

14. Optical Processes

The optical properties of nanostructures (as well as atoms and molecules) manifest themselves via optical processes. Most prominent among these is absorption, which is associated with the imaginary part of the susceptibility as discussed in the previous chapters. But other processes such as scattering and fluorescence are of importance. The processes are not independent. The energy emitted as scattering and fluorescence processes must originate from energy transferred from light to matter, ultimately absorption in a broad sense. In this chapter, we will study the balance between these processes and study their connection.

Quite generally, the exchange of energy between light and matter is governed by the balance of electromagnetic power density (the Poynting vector $\vec{S} = \vec{\mathcal{E}} \times \vec{\mathcal{H}}$) reaching matter, on the one hand, and energy stored in the fields (electromagnetic energy density u) plus absorbed power, on the other. The energy balance is expressed as

$$-\nabla \cdot \vec{S} = \frac{\partial u}{\partial t} + \vec{j} \cdot \vec{\mathcal{E}}.$$

The electromagnetic energy density u is given by $u = \frac{1}{2}(\vec{\mathcal{E}} \cdot \vec{\mathcal{D}} + \vec{\mathcal{B}} \cdot \vec{\mathcal{H}})$. We will make the simplifying assumption that all processes are elastic. Hence, if we restrict ourselves to monochromatic incident fields with a frequency ω all fields vary with this frequency and we find that u contains terms varying at twice the frequency 2ω as well as temporally constant terms. Taking the time derivative, the constant terms vanish. In addition, we will average the energy balance over one period of the field. This kills off the 2ω terms as well. It should be noted that the elastic assumption means that fluorescence is ignored. Also, conversion of electromagnetic energy into heat is neglected. We write the time-averaged quantities using pointed brackets such as $\langle \vec{S} \rangle$ and find

$$-\nabla \cdot \langle \vec{S} \rangle = \langle \vec{j} \cdot \vec{\mathcal{E}} \rangle.$$

Next, we integrate this relation over a finite volume V and use Gauss' theorem to transform into an integral over the bounding surface S

$$\begin{aligned} -\int_V \nabla \cdot \langle \vec{S} \rangle d^3r &= \int_V \langle \vec{j} \cdot \vec{\mathcal{E}} \rangle d^3r \\ \Downarrow \\ -\int_S \vec{e}_n \cdot \langle \vec{S} \rangle dS &= \int_V \langle \vec{j} \cdot \vec{\mathcal{E}} \rangle d^3r, \end{aligned}$$

where \vec{e}_n is the outward pointing normal. The left-hand side has a simple interpretation as the net electromagnetic intensity radiated into the volume. Also, the $\vec{j} \cdot \vec{\mathcal{E}}$ term is the absorbed optical power inside the volume. Both electric and magnetic fields contain an incident (subscript "0") and a scattered (subscript "scat") part and so the Poynting vector has three contributions

$$\vec{S} = \vec{S}_0 + \vec{S}_{scat} + \vec{S}_{ext}$$

$$\vec{S}_0 = \vec{\mathcal{E}}_0 \times \vec{\mathcal{H}}_0, \quad \vec{S}_{scat} = \vec{\mathcal{E}}_{scat} \times \vec{\mathcal{H}}_{scat}, \quad \vec{S}_{ext} = \vec{\mathcal{E}}_0 \times \vec{\mathcal{H}}_{scat} + \vec{\mathcal{E}}_{scat} \times \vec{\mathcal{H}}_0.$$

The integral over $\vec{e}_n \cdot \langle \vec{S}_0 \rangle$ vanishes because of conservation of electromagnetic power in the absence of matter. The integral of $\vec{e}_n \cdot \langle \vec{S}_{scat} \rangle$ is the power radiated by scattering. Hence, the energy balance yields

$$P_{ext} = P_{scat} + P_{abs},$$

where the three terms are, respectively, the extinction, scattered, and absorbed power given by

$$P_{ext} = - \int_S \vec{e}_n \cdot \langle \vec{S}_{ext} \rangle dS, \quad P_{scat} = \int_S \vec{e}_n \cdot \langle \vec{S}_{scat} \rangle dS, \quad P_{abs} = \int_V \langle \vec{j} \cdot \vec{\mathcal{E}} \rangle d^3r.$$

