f(r) \) is defined as

\[
\langle S(r, t) \rangle = \int d^3 \mathbf{r}' f(\mathbf{r}') S(\mathbf{r} - \mathbf{r}', t),
\]

where \( f(\mathbf{r}) \) is real, nonzero in the neighborhood of \( \mathbf{r} = 0 \), and normalized to unity over all space. The often used spherical averaging volume with radius \( R (R \approx \Lambda) \) is represented by

\[
f(\mathbf{r}) = \frac{3}{4\pi R^3} \Theta(R^2 - |\mathbf{r}|^2),
\]

where \( \Theta(x) \) is the step function, with \( \Theta(x) = 1 \) for \( x \geq 0 \) and \( \Theta(x) = 0 \) for \( x < 0 \).

Using the spatial averaging procedure, the macroscopic electric field \( \mathbf{E}_{\text{mac}}(\mathbf{r}, t) \) becomes

\[
\mathbf{E}_{\text{mac}}(\mathbf{r}, t) = \langle \mathbf{E}(\mathbf{r}, t) \rangle,
\]

where \( \mathbf{E}(\mathbf{r}, t) \) is the microscopic electric field. Likewise, the macroscopic polarization \( \mathbf{P}(\mathbf{r}, t) \) for a set of induced point dipoles \( \{ \mathbf{p}_i \} \) at positions \( \{ \mathbf{r}_i \} \) is

\[
\mathbf{P}(\mathbf{r}, t) = \langle \sum_i \mathbf{p}_i \delta^3(\mathbf{r} - \mathbf{r}_i) \rangle.
\]

For linear, isotropic, homogeneous dielectrics the macroscopic polarization \( \mathbf{P} \) and the macroscopic electric field \( \mathbf{E}_{\text{mac}} \) are related through

\[
\mathbf{P} = \chi(\omega) \mathbf{E}_{\text{mac}} \equiv (\varepsilon(\omega) - 1) \mathbf{E}_{\text{mac}},
\]

where \( \chi(\omega) \) is the electric susceptibility and \( \varepsilon(\omega) \) the dielectric function, for \( \omega = 0 \) known as the dielectric constant \( \varepsilon(0) \). Equation 2.16 is the macroscopic analogon of...
\( \mathbf{p} = \alpha(\omega) \mathbf{E} \). The macroscopic response of a homogeneous dielectric is completely captured in \( \chi(\omega) \), or equivalently \( \varepsilon(\omega) \). This macroscopic response originates from the microscopic one: \( \chi(\omega) \), \( \varepsilon(\omega) \), depends on how the dipoles are spatially arranged, the density of the dipoles \( \rho \), and their polarizability \( \alpha(\omega) \).

2.3 The small dielectric sphere

In order to further clarify the properties of a point dipole, the small dielectric sphere is discussed. The two, the point dipole and the small dielectric sphere, are shown to be analogous.

Consider a small dielectric sphere with radius \( a \) and dielectric constant \( \varepsilon \) in a homogeneous external electric field \( \mathbf{E}_0 \). Small means that \( a \) is much smaller than the wavelength \( \lambda \), so that electrostatic approach is applicable (also known as the long wavelength limit or dipole approximation). The dielectric sphere is polarized by the external electric field \( \mathbf{E}_0 \). As a result, the total electric field is different from the external field. The electric field \( \mathbf{E}_{\text{in}} \) inside the dielectric is homogeneous and given by

\[
\mathbf{E}_{\text{in}} = \frac{3}{\varepsilon + 2} \mathbf{E}_0 = \mathbf{E}_0 + \mathbf{E}_{\text{depol}}, \tag{2.17}
\]

where \( \mathbf{E}_{\text{depol}} \) is the depolarization field produced by the dielectric sphere. Outside the sphere, the total field is the sum of \( \mathbf{E}_0 \) and the field of an electric dipole (see Eq. 2.9) at the center of the sphere with dipole moment

\[
\mathbf{p}_{\text{sph}} = 4\pi \frac{\varepsilon - 1}{\varepsilon + 2} \frac{1}{a^3} \mathbf{E}_0 = 3 \frac{\varepsilon - 1}{\varepsilon + 2} \Omega \mathbf{E}_0, \tag{2.18}
\]

where \( \Omega = 4\pi a^3/3 \) is the volume of the sphere. The dipole moment \( \mathbf{p}_{\text{sph}} \) can be interpreted as the volume integral of polarization \( \mathbf{P} \), as the polarization is (see Eq. 2.16),

\[
\mathbf{P} = (\varepsilon - 1) \mathbf{E}_{\text{in}} = 3 \frac{\varepsilon - 1}{\varepsilon + 2} \mathbf{E}_0. \tag{2.19}
\]

Combining Eqs. 2.17 and 2.18 gives for the depolarization field

\[
\mathbf{E}_{\text{depol}} = -\frac{1}{3\Omega} \mathbf{p}_{\text{sph}} = -\frac{1}{3} \mathbf{P}, \tag{2.20}
\]

baring close resemblance to the delta function term in Eqs. 2.7 and 2.9. In fact, in the limit \( a \downarrow 0 \) the dielectric sphere, or point scatterer, is equivalent to a point
dipole in the quasi-static regime \((\omega \ll \omega_0)\). The analogy is complete when the static polarizability in Eq. 2.6 is identified as

\[
\alpha(0) = 3\Omega \frac{\varepsilon - 1}{\varepsilon + 2},
\]

(2.21)

The dynamic polarizability \(\alpha(\omega)\) also depends on \(\omega_0\) and \(\Gamma_0\). The exact value for \(\omega_0\) is irrelevant, as long as \(\omega_0 \gg \omega\). The damping rate \(\Gamma_0\) follows from the optical theorem, as elastic point scatterers are considered, see Eq. 2.5. Contrary to the quasi-static regime, the analogy in the resonant regime is more complicated [27].

Particles much smaller than the wavelength of light \(\lambda\) are also called Rayleigh scatterers [2]. The present treatment breaks down when the size \(s\) of the scatterer becomes comparable or larger than \(\lambda\). The regime \(s \approx \lambda\) is governed by Mie scattering, whereas for \(s \gg \lambda\) geometrical scattering is important [2].

### 2.3.1 The small dielectric cavity

The properties of a small dielectric cavity with radius \(a\) inside an otherwise homogeneous dielectric with dielectric constant \(\varepsilon\) are very similar to the above described dielectric sphere. The macroscopic field outside the cavity can be represented by the sum of the macroscopic applied field \(E_{\text{mac}}\) and the field of a dipole placed at the center of the cavity with dipole moment

\[
p_{\text{cav}} = 3\varepsilon \frac{1 - \varepsilon}{2\varepsilon + 1} \Omega E_{\text{mac}},
\]

(2.22)

where of course \(\Omega\) is the volume of the cavity. Note that \(p_{\text{cav}}\) is oppositely directed to \(E_{\text{mac}}\) for \(\varepsilon > 1\). It should also be emphasized that the field produced by \(p_{\text{cav}}\) is the field of a dipole in a host medium with dielectric constant \(\varepsilon\). The electric field \(E_{\text{in}}\) inside the cavity is homogeneous and given by

\[
E_{\text{in}} = \frac{3\varepsilon}{2\varepsilon + 1} E_{\text{mac}} = E_{\text{mac}} + E_{\text{depol}} = L_{\text{emp}} E_{\text{mac}}.
\]

(2.23)

Here \(E_{\text{depol}} = -1/(3\varepsilon\Omega)p_{\text{cav}}\), similar to Eq. 2.20, and the empty cavity factor \(L_{\text{emp}}\) is defined for later convenience.

### 2.4 The dielectric function

As already mentioned, the dielectric function \(\varepsilon(\omega)\) of a homogeneous dielectric depends on the density \(\rho\) and polarizability \(\alpha(\omega)\) of the dipoles that constitute the dielectric. For simplicity it assumed that the dielectric consists of only one type of polarizable dipoles, with a density that is independent of position. Here several derivations for \(\varepsilon(\omega)\) are presented.
2.4.1 Linear response

First the linear response approach is discussed. The dipoles are polarized by a homogeneous external field $E_0$. In the approximation of the linear response model, the electric field produced by these dipoles is disregarded. As a result, the macroscopic electric field $E_{\text{mac}}$ equals the microscopic one: $E_{\text{mac}} = E_0$, as $E_0$ is the only microscopic field present. The macroscopic polarization $P$ is given by (see Eq. 2.15)

$$P = \langle \sum \alpha(\omega)E_0 \delta^3 (r - r_i) \rangle = \rho \alpha(\omega)E_{\text{mac}},$$

(2.24)

using $p_i = p = \alpha(\omega)E_0$, $E_{\text{mac}} = E_0$, and

$$\rho = \langle \sum \delta^3 (r - r_i) \rangle.$$

(2.25)

Hence, combining Eqs. 2.16 and 2.24, the dielectric function is found to be

$$\varepsilon(\omega) = 1 + \rho \alpha(\omega).$$

(2.26)

The linear response approximation is valid for $\varepsilon$ close to 1, or equivalently $\rho \alpha \ll 1$.

2.4.2 A random collection of dipoles; fluids

For dense dielectrics, that is $\rho \alpha(\omega) \sim 1$, the linear response approximation breaks down: the dipolar electric fields may not be neglected. In general, the total static microscopic field $E_{\text{mic}}(r)$ for a collection of dipoles $\{p_i\}$ at positions $\{r_i\}$ is

$$E_{\text{mic}}(r) = E_0 + \sum E_{\text{dip}}^\text{nf}(p_i, r - r_i),$$

(2.27)

where again $E_0$ is the homogeneous external electric field and $E_{\text{dip}}^\text{nf}$ is given by Eq. 2.9. This summation over dipolar fields consists of two contributions: the scattered fields $E_{\text{scat}}$ and the depolarization fields $E_{\text{depol}}$, explicitly given by

$$E_{\text{scat}} = \sum \frac{1}{4\pi} \left[ 3n^2_i (n_i \cdot p_i) - p_i \right] \frac{1}{r_i^3}$$

(2.28)

and

$$E_{\text{depol}} = - \sum \frac{1}{3} p_i \delta^3 (r - r_i),$$

(2.29)

where the notation is used as explained below Eq. 2.7. For randomly positioned dipoles, as is the case for fluids, it is assumed that $E_{\text{scat}}$ averages out to zero. Later,
this will be shown explicitly for dipoles on a square lattice. Using this assumption, the total microscopic field resides to

\[ \mathbf{E}_{\text{mic}}(\mathbf{r}) = \mathbf{E}_0 - \sum_i \frac{1}{3} \mathbf{p}_i \delta^3(\mathbf{r} - \mathbf{r}_i). \] (2.30)

As the discussion is concerned with homogeneous and isotropic media, all dipole moments are the same, that is \( \mathbf{p}_i = \mathbf{p} \). Hence, the macroscopic electric field \( \mathbf{E}_{\text{mac}} \), using Eqs. 2.14 and 2.25, is given by

\[ \mathbf{E}_{\text{mac}} = \mathbf{E}_0 - \frac{1}{3} \rho \mathbf{p}. \] (2.31)

Similarly, the macroscopic polarization \( \mathbf{P} \) becomes, see Eq. 2.15,

\[ \mathbf{P} = \rho \mathbf{p}. \] (2.32)

The only unknown parameter left, is the dipole moment \( \mathbf{p} \) that is induced by the microscopic field at the position of the dipole. This field is \( \mathbf{E}_0 - (1/3) \rho \delta^3(0) \), where the delta function represents an unphysical self interaction and will be neglected. Here, it is implicitly assumed that two or more dipoles are not on the same position. Consequently, \( \mathbf{p} = \alpha(\omega) \mathbf{E}_0 \). Combining Eqs. 2.16, 2.31, and 2.32, finally the desired result for the dielectric function is obtained

\[ \varepsilon(\omega) = 1 + \frac{\rho \alpha(\omega)}{1 - \frac{1}{3} \rho \alpha(\omega)}. \] (2.33)

It should be noted that this derivation is done in the static limit. However, it also holds for dynamic fields, under the assumption that the size of the sphere used in the spatial averaging procedure to obtain macroscopic quantities, see Eq. 2.13, is much smaller than the wavelength involved. Furthermore, it is clear that for \( \rho \alpha(\omega) \ll 1 \) the linear response result, Eq. 2.26, is regained.