14.1 Single Dipole

We now specialize to a single point dipole, that is, a single nanostructure, atom or molecule that is sufficiently small compared to the optical wavelength that it can be regarded as a point source. The dipole moment varies with time as $\vec{p}(t) = \frac{1}{2}(\vec{p}(\omega)e^{-i\omega t} + c.c.)$ and taking the dipole position as the origin, the associated density is $\vec{p}(t)\delta(\vec{r})$. The accompanying current density is

$$\vec{j}(\vec{r}, t) = \frac{\partial \vec{p}(t)}{\partial t} \delta(\vec{r}) = \frac{1}{2}(-i\omega \vec{p}(\omega)e^{-i\omega t} + c.c.)\delta(\vec{r}). \quad (14.1)$$

With an electric field $\vec{\mathcal{E}}(\vec{r}, t) = \frac{1}{2}(\vec{\mathcal{E}}(\vec{r}, \omega)e^{-i\omega t} + c.c.)$ it then readily follows that

$$P_{abs} = \int_V \frac{1}{4}(-i\omega \vec{p}(\omega) \cdot \vec{\mathcal{E}}^*(\vec{r}, \omega) + i\omega \vec{p}^*(\omega) \cdot \vec{\mathcal{E}}(\vec{r}, \omega))\delta(\vec{r}) d^3r$$

$$= \frac{1}{2}\omega \text{Im} \{ \vec{p}(\omega) \cdot \vec{\mathcal{E}}^*(0, \omega) \}.$$

In our case, the dipole is induced by the electric field and we therefore write $\vec{p}(\omega) = \vec{\alpha}_0(\omega) \cdot \vec{\mathcal{E}}(0, \omega)$, where $\vec{\alpha}_0$ is the polarizability (tensor). The subscript “0” signifies that it is the “bare” polarizability, which relates the dipole moment to the total driving field. Writing the field vector as $\vec{\mathcal{E}}(\vec{r}, \omega) = \mathcal{E}(\vec{r}, \omega) \vec{e}$ we subsequently have

$$P_{abs} = \frac{1}{2} \omega \text{Im} \{ \vec{e} \cdot \vec{\alpha}_0(\omega) \cdot \vec{e} \} | \mathcal{E}(0, \omega) |^2. \quad (14.2)$$

This result demonstrates that the absorbed power is proportional to the imaginary part of the polarizability.

Our next step is to compute the fields radiated by the dipole, i.e. the scattered fields. The simplest strategy is to obtain the vector potential $\vec{\mathcal{A}}$ (choosing Lorentz gauge) and then find the magnetic field via $\vec{\mathcal{B}} = \nabla \times \vec{\mathcal{A}}$ and finally the electric field from $\partial \vec{\mathcal{E}} / \partial t = c^2 \nabla \times \vec{\mathcal{B}}$. The relation between scattered vector potential and current density is [1]

$$\vec{\mathcal{A}}_{scat}(\vec{r}, t) = \frac{1}{4\pi\epsilon_0 c^2} \int \frac{\vec{j}(\vec{r}', t - |\vec{r} - \vec{r}'|/c)}{|\vec{r} - \vec{r}'|} d^3 r',$$

where $t - |\vec{r} - \vec{r}'|/c$ is the so-called retarded time. With Eq.(14.1) we then find $\vec{\mathcal{A}}_{scat}(\vec{r}, t) = \frac{1}{2} (\vec{\mathcal{A}}_{scat}(\vec{r}, \omega) e^{-i\omega t} + c.c.)$ with

$$\vec{\mathcal{A}}_{scat}(\vec{r}, \omega) = -\frac{ik_0}{4\pi\epsilon_0 c} \vec{p}(\omega) \frac{e^{ik_0 r}}{r}, \quad k_0 \equiv \frac{\omega}{c}. \quad (14.3)$$

In turn, the magnetic field becomes $\vec{\mathcal{B}}_{scat}(\vec{r}, t) = \frac{1}{2} (\vec{\mathcal{B}}_{scat}(\vec{r}, \omega) e^{-i\omega t} + c.c.)$ with

$$\begin{aligned} \vec{\mathcal{B}}_{scat}(\vec{r}, \omega) &= \nabla \times \vec{\mathcal{A}}_{scat}(\vec{r}, \omega) = -\frac{ik_0}{4\pi\epsilon_0 c} \nabla \left(\frac{e^{ik_0 r}}{r} \right) \times \vec{p}(\omega) \\ &= -\frac{ik_0}{4\pi\epsilon_0 c} \frac{\partial}{\partial r} \left(\frac{e^{ik_0 r}}{r} \right) \vec{e}_r \times \vec{p}(\omega) \\ &\approx \frac{k_0^2 e^{ik_0 r}}{4\pi\epsilon_0 c r} \vec{e}_r \times \vec{p}(\omega), \end{aligned}$$