### 2.4.3 A square lattice of dipoles; exact result for electrostatics

Consider a dielectric with the dipoles \( \mathbf{p} \) placed on a square lattice. The positions of the dipoles are thus given by the set of coordinates \( \{ \mathbf{R} \} \), with components along the cartesian coordinate axes \( (a_i, a_j, a_k) \), where \( a \) is the lattice spacing, and \( i, j, \) and \( k \) each take on positive and negative integer values. Hence, the total static microscopic field is, see Eq. 2.27,

\[ \mathbf{E}_{\text{mic}}(\mathbf{r}) = \mathbf{E}_0 + \sum_{\{ \mathbf{R} \}} \mathbf{E}_{\text{dip}}^{\text{nf}}(\mathbf{p}, \mathbf{r} - \mathbf{R}). \] (2.34)
Contrary to the treatment of fluids, where the dipoles were randomly positioned, it is now not assumed that the scattered fields of the dipoles average out to zero. Here, of course within the limits of the static approximation, the derivation will be exact using the explicit form of Eq. 2.34.

As the lattice of point dipoles is homogeneous, the macroscopic field is also homogeneous. Therefore, it is sufficient to calculate the macroscopic field at the origin

$$\mathbf{E}_{\text{macro}}(0) = \frac{3}{4\pi R^3} \int_{r < R} d^3 r \left[ \mathbf{E}_0 + \sum_{\{\mathbf{R}\}} \mathbf{E}_{\text{dip}}^{\text{nf}}(\mathbf{p}, \mathbf{r} - \mathbf{R}) \right],$$

where the spherical integration volume is centered at the origin and using Eqs. 2.12-2.14 and 2.34. As the external field \( \mathbf{E}_0 \) is independent of position, the contribution of this field is just (as always) \( \mathbf{E}_0 \). The other contribution to the microscopic field in the sphere is a superposition of fields from the dipoles both in and outside the sphere. The entire set of \( \{\mathbf{R}\} \) dipoles can be divided into two subsets: the dipoles in the sphere \( \{\mathbf{R}_{\text{in}}\} \) and the dipoles outside the sphere \( \{\mathbf{R}_{\text{out}}\} \): \( \Sigma_{\{\mathbf{R}\}} = \Sigma_{\{\mathbf{R}_{\text{in}}\}} + \Sigma_{\{\mathbf{R}_{\text{out}}\}} \).

First consider the contribution of \( \{\mathbf{R}_{\text{in}}\} \) to the macroscopic field. As all the dipoles are inside the sphere, Eq. 2.10 is applicable,

$$\int_{r < R} d^3 r \sum_{\{\mathbf{R}_{\text{in}}\}} \mathbf{E}_{\text{dip}}^{\text{nf}}(\mathbf{p}, \mathbf{r} - \mathbf{R}_{\text{in}}) = -\frac{1}{3} \sum_{\{\mathbf{R}_{\text{in}}\}} \mathbf{p}. \quad (2.36)$$

Hence, the contribution to the macroscopic field of the dipoles inside the sphere is \(- (1/3) \mathbf{p}\), where \( \mathbf{p} \) is identified as \((3/4\pi R^3) \Sigma_{\{\mathbf{R}_{\text{in}}\}} \).

Similarly, for the dipoles outside the sphere Eq. 2.11 applies,

$$\int_{r < R} d^3 r \sum_{\{\mathbf{R}_{\text{out}}\}} \mathbf{E}_{\text{dip}}^{\text{nf}}(\mathbf{p}, \mathbf{r} - \mathbf{R}_{\text{out}}) = \frac{4\pi R^3}{3} \sum_{\{\mathbf{R}_{\text{out}}\}} \mathbf{E}_{\text{dip}}^{\text{nf}}(\mathbf{p}, 0 - \mathbf{R}_{\text{out}}). \quad (2.37)$$

Instead of the volume integral, the summation over \( \{\mathbf{R}_{\text{out}}\} \) of the dipole fields in the origin has to be performed. It will be proven at the end of this subsection that this summation adds up to zero, so that the macroscopic field \( \mathbf{E}_{\text{mac}} \) is

$$\mathbf{E}_{\text{mac}} = \mathbf{E}_0 - \frac{1}{3} \mathbf{p}, \quad (2.38)$$

which is identical to Eq. 2.31.

The microscopic field at the position of a dipole, or equivalently at the origin \( \mathbf{E}_{\text{mic}}(0) \), is given by Eq. 2.34, where the field of the dipole at the origin is excluded for reasons of the unphysical self interaction,

$$\mathbf{E}_{\text{mic}}(0) = \mathbf{E}_0 + \sum_{\{\mathbf{R} \neq 0\}} \mathbf{E}_{\text{dip}}^{\text{nf}}(\mathbf{p}, 0 - \mathbf{R}). \quad (2.39)$$
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Figure 2.2 Two spherically symmetric subsets of dipoles on a cubic lattice: Left the subset \( \{ \mathbf{R} \neq 0 \} \), right \( \{ \mathbf{R}_{\text{out}} \} \), corresponding to Eqs. 2.39 and 2.37, respectively. Both subsets are captured by \( \{ \mathbf{R}' \} \).

It is clear that this summation resembles the second summation in Eq. 2.37, the only difference is the set of dipoles over which the summation runs. As will be proven, the summation in Eq. 2.39 is also zero. As a result, the microscopic electric field at the position of a dipole is \( \mathbf{E}_0 \). Consequently \( \mathbf{p} = \alpha(0)\mathbf{E}_0 \), where \( \alpha(0) \) is used as the derivation is for the static limit. Similar as in the random case, combining Eqs. 2.16, 2.32, and 2.38 gives

\[
\varepsilon(0) = 1 + \frac{\rho \alpha(0)}{1 - \frac{1}{3} \rho \alpha(0)}.
\]  (2.40)

identical to the static limit of Eq. 2.33. It should be stressed that the derivation of Eq. 2.40 is exact, whereas in the derivation for randomly positioned dipoles it had to be assumed that the scattered fields, see Eq. 2.28, average out to zero. Nevertheless, this assumption seems valid as both the random system and the square lattice are highly symmetric positional realizations, and should therefore have the same dependence of \( \varepsilon \) on \( \rho \) and \( \alpha \), compare Eqs. 2.33 and 2.40.