where we have applied the far-field assumption that $e^{ik_0 r}$ is much faster varying than r^{-1} , which is clearly the case whenever $k_0 r \gg 1$. Similarly, the electric field in the far-field limit becomes

$$\vec{\mathcal{E}}_{scat}(\vec{r}, \omega) = ic^2 / \omega \nabla \times \vec{\mathcal{B}}_{scat}(\vec{r}, \omega) \approx -\frac{k_0^2 e^{ik_0 r}}{4\pi\epsilon_0 r} \vec{e}_r \times [\vec{e}_r \times \vec{p}(\omega)] = \frac{k_0^2 e^{ik_0 r}}{4\pi\epsilon_0 r} [\vec{U} - \vec{e}_r \vec{e}_r] \cdot \vec{p}(\omega).$$

The last form is obtained by considering the direction of $\vec{e}_r \times [\vec{e}_r \times \vec{p}(\omega)]$, c.f. Fig. 14.1. From these fields we now compute the time-averaged Poynting vector of the dipole radiation

$$\langle \vec{S}_{scat} \rangle = \frac{\epsilon_0 c^2}{2} \text{Re} \left\{ \vec{\mathcal{E}}_{scat}(\vec{r}, \omega) \times \vec{\mathcal{B}}_{scat}^*(\vec{r}, \omega) \right\} = -\frac{\epsilon_0 c^2}{2} \text{Re} \left\{ \mathcal{E}_{scat}(\vec{r}, \omega) \mathcal{B}_{scat}^*(\vec{r}, \omega) \right\} \vec{e}_r.$$

The last equality follows from the direction of the cross product between $\vec{e}_r \times \vec{p}(\omega)$ and $\vec{e}_r \times [\vec{e}_r \times \vec{p}(\omega)]$. Introducing θ as the angle between \vec{e}_r and $\vec{p}(\omega)$ as illustrated in Fig. 14.1 we realize that $|\vec{e}_r \times \vec{p}(\omega)| = |\vec{e}_r \times [\vec{e}_r \times \vec{p}(\omega)]| = p(\omega) \sin \theta$ and so

$$\langle \vec{S}_{scat} \rangle = \frac{ck_0^4}{32\pi^2 \epsilon_0} |p(\omega)|^2 \frac{\sin^2 \theta}{r^2} \vec{e}_r.$$

This result can be integrated over a large sphere to provide the scattered power

$$\begin{aligned} P_{scat} &= \int_S \frac{ck_0^4}{32\pi^2 \epsilon_0} |p(\omega)|^2 \frac{\sin^2 \theta}{r^2} dS = \frac{ck_0^4}{12\pi\epsilon_0} |p(\omega)|^2 \\ &= \frac{ck_0^4}{12\pi\epsilon_0} |\vec{e} \cdot \vec{\alpha}_0(\omega) \cdot \vec{e}|^2 |\mathcal{E}(0, \omega)|^2 \end{aligned} \quad (14.4)$$

using the fact that $\int_S \frac{\sin^2 \theta}{r^2} dS = 8\pi/3$.

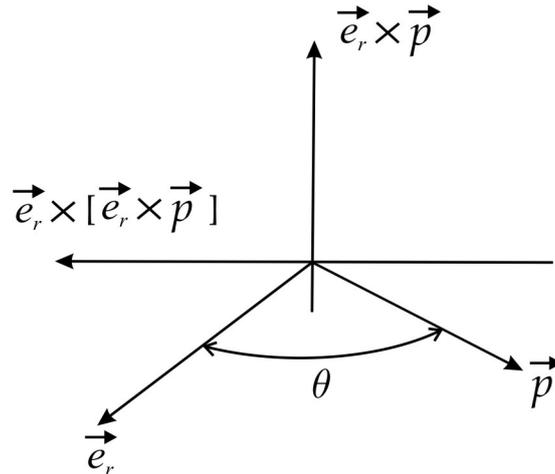


Figure 14.1 Vector diagram for the directions of scattered vector potential (\vec{p}), magnetic field ($\vec{e}_r \times \vec{p}$) and electric field ($\vec{e}_r \times [\vec{e}_r \times \vec{p}]$).