Still left to prove is that the summations in Eq. 2.37 and 2.39 of the dipole fields in the origin are zero. Considering Eq. 2.9, it is clear that the delta function terms do not contribute to the sum, since the summation either runs over all dipoles excluding a sphere of many dipoles centered around the origin [Eq. 2.37] or all dipoles excluding the one positioned at the origin [Eq. 2.39], see Fig. 2.2. As a result, the summation \( S \) is explicitly given by, where the prefactor \( 1/(4\pi) \) is left out,

\[
S = \sum_{\{\mathbf{R}'\}} \frac{3\mathbf{R}(\mathbf{R} \cdot \mathbf{p}) - |\mathbf{R}|^2 \mathbf{p}}{|\mathbf{R}|^{5/2}}.
\]  (2.41)
Here the prime in \( \{\mathbf{R}'\} \) denotes that the summation is constraint to a spherical symmetric subset of \( \{\mathbf{R}\} \) centered around the origin, covering both Eqs. 2.37 and 2.39. The \( x \) component of \( \mathbf{S}, S_1 \), can be written in the form

\[
S_1 = \sum_{(ijk)} \frac{3(i^2p_1 + ijp_2 + ikp_3) - (i^2 + j^2 + k^2)p_1}{a^3(i^2 + j^2 + k^2)^{5/2}}, \tag{2.42}
\]

where \( \mathbf{p} = (p_1, p_2, p_3) \). Since the indices run equally over positive and negative values, even when relaxing the spherical symmetrically constraint, the cross terms involving \( (ijp_2 + ikp_3) \) vanish.

Consider a specific lattice vector \((s, t, u)\), which has a length \(|(s, t, u)| = \sqrt{s^2 + t^2 + u^2}\), where \( s, t, \) and \( u \) can have both positive and negative integer values. This vector is part of a subset of vectors, labeled as \( \{(s, t, u)\} \), which can be generated from \((s, t, u)\) by permutation of the components \( s, t, \) and \( u \). Thus all the vectors in \( \{(s, t, u)\} \) have the same length. Note that there are different subsets with vectors of the same length, but these subsets will be treated independently. For example, a vector from \( \{(-s, -t, u)\} \) has the same length as a vector from \( \{(s, t, u)\} \). It is sufficient to prove that summation over the subset \( \{(s, t, u)\} \) yields zero in order to prove that the entire sum Eq. 2.42 is zero, as \( \{\mathbf{R}'\} \) is a superposition of many different \( \{(s, t, u)\} \).

The subset \( \{(s, t, u)\} \) contains six vector (six permutations). The first component of these vectors is twice \( s \), twice \( t \), and also twice \( u \). The summation over this subset thus yields, see Eq. 2.42,

\[
\frac{3 \cdot 2(s^2 + t^2 + u^2)p_1 - 6|(s, t, u)|^2p_1}{a^3|(s, t, u)|^{5/2}} = 0. \tag{2.43}
\]

This completes the prove that the summation \( S_1 \) is zero. If the summation of one component of \( \mathbf{S}, S_1 \), is zero, then by symmetry this also holds for the other components, and thus \( \mathbf{S} = 0 \).

### 2.4.4 A square lattice of dipoles; virtual cavity approach

In this section a more generally employed derivation of Eqs. 2.33 and 2.40 is sketched. In this approach a sphere is imagined inside the dielectric, the virtual cavity, centered at a particular dipole. The dipoles nearby the central dipole, that is the dipoles in the sphere with dipole moment \( \mathbf{p} \), are treated individually. The dipoles outside the sphere are considered in the continuum approximation described by the polarization \( \mathbf{P} \). By use of the superposition principle the field at the central dipole, \( \text{i.e.} \) the local field \( \mathbf{E}_{\text{loc}} \), can be derived. This local field is the sum of: i) the macroscopic field \( \mathbf{E}_{\text{mac}} \), with corresponding polarization \( \mathbf{P} \); ii) the field \( \mathbf{E}_p \) inside a dielectric sphere with polarization \( -\mathbf{P} \); iii) the total field \( \mathbf{E}_{\text{near}} \) produced by the discrete
dipoles inside the cavity, see Fig 2.3. In fact, the homogeneous polarization $\mathbf{P}$ inside the cavity is replaced by the field of the individual dipoles. The field inside a polarized dielectric sphere $\mathbf{E}_P$, without external field, is just given by the depolarization field $\mathbf{E}_{\text{depol}}$, see Eqs. 2.17 and 2.20. The fields due to the discrete dipoles inside the cavity add up to zero, for the contribution of these fields is given by the summation of Eq. 2.41, that is $\mathbf{E}_\text{near} = 0$. As a result, the local field, expressed in only macroscopic quantities, reduces to

$$\mathbf{E}_\text{loc} = \mathbf{E}_\text{mac} + \frac{1}{3}\mathbf{P}. \quad (2.44)$$

Combining $\mathbf{P} = \rho \alpha \mathbf{E}_\text{loc} = \rho \alpha [\mathbf{E}_\text{mac} + (1/3)\mathbf{P}]$ and $\mathbf{P} = (\varepsilon - 1)\mathbf{E}_\text{mac}$ readily gives the by now well-known result of Eqs. 2.33 and 2.40. It should be stressed that the approach presented here resides on the use of macroscopic quantities that are not derived from microscopic ones, in contrast with the method of the previous sections. Note that the local field differs from the macroscopic field by the so called Lorentz local-field factor $L_{\text{Lor}}$:

$$\mathbf{E}_\text{loc} \equiv L_{\text{Lor}} \mathbf{E}_\text{mac} = \frac{\varepsilon + 2}{3} \mathbf{E}_\text{mac}. \quad (2.45)$$

For $\varepsilon \approx 1$, that is $\rho \alpha \ll 1$, the local field approximately equals the macroscopic field, establishing the applicability of the linear response approach in this regime.

### 2.4.5 The Onsager-Böttcher approach; the reaction field

In the Onsager-Böttcher approach an impurity dipole $\mathbf{p}_i$ is considered to be at center of a real spherical cavity with radius $a$ in an otherwise homogeneous dielectric with dielectric constant $\varepsilon$ [14], see Fig. 2.4. The field at the site of the dipole $\mathbf{E}_\text{loc}$ is given by the sum of the field inside the cavity $\mathbf{E}_\text{in}$ [Eq. 2.23] due to an external...
Figure 2.4 The Onsager-Böttcher treatment: An impurity dipole with polarizability $\alpha_1$, the dipole in question, is placed at the center of a real spherical cavity (radius $a$) in a homogeneous medium with dielectric constant $\varepsilon$.

macroscopic field $E_{\text{mac}}$ and the reaction field $R$. The reaction field originates from the polarization of the surrounding dielectric induced by the central dipole. This field $R$ is uniform throughout the cavity and proportional to the dipole moment $p_1$ [14]:

$$ R = \frac{1}{3\Omega} \frac{2(\varepsilon - 1)}{2\varepsilon + 1} p_1 \equiv \int p_1, \quad (2.46) $$

where $\Omega = (4\pi a^3)/3$ is the volume of the cavity. The dipole moment $p_1$ is induced by the total field at the center of the cavity $E_{\text{loc}} = E_{\text{in}} + R$: $p_1 = \alpha_1 E_{\text{loc}}$. Hence, the reaction field is given by

$$ R = \int p_1 = f\alpha_1 (E_{\text{in}} + R), \quad (2.47) $$

from which it follows that

$$ E_{\text{loc}} = \frac{1}{1 - f\alpha_1} E_{\text{in}} = \frac{1}{1 - f\alpha_1} \frac{3\varepsilon}{2\varepsilon + 1} E_{\text{mac}}, \quad (2.48) $$

where Eq. 2.23 is used. Rewriting this equation, using the explicit form for $f$, resides for the local field to

$$ E_{\text{loc}} = \frac{3\varepsilon}{2\varepsilon + 1 - \frac{2\alpha_1}{3\Omega}(\varepsilon - 1)} E_{\text{mac}} \equiv L_{\text{OB}}(\alpha_1/\Omega) E_{\text{mac}}, \quad (2.49) $$

where $L_{\text{OB}}(\alpha_1/\Omega)$ is defined in analogy with $L_{\text{emp}}$ and $L_{\text{Lor}}$. The field outside the cavity is given by the sum of $E_{\text{mac}}$ and the field of a dipole embedded in a host material with dielectric constant $\varepsilon$ with dipole moment

$$ p_{\text{tot}} = [\alpha_1 L_{\text{emp}} L_{\text{OB}}(\alpha_1/\Omega) + (1 - \varepsilon)L_{\text{emp}} \Omega] E_{\text{mac}}, \quad (2.50) $$
where the first term presents the dipole field produced by the central impurity dipole and the second term corresponds to dipole field of an empty cavity, see Eq. 2.22. The volume of the cavity $\Omega$ is the only unknown parameter left. In contrast to the virtual cavity approach, two cases can be distinguished: the dipole inside the cavity is either equivalent to or different from the ones forming the dielectric. Considering the former case ($\alpha_i = \alpha$, where $\alpha$ is the polarizability of the dipoles that form the dielectric), Eq. 2.33 and 2.40 are regained upon Onsager’s assumption [15] that the volume of the cavity obeys $\rho\Omega = 1$ and realizing that $\mathbf{P} = \rho\alpha\mathbf{E}_{\text{loc}} = (\varepsilon - 1)\mathbf{E}_{\text{mac}}$. Here $\rho$ is the density of the dipoles in the dielectric. In other words, the average polarization in the cavity, $\mathbf{p}_i/\Omega = \rho\mathbf{p}$, equals the polarization of the dielectric, see for example Eq. 2.32. As a result, $\mathbf{p}_{\text{tot}}$ in Eq. 2.50 is zero, as it should for a homogeneous medium.

In the case of an impurity dipole, the volume $\Omega$ is generally taken to be the real volume of the molecule or atom the dipole represents. Note that for impurity dipoles with a very low polarizability, $\alpha_i/\Omega \ll 1$, the empty cavity result [Eq. 2.23] is obtained: $L_{\text{OB}}(0) = L_{\text{emp}}$.

**2.4.6 Historical overview on local fields**

The concept of local fields, the field experienced by a dipole in a dielectric medium, has been a subject of interest for over 150 years, see for reviews [28, 29, 30]. The first familiar results were obtained by Mossotti [31] who considered small metal particles in an ‘ether’ and by Clausius [32] who extended Mossotti’s results to conducting particles in an insulating medium. In fact, to be more precise, they established that, for any given substance, $(\varepsilon - 1)/(\varepsilon + 2)$ should be proportional to the density of the substance. Rewriting Eqs. 2.33 and 2.40 indeed confirms such a relation:

$$\rho\alpha = \frac{3}{\varepsilon + 2},$$

(2.51)

known as the *Clausius-Mossotti equation*. This equation can be generalized to the case of mixtures of different types of dipoles with polarizabilities $\alpha_i$ and densities $\rho_i$. It then reads

$$\frac{\varepsilon - 1}{\varepsilon + 2} = \frac{1}{3} \sum_i \rho_i \alpha_i,$$

(2.52)

which is the more familiar form.

Lorenz [33] studied dielectric particles surrounded by a medium with a different refractive index and solved the problem for optical vibrations. He was the first to introduce the idea that, in a cubic or random distribution, the contributions of
near neighbors to the local field sum to zero, although this was an assumption rather than a proven result. Lorentz [34] used the by now familiar method (see previous section) of cutting out a virtual sphere about the site in question. He was able to show that indeed the contribution of the neighbors within the sphere in a cubic lattice is zero. For dynamical fields, Eq. 2.52 is better known as the Lorentz-Lorenz equation.

Over the last century, several rederivations of Lorentz’s original result have been given [15, 28, 35, 36]. All of these derivations, however, use the concept of a local field and apply the macroscopic Maxwell equations to achieve the result. Recently, an exact microscopic derivation for fluids has been presented by Lagendijk et al. using the formalism of multiple-scattering theory taking into account hard-sphere particle correlations to all orders of the density [37]. For static fields, a similar approach was adopted by Felderhof et al. [38]. It should be noted, that these correlations were implicitly included in the derivations of sections 2.4.2 and 2.4.3, as the field felt by a particular dipole is just the sum of the external field and the scattered fields of all the other dipoles, excluding the depolarization fields, see Eqs. 2.28 and 2.29. That is to say: the dipoles were not at the same position.

2.5 Wave propagation and the dielectric function

So far, only the dielectric function $\varepsilon(\omega)$ has been calculated from microscopic quantities. The implications of such a dielectric function on the properties of light wave propagation through dielectrics will be discussed now.