14.2 Bare and Dressed Polarizabilities

Will a particle be influenced by the scattered field that it emits? This may sound as a strange question but, in fact, it's important for a full understanding of optical processes. The answer is yes and the basic reason is simple. In the process of emitting light, momentum is lost and so a force acts on the particle. This effect, however, can be incorporated into the response of the particle. Hence, instead of a "bare" particle interacting with both incident and scattered fields we find an equivalent picture of a "dressed" particle interacting with the incident field only. To set up this equivalent picture, a careful analysis of external and local fields is needed. Primarily, we need to consider the fields without using the far-field approximation. To this end, we use the identity

$$\frac{e^{ik_0 r}}{r} = \frac{1}{2\pi^2} \int \frac{e^{i\vec{k}\cdot\vec{r}}}{k^2 - k_0^2} d^3k$$

and write the vector potential as

$$\vec{A}_{\text{scat}}(\vec{r}, \omega) = -\frac{ik_0}{8\pi^3 \epsilon_0 c} \int \frac{e^{i\vec{k}\cdot\vec{r}}}{k^2 - k_0^2} \vec{p}(\omega) d^3k.$$

Taking various curls, the electric field is then readily found as

$$\begin{aligned} \vec{\mathcal{E}}_{\text{scat}}(\vec{r}, \omega) &= -\frac{1}{8\pi^3 \epsilon_0} \int \frac{e^{i\vec{k}\cdot\vec{r}}}{k^2 - k_0^2} \vec{k} \times \vec{k} \times \vec{p}(\omega) d^3k \\ &= \frac{1}{8\pi^3 \epsilon_0} \int \frac{e^{i\vec{k}\cdot\vec{r}}}{k^2 - k_0^2} [k^2 \vec{U} - \vec{k} \vec{k}] d^3k \cdot \vec{p}(\omega). \end{aligned}$$

This field, which is radiated by the dipole, also acts on the dipole! In fact, the total local field is the sum of the incident field and this radiated field evaluated at $\vec{r} = 0$. The imaginary part is particularly important because it acts as a damping force being 90 degrees out of phase with the dipole. The real part (which, incidentally, cannot be correctly handled in a classical scheme but requires a fully quantum-electrodynamical theory) leads to a frequency shift of the resonance, the so-called Lamb shift. The imaginary part of the field evaluated at $\vec{r} = 0$ is called the Radiation-Reaction field $\vec{\mathcal{E}}_{RR}(\omega)$. It is obtained from the imaginary part of the pole, i.e.

$$\begin{aligned}
\vec{\mathcal{E}}_{RR}(\omega) &= \frac{i}{8\pi^2\epsilon_0} \int \delta(k^2 - k_0^2) [k^2 \vec{\mathcal{U}} - \vec{k} \vec{k}] d^3k \cdot \vec{p}(\omega) \\
&= \frac{ik_0^3}{6\pi\epsilon_0} \vec{p}(\omega).
\end{aligned} \tag{14.5}$$

The effects of radiation reaction are clear if we note that the total field driving the dipole becomes $\vec{\mathcal{E}}(0, \omega) = \vec{\mathcal{E}}_0(0, \omega) + \vec{\mathcal{E}}_{RR}(\omega)$. Hence, the induced dipole moment is

$$\vec{p}(\omega) = \vec{\alpha}_0(\omega) \cdot \left\{ \vec{\mathcal{E}}_0(0, \omega) + \vec{\mathcal{E}}_{RR}(\omega) \right\}.$$

Applying the expression for the radiation-reaction field, this result can be rearranged as

$$\begin{aligned}
\vec{p}(\omega) &= \left\{ \vec{\mathcal{U}} - \frac{ik_0^3}{6\pi\epsilon_0} \vec{\alpha}_0(\omega) \right\}^{-1} \cdot \vec{\alpha}_0(\omega) \cdot \vec{\mathcal{E}}_0(0, \omega) \\
&\equiv \vec{\alpha}(\omega) \cdot \vec{\mathcal{E}}_0(0, \omega).
\end{aligned}$$