For homogeneous media and monochromatic light with frequency $\omega$, the Helmholtz equation reads

$$\nabla^2 \mathbf{E}_\text{mac}(\mathbf{r}) - \varepsilon(\omega) \frac{\omega^2}{c_0^2} \mathbf{E}_\text{mac}(\mathbf{r}) = 0, \quad (2.53)$$

where it is understood that the time dependence of the macroscopic field is $e^{-i\omega t}$. The solution of Eq. 2.53 is a transverse plane wave

$$\mathbf{E}_\text{mac}(\mathbf{r}, t) = \mathbf{E}_0 e^{i\mathbf{n} \cdot \mathbf{r} - i\omega t}, \quad (2.54)$$

where $\mathbf{E}_0$ is the amplitude of the wave, $\mathbf{n}$ a unit vector pointing in the direction of propagation and

$$k = \sqrt{\varepsilon(\omega)} \frac{\omega}{c_0} \quad (2.55)$$

the wavevector in the medium. Note that $\mathbf{E}_0 \cdot \mathbf{n} = 0$. In general, $\varepsilon(\omega)$ is a complex function: $\varepsilon = \varepsilon_R + i\varepsilon_I$. The real part of dielectric function $\varepsilon_R$ relates to the refractive
index \( m \), whereas the imaginary part \( \varepsilon_i \) describes both absorption and scattering, \textit{i.e.} extinction. As a result \( k \) is complex: \( k = \beta + i \kappa / 2 \). So that the \textit{intensity} of the wave falls off as \( e^{-k \rho} \), see Eq. 2.54. Consequently, \( \kappa \) is identified as the extinction coefficient, that is the inverse of extinction length \( \ell_{ex} : \kappa = \ell_{ex}^{-1} \). Both \( \beta \) and \( \kappa \) can be expressed in terms of \( \varepsilon_R \) and \( \varepsilon_i \) using Eq. 2.55. If \( \kappa \ll \beta \), which is the case for nearly all media unless they are extremely strongly absorbing and/or scattering, it is found that

\[
\beta = \sqrt{\varepsilon_R \varepsilon_i}, \quad \kappa = \frac{\varepsilon_i}{\varepsilon_R} \beta,
\]

from which it follows that the refractive index \( m \) is \( \sqrt{\varepsilon_R} \). Using Eq. 2.56, it is clear how the refractive index \( m \) and the extinction length \( \ell_{ex} \) depend on microscopic quantities like the dipole density \( \rho \) and dynamic polarizability \( \alpha(\omega) \).

The imaginary part of the dielectric function given by Eq. 2.33 arises from a complex dynamic polarizability \( \alpha(\omega) \), see Eq. 2.6. Note that in the static limit, \( \omega \downarrow 0 \), \( \alpha(\omega) \) becomes real and extinction disappears \( (\kappa = 0) \). In other words, absorption and scattering are essentially dynamic properties.

### 2.6 Mixtures of dielectrics

As the origin of the refractive index and extinction coefficient of \textit{homogeneous} dielectrics is clear, it is interesting to investigate \textit{inhomogeneous} dielectrics. For this purpose, consider a mixture of two dielectrics, with volume fractions \( \phi_1 \) and \( \phi_2 \), and dielectric constants \( \varepsilon_1 \) and \( \varepsilon_2 \), respectively. Aside from the dielectric constants and the volume fractions, the \textit{average} refractive index \( \varepsilon_{av} \) and the extinction length depend on how the two dielectric components are organized and their dimensions. In the electrostatic limit, the components always have dimensions much smaller than the (infinitely) long wavelength, leading to a well-defined average refractive index. However, the extinction \( (\ell_{ex} \rightarrow \infty) \) is zero in this limit. So in order to grasp both the extinction and average refractive index, the derivations will be in the quasi-static approximation.

As already mentioned, the morphology of the mixture influences both \( m \) and \( \ell_{ex} \). Three different effective medium models will be discussed: The Lorentz-Lorenz model [29], Maxwell Garnett theory [39] and Bruggeman’s approach [40]. In the Lorentz-Lorenz model two types of dielectric spheres in vacuum are treated. Garnett considered spherical inclusions, \textit{i.e.} scatterers, in a homogeneous dielectric background (cermet topology), whereas Bruggeman treated both dielectric components on an equal basis, more appropriate for the so-called aggregate topology [41]. In the cermet topology each inclusion is completely surrounded by the host dielectric, whereas in the aggregate topology the connectedness of the two components
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Figure 2.5 Two topologies of two-component dielectrics. The lighter and darker areas correspond to the different dielectric constant materials. Left a collection of spherical inclusions is depicted, the cermet topology, related to the Maxwell Garnett formalism. Right the aggregate topology is shown, considered by Bruggeman, which is symmetric in the statistical sense: i.e. an interchange of the two components results in the same type of medium with interchanged volume fractions. This symmetry is absent in the Maxwell Garnett type of mixture (left).

is treated on the same footing, see Fig. 2.5. For recent investigations of effective medium models for different morphologies see [42].

2.6.1 Quasi-static properties of a small dielectric sphere

In order to derive Maxwell Garnett results, first the small dielectric sphere is discussed; the results will be very similar to those in section 2.3. Consider a small dielectric sphere with dielectric constant \( \varepsilon_1 \) in otherwise homogeneous medium with dielectric constant \( \varepsilon_2 \). The sphere has a radius \( a \) (volume \( \Omega = (4\pi a^3)/3 \)), much smaller than the wavelength involved, so that the quasi-static approach applies. In the host medium the macroscopic electric field far away from the sphere is homogeneous and given by \( \mathbf{E}_2 \). Analogous to Eq. 2.17, the macroscopic field inside the sphere \( \mathbf{E}_1 \) is homogeneous and reads

\[
\mathbf{E}_1 = \frac{3}{\varepsilon + 2} \mathbf{E}_2, \tag{2.57}
\]

where \( \varepsilon = \varepsilon_1/\varepsilon_2 \) is the dielectric constant ratio. The total field outside the dielectric sphere is the sum of \( \mathbf{E}_2 \) and the field of dipole in a background medium with dielectric constant \( \varepsilon_2 \) and dipole moment

\[
\mathbf{p} = 3\varepsilon_2 \Omega \frac{\varepsilon - 1}{\varepsilon + 2} \mathbf{E}_2 = \alpha_{\varepsilon_1,\varepsilon_2}(0) \mathbf{E}_2 = \varepsilon_2 \alpha_\varepsilon(0) \mathbf{E}_2, \tag{2.58}
\]

where \( \alpha_{\varepsilon_1,\varepsilon_2}(0) \) is the static polarizability of the sphere and \( \alpha_\varepsilon(0) \) is defined for later convenience.
In the quasi-static limit, the dynamic polarizability (necessary to describe extinction) is given by Eq. 2.6, where it is assumed that $\omega \ll \omega_0$. Keeping only the first order terms for both the real and imaginary part of the polarizability, it is found that

$$\alpha_{\varepsilon_1,\varepsilon_2}(\omega) \approx \alpha_{\varepsilon_1,\varepsilon_2}(0) \left[ 1 + i \frac{\Gamma_0(\varepsilon_2) \omega^2}{\omega_0^4} \right].$$

(2.59)

Here $\Gamma_0(\varepsilon_2)$ is the damping rate of a dipole in a background medium with dielectric constant $\varepsilon_2$. In order to fulfill the optical theorem, this damping rate relates to vacuum damping rate, see Eq. 2.5, as

$$\Gamma_0(\varepsilon_2) = \sqrt{\varepsilon_2} \Gamma_0,$$

(2.60)

which is the general result for a dipole in a dielectric host medium. Of course, the static polarizability in Eq. 2.5 is now given by $\alpha_{\varepsilon_1,\varepsilon_2}(0)$. Note that although Eq. 2.59 seems to depend on $\omega_0$, this dependence is completely canceled by $\Gamma_0$, see Eq. 2.5: the quasi-static polarizability $\alpha_{\varepsilon_1,\varepsilon_2}(\omega)$ is completely independent of $\omega_0$. The imaginary part of $\alpha_{\varepsilon_1,\varepsilon_2}(\omega)$ represents scattering and not absorption, as the scatterer is constructed to be fully elastic on enforcing the optical theorem.

### 2.6.2 The average dielectric constant

**Lorentz-Lorenz expression**  Consider a collection of two types of spheres characterized by the densities $\rho_i$, dielectric constants $\varepsilon_i$, and volumes $\Omega_i$ ($i=1,2$) embedded in vacuum. The average dielectric constant $\varepsilon_{av}$ of such a mixture can be calculated from Eq. 2.52 giving

$$\frac{\varepsilon_{av} - 1}{\varepsilon_{av} + 2} = \frac{1}{3} \left[ \rho_1 \alpha_1 + \rho_2 \alpha_2 \right],$$

(2.61)

where $\alpha_i$ is polarizability of sphere $i$. Using Eq. 2.21, the Lorentz-Lorenz effective medium expression resides to

$$\frac{\varepsilon_{av} - 1}{\varepsilon_{av} + 2} = \phi_1 \frac{\varepsilon_1 - 1}{\varepsilon_2 + 2} + \phi_2 \frac{\varepsilon_2 - 1}{\varepsilon_2 + 2},$$

(2.62)

where $\rho_i \Omega_i$ is identified as the volume fraction $\phi_i$. If the phases $\varepsilon_1$ and $\varepsilon_2$ completely fill the entire space, $\phi_1 + \phi_2 = 1$. Obviously Eq. 2.62 can be generalized to systems containing more than two phases by adding more terms.
Maxwell Garnett theory  Maxwell Garnett theory treats an inhomogeneous medium that consists of spheres with dielectric constant \( \varepsilon_1 \) and volume fraction \( \phi_1 \) embedded in a background material with dielectric constant \( \varepsilon_2 \) and corresponding volume fraction \( \phi_2 = 1 - \phi_1 \). The derivation of the average dielectric constant \( \varepsilon_{av} \) presented here essentially follows the approach of Bohren and Huffman [43].

The average macroscopic electric field \( \langle \mathbf{E} \rangle \) can be found by using the spatial averaging procedure, see section 2.2 and especially Eq. 2.12. The spatial averaging volume is large enough to contain many of the spherical inclusions. As a result

\[
\langle \mathbf{E} \rangle = (1 - \phi_1) \langle \mathbf{E}_2 \rangle + \phi_1 \langle \mathbf{E}_1 \rangle, \tag{2.63}
\]

where \( \langle \mathbf{E}_2 \rangle \) and \( \langle \mathbf{E}_1 \rangle \) are the average macroscopic fields in the background medium and the sphere, respectively. Similarly, the average polarization is given by

\[
\langle \mathbf{P} \rangle = (1 - \phi_1) \langle \mathbf{P}_2 \rangle + \phi_1 \langle \mathbf{P}_1 \rangle. \tag{2.64}
\]

The average polarization in the spheres and in the host material relate to the corresponding average macroscopic fields as

\[
\langle \mathbf{P}_2 \rangle = (\varepsilon_2 - 1) \langle \mathbf{E}_2 \rangle, \quad \langle \mathbf{P}_1 \rangle = (\varepsilon_1 - 1) \langle \mathbf{E}_1 \rangle. \tag{2.65}
\]

The average dielectric constant \( \varepsilon_{av} \) of the composite medium is defined by

\[
\langle \mathbf{P} \rangle = (\varepsilon_{av} - 1) \langle \mathbf{E} \rangle. \tag{2.66}
\]

Combining Eqs. 2.63-2.66 yields

\[
(1 - \phi_1)(\varepsilon_{av} - \varepsilon_2) \langle \mathbf{E}_2 \rangle + \phi_1(\varepsilon_{av} - \varepsilon_1) \langle \mathbf{E}_1 \rangle = 0. \tag{2.67}
\]