Here, $\vec{\alpha}$ is the so-called dressed polarizability relating the dipole moment to the incident field alone. Hence, the effects of radiation reaction have been absorbed into the dressed polarizability. The bare polarizability was calculated previously in chapter 7

$$\vec{\alpha}_0(\omega) = 2e^2 \sum_n \frac{E_n}{E_n^2 - \hbar^2 \omega^2} \vec{D}_{0n} \vec{D}_{n0}.$$

Here, E_n is the many body energy eigenvalue of the n 'th state measured relative to the ground state. Also, $\vec{D}_{0n} = \langle 0 | \sum_e \vec{r}_e | n \rangle$ is the many-electron transition dipole moment. We now make the simplifying assumption of isotropy in the polarizability as appropriate for atoms or spherical nanostructures. Also, the approximations applied above are only expected to hold when we are close to a resonance $\omega \approx E_n / \hbar \equiv \omega_n$. Hence,

$$\vec{\alpha}_0(\omega) \approx \frac{e^2 |D_{0n}|^2}{\hbar \omega_n - \omega} \vec{\mathcal{U}}$$

and, thereby, with $k_n \equiv \omega_n / c$

$$\vec{\alpha}(\omega) = \left\{ 1 - \frac{ik_n^3}{6\pi\epsilon_0} \frac{e^2 |D_{0n}|^2}{\hbar \omega_n - \omega} \right\}^{-1} \cdot \frac{e^2 |D_{0n}|^2}{\hbar \omega_n - \omega} \vec{\mathcal{U}}.$$

Using simple manipulations, this result can be rewritten as

$$\vec{\alpha}(\omega) = \frac{e^2}{\hbar} \frac{|D_{0n}|^2}{\omega_n - \omega - i\frac{1}{2}\Gamma_n} \vec{U}, \quad (14.6)$$

where

$$\Gamma_n = \frac{e^2 k_n^3 |D_{0n}|^2}{3\pi\epsilon_0 \hbar}. \quad (14.7)$$

This quantity, which is actually the spontaneous decay rate of the n 'th excited state [2], then results in a finite line width equal to Γ_n for the resonance. Without Γ_n , the resonance would diverge precisely at $\omega = \omega_n$. This modification should be done for every transition and so

$$\vec{\alpha}(\omega) = \frac{e^2}{\hbar} \sum_n \frac{|D_{0n}|^2}{\omega_n - \omega - i\frac{1}{2}\Gamma_n} \vec{U}.$$

We have defined the dressed polarizability so that $\vec{\alpha}_0(\omega) \cdot \vec{\mathcal{E}}(0, \omega) = \vec{\alpha}(\omega) \cdot \vec{\mathcal{E}}_0(0, \omega)$. This means that the correct versions of Eq.(14.2) and (14.4) can be written as

$$P_{abs} = \frac{1}{2} \omega \text{Im} \{ \vec{e} \cdot \vec{\alpha}(\omega) \cdot \vec{e} \} | \mathcal{E}_0(0, \omega) |^2$$

$$P_{scat} = \frac{ck_0^4}{12\pi\epsilon_0} | \vec{e} \cdot \vec{\alpha}(\omega) \cdot \vec{e} |^2 | \mathcal{E}_0(0, \omega) |^2.$$

We wish to introduce cross sections for the two processes and, to this end, need the intensity of the incident field $I_{inc} = | \vec{S}_0 | = \frac{1}{2} \epsilon_0 c | \mathcal{E}_0 |^2$. Dividing the power expressions above by this intensity provides absorption and scattering cross sections

$$\sigma_{abs} = \frac{k_0}{\epsilon_0} \text{Im} \{ \vec{e} \cdot \vec{\alpha}(\omega) \cdot \vec{e} \}$$

$$\sigma_{scat} = \frac{k_0^4}{6\pi\epsilon_0^2} | \vec{e} \cdot \vec{\alpha}(\omega) \cdot \vec{e} |^2.$$

It may be noted that if the dipole is embedded in a homogeneous dielectric with a (real-valued) refractive index n_1 the above relations remain valid provided k_0 is replaced by $k_1 = n_1 k_0$. Now, if energy is not accumulated in the particle and it is not dissipated by other means, the absorbed power must equal the scattered power. Thus, equating the above cross sections yields

$$\text{Im} \{ \vec{e} \cdot \vec{\alpha}(\omega) \cdot \vec{e} \} \approx \frac{k_0^3}{6\pi\epsilon_0} | \vec{e} \cdot \vec{\alpha}(\omega) \cdot \vec{e} |^2. \quad (14.8)$$

This condition is only expected to hold exactly at a resonance $\omega = \omega_n$ so that Eq.(14.6) yields $\vec{\alpha}(\omega_n) = 2ie^2 |D_{0n}|^2 / (\hbar\Gamma_n)\vec{U}$. Plugging this into Eq.(14.8) shows that the requirement is precisely obeyed if Γ_n is given by the expression Eq.(14.7). Hence, our expression for the spontaneous decay rate is consistent with all absorbed power eventually being re-emitted as scattering.