For spherical inclusions the relation between \( \langle \mathbf{E}_2 \rangle \) and \( \langle \mathbf{E}_1 \rangle \) is known and given by Eq. 2.57. Here it is assumed that the fields scattered by the spheres average out to zero, similar to the treatment of fluids in section 2.4.2. The Maxwell Garnett result for the average dielectric constant follows:

\[
\varepsilon_{av} = \varepsilon_2 \left[ 1 + \frac{3\phi_1(\varepsilon_1 - 1)}{\varepsilon_1 + 2} \right], \tag{2.68}
\]

where again \( \varepsilon = \varepsilon_1 / \varepsilon_2 \). Identifying \( \phi_1 \) as \( \rho \Omega \), where \( \rho \) the density and \( \Omega \) the volume of the spheres, and using the definition of \( \alpha_\varepsilon(0) \) from Eq. 2.58, leads to

\[
\varepsilon_{av} = \varepsilon_2 \left[ 1 + \frac{\rho \alpha_\varepsilon(0)}{1 - \frac{1}{3} \rho \alpha_\varepsilon(0)} \right], \tag{2.69}
\]

clearly establishing the connection to the polarizability of a dielectric sphere, see Eq. 2.58. Note that the form of Eq. 2.69 is identical to Eqs. 2.33 and 2.40.
Equation 2.68 can be rewritten in a form similar to Eq. 2.62 yielding

$$\frac{\varepsilon_{av} - \varepsilon_2}{\varepsilon_{av} + 2\varepsilon_2} = \phi_1 \frac{\varepsilon_1 - \varepsilon_2}{\varepsilon_1 + 2\varepsilon_2}, \quad (2.70)$$

so that both Eqs. 2.62 and 2.70 are identified to stem from the same general formula

$$\frac{\varepsilon_{av} - \varepsilon_h}{\varepsilon_{av} + 2\varepsilon_h} = \phi_1 \frac{\varepsilon_1 - \varepsilon_h}{\varepsilon_1 + 2\varepsilon_h} + \phi_2 \frac{\varepsilon_2 - \varepsilon_h}{\varepsilon_2 + 2\varepsilon_h}, \quad (2.71)$$

where $\varepsilon_h$ is the dielectric constant of a host dielectric. Thus $\varepsilon_h$ equals 1 and $\varepsilon_2$ for the Lorentz-Lorenz and Maxwell Garnett expressions, respectively. If $\phi_1 > \phi_2$, then a more appropriate choice for $\varepsilon_h$ in the Maxwell Garnett case is $\varepsilon_1$. However, the resulting values of $\varepsilon_{av}$ are different for the two choices. Bruggeman resolved this dilemma.

**Bruggeman’s approach**  Bruggeman proposed that neither phase should be given preference (as in the Maxwell Garnett treatment), but that the inclusions should be considered as being embedded in the averaged medium itself. In the above formulation this is equivalent to choosing $\varepsilon_h = \varepsilon_{av}$, in which case Eq. 2.71 becomes

$$0 = \phi_1 \frac{\varepsilon_1 - \varepsilon_{av}}{\varepsilon_1 + 2\varepsilon_{av}} + \phi_2 \frac{\varepsilon_2 - \varepsilon_{av}}{\varepsilon_2 + 2\varepsilon_{av}}, \quad (2.72)$$

known as the Bruggeman effective medium expression. Although Eqs. 2.62, 2.70, and 2.72 are superficially quite different, the above discussion shows that they all are related and differ only in the choice of the host material. The generalization to mixtures of more than two dielectrics is obvious.

### 2.6.3 Light scattering in mixtures

Scattering of light in dielectrics originates from the complex dynamic polarizability. To indicate how this really works, the extinction coefficient $k$ is calculated for the Maxwell Garnett result in the linear response approximation, that is $\rho \alpha_\varepsilon \ll 1$. The quasi-static dielectric function $\varepsilon(\omega)$ then reads

$$\varepsilon(\omega) = \varepsilon_2 + \rho \alpha_{\varepsilon_1, \varepsilon_2}(\omega), \quad (2.73)$$

where $\alpha_{\varepsilon_1, \varepsilon_2}(\omega)$ is the complex quasi-static polarizability given by Eq. 2.59. Again, it is stressed that this complex polarizability is constructed via the optical theorem, so that the spheres are fully elastic scatterers. The real ($\varepsilon_R$) and imaginary ($\varepsilon_I$) part of $\varepsilon(\omega)$ thus are

$$\varepsilon_R = \varepsilon_2 + \rho \alpha_{\varepsilon_1, \varepsilon_2}(0), \quad \varepsilon_I = \rho \sqrt{\varepsilon_2} \left[\alpha_{\varepsilon_1, \varepsilon_2}(0)\right] \frac{\omega^3}{6\pi\varepsilon_0^3}, \quad (2.74)$$
where $\Gamma(\varepsilon_2)$ and $\omega_0$ are eliminated by use of Eqs. 2.5 and 2.60. The refractive index $m$ is just given by $\sqrt{\varepsilon_R} = \sqrt{\varepsilon_2 + \rho\alpha_{\varepsilon_1,\varepsilon_2}(0)}$, which approximates to $\sqrt{\varepsilon_2}$ for $\rho\alpha_{\varepsilon_1,\varepsilon_2}(0) \ll \varepsilon_2$. The extinction coefficient $\kappa$, or equivalently the inverse of the extinction length $\ell_{\text{ex}}$, follows from Eqs. 2.56, and 2.74 and reads

$$\kappa = \rho \left[ \alpha_{\varepsilon_1,\varepsilon_2}(0) \right]^2 \frac{\omega^4}{6\pi\varepsilon_0^2}. \quad (2.75)$$

This equation is related to the extinction cross-section $\sigma_{\text{ex}}$, which is defined as $\rho\sigma_{\text{ex}} = \kappa = \ell_{\text{ex}}^{-1}$. Using Eq. 2.75 and the explicit form of $\alpha_{\varepsilon_1,\varepsilon_2}(0)$ [Eq. 2.58] the well-known extinction cross-section for a spherical Rayleigh scatterer is readily obtained

$$\sigma_{\text{ex}} = \frac{8}{3} x^4 \left[ \frac{\varepsilon - 1}{\varepsilon + 2} \right]^2 \pi a^2 \equiv Q_{\text{ex}} \pi a^2 \quad (2.76)$$

Here $x \equiv k \varepsilon_2 a$, where $k \varepsilon_2 = \sqrt{\varepsilon_2 (\omega/c_0)}$ is the wavevector in the background dielectric $\varepsilon_2$ and $a$ the radius of the sphere. Furthermore, the extinction efficiency factor $Q_{\text{ex}}$ is defined as the ratio of the extinction cross-section $\sigma_{\text{ex}}$ to the geometrical cross-section $\pi a^2$. This completes the derivation of extinction by a low concentration of small dielectric spheres in a dielectric host material.