Exercise: Near-field relations

The calculation of the scattered field above relied on the far-field approximation $k_0r \gg 1$. If all terms are retained, a somewhat tedious computation shows that

$$\vec{\mathcal{E}}_{scat}(\vec{r}, \omega) = \frac{k_0^2 e^{ik_0r}}{4\pi\epsilon_0 r} \left\{ \left[1 + \frac{i}{k_0r} - \frac{1}{k_0^2 r^2} \right] \vec{U} - \left[1 + \frac{3i}{k_0r} - \frac{3}{k_0^2 r^2} \right] \vec{e}_r \vec{e}_r \right\} \cdot \vec{p}(\omega).$$

a) Show by expansion around $x = 0$ that

$$e^{ix} \left[\frac{1}{x} + \frac{i}{x^2} - \frac{1}{x^3} \right] \approx -\frac{1}{x^3} + \frac{1}{2x} + \frac{2i}{3}$$

$$e^{ix} \left[\frac{1}{x} + \frac{3i}{x^2} - \frac{3}{x^3} \right] \approx -\frac{3}{x^3} - \frac{1}{2x}.$$

b) Use this result to show that the radiation-reaction field is precisely the imaginary part of the scattered field in the limit $r \rightarrow 0$.

c) Show that the near-field, i.e. the electric field very close to the dipole, is approximately given by

$$\vec{\mathcal{E}}_{near-field}(\vec{r}, \omega) \approx \frac{1}{4\pi\epsilon_0 r^3} \left\{ 3\vec{e}_r \vec{e}_r - \vec{U} \right\} \cdot \vec{p}(\omega).$$

The same expression is obtained for the electrostatic field produced by a dipole. In a static calculation, we put $\vec{\mathcal{E}} = -\nabla\Phi$, where Φ is the electrostatic potential.

d) Show that the accompanying near-field potential is

$$\Phi_{near-field}(\vec{r}, \omega) \approx \frac{1}{4\pi\epsilon_0 r^2} \vec{e}_r \cdot \vec{p}(\omega).$$

We now consider a small nanosphere of radius a and refractive index n_2 embedded in a medium with refractive index n_1 subjected to a constant incident field $\vec{\mathcal{E}}_0 = \mathcal{E}_0 \vec{e}_z$. Hence,

the incident potential must be $\Phi_0 = -\mathcal{E}_0 z$. In polar coordinates, $\Phi_0 = -\mathcal{E}_0 r \cos \theta$ and we therefore write the full solution as $\Phi(r, \theta) = f(r) \cos \theta$. Laplace's equation for the potential $\nabla^2 \Phi(r, \theta) = 0$ consequently simplifies to $r \partial^2 (rf) / \partial r^2 = 2f$.

d) Show that $f(r) = r$ and $f(r) = 1/r^2$ are solutions to Laplace's equation.

e) Of the above, only the first type is allowed inside the sphere while both forms are applicable outside. Apply the boundary conditions $f(a_-) = f(a_+)$ and $n_2^2 f'(a_-) = n_1^2 f'(a_+)$ to demonstrate that the full solution outside the sphere is $\Phi = \Phi_0 + \Phi_{scat}$ with

$$\Phi_{scat}(r, \theta) \approx \frac{a^3}{r^2} \frac{n_2^2 - n_1^2}{n_2^2 + 2n_1^2} \mathcal{E}_0 \cos \theta.$$

Comparing to the general expression for the near-field potential, this demonstrates that the polarizability is $\alpha(\omega) \approx 4\pi\epsilon_0 a^3 \frac{n_2^2 - n_1^2}{n_2^2 + 2n_1^2}$.

References

- [1] J.R. Reitz, F.J. Milford, and R.W. Christy *Foundations of Electromagnetic Theory* (Addison-Wesley, Massachusetts, 1979).
- [2] R. Loudon *The Quantum Theory of Light* (Oxford University Press, Oxford, 1991)